

# Physical Chemistry for Energy Engineering (16<sup>th</sup>: 2018/11/12)

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\*The class follows the text book: D.A. McQuarrie, J.D. Simon, "Physical Chemistry: A Molecular Approach", University Science Books (1997).

# Course schedule (as of Nov. 5)

Deadline for appealing on exam-1 result: Nov. 12

Submission time of the homework-2: beginning of the class on Nov. 12.

	29-Oct	No lecture
	31-Oct	
14	5-Nov	2. Phase equilibrium-1
15	7-Nov	2. Phase equilibrium-2
16	12-Nov	3. Chemical equilibrium-1
17	14-Nov	Answers of homework-2
18	19-Nov	Exam-02 (2 hour)
19	21-Nov	3. Chemical equilibrium-2
20	26-Nov	3. Chemical equilibrium-3
21	28-Nov	3. Chemical equilibrium-4
22	3-Dec	3. Chemical kinetics-1
23	5-Dec	3. Chemical kinetics-2
24	10-Dec	3. Chemical kinetics-3
25	12-Dec	Answers of homework-3
26	17-Dec	Exam-03 (2 hour)

# Contents of today

## <Last class>

- 2.3. Phase equilibrium-1: a typical case (1 component)
  - 2.3.1. Chemical potential and phase rule

## <Today's class>

- 2.3. Phase equilibrium-1: a typical case (1 component)
  - 2.3.1. Chemical potential and phase rule
  - 2.3.2. Freezing mechanism
- 3.1. Chemical equilibrium for gases

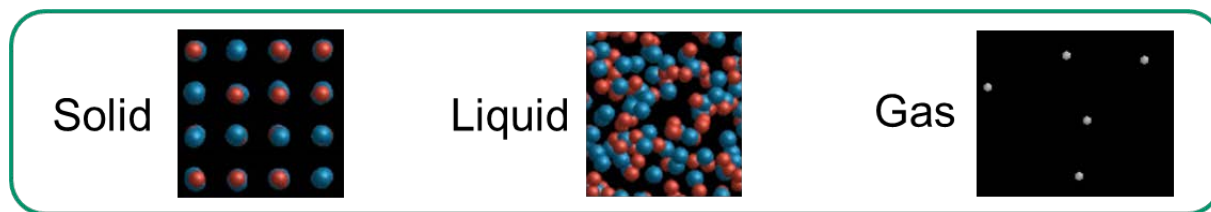
## (Review) 2.3. Phase equilibrium-1: a typical case (1 component)

- \$23-2: The Gibbs energy of a substance has a close connection to its phase diagram -

- ✓ As we have learned, the (molar) Gibbs energy indicates which state (phase) appears at equilibrium under constant-T constant-P condition.
  - ✓ Be careful that a smaller Gibbs energy means more stable.
- ✓ As  $G = H - TS$  ( $\bar{G} = \bar{H} - T\bar{S}$ ), the enthalpy term ( $H$ ) plays a dominant role at low temperatures, while the entropy term ( $-TS$ ) at high temperatures.
- ✓ In comparison of gas/liquid/solid phases, as we have learned:

$$\bar{S}^g \gg \bar{S}^l > \bar{S}^s (\geq 0) \quad (\text{due to disorder})$$

$$\Delta_f H^g > \Delta_f H^l > \Delta_f H^s \quad (\text{due to bonding nature})$$



- ✓  $\left(\frac{\partial G}{\partial T}\right)_P = -S$  and  $\left(\frac{\partial G}{\partial P}\right)_T = V$

## (Review) 2.3. Phase equilibrium-1: a typical case (1 component)

- §23-3: The chemical potentials of a pure substance in two phases in equilibrium are equal -

We consider a system consisting of two phases of a pure substance (1-component) in equilibrium each other. (liquid and gas, for example here)

$$dG = [\mu^g - \mu^l]dn^g \quad (\text{constant } T \text{ and } P)$$

where *chemical potentials* are  $\mu^g = \left(\frac{\partial G^g}{\partial n^g}\right)_{P,T}$  and  $\mu^l = \left(\frac{\partial G^l}{\partial n^l}\right)_{P,T}$ .

- ✓ If the two phases are in equilibrium with each other, then  $dG = 0$ .
- ✓ And because we suppose some amount of the liquid phase is transferred to the gas phase ( $dn^g$ ) here, to make  $dG = 0$  in this condition,  $\mu^g = \mu^l$  is needed.
  - If  $\mu^g < \mu^l$ ,  $[\mu^g - \mu^l] < 0$ . Thus, the process of  $dn^g > 0$  (transfer from the liquid phase to the gas phase) spontaneously takes place as  $dG < 0$  is achieved by the transfer.
  - Likewise, if  $\mu^g > \mu^l$ ,  $dn^g < 0$ .
  - Hence, in general, the mass transfer occurs from the phase with higher chemical potential to the phase with lower chemical potential.

## 2.3.1. Chemical potential and phase rule

### - theoretical background of Gibbs' phase rule -

<(Gibbs') phase rule> The degree of freedom (of intensive properties)  $f$  is described as:  $f = c - p + 2$ , where  $c$  is the number of components,  $p$  is the number of phase that coexist at equilibrium at that point.

- ✓ If 1 component and 1 phase,  $f = 1 - 1 + 2 = 2$ . It means we need to set 2 thermodynamic quantities (intensive, such as T and P) to specify the state.
- ✓ If 1 component and 2 phases (e.g. gas and liquid for water),  $f = 1 - 2 + 2 = 1$ . The reduction of the freedom is due to an additional condition in chemical potential:  $\mu^g = \mu^l$ .

We consider a system consisting of two phases of a pure substance (1-component) in equilibrium each other. (liquid and gas, for example here)

$$dG = [\mu^g - \mu^l]dn^g \quad (\text{constant T and P})$$

where *chemical potentials are*  $\mu^g = \left(\frac{\partial G^g}{\partial n^g}\right)_{P,T}$  and  $\mu^l = \left(\frac{\partial G^l}{\partial n^l}\right)_{P,T}$ .

At an equilibrium,  $\mu^g = \mu^l$  is needed to achieve  $dG = 0$ .

\*Because the chemical potential is molar Gibbs energy at const.-P const.-T condition, " $G = G(n, P, T)$ " & " $\mu = \frac{G}{n} = \mu(P, T)$ ", it is an intensive quantity, though Gibbs energy is an extensive quantity.

## 2.3.1. Chemical potential and phase rule

### - theoretical background of Gibbs' phase rule -

<(Gibbs') phase rule> The degree of freedom (of intensive properties)  $f$  is described as:  $f = c - p + 2$ , where  $c$  is the number of components,  $p$  is the number of phase that coexist at equilibrium at that point.

- ✓ If 2 components and 1 phase,  $f = 2 - 1 + 2 = 3$ . It means we need to set 3 thermodynamic quantities (e.g. T, P and molar fraction) to specify the state.
  - ✓ Normally to determine a state, we need to fix 3 quantities: for example,  $n, T, P$ .
  - ✓ If 2 components exist, we need to specify the amount of each specie. Then, not " $n$ " ( $= n_1 + n_2$ ), but " $n_1$  and  $n_2$ " may be needed.
  - ✓ However, the phase equilibrium between multiple phases are governed by chemical potential, not by Gibbs energy. And chemical potential does not depend on the amount (in mole), as it is an intensive quantity.
  - ✓ Hence, not " $n_1$  and  $n_2$ ", but their relation is enough for evaluating chemical potential. Their relation is given by molar fraction.
    - ✓  $x_1 = \frac{n_1}{n_1+n_2}$  and  $x_2 = \frac{n_2}{n_1+n_2} = 1 - x_1$ . Then only 1 variable " $x_1$ ", is independent.
- ✓ As a result, " $f = 3$ " (not " $f = 4$ ") is proved as the degree of freedom to specify the state of "2-components and 1-phase system". Note that all of them are intensive properties.

