

# ***Physical Chemistry II***

## ***2021 Class Notes***

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## Introduction to the note

This class note is written for the Physical Chemistry II course in University of Science and Technology of China (USTC). In 2020 spring, the course was first set as English class for *Talented Elite class* of School of Chemistry and Materials, where Prof. YiJing Yan, Chu-Sheng Chen and Xiao Zheng gave lectures on chemical kinetics, electrochemistry and surface chemistry individually. I, as a student, was very fortunate to attend the class at that time and was deeply impressed by the class. The class was taken a much modern form to inform students of the most advanced frontiers in physical chemistry. In 2021 spring, I start to write a note to help students learn the lesson better, as the role of teaching assistant.

# Transport Properties of Substances

PART

I

## 1 Transport properties

The description of transport properties provides a phenomena theory to formulate the long term changes, with regardless of the detailed motions that happen in every moment. Although the theories seem to be rather rough, they are still able to give us a good result.

### 1.1 Current

One core quantity in transport is current. The current is defined as the number of one matter that goes through an area in unit time, that is

$$\text{Current} = \frac{\# \text{ of matter that passes through an area}}{\text{Time interval}}. \quad (1.1)$$

The often used quantity is current density, which is defined as current divided by the cross area. The current density is usually treated as a vector  $\vec{J}$ , in which case, the definition could be given by

$$\iint_S d\vec{\sigma} \cdot \vec{J} = -\frac{dQ}{dt}, \quad (1.2)$$

where  $dQ/dt$  stands for the rate of change of matter  $Q$ , and the left hand side represents for the flux that the current density passes a certain area  $S$ . So far, the current has been defined in a good manner.

For a certain matter, the current density could be expressed by different empirical laws. Below list some important examples.

1. For the transport of matter, the current density (or flux) is given by Fick's 1<sup>st</sup> law, which reads

$$\vec{J}(\text{matter}) = -D\nabla C. \quad (1.3)$$

Here  $D$  is the diffusion constant and  $\nabla C$  is the gradient of concentration. The Fick's law just says that the flux induced by the difference of concentration is proportional to the gradient of concentration. Note that here we use capital  $C$  to stand for number concentration and  $c = C/N_A$  to stand for mole concentration.

2. For transport of heat, the current density is proportional to the temperature gradient  $\nabla T$ , that is

$$\vec{J}(\text{heat}) = -\kappa\nabla T, \quad (1.4)$$

where  $\kappa$  is the thermal conductivity constant.

3. For electron conductivity, the current density follows the Ohm's law, that is

$$\vec{J}(\text{electron}) = \sigma \vec{f}. \quad (1.5)$$

The current density is called “flux” in Atkins' book. But in electromagnetism, the term “current density” is preferred.

Here  $\sigma$  is the conductivity and  $\vec{f}$  is the force that unit charge feels. When only electric field exists,  $\vec{f} = \vec{E}$ . For static field, the electric field is just the minus gradient of scalar potential  $\varphi$ , then

$$\vec{J}(\text{electron}) = \sigma \vec{E} = -\sigma \nabla \varphi. \quad (1.6)$$

4. For the transport of momenta, the velocity difference in  $z$  direction could lead to the transport of momentum in  $x$  direction, that is

$$J(p_x) = -\eta \frac{\partial v_x}{\partial z}. \quad (1.7)$$

The constant  $\eta$  is called viscosity.

**Remark.** Note that the unit of each transport constant:

$$\begin{aligned} [D] &= \text{m}^2 \cdot \text{s}^{-1}, \\ [\kappa] &= \text{J} \cdot \text{K}^{-1} \text{m}^{-1} \text{s}^{-1}, \\ [\sigma] &= \text{S} \cdot \text{m}^{-1}, \\ [\eta] &= \text{kg} \cdot \text{m}^{-1} \text{s}^{-1} = \text{Pa} \cdot \text{s}. \end{aligned}$$

**Remark.** Other transport phenomena.

To be...

Next, an example to evaluate the transport constant is quite important. Here let us consider the idea gases. Recall the PChemI course. The velocity of idea gas could be obtained easily by Boltzmann distribution, that is

$$f(\vec{v}) = f(v_x)f(v_y)f(v_z) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{mv^2}{2k_B T}\right). \quad (1.8)$$

By changing the variables from Cartesian  $(v_x, v_y, v_z)$  to spherical  $(v, \theta, \phi)$  and integrating the solid angle, one could readily get the Maxwell distribution, reading

$$f(v) = 4\pi v^2 \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{mv^2}{2k_B T}\right). \quad (1.9)$$

The collision frequency  $z$  is given by

$$z = \frac{\sigma C \bar{v}_{\text{rel}} \Delta t \Delta A}{\Delta t \Delta A} = \sigma C \bar{v}_{\text{rel}}, \quad (1.10)$$

where  $\sigma$  is the cross section of collision,  $C$  is the number density (the same symbol as before) and  $\bar{v}_{\text{rel}}$  is the mean relative velocity. Then the mean free path could be obtained by

$$\lambda = \frac{\bar{v}}{z} = \frac{1}{\sqrt{2}\sigma C} = \frac{k_B T}{\sqrt{2}\sigma p}. \quad (1.11)$$

Here we used the equality

$$\bar{v}_{\text{rel}} = \sqrt{2}\bar{v}, \quad (1.12)$$

for the case where only one kind of molecules are considered.

A complete description of momentum flux needs something advanced in tensor analysis, due to the fact that the gradient of velocity is a tensor with 2 indices.

The diffusion constant for idea gases could be evaluated by

$$D = \frac{1}{3} \lambda \bar{v}. \quad (1.13)$$

And

$$\kappa = \frac{1}{3} \lambda \bar{v} C_{V,m} c_A, \quad (1.14)$$

$$\eta = \frac{1}{3} \lambda \bar{v} m C_A, \quad (1.15)$$

where  $C_{V,m}$  is the molar volume heat capacity and  $m$  is the mass of a single molecule.

**Proof.** Below we are going to prove Eq. (1.13).

To be...

□

**Remark.** Heat transport versus Heat transfer.

To be...

## 1.2 Thermodynamic view on diffusion

Recall on the chemical potential of one substance  $B_i$ ,

$$\mu_i = \mu_i^\ominus + RT \ln a_i, \quad (1.16)$$

where  $\mu_i^\ominus$  is the standard chemical potential and  $a_i$  is the activity of  $B_i$ . Define the thermodynamic force

$$\mathcal{F}_{i,x} \equiv - \left( \frac{\partial \mu_i}{\partial x} \right)_{p,T}. \quad (1.17)$$

The force that one particle feels is defined as

$$F_i \equiv \frac{\mathcal{F}_i}{N_{\text{avo}}}. \quad (1.18)$$

Here we define the drift speed

$$\vec{v} \equiv \frac{1}{N} \sum_{i=1}^N \vec{u}_i, \quad (1.19)$$

which stands for the average of velocity of all particles with same properties. Then we can write down another expression for flux, namely

$$\vec{J}(\text{mole}) = c \vec{v} = -D \nabla c. \quad (1.20)$$

On the other hand, the thermodynamic force is recast as

$$\vec{\mathcal{F}} = -\nabla \mu = -RT \nabla \ln a = -RTW \nabla \ln c, \quad (1.21)$$

where

$$W \equiv \frac{\partial \ln a}{\partial \ln c}. \quad (1.22)$$

For ideal cases,  $W$  is approximately equal to 1. Thus we get

$$\vec{v} = \frac{D}{RT} \vec{\mathcal{F}} = \frac{D}{k_B T} \vec{F}. \quad (1.23)$$

So far, we have deduced the Einstein–Stokes equation, which is very useful in the discussion of electrical conductivity in Section 1.4.

