Physical Chemistry for Energy Engineering
(20th: 2018/11/26)

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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)

	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)

3.1. Chemical equilibrium for gases

- \$26-6: The sign of $\Delta_r G$ and not that of $\Delta_r G^\circ(T)$ determines the direction of reaction spontaneity -

(Example-6) Consider " H_2 (g) + ½ O_2 (g) ⇌ H_2O (l) ",
for which $\Delta_r G^\circ = -237\ \text{kJ}\ mol^{-1}$ at 298.15 K.

In this case, $\Delta_r G^\circ$ has a large negative value, thus basically H_2O (l) is much more stable than the reactants at 298.15 K. However, a mixture of H_2 (g) and O_2 (g) remains unchanged.

If a spark or a catalyst is introduced, then the reaction occurs explosively.

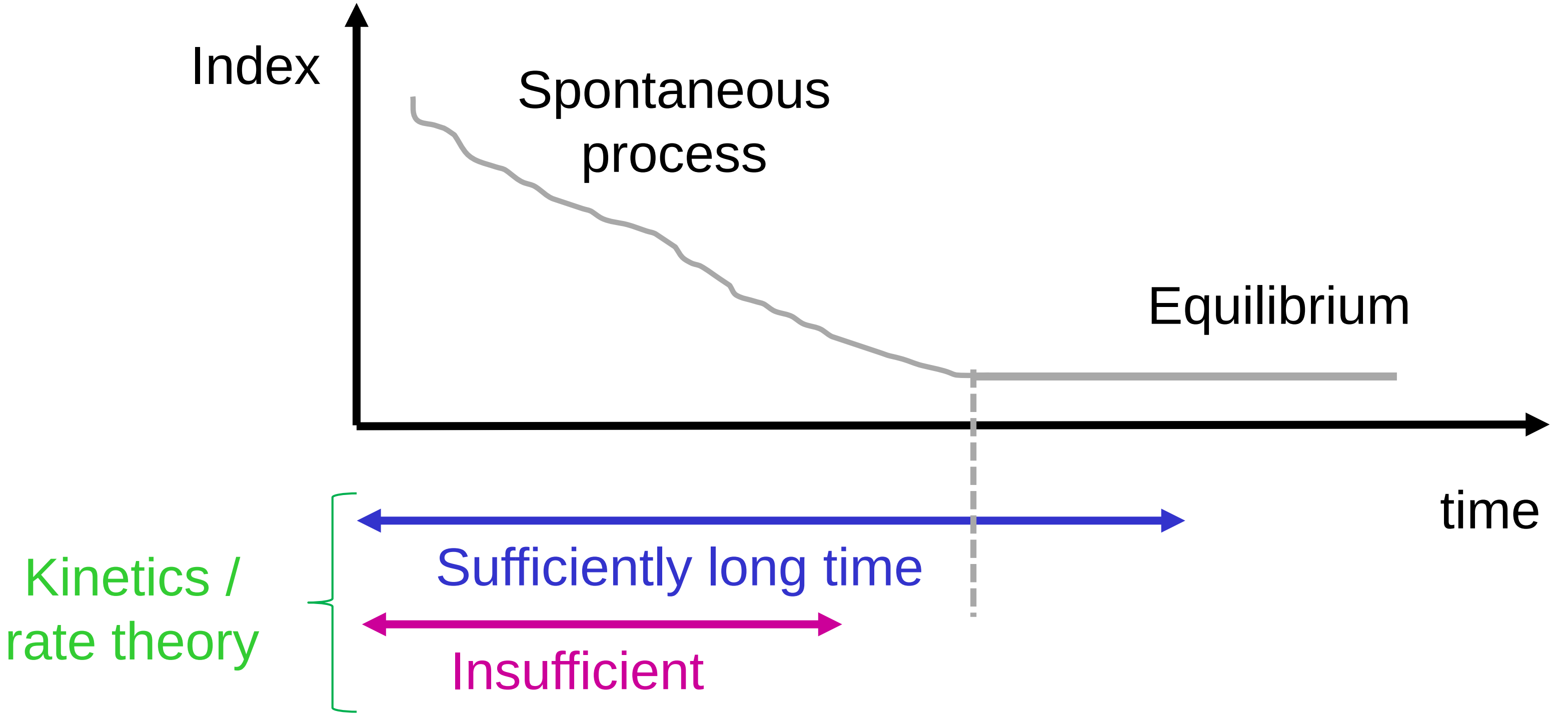
- ✓ The "no" is emphatic in thermodynamics: If thermodynamics insists that a certain process will not occur spontaneously, then it will not occur.
- ✓ On the other hand, the "yes" is actually "maybe". The fact that a process will occur spontaneously does not imply that it will occur at a detectable rate.
  - ➢ Diamond remains its form, although a graphite is more favorable energetically, is another example.