## 2.3.1. Chemical potential and phase rule

### - theoretical background of Gibbs' phase rule -

<(Gibbs') phase rule> The degree of freedom (of intensive properties)  $f$  is described as:  $f = c - p + 2$ , where  $c$  is the number of components,  $p$  is the number of phase that coexist at equilibrium at that point.

More clearly written, it becomes:  $f = \underbrace{2}_{(1)} + \underbrace{(c - 1)p}_{(2)} - \underbrace{(p - 1)c}_{(3)} = c - p + 2$

- ✓ (1) the equilibrium of multiple phase is determined by chemical potential (molar Gibbs energy for const.-P const.-T condition). And as chemical potential is intensive quantity and expressed as  $\mu = \mu(P, T)$ , 2 quantities are enough to determine it. (\*If extensive, 3 quantities are needed, e.g.  $n$  in addition)
- ✓ (2) if multiple component, we need to know how many amount is for each component for each phase. However, again, as the chemical potential is intensive, we do not need to know the absolute amount: compositions (specified by "molar fraction") are enough. The number of independent molar fractions is  $(c - 1)$  for each phase, then  $(c - 1)p$  for all:
  - ✓ if  $c = 1$ , it becomes 0 for each phase, because the molar fraction is always  $x_1 = 1$ .
  - ✓ If  $c = 2$ , it becomes 1 for each phase, because  $x_1 = \frac{n_1}{n_1+n_2}$  &  $x_2 = \frac{n_2}{n_1+n_2} = 1 - x_1$ . If 2 phases, we need another  $x'_1$  for the 2<sup>nd</sup> phase.



## 2.3.1. Chemical potential and phase rule - theoretical background of Gibbs' phase rule -

<**(Gibbs') phase rule**> The degree of freedom (of intensive properties)  $f$  is described as:  $f = c - p + 2$ , where  $c$  is the number of components,  $p$  is the number of phase that coexist at equilibrium at that point.

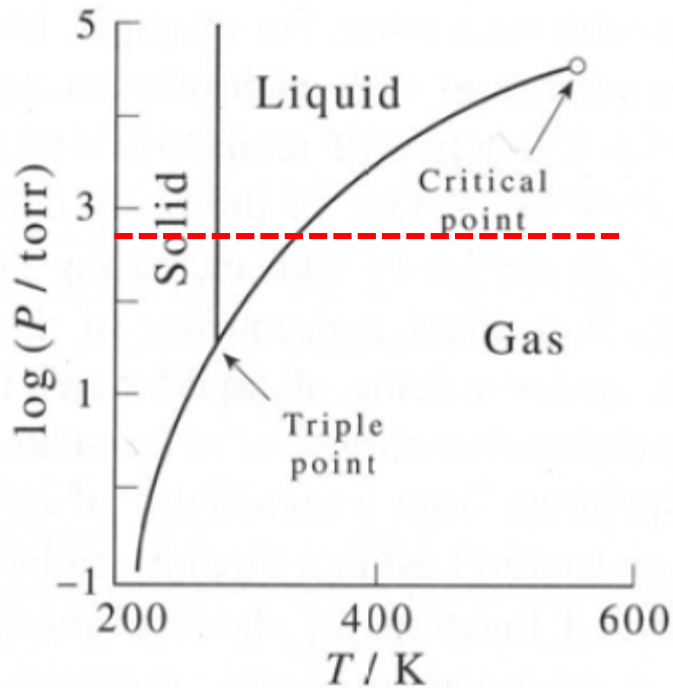
More clearly written, it becomes:  $f = \underbrace{2}_{(1)} + \underbrace{(c - 1)p}_{(2)} - \underbrace{(p - 1)c}_{(3)} = c - p + 2$

- ✓ (3) This is due to the number of constraints in chemical potential for equilibrium states. The number of constraints is  $(p - 1)$  for each **component**, then  $(p - 1)c$  for all:
  - ✓ If 2 phases coexist ( $p = 2$ ) for 1-component system ( $c = 1$ ),  $(p - 1)c$  becomes 1, because  $\mu_1 = \mu_2$ .
  - ✓ If 3 phases coexist ( $p = 3$ ) for 1-component system ( $c = 1$ ),  $(p - 1)c$  becomes 2, because  $\mu_1 = \mu_2 = \mu_3$ .
  - ✓ If 3 phases coexist ( $p = 3$ ) for 2-component system ( $c = 2$ ),  $(p - 1)c$  becomes 4, because  $\mu_1 = \mu_2 = \mu_3$  for 1 component and  $\mu'_1 = \mu'_2 = \mu'_3$  for another component.

## 2.3.1. Chemical potential and phase rule - theoretical background of Gibbs' phase rule -

<(Gibbs') phase rule> The degree of freedom (of intensive properties)  $f$  is described as:  $f = c - p + 2$ , where  $c$  is the number of components,  $p$  is the number of phase that coexist at equilibrium at that point.

*The phase diagram of benzene  
(P is in logarithm)*

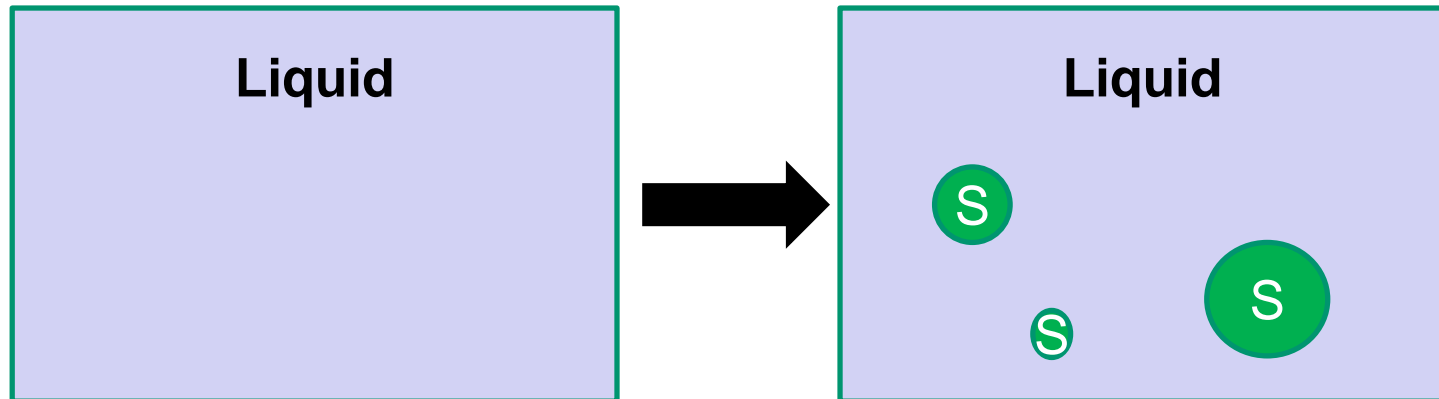


- (1) If we look at the region of liquid phase, the phase rule indicates  $f=2$  as  $c = 1$  and  $p = 1$ . This is reasonable because, for example, even if we set  $T = 400$  K, the pressure is not fully determined: there still is a degree of freedom for  $P$ .
- (2) If we look at the liquid-gas coexistence curve, the phase rule indicates  $f=1$  as  $c = 1$  and  $p = 2$ . This is reasonable because, for example, if we set  $T = 400$  K, the pressure is fully determined: thus, there is no degree of freedom for  $P$ .
- (3) If we look at the triple point,  $f=0$  as  $c = 1$  and  $p = 3$ . This is reasonable because the pressure and temperature are unique: thus, there is no degree of freedom for both  $T$  and  $P$ .