Note that for spherical particle, the friction force is given by Stokes equation

$$\vec{f} = 6\pi a \eta \vec{v}, \quad (1.24)$$

where  $a$  is the radius of the particle. Then

$$D = \frac{k_B T}{6\pi a \eta}. \quad (1.25)$$

### 1.3 Diffusion equation

Below, we focus on the transport processes of substances. Therefore, the conservation law of substances exists, reading

$$-\frac{dN}{dt} = \iint_{S=\partial V} d\vec{\sigma} \cdot \vec{J} = - \iiint_V dV \frac{\partial C}{\partial t}, \quad (1.26)$$

where  $C$  is concentration and total amount of substances in area  $V$  is  $N = \int_V dV C$ . Together with the equality

$$\iint_S d\vec{\sigma} \cdot \vec{J} = \iiint_V dV \nabla \cdot \vec{J}, \quad (1.27)$$

one could readily get the continuity equation

$$\nabla \cdot \vec{J} + \frac{\partial C}{\partial t} = 0. \quad (1.28)$$

If the flux satisfies the Fick's 1st law, then combine with Eq. (1.28), one could have the diffusion equation

$$\frac{\partial C}{\partial t} = D \nabla^2 C, \quad (1.29)$$

named Fick's 2nd law. The probability density function  $\rho$  is defined as the probability of finding particles in  $\vec{x} \rightarrow \vec{x} + d\vec{x}$ , then it could be written as

$$\rho = \frac{C}{\int_V dV C}. \quad (1.30)$$

Then, the diffusion equation becomes

$$\frac{\partial \rho}{\partial t} = D \nabla^2 \rho. \quad (1.31)$$

For one dimension case, consider the boundary conditions:

$$\rho|_{t=0} = \delta(x) \quad \text{and} \quad \lim_{x \rightarrow \pm\infty} \rho = 0. \quad (1.32)$$



The solution has the Gaussian form

$$\rho(t, x) = \frac{1}{\sqrt{4\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right). \quad (1.33)$$

Thus the average and fluctuation of  $x$  can be evaluated directly, namely

$$\langle x \rangle = 0, \quad (1.34)$$

$$\langle x^2 \rangle = 2Dt. \quad (1.35)$$

For multi-dimension case,

$$\langle r^2 \rangle = 2dDt, \quad (1.36)$$

with  $d = 1, 2, 3$ .

One instructive approach to seizing such a result is the Brownian motion. The Brownian motion is defined as a random motion mode for a particle in an environment. The environment will give the particle random forces and friction force. Thus we could write down the equation of motion of the particle, called Langevin equation, through Newton equation (with absence of potential energy), that is

$$m\dot{v} = -\zeta v + \delta F(t), \quad (1.37)$$

where  $v = \dot{x}$ ,  $\zeta$  is a constant describing the friction and  $\delta F(t)$  is the random force. The random force  $\delta F(t)$  is a random variable depending on time, which is called stochastic process in mathematics. For Brownian motion, the random force is required to satisfy

$$\langle \delta F(t) \rangle = 0, \quad (1.38)$$

$$\langle \delta F(t) \delta F(t') \rangle = 2B\delta(t - t'). \quad (1.39)$$

Here  $B$  is a constant used to measure the intensity of random force. In mathematics, such a stochastic process is called Wiener process. The fluctuation–dissipation theorem tells us<sup>1</sup>

$$B = \zeta k_B T. \quad (1.40)$$

In over-damped case, where  $\dot{v} \simeq 0$ ,

$$v = \frac{\delta F(t)}{\zeta}. \quad (1.41)$$

Then the displacement could be evaluated by integrating  $v$ , which is

$$x(t) = x(0) + \int_0^t dt' \frac{\delta F(t')}{\zeta}. \quad (1.42)$$

If we set  $x(0) = 0$ , then

$$x(t) = \frac{1}{\zeta} \int_0^t dt' \delta F(t'). \quad (1.43)$$

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<sup>1</sup>The detail could be found in appendix

The average of  $x(t)$  is

$$\langle x(t) \rangle = 0. \quad (1.44)$$

The fluctuation of  $x(t)$  is

$$\langle x^2(t) \rangle = \frac{1}{\zeta^2} \int_0^t d\tau \int_0^t d\tau' \langle \delta F(\tau) \delta F(\tau') \rangle = \frac{2k_B T}{\zeta} t. \quad (1.45)$$

Then the average and fluctuation mutually give us the probability density function

$$\rho(t, x) = \frac{1}{\sqrt{4\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right), \quad (1.46)$$

with Stokes–Einstein relation

$$D = \frac{k_B T}{\zeta}. \quad (1.47)$$

The result is just identical to the previous one given by Fick's 2nd law.

**Remark.** The Langevin equation gives an equation that describes the time evolution of random variables. And the diffusion equation focuses on describing the probability density functions. The general case of diffusion equation is called Fokker–Planck equation, which could be derived by Langevin equation. You could find the derivation in appendix.

## 2 Diffusion and Electrical Conduction

### 2.1 Electrical force involved diffusion

#### General remarks

Recall the basic thermodynamic relation

$$dU = TdS - pdV + \mu dn + \delta w_{\text{non-}pV}. \quad (2.1)$$

If we only consider the electric non- $pV$  reversible work, then

$$dU = TdS - pdV + \mu dn + \varphi dq, \quad (2.2)$$

where  $q$  is electric charge and  $\varphi$  is the electric potential. By using Legendre transformation, one could get

$$dG = Vdp - SdT + \mu dn + \varphi dq. \quad (2.3)$$

Besides, the chemical potential of a certain substance  $B_i$  reads

$$\mu_i = \mu_i^\ominus + RT \ln a_i. \quad (2.4)$$

Then we can define the electrochemical potential to satisfy the relation Eq. (2.3) as

$$\tilde{\mu}_i \equiv \mu_i + z_i F \varphi, \quad (2.5)$$

where  $z_i$  is the valence of  $B_i$  and  $F$  is the Faraday constant. Thus the corresponding thermodynamic force is given by

$$\vec{F}_i = \frac{\vec{\mathcal{F}}_i}{N_{\text{avo}}} = -\frac{1}{N_{\text{avo}}} \nabla \tilde{\mu}_i. \quad (2.6)$$

To relate the thermodynamic force and drift speed, we define the absolute mobility  $B$  as

$$\vec{v}_i = B_i \vec{F}_i. \quad (2.7)$$

Consider the flux

$$\vec{J}_i = c_i \vec{v}_i = -\frac{c_i B_i}{N_{\text{avo}}} \nabla \tilde{\mu}_i. \quad (2.8)$$

Due to the fact that  $\tilde{\mu}$  is made of two parts, we could discuss them respectively, which will be discussed in the following content.

#### Chemical potential gradient

The flux induced by chemical potential reads

$$\vec{J}_i^{\text{chem}} = -\frac{c_i B_i}{N_{\text{avo}}} \nabla \mu_i. \quad (2.9)$$

Combine with

$$\mu_i = \mu_i^\ominus + RT \ln a_i, \quad (2.10)$$

we obtain

$$\vec{J}_i^{\text{chem}} = -\frac{c_i B_i R T}{N_{\text{avo}}} \nabla \ln a_i = -B_i k_B T W_i \nabla c_i. \quad (2.11)$$

Thus, the diffusion constant caused by chemical potential is

$$D_i^{\text{chem}} \equiv B_i k_B T W_i \equiv D_i. \quad (2.12)$$

For ideal case,  $W_i \simeq 1$ , then

$$D_i \simeq B_i k_B T. \quad (2.13)$$

### Electric potential gradient

The flux result from electric potential gradient reads

$$\vec{J}_i^{\text{ele}} = -\frac{c_i B_i z_i F}{N_{\text{avo}}} \nabla \varphi. \quad (2.14)$$

Here we assume that the electric potential for every species is identical. (i.e. we assume that the extent of the change of electrical potential is much greater than that of concentration.)

Recall the Ohm's law, reading

$$\vec{J}_i^{\text{current}} = \sigma_i \vec{E} = z_i F \vec{J}_i^{\text{ele}}. \quad (2.15)$$

Here  $\vec{E} = -\nabla \varphi$  is the electric field. Then we can write down expressions of electric conductivity  $\sigma_i$ , which is

$$\sigma_i = \frac{c_i z_i^2 F^2 B_i}{N_{\text{avo}}}. \quad (2.16)$$

On the other hand, we define the electric mobility as

$$\vec{v}_i = u_i \vec{E}. \quad (2.17)$$

Then together with the Einstein relation

$$D = \frac{k_B T}{\zeta}, \quad (2.18)$$

where  $\zeta$  is defined in Langevin equation, then

$$D = \frac{u_i k_B T}{z_i e}, \quad (2.19)$$

and

$$u_i = B_i k_B T, \quad (2.20)$$

which is the Einstein–Nernst equation.

### Combined situation

The total flux is given by

$$\vec{J}_i = \vec{J}_i^{\text{chem}} + \vec{J}_i^{\text{ele}}. \quad (2.21)$$

For galvanic cells, the first term given by chemical potential is greater than the contribution of electric potential. And the reverse situation, it is called electrolytic cells.

## **2.2 Conductivities and mobilities of ions in liquid**

# Reaction Rate Theories

## 3 Kinetic Rate and Laws

Chemical reactions are defined as the processes that involve break and formation of chemical bonds. A general expression of chemical reactions reads

$$0 = \sum_i \nu_i B_i, \quad (3.1)$$

where  $B_i$  stand for all the species that participate in the reaction and  $\nu_i$  are the corresponding stoichiometry. Reaction extent  $\xi$  is a quantity to characterize the extent that the reaction occurs, which is defined as

$$\xi \equiv \frac{\Delta n_i}{\nu_i}. \quad (3.2)$$

For products,  $\nu_i > 0$ ; for reactants,  $\nu_i < 0$ .