The speed of reaction can be analyzed in the framework of rate theory. (next topic)

3.1. Chemical equilibrium for gases

- \$26-6: The sign of $\Delta_r G$ and not that of $\Delta_r G°(T)$ determines the direction of reaction spontaneity -

Theory of equilibrium is powerful, but it cannot indicate how long it take to reach the equilibrium state.
Kinetics and rate theory can analyze and give information on the speed of a reaction.



Kinetics and rate theory are often based on thermodynamics, but sometimes extended to microscopic systems (via statistics mechanics/thermodynamics).

3.1. Chemical equilibrium for gases

- $26-7: The variation of an equilibrium constant with temperature is given by the Van’t Hoff Equation -

We utilize the Gibbs-Helmholtz equation: $\left(\frac{\partial \Delta G^\circ/T}{\partial T}\right)_P = -\frac{\Delta H^\circ}{T^2}$

Substitute $\Delta_r G^\circ = -RT \ln K_P$ (note this is a definition of $\Delta_r G^\circ$, not a condition achieved at equilibrium state) for this equation:

$$\left(\frac{\partial \ln K_P(T)}{\partial T}\right)_P = \frac{d \ln K_P(T)}{dT} = \frac{\Delta_r H^\circ}{RT^2}$$

This means that

- ✓ If $\Delta_r H^\circ > 0$ (endothermic reaction), $K_P(T)$ increases with temperature.
- ✓ If $\Delta_r H^\circ < 0$ (exothermic reaction), $K_P(T)$ decreases with temperature.

Integrate the equation: $$\ln \frac{K_P(T_2)}{K_P(T_1)} = \int_{T_1}^{T_2} \frac{\Delta_r H^\circ(T)}{RT^2} dT$$

If the temperature range is small enough to consider $\Delta_r H^\circ$ constant:

$$\ln \frac{K_P(T_2)}{K_P(T_1)} = -\frac{\Delta_r H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

3.1. Chemical equilibrium for gases

- $26-7: The variation of an equilibrium constant with temperature is given by the Van't Hoff Equation -

(Example-7) Consider " PCl_3 (g) + Cl_2 (g) $\rightleftharpoons$ PCl_2 (g) ".
Given that $\Delta_r H°$ has an average value of -69.8 kJ mol^{-1} over 500-700 K and K_P is 0.0408 at 500K, evaluate K_P at 700K.

As $\Delta_r H°$ can be assumed as a constant over the concerned temperatures,

$$\ln \frac{K_P(T_2)}{K_P(T_1)} = -\frac{\Delta_r H°}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Substituting provided values gives:

$$\ln \frac{K_P(700\ K)}{K_P(500\ K)} = \ln \frac{K_P(700\ K)}{0.0408} = -\frac{-69.8 \times 10^3}{R}\left(\frac{1}{700} - \frac{1}{500}\right)$$

$$K_P(700\ K) = 3.36 \times 10^{-4}$$

Note that since the reaction is exothermic, $K_P(700\ K)$ is less than $K_P(500\ K)$; namely less product (PCl_2) at higher temperatures as $K_P = {}^{p_{PCl_2}}/_{p_{PCl_3} p_{Cl_2}}$.