## 2.3.2. Freezing mechanism

### - realistic phenomena in the beginning of freezing process-

- ✓ In the beginning of freezing process, some small solids are formed in liquid phase.
- ✓ When a solid phase is partly formed in liquid phase, boundaries between solid and liquid regions emerge.
- ✓ Such boundaries have **an interface energy** (which is normally  $>0$ ), and thus the total energy (internal energy) of the system is increased. Hence, freezing process contain 2 phenomena to change the internal energy (and free energy).
  - [Interface energy] To increase the energy, which means the formation of interface due to the formation of solid is not energetically favorable.
  - [Energy by phase transition from liquid to solid] To increase or decrease the energy, according to the temperature.



## 2.3.2. Freezing mechanism

### - realistic phenomena in the beginning of freezing process-

- ✓ Here, we consider that a spherical solid region is formed in the liquid. Then, we assume that “per-volume Gibbs energy gain” due to the formation of the solid phase is  $\Delta G_v$  (defined as a gain, not as a difference), then:

$$\Delta G_{\text{phase-transition}} = \frac{4}{3}\pi r^3 \Delta G_v$$

- the per-volume Gibbs energy gain is almost equal to per-mole Gibbs energy gain (chemical potential when constant P,V), because the volumes of liquid and solid are comparable each other.

$$\Delta G_v \sim \alpha (\bar{G}^s - \bar{G}^l)$$

where  $\alpha$  [mol/m<sup>3</sup>] is a constant proportional to the density [kg/m<sup>3</sup>].

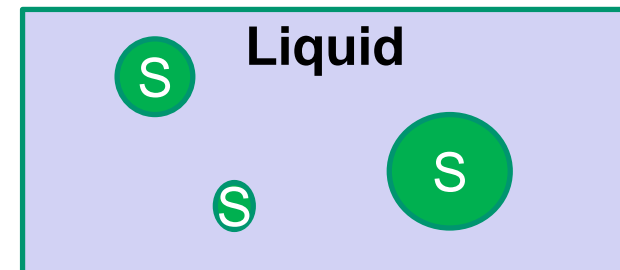
- Below the melting point,  $\Delta G_v < 0$  (energy decrease by transition to solid)

- ✓ In addition, the Gibbs energy change due to the formation of solid-liquid interface is:  $\Delta G_{\text{interface}} = 4\pi r^2 \gamma$

where we assume that per-area interface energy is  $\gamma$  (always  $\gamma > 0$ ).

- ✓ Accordingly, the Gibbs energy change in the system is:

$$\begin{aligned} \Delta G &= \Delta G_{\text{phase-transition}} + \Delta G_{\text{interface}} \\ &= \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma \end{aligned}$$



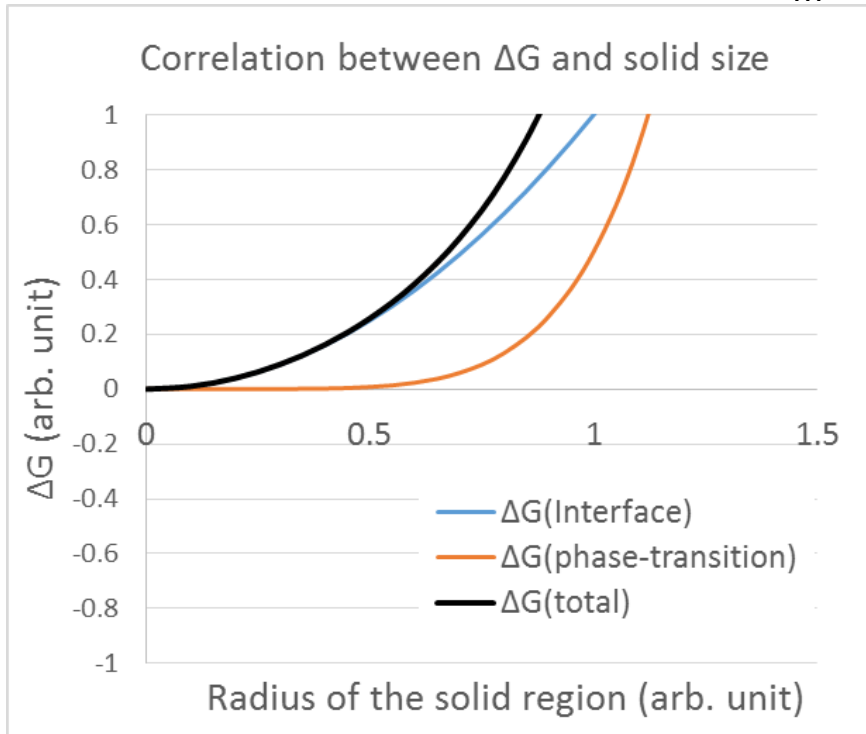
## 2.3.2. Freezing mechanism

### - realistic phenomena in the beginning of freezing process-

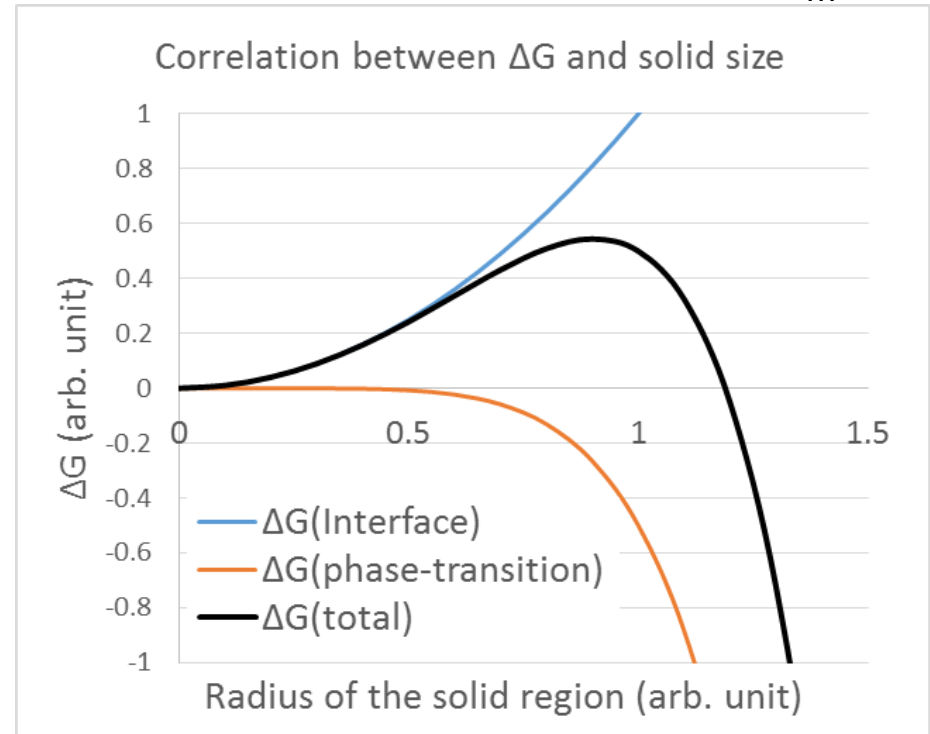
$$\Delta G = \Delta G_{\text{phase-transition}} + \Delta G_{\text{interface}} = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma$$

- Always  $\gamma > 0$  thus  $\Delta G_{\text{interface}} > 0$ .
- If above the melting point ( $T > T_m$ ),  $\Delta G_v > 0$  and  $\Delta G_{\text{phase-transition}} > 0$ . Thus,  $\Delta G > 0$  is always achieved,
- If below the melting point ( $T < T_m$ ),  $\Delta G_v < 0$  then  $\Delta G_{\text{phase-transition}} < 0$ . Thus,  $\Delta G < 0$  may be achieved at some conditions.