At constant temperature and pressure, the infinitesimal change of Gibbs energy is

$$dG = \sum_i \mu_i dn_i = \sum_i \nu_i \mu_i d\xi. \quad (3.3)$$

The reaction Gibbs energy is defined as

$$\Delta_r G \equiv \left( \frac{\partial G}{\partial \xi} \right)_{p,V} = \sum_i \nu_i \mu_i. \quad (3.4)$$

The criterion of determining whether a reaction could occur is whether  $\Delta_r G > 0$ . If  $\Delta_r G > 0$ , the reaction cannot occur; otherwise, the reaction could take place.

The Gibbs energy tells us how to tell a reaction could take place from the thermodynamic aspect. However, the thermodynamic favour reaction sometimes cannot observe the occurrence of it due to the limit of the reaction rate. Thus a detailed consideration of chemical reaction rates is necessary. The reaction rate is defined as

$$v \equiv \frac{1}{V} \frac{d\xi}{dt}, \quad (3.5)$$

where  $V$  is the volume of the container in which reaction occurs. Note that the unit of  $v$  is  $\text{mol m}^{-3} \text{s}^{-1}$ . For specific species,

$$\frac{d[B_i]}{dt} = \nu_i v. \quad (3.6)$$

The discussion of chemical kinetics and chemical dynamics focus on the study of the rate equation. The chemical kinetics focuses on the macroscopic description of reaction rates mainly based on the empirical laws and formulas together with physical picture. The chemical dynamics deduces the reaction rate laws from a microscopic aspect, resorting to more basic physical laws (Newtonian laws or quantum theory combined with statistical mechanics).

### 3.1 Chemical Kinetics Laws

Experiments provide us rate law for different chemical reactions in an empirical way. Generally, the rate law says the reaction rate is a function of concentrations of reactants and products together with some other parameters  $\{q\}$  (such as temperature), that is

$$v = f(\{[B]\}; \{q\}). \quad (3.7)$$

The results of experiments always tell us that the rate law takes the form

$$v = k_r(\{q\}, \{[B]\}) \prod_i [B_i]^{\alpha_i}. \quad (3.8)$$

Here,  $k_r(\{q\}, \{[B]\})$  is the reaction constant and  $\alpha_i$  are also constants. This kind of form of reaction rates separate the different reactants' and products' concentrations and the parameter groups  $\{q\}$ , which enormously simplifies the rate law. The reaction order is defines as the summation of  $\alpha_i$ , that is  $\sum_i \alpha_i$ . This kind assumption or observation of rate law takes a lot of approximations and is not necessarily true.

Note that  $\alpha_i$  are not required to equal to  $\nu_i$ . And the reaction order does not need to be integers all the time.

The simplest rate law is just the mass action law, which says

$$v = k_r(\{q\}) \prod_i [B_i]^{\nu_i}. \quad (3.9)$$

Based on the mass action law, we define the elementary reactions as the reactions whose rate law takes the form of Eq. (3.9). However, the reaction that satisfies the mass action law is not necessary to be an elementary reaction. When propose a reasonable mechanism of a reaction, the elementary reaction assumption is always applied. This consideration comes from the microscopic view on reactions, that is the physics picture that the elementary steps are always concerning the collisions or other interactions between reactants. Therefore, the rate *should* be proportional to the number of reactants.

The parameter dependence of  $k_r$  is always supposed to be the Arrhenius form. The Arrhenius' law of reaction constant reads

$$k_r = A e^{-E_a/RT}, \quad (3.10)$$

where  $A$  is some other constant that has nothing to do with  $T$ ,  $E_a$  is the activation energy and  $R$  is the ideal gas constant. The inner physics picture is well dictated by transition state theory (TST). For a reaction, if it has to occur, it has to overcome a obstacle in the potential energy-reaction coordinates plot. The obstacle represents for the transition state and the energy difference between transition state and reactant is related to  $E_a$  or sometimes  $E_a$  plus a constant.

So far, two important empirical laws are raised. One focuses on the concentration dependence and the other focuses on the temperature dependence. Thus given a rate law with all quantities specified, the problem of chemical kinetics is to solve the derivative equation

$$\frac{1}{V} \frac{d\xi}{dt} = f(\{q\}; \{\nu\}; \xi). \quad (3.11)$$

### 3.2 Detailed-Balance Relation

The detailed-balance *states* that in equilibrium, the times that the reaction occurs are identical to the times that the reverse reaction occurs.

Let us consider a reaction that reaches equilibrium



The detailed-balance relation just tells us

$$k[\text{R}] = k'[\text{P}]. \quad (3.13)$$

Here we assumed that the mass action law holds. Or in term of equilibrium constant  $K_c$ ,

$$K_c = \frac{[\text{P}]}{[\text{R}]} = \frac{k}{k'}. \quad (3.14)$$

The detailed-balance relation could be obtained from the time-reversal symmetry of an equilibrium system. The laws of motion of molecules are invariant under time reversal operation, so as the time goes reversely, the system looks the same as origin. Thus the detailed-balance relation must hold. Some detailed discussion is enclosed in the appendix.

### 3.3 Basic Skills

The experiment results give us a rate law. Next, we have to explain why the reaction takes such a form. Specifically, one has to propose a reasonable mechanism to account for the results. Please note, one mechanism could give you the rate law in consistent with the experiment but it cannot to be a truth enough. More test should be performed in order to determine whether your mechanism is correct.

To be...



## 4 Reaction Mechanism

### 4.1 Bimolecular Reactions

To be...

### 4.2 Unimolecular Reactions

The unimolecular reactions are those reactions in which only one kinds of molecules involve and react, that is



**Remark.** The differences between unimolecular reactions and single-molecular reactions.

To be...

The Lindemann-Hinshelwood mechanism is the most important one to account for the unimolecular reactions' occurring in gas phase. The mechanism takes three steps: generation of energized/excited molecules  $A^*$ , de-excitation, and termination. And each step is an elementary one. In detail,



Use the steady-state approximation, and we get

$$\frac{d}{dt}[A^*] = k_a[A]^2 - k'_a[A^*][A] - k_b[A^*] \simeq 0. \quad (4.5)$$

Or

$$[A^*] = \frac{k_a[A]^2}{k'_a[A] + k_b}. \quad (4.6)$$

Then the reaction rate is given by

$$v = \frac{d[P]}{dt} = k_b[A^*] = \frac{k_a k_b}{k'_a[A] + k_b} [A]^2. \quad (4.7)$$

If the last step is the rate-determination one, i.e.  $k'_a[A] \gg k_b$ , then the rate becomes

$$v \simeq \frac{k_a k_b}{k'_a} [A]. \quad (4.8)$$

The result shows that under the approximation stated before, the unimolecular reaction is a first-order reaction and satisfies the mass action law. Note that, in this case, the activation energy is  $E_a = E_a(k_a) + E_a(k_b) - E_a(k'_a)$ , which indicates that  $E_a$  could be negative.

From another aspect, as the pressure is low, i.e.  $k'_a[A] \ll k_b$ , then

$$v \simeq k_a[A]^2, \quad (4.9)$$

that shows the reaction rate takes the second-order form.

The Lindemann-Hinshelwood treatment establishes a reasonable mechanism that agrees with experiment in a not bad manner. The more detailed treatment of the reaction constant will be discussed in the following chapters, which will follow the Hinshelwood's and RRK's statistical mechanics involved consideration.

### 4.3 Hinshelwood v.s. RRK Theories

The deduction of reaction constant in Hinshelwood and RRK theories is only established on the statistical treatment without any consideration step from the microscopic motions of molecules.