3.1. Chemical equilibrium for gases

- $26-7: The variation of an equilibrium constant with temperature is given by the Van't Hoff Equation -

Finally, we consider the temperature dependence of $\Delta_r H°$ constant in:

$$\ln \frac{K_P(T_2)}{K_P(T_1)} = \int_{T_1}^{T_2} \frac{\Delta_r H°(T)}{RT^2} dT$$

This equation can write down as:

$$\ln K_P(T) = \ln K_P(T_1) + \int_{T_1}^{T} \frac{\Delta_r H°(T')}{RT'^2} dT'$$

For example, as we learned, the temperature dependence of $\Delta_r H°$ may be written as:

$$\Delta_r H°(T_2) = \Delta_r H°(T_1) + \int_{T_1}^{T_2} \Delta C°_P(T) dT$$

or expanded in respect to temperature as:

$$\Delta_r H°(T) = \alpha + \beta T + \gamma T^2 + \delta T^3 + \cdots$$

In this latter case, $\ln K_P(T)$ becomes:

$$\ln K_P(T) = -\frac{\alpha}{RT} + \frac{\beta}{R}\ln T + \frac{\gamma}{R} T + \frac{\delta}{2R} T^2 + (integration\_constant) \ldots$$

3.1. Chemical equilibrium for gases

- $26-7: The variation of an equilibrium constant with temperature is given by the Van’t Hoff Equation -

(Example-8) Consider “ ½ N_2 (g) + 3/2 H_2 (g) ⇌ NH_3 (g) ”.
The molar heat capacities of these species are give over 300-1500K as:

$$C_P°[N_2(g)]/J\ K^{-1}\ mol^{-1} = 24.98 + 5.912 \times 10^{-3}T - 0.03376 \times 10^{-6}T^2$$

$$C_P°[H_2(g)]/J\ K^{-1}\ mol^{-1} = 29.07 - 0.8368 \times 10^{-3}T + 2.012 \times 10^{-6}T^2$$

$$C_P°[NH_3(g)]/J\ K^{-1}\ mol^{-1} = 25.93 + 32.58 \times 10^{-3}T - 3.046 \times 10^{-6}T^2$$

Given that $\Delta_f H°[NH_3(g)] = -46.11\ kJ\ mol^{-1} at\ 300\ K\ and\ K_P = 6.55 \times 10^{-3}$ at 725 K, derive the expression for the variation of $K_P(T)$ with temperature.

$$\Delta_r H°(T_2) = \Delta_r H°(T_1) + \int_{T_1}^{T_2} \Delta C°_P(T)dT$$

$$\Delta C_P° = C_P°[NH_3(g)] - {}^1/_2\, C_P°[N_2(g)] - {}^3/_2\, C_P°[H_2(g)]$$

Thus

$$\Delta_r H°(T) = -46.11 \times 10^{-3} + \int_{300}^{T} \Delta C°_P(T)dT$$

$$\ln K_P(T) = \ln K_P(725\ K) + \int_{725}^{T} \frac{\Delta_r H°(T')}{RT'^2} dT'$$

$$= 12.06 + 4583/T - 3.749 \ln T + 1.857 \times 10^{-3}T - 0.118 \times 10^{-6}T^2$$

Review of Chapter 3:
Comparison between phase equilibrium and chemical equilibrium

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

As the condition is cont.-T const.-P, the equilibrium system has the minimum Gibbs energy. This is the ground rule. Here, we consider conditions with which a two-phase system (liquid & gas here) as the minimum Gibbs energy.

The Gibbs energy of this system is given by

$$G = G^l + G^g$$

where G^l and G^g are the Gibbs energies of the liquid and the gas phase.

Now, if the liquid phase increases with dn^l mole (thus, the solid phase decreases with dn^g ($dn^l = -dn^g$)), the Gibbs energy change is:

$$dG = dG^l + dG^g = \left(\frac{\partial G^g}{\partial n^g}\right)_{P,T} dn^g + \left(\frac{\partial G^l}{\partial n^l}\right)_{P,T} dn^l = \left[\left(\frac{\partial G^g}{\partial n^g}\right)_{P,T} - \left(\frac{\partial G^l}{\partial n^l}\right)_{P,T}\right] dn^g$$

