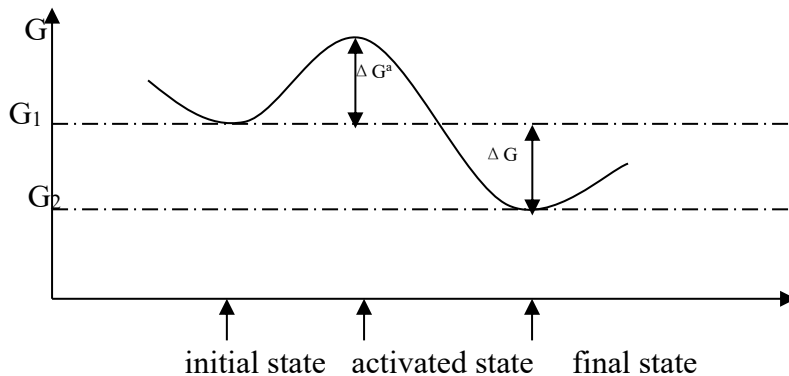


Lecture 2: Kinetics: as described as transformation rate between two equilibrium states

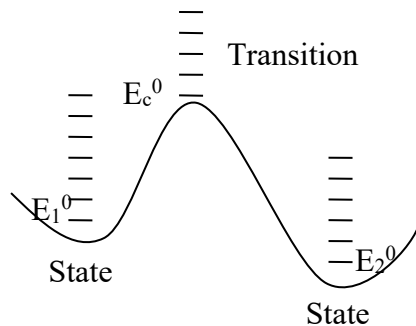
Today's topics

- As we learned in last Lecture: $\text{Rate} \propto (\text{Kinetic factor}) \times (\text{Thermodynamic factor})$. In this Lecture we will further describe this relationship in more analytical way, assuming a process going from one state to another (via passing through a transition state), which are all defined as quantized energy states.
- The number of particles distributed over the quantized levels will be described using the Boltzmann equation.
- Understand thermodynamic controlled process vs. kinetic controlled process, and how the transformation rate between two equilibrium states depends on the two key parameters, Gibbs free energy change or driving force (ΔG) and activation energy (ΔG_A).
- Under the kinetic controlled process, understand how the rate depends on temperature following the Arrhenius equation.

In last lecture, we talked about the difference and inter-relationship between Kinetics and Thermodynamics, and how to use the two concepts to describe the chemical reactions or materials transformations, regarding transition state, driving force, activation energy as illustrated in this diagram:



Now, let us assume the system in all states (initial, transition, and final) to be modeled by a linear harmonic oscillator.



The energy at different levels ($i = 0, 1, 2, 3 \dots$) is thus quantized, and can be written as

$$E^i = (i + 1/2) h\nu, \quad i = 0, 1, 2, \dots$$

where h is the Planck constant, and ν is the vibrational frequency.

When $T=0$, all frozen to the lowest level ($i=0$), then

$$E^0 = 1/2 h\nu \text{ --- the zero point of energy.}$$

Now,

$$E^i = E^0 + i h\nu$$

For the three states as illustrated above, state 1, state 2 and transition state, we have

$$E_1^i = E_1^0 + i h\nu_1$$

$$E_2^i = E_2^0 + i h\nu_2$$

$$E_c^i = E_c^0 + i h\nu_c$$

Now, for particles to go from state 1 to 2, they must have energy in excess of E_c^0 .

Using the Boltzmann distribution, the fractional number of particles in *state 1* having energy in excess of E_c^0 is given by

$$\frac{n_1(c)}{N_1} = \frac{e^{-E_c^0/KT} + e^{-(E_c^0+h\nu_1)/KT} + e^{-(E_c^0+2h\nu_1)/KT} + \dots}{e^{-E_1^0/KT} + e^{-(E_1^0+h\nu_1)/KT} + e^{-(E_1^0+2h\nu_1)/KT} + \dots}$$

$$\frac{n_1(c)}{N_1} = \frac{e^{-E_c^0/KT} (1 + e^{-h\nu_1/KT} + e^{-2h\nu_1/KT} + \dots)}{e^{-E_1^0/KT} (1 + e^{-h\nu_1/KT} + e^{-2h\nu_1/KT} + \dots)}$$

$$= e^{-(E_c^0 - E_1^0)/KT} \dots \dots \dots (1) \quad \text{Boltzmann factor}$$

where K stands for Boltzmann constant.

Similarly, the fraction number of atoms in state 2 having energy in excess of E_c^0 is

$$\frac{n_2(c)}{N_2} = e^{-(E_c^0 - E_2^0)/KT} \dots\dots\dots (2)$$

$$\frac{n_1(c)}{N_1} \text{ --- (thermodynamic) probability for system to go from 1 to 2}$$

$$\frac{n_2(c)}{N_2} \text{ --- (thermodynamic) probability for system to go from 2 to 1}$$

Thus, the net forward process rate is

$$\text{Rate} \propto \frac{n_1(c)}{N_1} - \frac{n_2(c)}{N_2} \propto e^{-(E_c^0 - E_1^0)/KT} - e^{-(E_c^0 - E_2^0)/KT}$$

Then,

$$\begin{aligned} \text{Rate} &= c \cdot \{ e^{-(E_c^0 - E_1^0)/KT} - e^{-(E_c^0 - E_2^0)/KT} \} \\ &= c \cdot e^{-(E_c^0 - E_1^0)/KT} \{ 1 - e^{-(E_1^0 - E_2^0)/KT} \} \end{aligned}$$

Note that for rate >0, (i.e., the process going from 1 to 2)

Then, the term $1 - e^{-(E_1^0 - E_2^0)/KT}$ must be > 0.