Consider Boltzmann distribution of energy of molecules,  $f(\varepsilon) = \beta e^{-\beta\varepsilon}$  with  $\beta = 1/k_B T$ , and the normalization reads

$$\int_0^\infty d\varepsilon f(\varepsilon) = 1. \quad (4.10)$$

The joint probability distribution of  $s$  molecules' energy  $\varepsilon_1, \varepsilon_2, \dots, \varepsilon_s$  is given by

$$f(\varepsilon_1, \varepsilon_2, \dots, \varepsilon_s) = \prod_{i=1}^s f(\varepsilon_i) = \beta^s e^{-\beta(\varepsilon_1 + \varepsilon_2 + \dots + \varepsilon_s)}. \quad (4.11)$$

And the normalization relation reads

$$\int_0^\infty d\varepsilon_1 \int_0^\infty d\varepsilon_2 \dots \int_0^\infty d\varepsilon_s f(\varepsilon_1, \varepsilon_2, \dots, \varepsilon_s) = 1. \quad (4.12)$$

We are only interested in the total energy  $\zeta \equiv \sum_i \varepsilon_i$  distribution, then we could make a variables' transformation and integral other useless variables. We will do this process in a more intuitive way. All we have to do is find a function  $G_s(\zeta)$  to satisfy

$$\int_0^\infty d\zeta G_s(\zeta) = 1. \quad (4.13)$$

Due to the consideration of the variables' transformation,  $G_s$  must be the product of  $F_s(\zeta) \equiv \beta^s e^{-\beta\zeta}$  and a function  $\rho_s$  related to the density of states in  $(\zeta, \zeta + d\zeta)$ . First of all,  $\rho_s \propto \zeta^{s-1}$ . This comes from fact that  $n^{\text{th}}$  dimensional object's surface area must be proportional to  $(n-1)^{\text{th}}$  power of its size. Combined with the normalization relation, one could easily get

$$G_s(\zeta) = \rho_s(\zeta) F_s(\zeta) = \underbrace{\frac{\zeta^{s-1}}{(s-1)!}}_{\rho_s} \times \underbrace{\beta^s e^{-\beta\zeta}}_{F_s}. \quad (4.14)$$

Let us go back to Hinshelwood's idea. The proportion of energized molecules is given by the integral

$$\frac{k_a}{k'_a} = \frac{[A^*]}{[A]} = \int_{\varepsilon_a}^\infty d\zeta \rho_s(\zeta) F_s(\zeta) = e^{-\beta\varepsilon_a} \sum_{n=0}^{s-1} \frac{(\beta\varepsilon_a)^n}{n!}. \quad (4.15)$$

Thus, the rate constant is

$$k \equiv \frac{k_a k_b}{k'_a} = k_b e^{-\beta\varepsilon_a} \sum_{n=0}^{s-1} \frac{(\beta\varepsilon_a)^n}{n!}. \quad (4.16)$$

However, the deficiencies of Hinshelwood theory are quite clear. The result of rate constant does not have the Arrhenius form, and the temperature dependence of  $k$  is complex. In fact, for a reaction, not all the freedoms take part in the reaction. Besides, the determination-step is not considered.

In light of Hinshelwood's shortcoming, RRK theory provides us a more sophisticated result. RRK theory assumes that from  $A^*$  to P, only molecules with specific freedoms (denoted as activated molecules  $A^\ddagger$ ) are able to become products, that is



RRK assume that the first step should be slow to satisfy the ergodicity, whereas the second step should be fast. Besides, the step  $A^* \longrightarrow A^\ddagger$  cannot go reverse. The ratio of  $A^\ddagger$  to  $A^*$  can be evaluated by resorting to the balls in draws problem. The reason why we could do this is that here we view chemical bonds as oscillators. Reaction engages only some bonds re-arranged or broken. The activated species stands for the key vibrating modes that could yield products. According to quantum physics, the energy of a harmonic oscillator is given by

$$\varepsilon_n = \hbar\omega \left( n + \frac{1}{2} \right), \quad n = 0, 1, 2, \dots, \quad (4.18)$$

where  $\omega$  is the angular frequency of the oscillator. Thus for a given energy  $\varepsilon_n$ ,  $n$  energy levels are available for molecules' degrees of freedoms. Therefore, the total number of configurations of  $A^*$  is given by the ways of putting  $J$  balls into  $s$  draws, that is

$$W = \frac{(J + s - 1)!}{J!(s - 1)!}. \quad (4.19)$$

The number of configurations of  $A^\ddagger$  is

$$W' = \frac{(J - M + s - 1)!}{(J - M)!(s - 1)!}, \quad (4.20)$$

where the number of balls becomes  $J - M$ . Thus

$$\begin{aligned} \frac{[A^\ddagger]}{[A^*]} &= \frac{W'}{W} = \frac{(J - M + s - 1)!J!}{(J + s - 1)!(J - M)!} \\ &\simeq \frac{(J - M + s - 1)^{J - M + s - 1} J^J}{(J + s - 1)^{J + s - 1} (J - M)^{J - M}} \\ &\simeq \left( 1 - \frac{M}{J} \right)^{s - 1}. \end{aligned} \quad (4.21)$$

Then the ratio is

$$g_s(\zeta; \varepsilon_a) = \left( 1 - \frac{\varepsilon_a}{\zeta} \right)^{s - 1}. \quad (4.22)$$

Therefore,

$$\tilde{k}_b(\zeta) = k^\ddagger g_s(\zeta; \varepsilon_a). \quad (4.23)$$

The rate constant could be evaluated from the ensemble average, that is

$$\begin{aligned}
 k_b/k^\ddagger &= \int_{\varepsilon_a}^{\infty} d\zeta \tilde{k}_b(\zeta) \rho_s(\zeta) F_s(\zeta) \\
 &= \int_{\varepsilon_a}^{\infty} d\zeta \left(1 - \frac{\varepsilon_a}{\zeta}\right)^{s-1} \frac{\zeta^{s-1}}{(s-1)!} \beta^s e^{-\beta\zeta} \\
 &= e^{-\beta\varepsilon_a}.
 \end{aligned} \tag{4.24}$$

The RRK theory's result has the Arrhenius' form. However, the assumptions of RRK theory are not self-consistent. The ergodicity assumption requires the reverse reaction of  $A^* \longrightarrow A^\ddagger$  should occur. The more acceptable theory RRKM combining transition state theory and RRK theory will be introduced in section 4.4.

## 5 Reaction Dynamics and Theories

### 5.1 Collision Theory v.s. Molecular Dynamics

Different from reaction kinetics, reaction dynamics focuses on the microscopic interactions between molecules and tries to establish theories to describe reaction constant from more basic physical principles.

The collision theory stems from considering the collisions of reactants by using the hard-sphere model, which presents us a great example of reaction dynamics.

In this section, we consider the reaction that involves two molecules



The contributions to  $v$  come from three parts: steric factor, collision rate and energetic factor. Let us examine them respectively.

(i) The energetic factor (EF) contributes to the Arrhenius' factor of reaction constant. The emergence of EF results from the fact that the reaction could occur, only it overcomes a barrier of energy. The energy is denoted as  $\varepsilon_a$ . Consider the collision of two spherical molecules, due to the differences of the velocity (magnitude and direction), the effective velocity  $v_{\text{eff}}$  for collision is the projection of velocity  $\vec{v}_{\text{rel}}$  on the line connecting two molecules' mass centers, which is  $v_{\text{rel}} \cos \theta$ . Thus, the real collision section is given by

$$\sigma' = \pi(d \cos \theta)^2 = \sigma \cos^2 \theta, \quad (5.2)$$

where  $d$  is the sum of radii of two molecules and  $\sigma \equiv \pi d^2$ . On the other side, the remaining energy must exceed  $\varepsilon_a$ , which means

$$\cos^2 \theta = 1 - \frac{v_a^2}{v_{\text{rel}}^2}, \quad (5.3)$$

where  $\varepsilon_a = \frac{1}{2} \mu v_a^2$ .

Then EF could be evaluated through

$$\begin{aligned} \text{EF} &= \frac{\# \text{ of molecules that could react}}{\# \text{ of molecules}} \\ &= \frac{\int_{\varepsilon_a}^{\infty} dv_{\text{rel}} f(v_{\text{rel}}) v_{\text{rel}} \sigma'}{\int_0^{\infty} dv_{\text{rel}} f(v_{\text{rel}}) v_{\text{rel}} \sigma} = \frac{1}{\bar{v}_{\text{rel}}} \int_{\varepsilon_a}^{\infty} dv_{\text{rel}} f(v_{\text{rel}}) v_{\text{rel}} \cos^2 \theta, \end{aligned} \quad (5.4)$$

where  $f$  is the Maxwell distribution of  $v_{\text{rel}}$ . Then, by calculating the integral, we have

$$\text{EF} = e^{-\varepsilon_a/k_B T}. \quad (5.5)$$

(ii) Collision rate could be obtained from intramolecular collision frequency per volume,

$$\mathcal{Z}_{AB} = \sigma \bar{v}_{\text{rel}} \frac{N_A}{V} \frac{N_B}{V}. \quad (5.6)$$

(iii) Since not every molecules are spherical and other effects (e.g. harpoon effect) exist, one correction factor is necessary, which is the steric factor  $\Phi$ .

Note that if  $A=A$ ,  $\mathcal{N}_{AA} = \frac{1}{2} \sigma \bar{v}_{\text{rel}} \frac{N_A}{V} \frac{N_A}{V}$ .