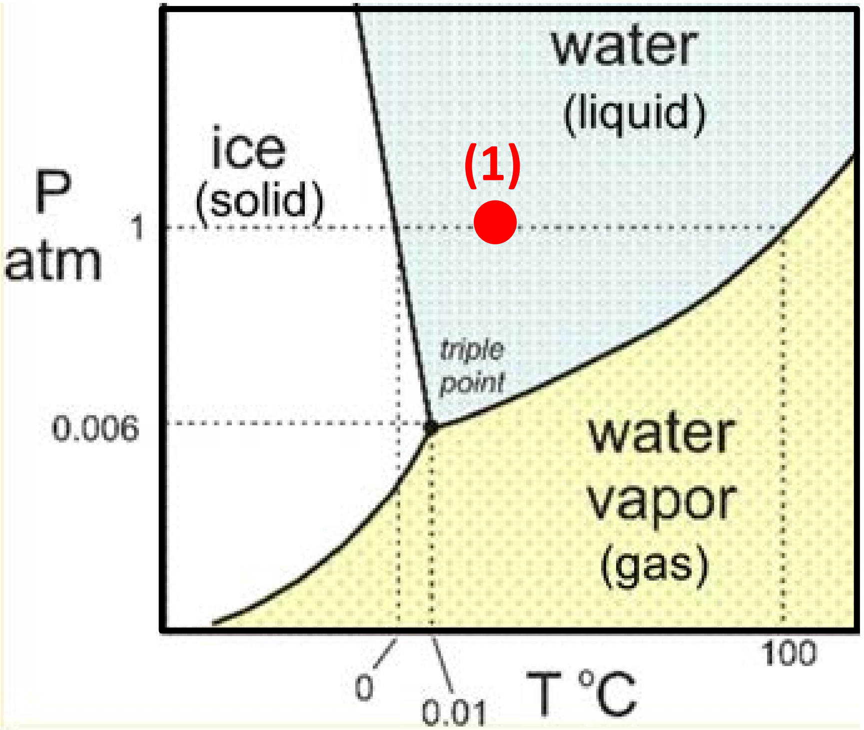
Here, we define *chemical potentials,* $\mu^g = \left(\frac{\partial G^g}{\partial n^g}\right)_{P,T}$ and $\mu^l = \left(\frac{\partial G^l}{\partial n^l}\right)_{P,T}$, then

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

As $dG = 0$ is the condition for an equilibrium state, $\mu^g = \mu^l$ is the condition.

Review of Chapter 3:
Comparison between phase equilibrium and chemical equilibrium

Phase diagram of water



(state-1) 300 K, 1 atm

- ✓ The phase diagram indicates that "at 300 K and 1 atm, the equilibrium phase of water is liquid water."
- ✓ It means "if water is at 300 K and 1 atm (and with a fixed amount), liquid phase has a smaller Gibbs energy than solid and gas phases."

- ✓ [Quiz] If there is a liquid water in this class room (assuming 300 K), do you think there are some ice (liquid) or vapor water (gas) coexisting?
  - ✓ Why do you think so and what is the mechanism of it?

http://cft.fis.uc.pt/eef/FisicaI01/fluids/thermo20.htm

Review of Chapter 3:
Comparison between phase equilibrium and chemical equilibrium

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \qquad [\mathrm{J}]/[\mathrm{K}]=[\mathrm{J/K}]$$