Above the melting point ( $T > T_m$ )



Below the melting point ( $T < T_m$ )



## 2.3.2. Freezing mechanism

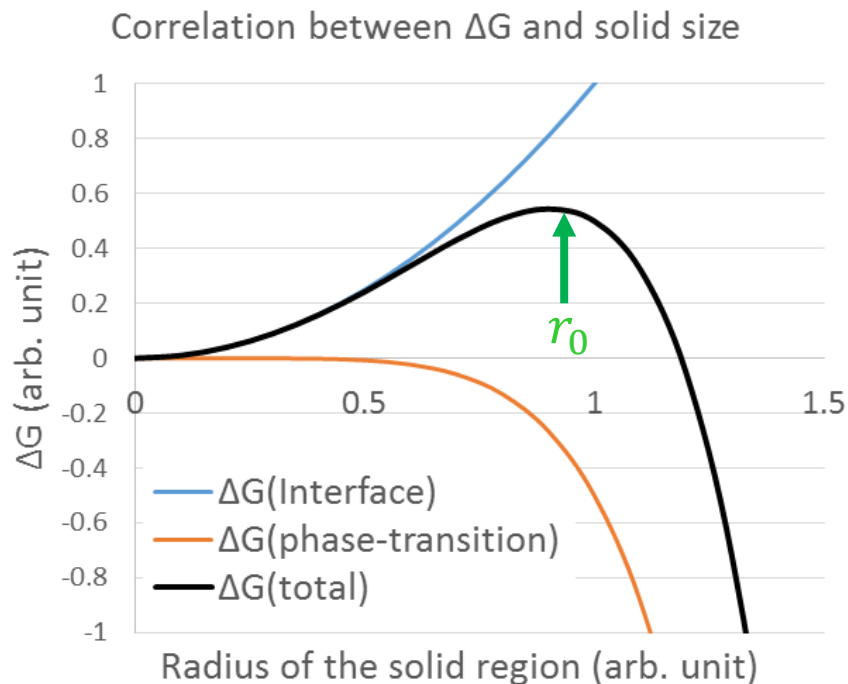
### - realistic phenomena in the beginning of freezing process-

✓ Accordingly, the Gibbs energy change in the system is:

$$\Delta G = \Delta G_{\text{phase-transition}} + \Delta G_{\text{interface}} = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma$$

- Always  $\gamma > 0$  thus  $\Delta G_{\text{interface}} > 0$ .
- If above the melting point,  $\Delta G_v > 0$  and  $\Delta G_{\text{phase-transition}} > 0$ .
- If below the melting point,  $\Delta G_v < 0$  and  $\Delta G_{\text{phase-transition}} < 0$ .

Below the melting point ( $T < T_m$ )



✓ There is a radius above which the solid spontaneously grows. This radius is called the “critical radius (of nucleation)”.

✓ To find it, taking derivative: as

$$\frac{d(\Delta G)}{dr} = 4\pi r^2 \Delta G_v + 8\pi r \gamma$$

✓ The condition “ $\frac{d(\Delta G)}{dr} = 0$ ” gives the critical radius of nucleation ( $r_0$ ):

$$\frac{d(\Delta G)}{dr} = 4\pi r_0^2 \Delta G_v + 8\pi r_0 \gamma = 0$$

$$\text{Thus } r_0 = -2\gamma / \Delta G_v$$

## 2.3.2. Freezing mechanism

### - realistic phenomena in the beginning of freezing process-

- ✓ Accordingly, the Gibbs energy change in the system is:

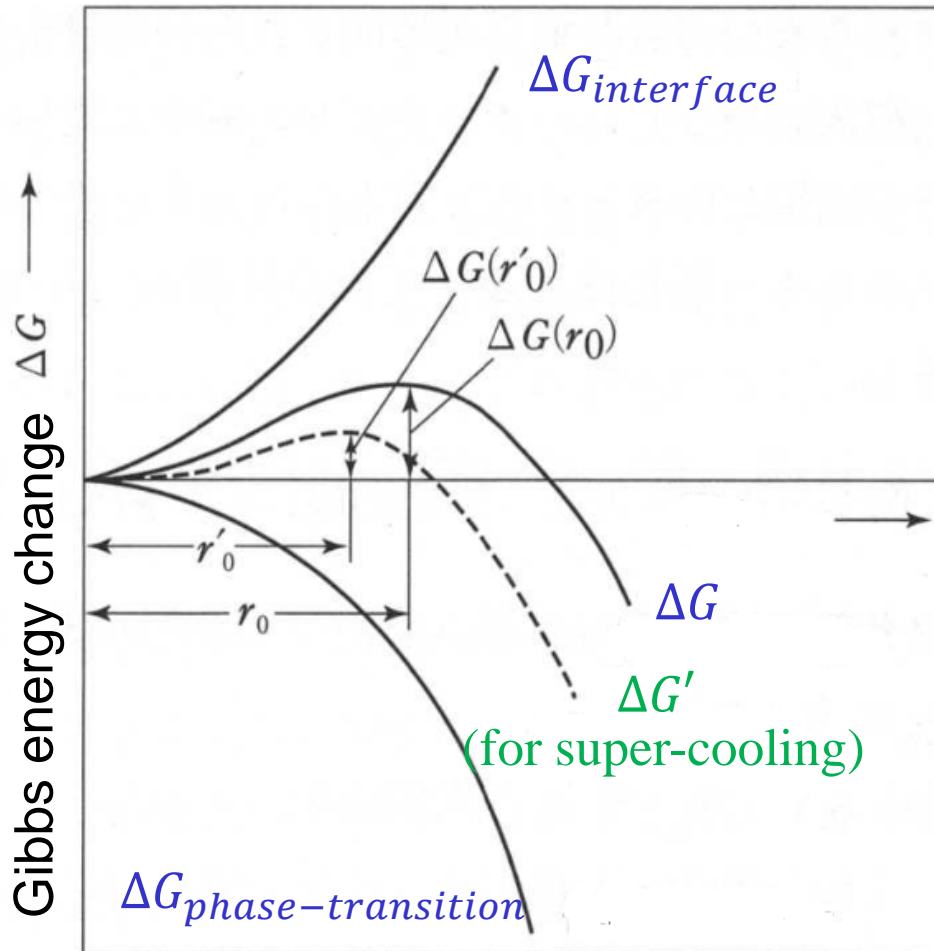
$$\Delta G = \Delta G_{interface} + \Delta G_{phase-transition} = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma$$

- ✓ In this case, a solid phase whose effective radius is smaller than  $r_0$  is called “embryo” while that larger than  $r_0$  is called “nucleus”.
- ✓ To achieve  $\frac{d(\Delta G)}{dr} = 0$ ,  $\Delta G_v$  ( $\Delta G_v \sim \alpha(\bar{G}^s - \bar{G}^l)$ , the Gibbs energy gain by phase transition from liquid to solid) must be negative because  $\gamma$  (interface energy) is always  $\gamma > 0$ .
  - ✓  $\Delta G_v < 0$  is achieved at temperatures below the melting point. Thus, the nucleation (as freezing process) can take place only below the melting point.
- ✓ This kind of model is also important when we consider the growth of defects in nuclear materials.
  - ✓ The size of solid in liquid  $\rightarrow$  the size of defect clusters in crystal

## 2.3.2. Freezing mechanism

- realistic phenomena in the beginning of freezing process-

The critical radius ( $r_0$ ) for nucleation is given as  $r_0 = -2\gamma/\Delta G_v$ .