In conclusion, the rate is just the product of the above terms, that is

$$-\frac{1}{V} \frac{dN_A}{dt} = \Phi \sigma \bar{v}_{\text{rel}} \frac{N_A}{V} \frac{N_B}{V} e^{-\varepsilon_a/kT}. \quad (5.7)$$

Change the unit from number to mole. Then

$$v = \Phi N_{\text{avo}} \sigma \bar{v}_{\text{rel}} e^{-\varepsilon_a/kT} [A][B]. \quad (5.8)$$

The rate constant is given by

$$k_r = \Phi N_{\text{avo}} \sigma \bar{v}_{\text{rel}} e^{-\varepsilon_a/kT}. \quad (5.9)$$

The expression has the Arrhenius' form, but note that  $\bar{v}_{\text{rel}}$  is temperature dependent. Now we introduce the concept of apparent activation energy, which is defined as

$$E_a^{\text{exp}} \equiv RT^2 \frac{d \ln k_r}{dT}. \quad (5.10)$$

Consider the result of collision theory, and we have

$$\begin{aligned} E_a^{\text{exp}} &= RT^2 \frac{d}{dT} \left[ \ln(\Phi N_{\text{avo}} \sigma \bar{v}_{\text{rel}}) - \frac{E_a}{RT} \right] \\ &= E_a + \frac{1}{2} RT. \end{aligned}$$

Here we used

$$\bar{v}_{\text{rel}} = \sqrt{\frac{8k_B T}{\pi \mu}}. \quad (5.11)$$

If  $RT \ll E_a$ , the apparent activation energy is equal to activation energy approximately.

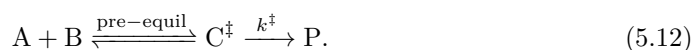
To be...

## 5.2 Solvent Effects

To be...

## 5.3 Transition State Theory

Transition state theory plays a pivot role in chemical rate theories. Let us start from the reaction mechanism,



The activated species (transition state)  $C^\ddagger$  is assumed to represent the saddle-point structure in reaction coordinates surface, which supports the normal-modes model analysis. Saddle-point in the potential surface indicates that  $C^\ddagger$  is a meta-stable structure along reaction-coordinate and the most stable in other paths.  $C^\ddagger$  reaches pre-equilibrium with reactants, and the rate-determination step is the second one.

The reaction rate could be easily evaluated from pre-equilibrium approximation, that is

$$k_r = k^\ddagger K_c^\ddagger, \quad (5.13)$$

where  $K_c^\ddagger = \frac{[C^\ddagger]_{\text{eq}}}{[A]_{\text{eq}}[B]_{\text{eq}}}$ . The rate constant  $k^\ddagger$  is just the rate at which the transition state yields products. The mode that  $C^\ddagger$  could become products must be the meta-stable one along reaction coordinate. Denote the frequency of this mode as  $\nu_r$ . Then  $k^\ddagger = \kappa\nu_r$ .  $\kappa$  is a parameter used to make a correction of  $\nu$  and is often assumed to equal to 1. In order to calculate the constant, we resort to the statistical mechanics to obtain the equilibrium constants.

For number equilibrium constant,

$$K_N = \frac{N_{C^\ddagger}}{N_A N_B} = \frac{q_{C^\ddagger}}{q_A q_B} e^{-\Delta E/RT}, \quad (5.14)$$

where  $N_i$  is the number of each molecule,  $q_i$  is the single-molecular partition function and  $\Delta E$  is the difference of zero-point energy. Thus,

$$K_c^\ddagger = \frac{[C^\ddagger]_{\text{eq}}}{[A]_{\text{eq}}[B]_{\text{eq}}} = N_{\text{avo}} \frac{q_{C^\ddagger}/V}{(q_A/V)(q_B/V)} e^{-\Delta E/RT}. \quad (5.15)$$

Recall the vibration partition function takes the form

$$q_{\text{vib}} = \frac{k_B T}{h\nu}. \quad (5.16)$$

Then we could separate the reaction degree of freedom from  $q_{C^\ddagger}$ , which means that  $q_{C^\ddagger} = \tilde{q}_{C^\ddagger} k_B T / h\nu_r$ . Then,

$$k_r = \kappa \frac{k_B T}{h} \tilde{K}_c^\ddagger, \quad (5.17)$$

where we denote

$$\tilde{K}_c^\ddagger = N_{\text{avo}} \frac{\tilde{q}_{C^\ddagger}/V}{(q_A/V)(q_B/V)} e^{-\Delta E/RT}. \quad (5.18)$$

To be...

## 5.4 RRKM Theory

The transition state theory only treats the normal-mode saddle-point case, which requires harmonic approximation. RRKM theory combines TST and RRK theory and provides us with a more effective method to calculate rate constant.

Consider the reaction mechanism



The first step shows that reactants R reach pre-equilibrium with transition state  $X^\ddagger$ . Then the transition state will yield products through some key modes. The ergodic property is assumed to be held in the process. Besides, the adiabatic approximation is required. The microcanonical rate constant  $k^\ddagger(\varepsilon)$  is given by

$$k^\ddagger(\varepsilon) = \frac{W^\ddagger(\varepsilon)}{h\rho(\varepsilon)}, \quad (5.20)$$

where  $W^\ddagger(\varepsilon)$  is the sum of states in transition states with energy  $\varepsilon \geq \varepsilon_a$  and  $\rho(\varepsilon)$  is the

density of states. Then, due to the equality  $\delta W(\varepsilon) = \delta\varepsilon \times \rho(\varepsilon)$ , then

$$k^\ddagger(\varepsilon) = \frac{\delta\varepsilon}{h} \cdot \frac{1}{\delta W(\varepsilon)} \cdot W^\ddagger(\varepsilon). \quad (5.21)$$

Here, we separate the expression into three parts. The first part corresponds to the reaction frequency  $\nu_r$  in TST, which means that all the modes in the energy interval  $\delta\varepsilon$  could contribute to the reaction rate. The second term accounts for the ergodicity, that is why we could use the conclusion of microcanonical ensemble. And the last term stands for the multiplicity of states.

Then the energy-independent rate constant is given by the canonical integral

$$k^\ddagger = \sigma \int_{\varepsilon_a}^{\infty} d\varepsilon k^\ddagger(\varepsilon) F(\varepsilon) = \sigma \int_{\varepsilon_a}^{\infty} d\varepsilon k^\ddagger(\varepsilon) \rho_s(\varepsilon) F_s(\varepsilon), \quad (5.22)$$

where  $\sigma$  is the number of paths to the same products. Consider the TST case, where  $\delta\varepsilon = h\nu$  and  $W^\ddagger(\varepsilon) = 1$ ,  $\delta W(\varepsilon) = 1$ . Then  $k^\ddagger(\varepsilon) = \nu$ , which is consistent with TST. In detail,

$$k_{\text{TST}}^\ddagger = \sigma \int_{\varepsilon_a}^{\infty} d\varepsilon \nu \beta e^{-\beta\varepsilon} = \sigma \nu e^{-\beta\varepsilon_a}. \quad (5.23)$$

## 5.5 Marcus' Electron Transfer Theory

It is notable that all the reaction rate theories mentioned above only deal with the rate in adiabatic representation. In the adiabatic representation, the energy potential surface is separated based on Born–Oppenheimer approximation, suggesting the Hamiltonian takes the diagonal form. The celebrated Marcus' electron transfer rate theory focuses on non-adiabatic representation, where the Hamiltonian takes the form

$$H_T = h_0|0\rangle\langle 0| + (h_1 + E^\circ)|1\rangle\langle 1| + V(|0\rangle\langle 1| + |1\rangle\langle 0|), \quad (5.24)$$

where  $|a\rangle$  ( $a = 0, 1$ ) stand for the state of donator or acceptor,  $h_a$  describe the solvation environment of donator and acceptor,  $E^\circ \simeq \Delta_r G$  is the standard reaction Gibbs energy and  $V$  is the coupling strength, assumed as a small quantity. The key issue of electron transfer process is the effect of solvation, which comes from the interaction of system's electronic state and environment. The environment is also characterized via canonical distribution,  $\rho_a^{\text{eq}} \equiv e^{-\beta h_a} / \text{tr} e^{-\beta h_a}$ , where  $\beta = k_B T$ . The initial state of total Hamiltonian is given by the density operator  $\rho_T(t_0) = \rho_0^{\text{eq}}|0\rangle\langle 0|$ . To describe the solvation process during the whole reaction, we define solvation coordinate as

$$U \equiv h_1 - h_0. \quad (5.25)$$

And also the solvation energy is also defined as

$$2\lambda \equiv \langle U \rangle_0 - \langle U \rangle_1 \equiv \text{tr}_0[U\rho_0^{\text{eq}}(T)] - \text{tr}_1[U\rho_1^{\text{eq}}(T)], \quad (5.26)$$

which is also called reorganization energy. Here the partial trace  $\text{tr}_a$  means that the corresponding degree of freedoms are reduced. It could be shown that  $\lambda > 0$ , thus  $\langle U \rangle_0 > 0$  and  $\langle U \rangle_1 < 0$ .