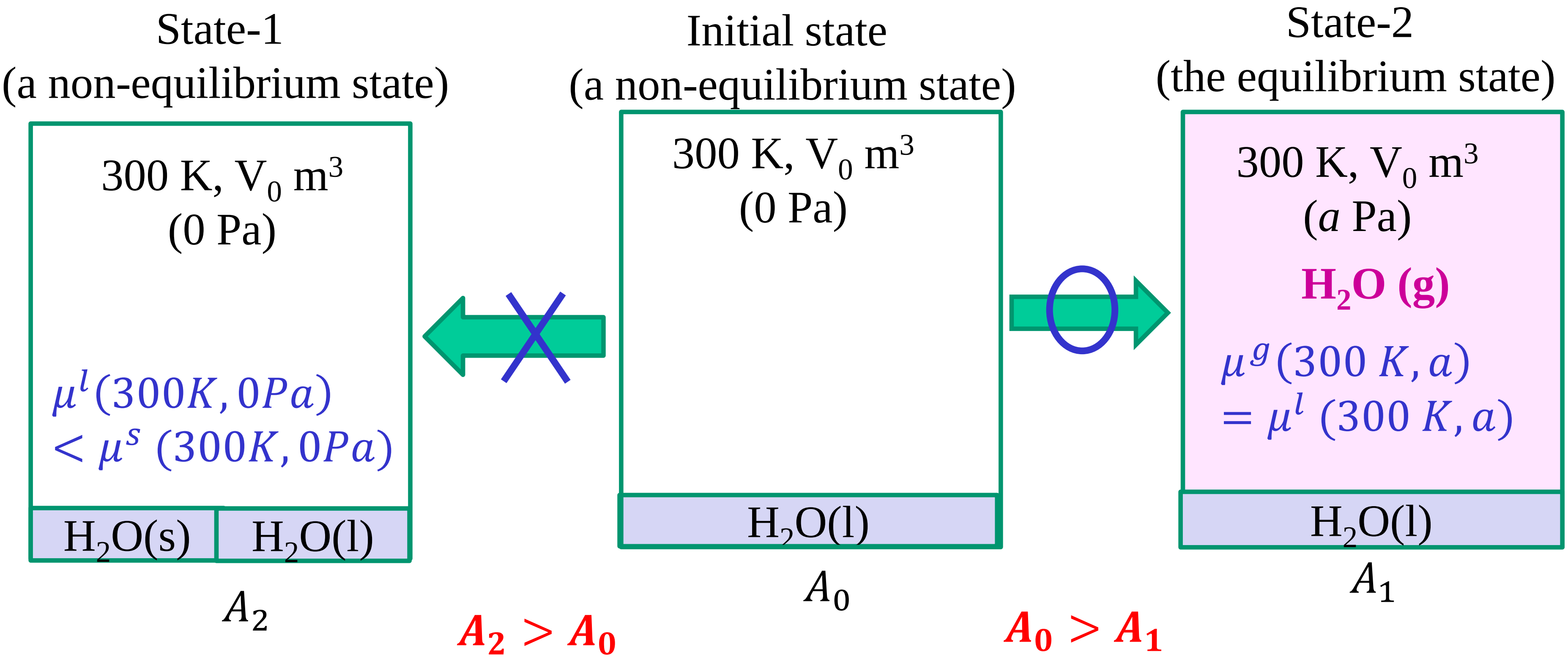
$$\left(\frac{\partial G}{\partial P}\right)_T = V \qquad [\mathrm{J}]/[\mathrm{Pa}]=[\mathrm{m}^3]$$

Substance	$\bar{V}$ (m^3/mol)	S$^\circ$ (J/mol/K)
$H_2O(l)$	0.018E-3	250.5
$H_2O(g)$	22.4E-3	188.8

- ✓ Typical pressure changes in chemistry are “1 atm → 0.5 atm”, “1atm → 10 atm”, for example, (“1E5 Pa → 0.5E5 Pa”, “1E5 Pa → 1E6 Pa”).
- ✓ Typical temperature changes are such as “300 K → 600 K”, etc.
- ✓ Thus, the difference between typical pressure and typical temperature (the their changes) are 3-4 orders of magnituede.
  - ✓ For gas, the difference between $\bar{V}$ and S° are 4 orders of magnitude. Thus, pressure change affect the Gibbs energy of gas in a comparable scale with temperature change.
- ✓ For liquid (solid), on the other hand, the difference between $\bar{V}$ and S° are 7 orders of magnitude. Thus, the Gibbs energy is hardly affected by pressure.