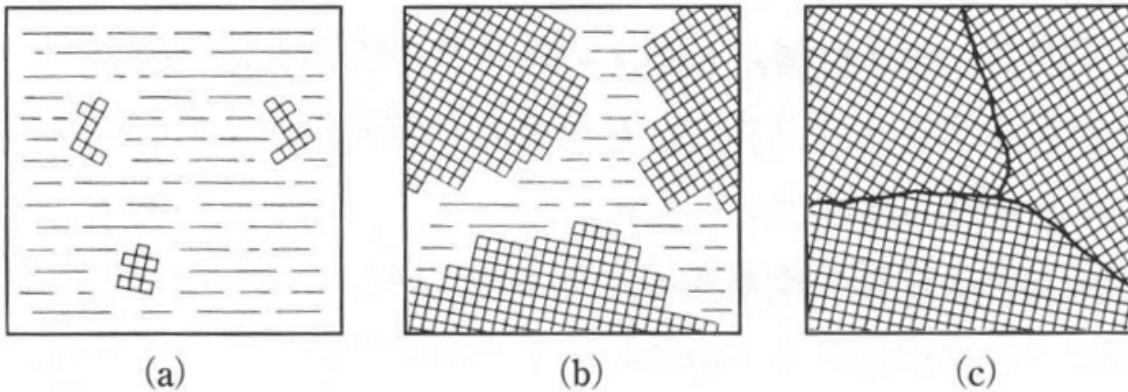
- ✓ Usually,  $\gamma$  is less sensitive to temperature while  $\Delta G_v$  is sensitive as  $\Delta G_v$  is the difference in Gibbs energy between liquid and solid phases.
- ✓ Thus, if the temperature is much lower than the melting temperature,  $\Delta G_v$  is more negative, then  $r_0$  becomes much smaller.
- ✓ In practice,
  - ✓ if we rapidly cool down liquid, we have smaller grains in created crystals.
  - ✓ If we very gently cool down, super-cooling may occur.



## 2.3.2. Freezing mechanism

### - phenomena in the beginning of freezing process-

- ✓ If many nucleuses grow in liquid, they collide each other and boundaries are formed between them. Finally, the liquid is totally transformed to solid. The solid contains multiple grains and grain boundaries: thus a **polycrystal**.



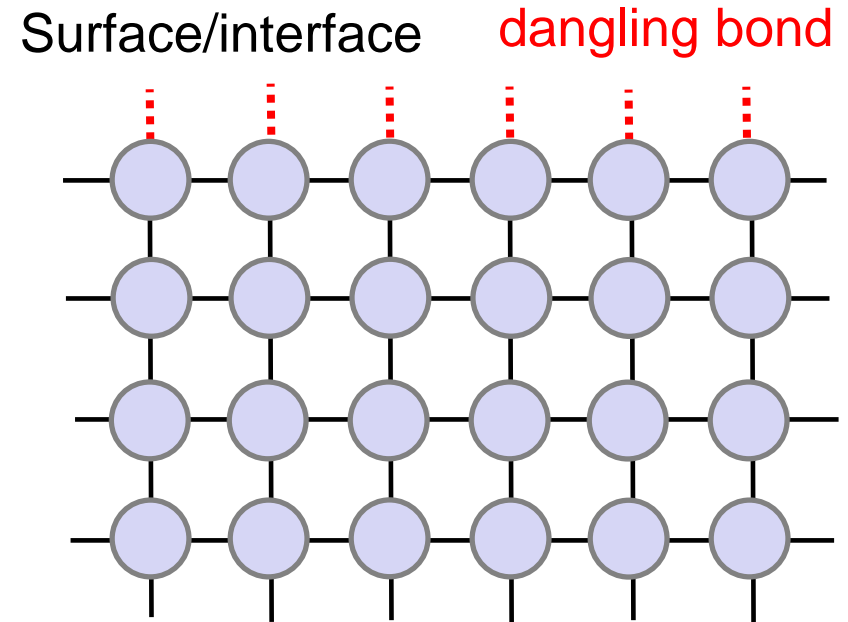
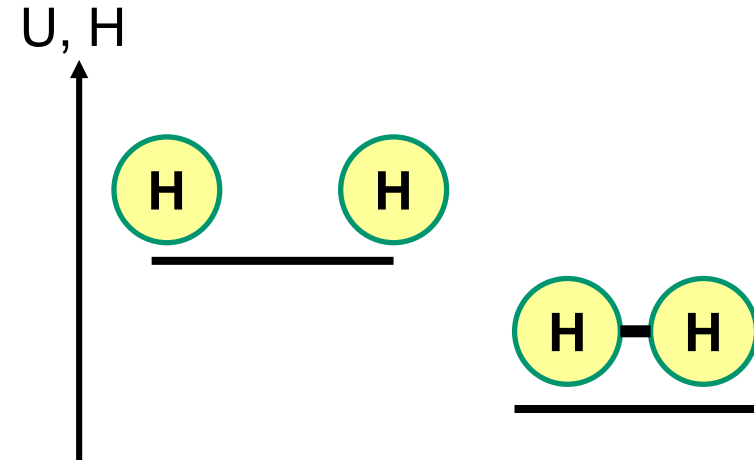
\*Shiro Kohara, “Metal materials”,  
Asakura Publishing Co., Ltd.,  
2012 (in Japanese).

- ✓ If some atoms are not soluble in the matrix (lattice) of the solid phase, they accumulate at grain boundaries because the boundaries freeze at last.
- ✓ Because interface energy is anisotropic, the growth speed characteristically depends on the surface direction. And there is a preferential direction to grow for each material, largely depending on the lattice structure.

	bcc	fcc			hcp			
Material	Fe	Al	Cu	Ag	Ag	Cd	Zn	Mg
Preferential direction	$\langle 100 \rangle$	$\langle 100 \rangle$			$\langle 0001 \rangle$	$\langle 0001 \rangle$	$\langle 2110 \rangle$	

# (Appendix) Why interface energy is always positive

- ✓ If there are bonds between atoms, the total energy (internal energy) decreases, as the substance becomes stable.
  - ✓ This is why enthalpy of substance is lower in solid than in liquid/gas.
- ✓ If there are interfaces, the bonding is cut, apparently from solid crystals. This bonding-cut creates so-called “**dangling bond**”, which is the reason why interface is unstable (“interfaces have positive energies”)
  - ✓ The number of dangling bonds are proportional to the surface area, thus the interface energy is proportional to it.