The other key point introduced by Marcus is the solvation thermodynamic potential mapping. The bath environments generate microscopic solvent potentials and all the potentials are projected onto solvation potentials  $\{u_a(U)\}_{a=0,1}$ . Thus the solvation coordinate



can be expressed as

$$U = u_1 - u_0. \quad (5.27)$$

Besides, due to the coordinate is linear, we could set

$$\langle U \rangle_0 = \lambda \quad (5.28)$$

and

$$\langle U \rangle_1 = -\lambda. \quad (5.29)$$

From another aspect, the fluctuation dissipation theorem tells us

$$\langle \delta U^2 \rangle_0 = \langle \delta U^2 \rangle_1 = 2k_B T \lambda. \quad (5.30)$$

All together give the solvation potential as

$$u_0(U) = \frac{1}{4\lambda}(U - \lambda)^2, \quad (5.31)$$

$$u_1(U) = \frac{1}{4\lambda}(U + \lambda)^2. \quad (5.32)$$

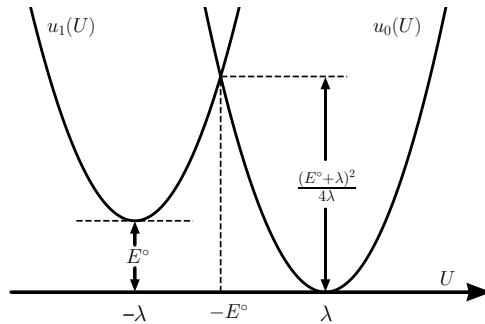
And the density follows

$$\rho_0(U) = \frac{1}{\mathcal{Z}} \exp \left[ -\frac{u_0(U)}{k_B T} \right], \quad (5.33)$$

with

$$\mathcal{Z} \equiv \int_{-\infty}^{\infty} dU e^{-\beta u_0(U)} = \sqrt{4\pi\lambda k_B T}. \quad (5.34)$$

All the relations are depicted in Fig. 1



**Figure 1.** Marcus' electron transfer plot.

The standard treatment of non-adiabatic electron transfer rate is the Fermi's Golden Rule (FGR) in the linear solvation scenario, where the time dependent perturbation theory is applied<sup>2</sup>, which gives the electron transfer rate as

$$k_{\text{ET}} = \frac{V^2/\hbar}{\sqrt{\lambda k_B T/\pi}} \exp \left[ -\frac{(E^0 + \lambda)^2}{4\lambda k_B T} \right]. \quad (5.35)$$

<sup>2</sup>The treatment could be found in appendix.

And it is remarkable that the result could also be obtained via RRKM analogue, where ergodicity assumption and solvation potentials are applied.

# Appendix

PART

III

## A Classical Mechanics Revision

The Newtonian equation of motion provides us a great way to calculate the motions in classical world. The problem of Newtonian motion is that it is a differential equation of vectors and the analyse of vectors is quite complex sometimes. Another trumps of classical mechanics are the Lagrange and Hamiltonian mechanics, which lays the foundation of analytical mechanics. Now we just give a simple glimpse on them.

The degree of freedoms of a system constituting with  $n$  freedom particles is  $3n$ . But in some cases, the inner constrains lower down the number of freedoms. If  $k$  constrains exist, the degree of freedoms  $s$  is  $3n - k$ . Then theoretically, we could choose  $s$  variables to describe the system, denotes as  $\{q_k\}_{k=1}^s$ . The  $s$  variables are called generalized coordinates, because for free particles,  $s = 3n$ , the chosen variables just are the Cartesian coordinates. The first order time derivative of  $q$  (In short, we use  $q$  to refer to  $\{q_k\}_{k=1}^s$  sometimes.) is the generalized velocity,  $\dot{q} = \{\dot{q}_i\} \equiv q'(t)$ . The equations of motion of  $q$  are the notable Lagrange equation,

$$\frac{d}{dt} \frac{\partial L}{\partial \dot{q}_i} - \frac{\partial L}{\partial q_i} = 0, \quad i = 1, 2, \dots, s. \quad (\text{A.1})$$

Here  $L$  is the Lagrangian, defined as  $L(q, \dot{q}, t) = T - V$ , with kinetic energy  $T$  and potential energy  $V$ . The equation is valid when only conservative forces exist. Define the generalized momenta

$$p_i \equiv \frac{\partial L}{\partial \dot{q}_i}, \quad (\text{A.2})$$

then

$$\frac{\partial L}{\partial q_i} = \dot{p}_i, \quad (\text{A.3})$$

which is similar to the Newton equation.

The Lagrangian is the function of  $q, \dot{q}$ . Then,

$$\begin{aligned} dL &= \sum_i \frac{\partial L}{\partial q_i} dq_i + \frac{\partial L}{\partial \dot{q}_i} d\dot{q}_i + \frac{\partial L}{\partial t} dt \\ &= \sum_i \dot{p}_i dq_i + p_i d\dot{q}_i + \frac{\partial L}{\partial t} dt. \end{aligned} \quad (\text{A.4})$$

If we are desired to transform the variables from  $q, \dot{q}$  to  $q, p$ , we could use the Legendre transformation. Define Hamiltonian as

$$H(q, p) = \sum_i p_i \dot{q}_i - L. \quad (\text{A.5})$$

Then,

$$dH = \sum_i \dot{q}_i dp_i - \dot{p}_i dq_i - \frac{\partial L}{\partial t} dt. \quad (\text{A.6})$$

Thus, we have a set of equations

$$\dot{q}_i = \frac{\partial H}{\partial p_i}, \quad (\text{A.7})$$

$$\dot{p}_i = -\frac{\partial H}{\partial q_i}, \quad (\text{A.8})$$

which are the Hamiltonian canonical equations. The space of  $q$  and  $p$  is called the phase space. The motion of a manifold in phase space is governed by Hamiltonian canonical equations.

For a given quantity  $A(p, q, t)$ , the time derivative of it is

$$\begin{aligned} \frac{dA}{dt} &= \sum_i \frac{\partial A}{\partial p_i} \dot{p}_i + \frac{\partial A}{\partial q_i} \dot{q}_i + \frac{\partial A}{\partial t} \\ &= \sum_i -\frac{\partial A}{\partial p_i} \frac{\partial H}{\partial q_i} + \frac{\partial A}{\partial q_i} \frac{\partial H}{\partial p_i} + \frac{\partial A}{\partial t}. \end{aligned} \quad (\text{A.9})$$

Define the Poisson bracket

$$\{A, B\} \equiv \frac{\partial A}{\partial q_i} \frac{\partial B}{\partial p_i} - \frac{\partial A}{\partial p_i} \frac{\partial B}{\partial q_i}. \quad (\text{A.10})$$

Then

$$\frac{dA}{dt} = \{A, H\} + \frac{\partial A}{\partial t}. \quad (\text{A.11})$$

If  $A$  does not contain  $t$  explicitly, then the statement that  $A$  is conservative is equivalent to  $\{A, H\} = 0$ . Note that

$$\{q_i, p_j\} = \delta_{ij}. \quad (\text{A.12})$$

In quantum mechanics, observables are all operators. One basic equality in quantum mechanics is

$$[q_i, p_j] \equiv q_i p_j - p_j q_i = i\hbar \delta_{ij}. \quad (\text{A.13})$$

The relation between quantum mechanics bracket and Poisson bracket is given by

$$\frac{[A, B]}{i\hbar} \longrightarrow \{A, B\}, \quad (\text{A.14})$$

as  $\hbar \rightarrow 0$ .

## B Review on Statistical Thermodynamics

The statistical mechanics establishes a way that connects microscopic states with macroscopic properties of a system. Through canonical ensemble, one could obtain the probability

that a macroscopic system is found at state  $\nu$  is given by

$$P_\nu = \frac{e^{-\beta E_\nu}}{Q}, \quad (\text{B.1})$$

where  $E_\nu$  is the corresponding energy and  $Q$  is the partition function, defined as

$$Q \equiv \sum_\nu e^{-\beta E_\nu}. \quad (\text{B.2})$$

The energy and microscopic states are given by the time-independent Schrödinger equation, that is

$$\hat{H}|\nu\rangle = E_\nu|\nu\rangle. \quad (\text{B.3})$$

Here  $\hat{H}$  is the Hamiltonian of the system.