Review of Chapter 3:
Comparison between phase equilibrium and chemical equilibrium

Const.-T const.-V condition



State-1
(a non-equilibrium state)

300 K, V_0 m^3
(0 Pa)

$\mu^l(300K, 0Pa)$
$< \mu^s(300K, 0Pa)$

$H_2O(s)$ $H_2O(l)$

A_2

$A_2 > A_0$

Initial state
(a non-equilibrium state)

300 K, V_0 m^3
(0 Pa)

$H_2O(l)$

A_0

$A_0 > A_1$

State-2
(the equilibrium state)

300 K, V_0 m^3
(*a* Pa)

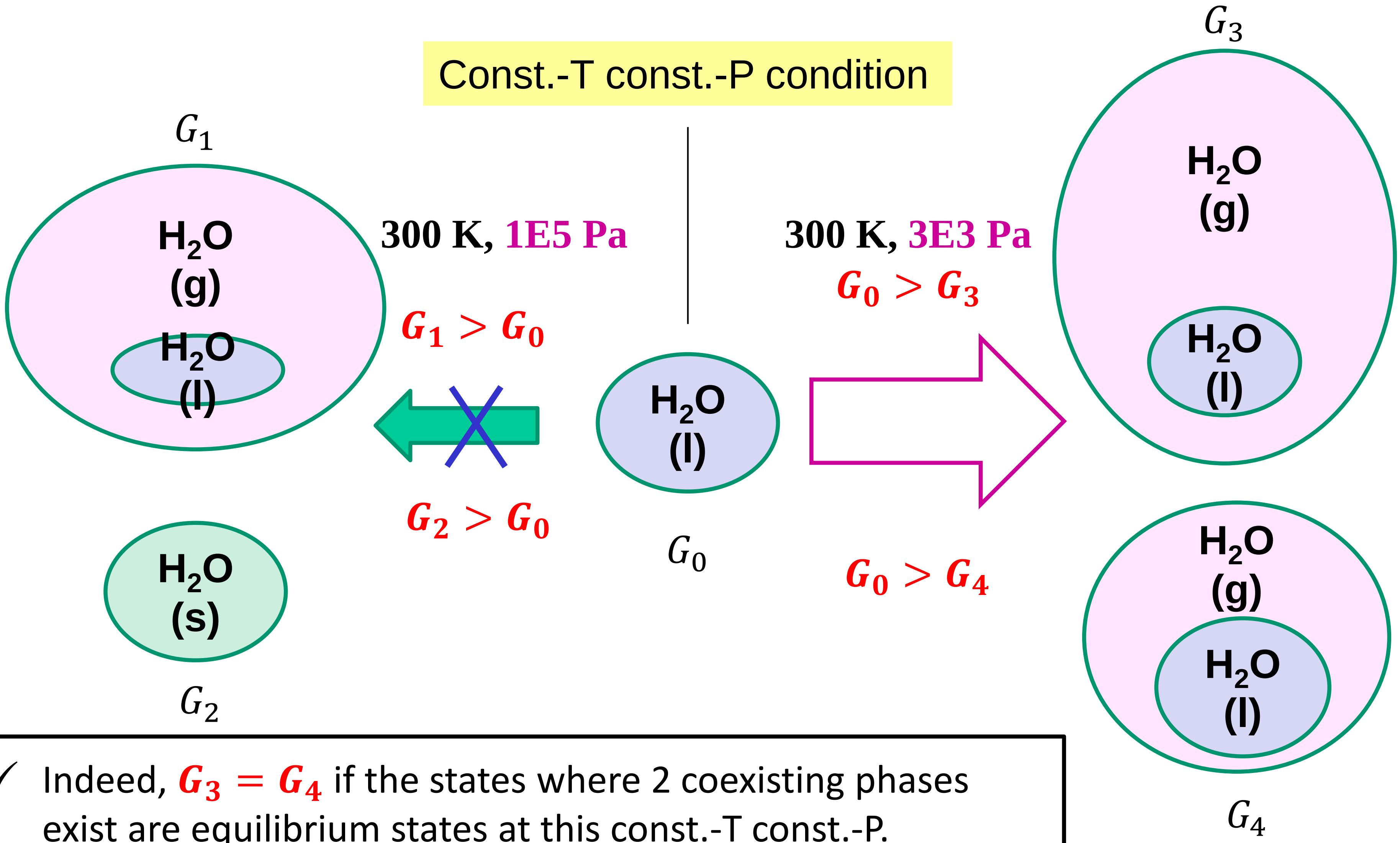
H_2O (g)

$\mu^g(300\ K, a)$
$= \mu^l(300\ K, a)$

$H_2O(l)$

A_1

Review of Chapter 3:
Comparison between phase equilibrium and chemical equilibrium