# **3.1. Chemical equilibrium for gases**

# 3.1. Chemical equilibrium for gases

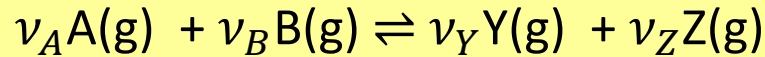
## - \$26: Introduction -

- ✓ Thermodynamics enables us to predict the equilibrium pressures or concentrations of reaction mixtures.
- ✓ In this chapter, we will derive a relation between the **standard Gibbs energy change** and the **equilibrium constant** for a chemical reaction.
- ✓ We will also learn how to predict the direction in which a chemical reaction will proceed if we start with arbitrary concentrations (thus, not equilibrium) of reactants and products.
  
- ✓ Although we need to utilize some equations specialized for gases, an important point is that chemical equilibrium (at const.-T const.-P condition) is governed by Gibbs energy as the same with phase equilibrium.
  - ✓ The equilibrium state is a state of the lowest Gibbs energy for chemical equilibrium, as the same with phase equilibrium (at const.-T const.-P)

### 3.1. Chemical equilibrium for gases

- §26-1: Chemical equilibrium results when the Gibbs energy is a minimum with respect to the extent of reaction -

Consider a general gas phase reaction, described by a balanced equation.



The amount of species  $i$  is  $n_i$  [mol]. The Gibbs energy for this multi-component system is a function of  $T, P, n_A, n_B, n_Y$  and  $n_Z$ , then the total differential is:

$$\begin{aligned} dG = & \left( \frac{\partial G}{\partial T} \right)_{P, n_A, n_B, n_Y, n_Z} dT + \left( \frac{\partial G}{\partial P} \right)_{T, n_A, n_B, n_Y, n_Z} dP + \left( \frac{\partial G}{\partial n_A} \right)_{T, P, n_B, n_Y, n_Z} dn_A \\ & + \left( \frac{\partial G}{\partial n_B} \right)_{T, P, n_A, n_Y, n_Z} dn_B + \left( \frac{\partial G}{\partial n_Y} \right)_{T, P, n_A, n_B, n_Z} dn_Y + \left( \frac{\partial G}{\partial n_Z} \right)_{T, P, n_A, n_B, n_Y} dn_Z \end{aligned}$$

Then, it can be re-written as:

$$dG = -SdT + VdP + \mu_A dn_A + \mu_B dn_B + \mu_Y dn_Y + \mu_Z dn_Z$$

$$\mu_A = \left( \frac{\partial G}{\partial n_A} \right)_{T, P, n_B, n_Y, n_Z}, \text{ etc}$$

If the reaction takes place in const.-T const.-P condition,

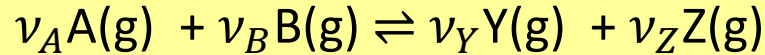
$$dG = \mu_A dn_A + \mu_B dn_B + \mu_Y dn_Y + \mu_Z dn_Z \quad (\text{constant T and P})$$

\*This “const.- $P$ ” is about total pressure (not partial pressure).

# 3.1. Chemical equilibrium for gases

- §26-1: Chemical equilibrium results when the Gibbs energy is a minimum with respect to the extent of reaction -

Consider a general gas phase reaction, described by a balanced equation.



We define a quantity  $\xi$ , called as the “extent of reaction”. Here  $n_{i0}$  is the initial number of moles for species  $i$ , then :

$$n_A = n_{A0} - \nu_A \xi \quad n_B = n_{B0} - \nu_B \xi \quad (\text{reactants})$$

$$n_Y = n_{Y0} + \nu_Y \xi \quad n_Z = n_{Z0} + \nu_Z \xi \quad (\text{products})$$

In this case,  $\xi$  has units of moles. Then, the variations of  $n_i$  is:

$$dn_A = -\nu_A d\xi \quad dn_B = -\nu_B d\xi \quad (\text{reactants})$$

$$dn_Y = \nu_Y d\xi \quad dn_Z = \nu_Z d\xi \quad (\text{products})$$

\*Note that the unit for  $d\xi$  is [mol].

which means that as the reaction (left to right) proceeds, the reactants decrease and the products increase according to the stoichiometry.

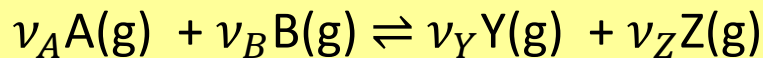
Using these equations:

$$\begin{aligned} dG &= \mu_A dn_A + \mu_B dn_B + \mu_Y dn_Y + \mu_Z dn_Z \\ &= (-\nu_A \mu_A - \nu_B \mu_B + \nu_Y \mu_Y + \nu_Z \mu_Z) d\xi \end{aligned} \quad (\text{constant T and P})$$

## 3.1. Chemical equilibrium for gases

- \$26-1: Chemical equilibrium results when the Gibbs energy is a minimum with respect to the extent of reaction -

Consider a general gas phase reaction, described by a balanced equation.



$$dG = (-\nu_A \mu_A - \nu_B \mu_B + \nu_Y \mu_Y + \nu_Z \mu_Z) d\xi \quad (\text{constant } T \text{ and } P)$$

$$\left( \frac{\partial G}{\partial \xi} \right)_{T,P} = \nu_Y \mu_Y + \nu_Z \mu_Z - \nu_A \mu_A - \nu_B \mu_B$$

Here, we define  $\left( \frac{\partial G}{\partial \xi} \right)_{T,P} = \Delta_r G$ , which is the change in Gibbs energy when the extent of reaction changes by one mole, and its unit is [J mol<sup>-1</sup>].

Assuming each species behaves as ideal gas, as the pressure dependence of chemical potential is written as  $\mu_j(T, P) = \mu^\circ_j(T) + RT \ln(P_j/P^\circ)$ , then:

$$\Delta_r G = \Delta_r G^\circ + RT \ln Q$$

$$Q = \frac{(P_Y/P^\circ)^{\nu_Y} (P_Z/P^\circ)^{\nu_Z}}{(P_A/P^\circ)^{\nu_A} (P_B/P^\circ)^{\nu_B}}$$

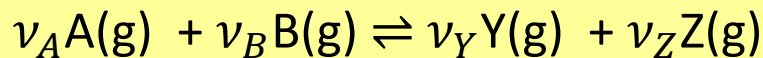
$P^\circ$  is the pressure of standard state (1 bar) and  $P_A$  is the partial pressure of species A.

$$\Delta_r G^\circ = \nu_Y \mu^\circ_Y(T) + \nu_Z \mu^\circ_Z(T) - \nu_A \mu^\circ_A(T) - \nu_B \mu^\circ_B(T)$$

## 3.1. Chemical equilibrium for gases

- \$26-1: Chemical equilibrium results when the Gibbs energy is a minimum with respect to the extent of reaction -

Consider a general gas phase reaction, described by a balanced equation.



$$\Delta_r G = \Delta_r G^\circ + RT \ln Q \quad (\text{ideal gas, constant } T \text{ and } P)$$

$$\Delta_r G^\circ = \nu_Y \mu^\circ_Y(T) + \nu_Z \mu^\circ_Z(T) - \nu_A \mu^\circ_A(T) - \nu_B \mu^\circ_B(T) \quad Q = \frac{(P_Y/P^\circ)^{\nu_Y} (P_Z/P^\circ)^{\nu_Z}}{(P_A/P^\circ)^{\nu_A} (P_B/P^\circ)^{\nu_B}}$$

Here, the quantity  $\Delta_r G^\circ$  is the change in standard Gibbs energy for the reaction between **unmixed reactants** to form **unmixed products**. All species in their standard states at  $T$  and  $P^\circ$ . Note that  $P^\circ = 1$  bar.