For a system made up with  $N$  indistinguishable particles ( $N$  is a very large number,  $\sim 10^{23}$ ), the partition function could be separated as the product of single-particle partition functions, that is

$$Q = \frac{1}{N!} \prod_k q_k = \frac{q^N}{N!}. \quad (\text{B.4})$$

Here the factor  $1/N!$  comes from the consideration of the fact that particles are indistinguishable. The single-particle partition function is evaluated by the single-particle Hamiltonian  $\hat{h}$ . Here, we assume the particles are so dilute that the interactions between them are neglected. Therefore,

$$q = \sum_\alpha e^{-\beta \varepsilon_\alpha}, \quad (\text{B.5})$$

with

$$\hat{h}|\alpha\rangle = \varepsilon_\alpha|\alpha\rangle. \quad (\text{B.6})$$

For a molecule, the motion of it is made of translation, rotation and vibration, and each part corresponds to a specific Hamiltonian and complete microscopic states. Then the partition function could be expressed the product of each motion modes, which is

$$q = \prod_k q_k. \quad (\text{B.7})$$

For instance, consider that a non-linear molecule that has  $n$  atoms, then it has 3 translation freedoms, 3 rotation ones, and  $3n - 6$  vibration ones, and the partition function is <sup>3</sup>

$$q = \prod_{i=1}^3 q_i^{\text{trans}} \prod_{j=1}^3 q_j^{\text{rot}} \prod_{k=1}^{3n-6} q_k^{\text{vib}}. \quad (\text{B.8})$$

So in order to determine the partition function, one has to evaluate all the partition functions.

The most convenient way to evaluate the partition functions is do the integral in phase

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<sup>3</sup>The separation of different partition functions is not generally true. It is just a kind of approximation.

space. The partition function in phase space is given by

$$q = \frac{1}{(2\pi\hbar)^s} \int_{\Omega} d^s \vec{p} d^s \vec{q} e^{-\beta h(\vec{q}, \vec{p})}, \quad (\text{B.9})$$

where  $s$  is the degree of freedoms and  $\Omega$  is the volume in phase space.

## C Kinetic Theory of Perfect Gases

To be ...

## D From Langevin Equation to Diffusion Equation

### D.1 Langevin equation approach to diffusion

We use the Newtonian equation to describe the Brownian motion. Consider a spherical particle moving one dimensionally in a fluid environment with one random force  $\delta F(t)$ . The corresponding Newtonian equation reads

$$m\dot{v} = -\zeta v + \delta F(t). \quad (\text{D.1})$$

where the coefficient  $\zeta$  describes the friction, which is equal to  $6\pi\eta a$  with fluid's viscosity  $\eta$  and particle's radius  $a$  according to Stokes equation.  $\delta F(t)$  is introduced by Langevin firstly, and is treated as a kind of random variable that depends on time. Mathematically, such a thing is called as stochastic process.

The common view on the stochastic force is to suppose that it results from the occasional interactions between Brownian particle with the molecules in environment. Two assumptions are made here for random force.

$$\langle \delta F(t) \rangle = 0, \quad (\text{D.2})$$

$$\langle \delta F(t) \delta F(t') \rangle = 2B\delta(t - t'). \quad (\text{D.3})$$

It's an approximation that the force at time  $t$ , is completely independent of any other time, while in fact the random forces have a non-zero correlation time when the molecules collide. However, the Langevin equation is used to describe the motion of “macroscopic” particles over long time scales, and in such extreme cases the  $\delta$  correlation function and the Langevin equation are accurate.

The formal solution of Langevin equation is

$$v(t) = v(0)e^{-\zeta t/m} + \frac{1}{m} \int_0^t dt' e^{-\zeta(t-t')/m} \delta F(t'). \quad (\text{D.4})$$

And according to Eq. (D.2), one could know

$$\langle v(t) \rangle = \langle v(0) \rangle e^{-\zeta t/m}. \quad (\text{D.5})$$

Thus  $\lim_{t \rightarrow +\infty} \langle v(t) \rangle = 0$ . From  $v(t)$ , one could know

$$\begin{aligned} v^2(t) &= v^2(0)e^{-2\zeta t/m} + \frac{2v(0)e^{-\zeta t/m}}{m} \int_0^t dt' e^{-\zeta(t-t')/m} \delta F(t') \\ &\quad + \frac{1}{m^2} \int_0^t dt' \int_0^t dt'' e^{-2\zeta t/m} e^{\zeta(t'+t'')/m} \delta F(t') \delta F(t'') \end{aligned}$$

Then

$$\langle v^2(t) \rangle = \langle v^2(0) \rangle e^{-2\zeta t/m} + \frac{B}{m\zeta} (1 - e^{-2\zeta t/m}). \quad (\text{D.6})$$

Therefore,  $\lim_{t \rightarrow +\infty} \langle v^2(t) \rangle = \frac{B}{m\zeta}$ . When the system approaches the thermal equilibrium,  $\langle v^2(t) \rangle = \frac{k_B T}{m}$ , then

$$B = \zeta k_B T, \quad (\text{D.7})$$

which is the fluctuation-dissipation theorem.

## D.2 From Langevin to Fokker-Planck

Consider a set of variables  $\vec{a} = (a_1, a_2, \dots)$ , and the corresponding Langevin equation reads

$$\frac{d}{dt} a_i = v_i(\vec{a}) + F_i(t). \quad (\text{D.8})$$

Just like Eq. (D.2),

$$\langle \delta F_i(t) \rangle = 0, \quad (\text{D.9})$$

$$\langle \delta F_i(t) \delta F_j(t') \rangle = 2B_{ij} \delta(t - t'). \quad (\text{D.10})$$

Now we are going to looking for the probability distribution  $f(\vec{a}, t)$  of  $\vec{a}$  at each time  $t$ . The probability distribution satisfies

$$\int d\vec{a} f(\vec{a}, t) = 1. \quad (\text{D.11})$$

Consider the conservation law, which leads to the continuous equation

$$\frac{\partial}{\partial t} f(\vec{a}, t) + \frac{\partial}{\partial \vec{a}} \cdot [\dot{\vec{a}} f(\vec{a}, t)] = 0. \quad (\text{D.12})$$

Then

$$\begin{aligned} \frac{\partial}{\partial t} f(\vec{a}, t) &= -\frac{\partial}{\partial \vec{a}} \cdot [\dot{\vec{a}} f(\vec{a}, t)] \\ &= -\frac{\partial}{\partial \vec{a}} \cdot [\vec{v}(\vec{a}) f(\vec{a}, t) + \vec{F}(t) f(\vec{a}, t)]. \end{aligned}$$

Define operator

$$\mathcal{L}\phi \equiv \frac{\partial}{\partial \vec{a}} \cdot [\vec{v}(\vec{a})\phi]. \quad (\text{D.13})$$

Then, the dormal solution of  $f(\vec{a}, t)$  is

$$f(\vec{a}, t) = e^{-t\mathcal{L}} f(\vec{a}, 0) - \int_0^t dt' e^{-\mathcal{L}(t-t')} \frac{\partial}{\partial \vec{a}} \cdot [\vec{F}(t') f(\vec{a}, t')]. \quad (\text{D.14})$$

Therefore,

$$\begin{aligned} \frac{\partial}{\partial t} f(\vec{a}, t) = & -\mathcal{L}f(\vec{a}, t) - \frac{\partial}{\partial \vec{a}} \cdot [\vec{F}(t)e^{-t\mathcal{L}} f(\vec{a}, 0)] \\ & + \frac{\partial}{\partial \vec{a}} \cdot \left\{ \vec{F}(t) \int_0^t dt' e^{-\mathcal{L}(t-t')} \frac{\partial}{\partial \vec{a}} \cdot [\vec{F}(t') f(\vec{a}, t')] \right\}. \end{aligned} \quad (\text{D.15})$$

Take the average over noise. Then,

$$\frac{\partial}{\partial t} \langle f(\vec{a}, t) \rangle = -\frac{\partial}{\partial \vec{a}} \cdot [\vec{v}(\vec{a}) \langle f(\vec{a}, t) \rangle] + \frac{\partial}{\partial \vec{a}} \cdot \overleftrightarrow{B} \cdot \frac{\partial}{\partial \vec{a}} \langle f(\vec{a}, t) \rangle. \quad (\text{D.16})$$

This is so-called Fokker-Planck equation.