Lets define $\Delta u^A = E_c^0 - E_1^0$ as the activation energy.

$\Delta u = E_2^0 - E_1^0$ as the change in internal energy from 1 to 2

Then, for rate >0, we must have $\Delta u = E_2^0 - E_1^0 < 0$ (i.e., negative energy change)

Now,

$$\text{Rate} = c \cdot e^{-\Delta u^A / KT} \{ 1 - e^{\Delta u / KT} \}$$

kinetic thermo
factor factor

The constant c is proportional to the vibrational frequency, ν

Recall what we learned in last Lecture: Rate \propto (Kinetic factor) \times (Thermodynamic factor)

Now lets consider two extreme situations:

1). If $|\Delta u| \ll KT$, then $e^{\Delta u / KT} \cong 1 + \frac{\Delta u}{KT}$

Then,

$$\text{Rate} \cong c \cdot e^{-\Delta u^A / KT} \left[-\frac{\Delta u}{KT} \right] \cong c \cdot e^{-\Delta u^A / KT} \left| \frac{\Delta u}{KT} \right| \quad (\text{since } \Delta u < 0, \text{ see above})$$

--- thermo controlled process, with small energy change.

2). If $|\Delta u| \gg KT$, then $e^{\Delta u / KT} \ll 1$ ($\Delta u < 0$)

Then,

$$\text{Rate} \cong c \cdot e^{-\Delta u^A / KT}$$

--- kinetic controlled process, with large energy change, highly favorable

In such a case, only kinetic factor is important. In other words, the reverse rate is negligible and the net forward rate equals the forward rate.

In general, at constant P, T, we use Gibbs energy (G) to replace the internal energy (u), and K can be replaced with R, the gas constant, $8.314 \text{ J} \cdot \text{mole}^{-1} \text{ K}^{-1}$, with the unit per mole, then, we have

$$\text{Rate} = c \cdot e^{-\Delta G_A / RT} \left| \frac{\Delta G}{RT} \right|, \quad \text{for } |\Delta G| \ll RT, \quad \text{--- thermo controlled process}$$

$$\text{Rate} = c \cdot e^{-\Delta G_A / RT}, \quad \text{for } |\Delta G| \gg RT, \quad \text{--- kinetic controlled process}$$

Note: For the *kinetic controlled process*, the rate equation becomes the **Arrhenius rate equation**, as learned from last lecture.

Additional reading:

Helmholtz free energy (F): In thermodynamics, the Helmholtz free energy is a thermodynamic potential which measures the “useful” work obtainable from a *closed* thermodynamic system at a *constant temperature and volume*. For such a system, the negative of the difference in the Helmholtz energy is equal to the maximum amount of work extractable from a thermodynamic process in which temperature and volume are held constant. Under these conditions, it is

minimized at equilibrium. The Helmholtz free energy was developed by Hermann von Helmholtz and is usually denoted by the letter A (from the German “Arbeit” or work).

$$F = U - TS$$

where: U is the internal energy, S the entropy, T is the absolute temperature

Gibbs free energy (G): In thermodynamics, the Gibbs free energy is a thermodynamic potential that measures the "useful" or process-initiating work obtainable from an *isothermal, isobaric thermodynamic system*. When a system changes from a well-defined initial state to a well-defined final state, the Gibbs free energy ΔG equals the work exchanged by the system with its surroundings, minus the work of the pressure forces, during a reversible transformation of the system from the same initial state to the same final state.

$$G(p,T) = H - TS = U + pV - TS$$

where: U is the internal energy (SI unit: joule), p is pressure (SI unit: pascal), V is volume (SI unit: m³), T is the absolute temperature (SI unit: kelvin), S is the entropy (SI unit: joule per kelvin), H is the enthalpy (SI unit: joule).

Compared to the Helmholtz free energy, the *isobaric* restriction on Gibbs free energy is inconvenient for some applications. For example, in explosives research, Helmholtz free energy is often used since explosive reactions by their nature induce pressure changes. On the other hand, Gibbs energy is often defined as the chemical potential that is minimized when a system reaches equilibrium at *constant pressure and temperature*. As such, it is a convenient criterion of spontaneity for processes with constant pressure and temperature.

The Gibbs free energy is given by $G = H - TS$, where H is the enthalpy, T is the absolute temperature, and S is the entropy. $H = U + pV$, where U is the internal energy, p is the pressure, and V is the volume. G is the most useful for processes involving a system at constant pressure p and temperature T, because, in addition to subsuming any entropy change due merely to heat, a change in G also excludes the p dV work needed to "make space for additional molecules" produced by various processes. Gibbs free energy change therefore equals work not associated with system expansion or compression, at constant temperature and pressure.

--- https://en.wikipedia.org/wiki/Thermodynamic_free_energy