When the reaction system is equilibrium, the Gibbs energy must be the minimum with respect to any change from the equilibrium state, thus

$$\left( \frac{\partial G}{\partial \xi} \right)_{T,P} = \Delta_r G = \Delta_r G^\circ + RT \ln Q_{eq} = 0 \text{ at an equilibrium state. Thus:}$$

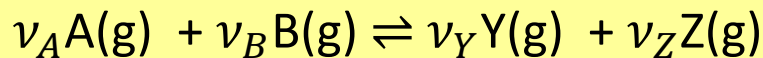
$$\Delta_r G^\circ = -RT \ln \left( \frac{P_Y^{\nu_Y} P_Z^{\nu_Z}}{P_A^{\nu_A} P_B^{\nu_B}} \right)_{eq} = -RT \ln K_P(T)$$



## 3.1. Chemical equilibrium for gases

- §26-1: Chemical equilibrium results when the Gibbs energy is a minimum with respect to the extent of reaction -

Consider a general gas phase reaction, described by a balanced equation.



$$\Delta_r G^\circ = -RT \ln K_P(T)$$

$$\Delta_r G^\circ = \nu_Y \mu^\circ_Y(T) + \nu_Z \mu^\circ_Z(T) - \nu_A \mu^\circ_A(T) - \nu_B \mu^\circ_B(T)$$

$$K_P(T) = Q_{eq} = \left[ \frac{(P_Y/P^\circ)^{\nu_Y} (P_Z/P^\circ)^{\nu_Z}}{(P_A/P^\circ)^{\nu_A} (P_B/P^\circ)^{\nu_B}} \right]_{eq} = \left( \frac{P_Y^{\nu_Y} P_Z^{\nu_Z}}{P_A^{\nu_A} P_B^{\nu_B}} \times P^{\circ(\nu_A + \nu_B - \nu_Y - \nu_Z)} \right)_{eq}$$

$P^\circ = 1 \text{ bar}$

\*the subscript *eq* emphasizes that the partial pressures are in an equilibrium.

- ✓  $K_P(T)$  is called as *equilibrium constant*. Be sure that  $K_P(T)$  has no unit.
- ✓ As seen in the definition, this constant is defined after the target equation is given.
  - ✓ For example, if the  $\nu_A$  in the equation is changed (even keeping the same meaning of reaction, like  $2\nu_A A(g) + 2\nu_B B(g) \rightleftharpoons 2\nu_Y Y(g) + 2\nu_Z Z(g)$ ),  $K_P(T)$  value is changed.

# 3.1. Chemical equilibrium for gases

-  $\mu_j(T, P) = \mu_j^\circ(T) + RT \ln(P_j/P^\circ)$  for an ideal gas -

$$\mu_j(T, P) = \mu_j^\circ(T) + RT \ln(P_j/P^\circ)$$

For an ideal gas:

$$PV = nRT$$

$$U = nC_V T + \text{constant.} = nC_V T + nU_0 \quad \text{then } dU = nC_V dT$$

For a path keeping some thermal equilibrium states (i.e. reversible process):

$$dU = TdS - PdV$$

$$dS = \frac{dU}{T} + \frac{PdV}{T} = nC_V \frac{dT}{T} + nR \frac{dV}{V}$$

$$S(T, V) = \int nC_V \frac{dT}{T} + \int nR \frac{dV}{V} = nS_0 + nC_V \ln T + nR \ln V$$

$$G(T, V) = U + PV - TS = nC_V T + nU_0 + nRT - T\{nS_0 + nC_V \ln T + nR \ln V\}$$

# 3.1. Chemical equilibrium for gases

-  $\mu_j(T, P) = \mu^\circ_j(T) + RT \ln(P_j/P^\circ)$  for an ideal gas -

$$\mu_j(T, P) = \mu^\circ_j(T) + RT \ln(P_j/P^\circ)$$

$$G(T, V) = U + PV - TS = nC_V T + nU_0 + nRT - T\{nS_0 + nC_V \ln T + nR \ln V\}$$

$$G(T, P) - G(T, P_0) = -T\{nR \ln V\} + T\{nR \ln V_0\} = T_1 \left\{ nR \ln \frac{V_0}{V} \right\}$$

$$P_1 V_1 = P_2 V_2$$

$$G(T, P) - G(T, P_0) = T_1 \left\{ nR \ln \frac{V_0}{V} \right\} = T_1 \left\{ nR \ln \frac{P}{P_0} \right\}$$

$$\mu = \left( \frac{\partial G}{\partial n} \right)_{P, T}$$

$$\mu(T, P) = \mu(T, P^\circ) + RT \ln \frac{P}{P^\circ} = \mu^\circ(T) + RT \ln \frac{P}{P^\circ}$$

Here  $P^\circ = 1$  bar for the standard chemical potential.

## 3.1. Chemical equilibrium for gases

- §26-1: Chemical equilibrium results when the Gibbs energy is a minimum with respect to the extent of reaction -

(Example-1a) For reaction " $3 \text{H}_2(\text{g}) + \text{N}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$ ", the equilibrium pressures are given as  $P_{\text{H}_2}$ ,  $P_{\text{N}_2}$ , and  $P_{\text{NH}_3}$ .

$$K_P(T) = \left( \frac{P_{\text{NH}_3}^2}{P_{\text{H}_2}^3 P_{\text{N}_2}} \right)_{eq}$$

\*Be sure that these pressures are pressures at equilibrium, as in the definition of equilibrium constant.

(Example-1b) For reaction " $3/2 \text{H}_2(\text{g}) + 1/2 \text{N}_2(\text{g}) \rightleftharpoons \text{NH}_3(\text{g})$ ", the equilibrium pressures are given as  $P_{\text{H}_2}$ ,  $P_{\text{N}_2}$ , and  $P_{\text{NH}_3}$ .

$$K_P(T) = \left( \frac{P_{\text{NH}_3}}{P_{\text{H}_2}^{3/2} P_{\text{N}_2}^{1/2}} \right)_{eq} \neq K_P(T) \text{ of example - 1a}$$

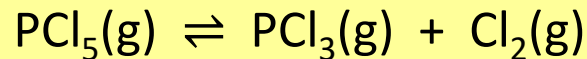


Although the reactions themselves are identical, the equilibrium constants are not the same, because the equilibrium constant depends on the expression of chemical reaction equation.

# 3.1. Chemical equilibrium for gases

- §26-2: An equilibrium constant is a function of temperature only -

Consider a general gas phase reaction, described by a balanced equation.