Then, let us go back to the Brownian motion. The Langevin equation is

$$m\ddot{x}(t) = -\zeta\dot{x}(t) - U'(x) + F_p(t). \quad (\text{D.17})$$

The corresponding Hamiltonian canonical equations are

$$\dot{x} = \frac{p}{m}, \quad (\text{D.18})$$

$$\dot{p} = -\zeta \frac{p}{m} - U'(x) + F_p(t). \quad (\text{D.19})$$

The random force satisfies

$$\langle F_p(t) F_p(t') \rangle = 2\zeta k_B T \delta(t - t'). \quad (\text{D.20})$$

Here  $\vec{a} = (x, p)$ ,

$$\vec{v}(\vec{a}) = \begin{pmatrix} p/m \\ -\zeta p/m - U'(x) \end{pmatrix}, \quad (\text{D.21})$$

and  $\vec{F}(t) = (0, F_p(t))$  with

$$\overleftrightarrow{B} = \begin{pmatrix} 0 & 0 \\ 0 & \zeta k_B T \end{pmatrix}. \quad (\text{D.22})$$

Then the F-P equation turns to be

$$\frac{\partial f}{\partial t} = -\frac{\partial f}{\partial x} \frac{p}{m} f + \frac{\partial}{\partial p} \left[ \frac{\zeta p}{m} + U'(x) f \right] + \zeta k_B T \frac{\partial^2 f}{\partial p^2}. \quad (\text{D.23})$$

with the approximation

$$\dot{x}(t) = -\frac{1}{\zeta} U'(x) + \frac{1}{\zeta} F_p(t). \quad (\text{D.24})$$

The corresponding F-P equation is

$$\frac{\partial f}{\partial t} = \frac{1}{\zeta} \frac{\partial}{\partial x} U'(x) f + \frac{k_B T}{\zeta} \frac{\partial^2 f}{\partial x^2}. \quad (\text{D.25})$$

That is the Smoluchowski equation. When  $U$  does not vary from  $x$ , Eq. (D.25) is exactly



the diffusion equation with the diffusion constant

$$D = \frac{k_B T}{\zeta}. \quad (\text{D.26})$$

As  $\zeta = 6\pi\eta a$ , it could be Einstein-Stokes equation. From

$$\frac{\partial}{\partial t} f(x, t) = D \frac{\partial^2}{\partial x^2} f(x, t), \quad (\text{D.27})$$

we could obtain

$$\begin{aligned} \frac{d}{dt} \langle x^2 \rangle &= \frac{d}{dt} \int_{-\infty}^{\infty} dx x^2 f(x, t) = \int_{-\infty}^{\infty} dx x^2 \frac{\partial}{\partial t} f(x, t) \\ &= D \int_{-\infty}^{\infty} dx x^2 \frac{\partial^2}{\partial x^2} f(x, t) = 2D. \end{aligned}$$

Then

$$\langle x^2 \rangle = 2Dt. \quad (\text{D.28})$$

## E Marcus' Electron Transfer Theory: the Fermi Golden Rule Approach

### E.1 Interaction Picture

Consider the system

$$\hat{H}(t) = \hat{H}_0 + \hat{H}'(t), \quad (\text{E.1})$$

whose Schrödinger equation reads

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = (\hat{H}_0 + \hat{H}'(t)) |\psi(t)\rangle. \quad (\text{E.2})$$

In the interaction picture,

$$i\hbar \frac{\partial |\psi(t)\rangle_I}{\partial t} = \hat{H}'_I(t) |\psi(t)\rangle_I, \quad (\text{E.3})$$

where  $|\psi(t)\rangle_I = e^{i\hat{H}_0 t/\hbar} |\psi(t)\rangle$  and  $\hat{H}'_I(t) = e^{i\hat{H}_0 t/\hbar} \hat{H}'(t) e^{-i\hat{H}_0 t/\hbar}$ . The formal solution of Eq. (E.3) is

$$|\psi(t)\rangle_I = |\psi(t_0)\rangle_I + \frac{1}{i\hbar} \int_{t_0}^t d\tau \hat{H}'_I(\tau) |\psi(\tau)\rangle_I. \quad (\text{E.4})$$

### E.2 Time-Dependent Perturbation Theory

Use the eigenfunction of  $\hat{H}_0$ , i.e.  $\hat{H}_0 |n\rangle = E_n^0 |n\rangle$ , and we have

$$\begin{aligned} |\psi(t)\rangle_I &= \sum_m c_m(t) |m\rangle, \\ |\psi(0)\rangle_I &= \sum_m c_m(0) |m\rangle. \end{aligned} \quad (\text{E.5})$$

The probability of the system collapses to  $|m\rangle$  at time  $t$ ,

$$P_m(t) = |c_m(t)|^2 = |\langle m|\psi(t)\rangle|^2. \quad (\text{E.6})$$

According to Eq. (E.4) and the completeness of  $\{|m\rangle\}$ , one could obtain

$$\begin{aligned} c_m(t) &= c_m(t_0) + \frac{1}{i\hbar} \int_{t_0}^t d\tau \langle m|\hat{H}'_I(\tau)|\psi(\tau)\rangle_I \\ &= c_m(t_0) + \sum_n \frac{1}{i\hbar} \int_{t_0}^t d\tau \langle m|e^{i\hat{H}_0\tau/\hbar} \hat{H}'(\tau) e^{-i\hat{H}_0\tau/\hbar} |n\rangle \langle n|\psi(\tau)\rangle_I \\ &= c_m(t_0) + \sum_n \frac{1}{i\hbar} \int_{t_0}^t d\tau \hat{H}'(\tau)_{mn} e^{i\omega_{mn}\tau} c_n(\tau), \end{aligned} \quad (\text{E.7})$$

where  $\omega_{mn} = (E_m(0) - E_n(0))/\hbar$ . If  $|\psi(t=0)\rangle = |l\rangle$ ,

$$c_{m,l}(t) = \delta_{m,l} + \sum_n \frac{1}{i\hbar} \int_{t_0}^t d\tau \hat{H}'(\tau)_{mn} e^{i\omega_{mn}\tau} c_{n,l}(\tau). \quad (\text{E.8})$$

For the first order approximation,  $c_{n,l}(\tau) = \delta_{n,l}$ , then

$$c_{m,l}(t) = \frac{1}{i\hbar} \int_{t_0}^t d\tau \hat{H}'(\tau)_{ml} e^{i\omega_{ml}\tau}. \quad (\text{E.9})$$

### E.3 Fermi Golden Rule

For the constant perturbation  $\hat{H}'$ , during the long enough time interval  $(-\frac{T}{2}, \frac{T}{2})$ , the transition rate from  $|n\rangle$  to  $|m\rangle$

$$\begin{aligned} p_{mn} &= \lim_{T \rightarrow \infty} \frac{P_{mn}}{T} = \lim_{T \rightarrow \infty} \frac{|\hat{H}'_{mn}|^2}{T\hbar^2} \cdot \left| \int_{-\frac{T}{2}}^{\frac{T}{2}} e^{i\omega_{mn}t} dt \right|^2 \\ &= \lim_{T \rightarrow \infty} \frac{|\hat{H}'_{mn}|^2}{T\hbar^2} \cdot T \cdot 2\pi\delta(\omega_{mn}) = \frac{2\pi}{\hbar^2} |\hat{H}'_{mn}|^2 \delta(\omega_{mn}), \end{aligned} \quad (\text{E.10})$$

which also reads

$$p_{mn} = \frac{2\pi}{\hbar} |\hat{H}'_{mn}|^2 \delta(E_m^{(0)} - E_n^{(0)}). \quad (\text{E.11})$$

### E.4 Marcus' Electron Transfer Theory

For the electron transferring from the donor ( $|0\rangle$ , reactant) to the acceptor ( $|1\rangle$ , product) state, the minimum model for the total ET composite Hamiltonian assumes

$$H_{ET} = h_0|0\rangle\langle 0| + (E^\circ + h_1)|1\rangle\langle 1| + V(|1\rangle\langle 0| + |0\rangle\langle 1|), \quad (\text{E.12})$$

In the linear solvation scenarios, the solvation coordinate  $X$  is

$$X = U \equiv h_1 - h_0, \quad (\text{E.13})$$

The reorganization energy

$$\lambda = \langle U \rangle_0 = -\langle U \rangle_1 > 0 \quad (\text{E.14})$$

and

$$\begin{aligned} u_0(U) &= \frac{1}{4\lambda}(U - \lambda)^2, \\ u_1(U) &= \frac{1}{4\lambda}(U + \lambda)^2. \end{aligned} \tag{E.15}$$

According to Eq. (E.11), the FGR rate formula reads

$$k = \frac{2\pi V^2}{\hbar} \langle \delta(u_1(U) - u_0(U) + E^\circ) \rangle, \tag{E.16}$$

Together with  $\rho_0(U) = e^{-\beta u_0(U)} / \sqrt{4\pi\lambda k_B T}$ , we know

$$\begin{aligned} k &= \frac{2\pi V^2}{\hbar} \frac{1}{\sqrt{4\pi\lambda k_B T}} \int dU \delta(u_1(U) - u_0(U) + E^\circ) e^{-\beta u_0(U)} \\ &= \frac{V^2 \hbar}{\sqrt{\lambda k_B T / \pi}} \exp \left[ -\frac{(E^\circ + \lambda)^2}{4\lambda k_B T} \right], \end{aligned} \tag{E.17}$$

which is exactly the celebrated Marcus' non-adiabatic electron transfer rate.