The equilibrium-constant expression for this reaction is:

$$K_P(T) = \left( \frac{P_{\text{PCl}_3} P_{\text{Cl}_2}}{P_{\text{PCl}_5}} \right)_{eq}$$

Suppose we have 1 mol of  $\text{PCl}_5$  (g) and no  $\text{PCl}_3$  or  $\text{Cl}_2$  at the beginning. When the reaction occurs to an extent  $\xi$ ,

$$\text{PCl}_5: \quad 1 \text{ mol} \rightarrow (1 - \xi) \text{ mol}$$

$$\text{PCl}_3: \quad 0 \text{ mol} \rightarrow \xi \text{ mol}, \quad \text{Cl}_2: \quad 0 \text{ mol} \rightarrow \xi \text{ mol}$$

$$\text{Total:} \quad 1 \text{ mol} \rightarrow (1 + \xi) \text{ mol}$$

If  $\xi_{eq}$  is the extent of reaction at equilibrium, then the partial pressures are:

$$P_{\text{PCl}_3} = P_{\text{Cl}_2} = (\xi_{eq} P) / (1 + \xi_{eq}), \quad P_{\text{PCl}_5} = ((1 - \xi_{eq}) P) / (1 + \xi_{eq})$$

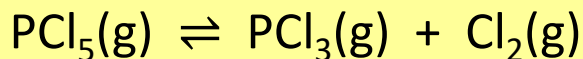
where  $P$  is the total pressure. Then, the equilibrium constant is:

$$K_P(T) = \left( \frac{\xi_{eq}^2}{1 - \xi_{eq}^2} \right) P$$

# 3.1. Chemical equilibrium for gases

- \$26-2: An equilibrium constant is a function of temperature only -

Consider a general gas phase reaction, described by a balanced equation.



$$K_P(T) = \left( \frac{\xi_{eq}^2}{1 - \xi_{eq}^2} \right) P$$

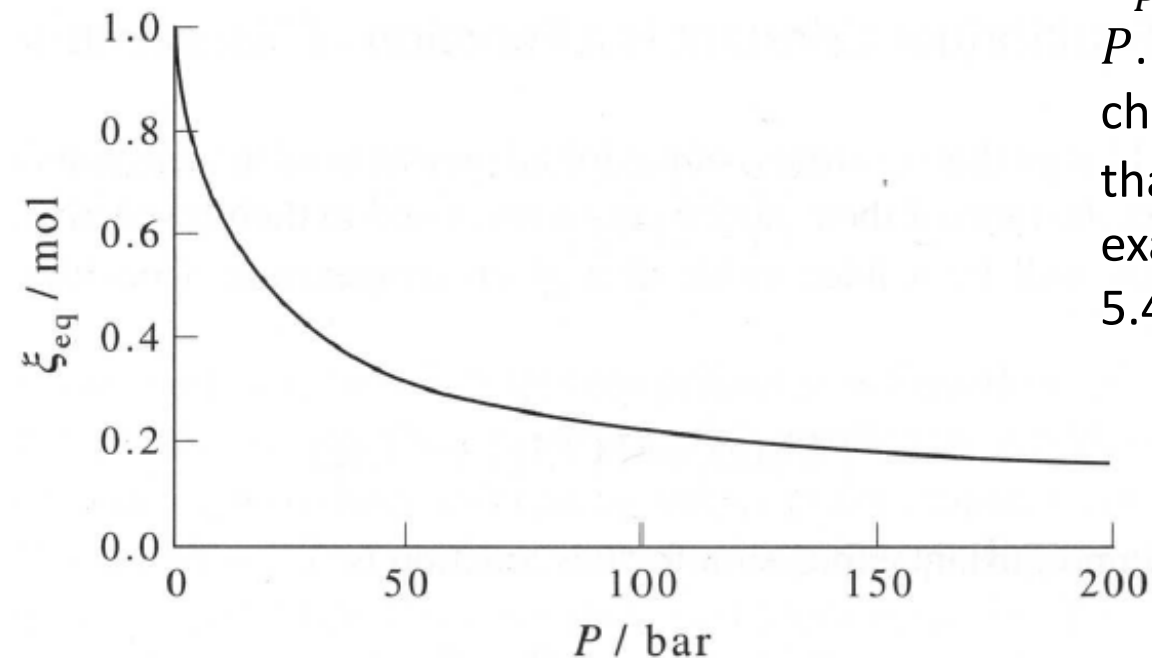
PCl<sub>5</sub>: 1 mol → (1 - ξ) mol

PCl<sub>3</sub>, Cl<sub>2</sub>: 0 mol → ξ mol,

Total: 1 mol → (1 + ξ) mol

$K_P(T)$  only depends on  $T$ , but not  $P$ . So, if  $P$  (total pressure) is changed,  $\xi_{eq}$  must be changed so that  $K_P(T)$  is kept constant. For example,  $K_P(T)$  of this reaction is 5.4 (*no unit*) at 200°C.

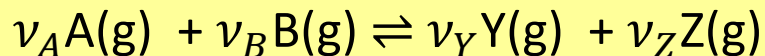
\*If gases interact each other,  $K_P(T)$  also depends on  $P$ . However, in practice, we can assume that gases behave like ideal gasses.



# 3.1. Chemical equilibrium for gases

- \$26-2: An equilibrium constant is a function of temperature only -

Consider a general gas phase reaction, described by a balanced equation.



So far, we express the equilibrium constant regarding pressure. We can also express the equilibrium constant in terms of concentrations, etc, by using the ideal-gas relation " $P = cRT$ ", where  $c = n/V$  is the concentration:

$$\Delta_r G^\circ = -RT \ln K_P(T)$$

$$K_P(T) = Q_{eq} = \left[ \frac{(P_Y/P^\circ)^{\nu_Y} (P_Z/P^\circ)^{\nu_Z}}{(P_A/P^\circ)^{\nu_A} (P_B/P^\circ)^{\nu_B}} \right]_{eq} = \left[ \frac{C_Y^{\nu_Y} C_Z^{\nu_Z}}{C_A^{\nu_A} C_B^{\nu_B}} \right]_{eq} \left( \frac{RT}{P^\circ} \right)^{\nu_Y + \nu_Z - \nu_A - \nu_B}$$

Here, we consider some standard concentration  $c^\circ$  (like  $P^\circ$ ), often taken to be " $1 \text{ mol L}^{-1}$ ". Then:

$$K_P(T) = K_C(T) \left( \frac{c^\circ RT}{P^\circ} \right)^{\nu_Y + \nu_Z - \nu_A - \nu_B}$$

$$K_C(T) = \left[ \frac{(C_Y/c^\circ)^{\nu_Y} (C_Z/c^\circ)^{\nu_Z}}{(C_A/c^\circ)^{\nu_A} (C_B/c^\circ)^{\nu_B}} \right]_{eq}$$

\*As the same with  $K_P$ ,  $K_C$  has also no unit.

# 3.1. Chemical equilibrium for gases

- \$26-2: An equilibrium constant is a function of temperature only -

(Example-2) For reaction " $\text{NH}_3(\text{g}) \rightleftharpoons 3/2 \text{H}_2(\text{g}) + 1/2 \text{N}_2(\text{g})$ ",  $K_P(T) = 1.36 \times 10^{-3}$  at 298.15 K. Determine the corresponding  $K_C(T)$ .

$$K_P(T) = K_C(T) \left( \frac{c^\circ RT}{P^\circ} \right)^{3/2+1/2-1} = K_C(T) \left( \frac{c^\circ RT}{P^\circ} \right)^1$$

$$K_C(T) = K_P(T) \left( \frac{c^\circ RT}{P^\circ} \right)^{-1}$$

$$= 1.36 \times 10^{-3} \times \left[ \frac{(1 \text{ mol L}^{-1}) \times (0.0831 \text{ L bar mol}^{-1} \text{K}^{-1}) \times (298.15 \text{ K})}{1 \text{ bar}} \right]^{-1}$$
$$= 5.49 \times 10^{-5}$$