Const.-T const.-P condition

G_1

H_2O (g)

H_2O (l)

300 K, 1E5 Pa

$G_1 > G_0$

$G_2 > G_0$

H_2O (s)

G_2

H_2O (l)

G_0

300 K, 3E3 Pa

$G_0 > G_3$

G_3

H_2O (g)

H_2O (l)

$G_0 > G_4$

H_2O (g)

H_2O (l)

G_4

- ✓ Indeed, $G_3 = G_4$ if the states where 2 coexisting phases exist are equilibrium states at this const.-T const.-P.
- ✓ In this case, $\mu^g(300\ K, 3E3\ Pa) = \mu^l\ (300\ K, 3E3\ Pa)$

Review of Chapter 3:
Comparison between phase equilibrium and chemical equilibrium

<Saturation pressure of water vapor>

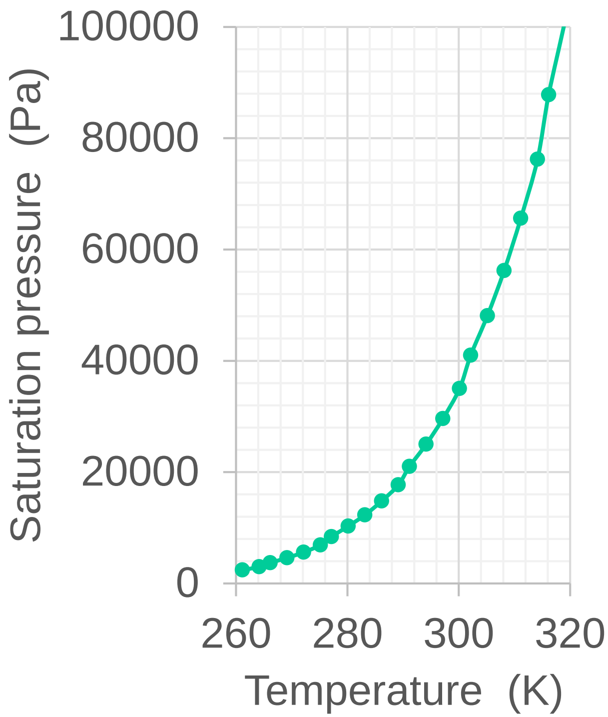
- ✓ The saturation pressure is the pressure where chemical potential of liquid and gas phases become identical at a given temperature.

$$\mu^g(T\ K, P_{sat}\ Pa) = \mu^l\ (T\ K, P_{sat}\ Pa)$$

- ✓ For practice, it may also be defined as

$$\mu^g(T\ K, P_{sat}\ Pa) = \mu^l\ (T\ K, 1\ atm) \sim \mu^l\ (T\ K, P_{sat}\ atm)$$

  - ✓ This equation is more useful when we want to know the saturation pressure of water vapor in a class room, for example.
  - ✓ Note that (molar) Gibbs energy of water vapor depends on partial pressure of water vapor, not on the total pressure of system. (assuming ideal gas)



So, even when the total pressure of the system is fixed, we may change the Gibbs energy (of the system) by adjusting partial pressures.

- ✓ For example, if we initially have 1 mol of H_2O(g), a state where H_2O(g), H_2(g) and O_2(g) coexist may have the minimum Gibbs energy under const.-P const.-T condition.

3.0. Pressure dependence of chemical potential-

-$\mu(T,P) = \mu°(T) + RT\, ln\left(P_j/P°\right)$ for pure substance of an ideal gas -

We consider the pressure dependence of gas of pure substance (single-component).

$$\boxed{\mu(T,P) = \mu°(T) + RT\ln(P/P°)}$$

For reversible processes (thus for thermodynamical equilibrium states)

$$dG = VdP - SdT$$

Assuming const.-T condition, and dividing both sides with dP

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

Then, keeping T and P constant, taking derivative regarding n

$$\left[\frac{\partial}{\partial n}\left(\frac{\partial G}{\partial P}\right)_T\right]_{T,P} = \left(\frac{\partial V}{\partial n}\right)_{T,p}$$

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

3.0. Pressure dependence of chemical potential-

-$\mu(T,P) = \mu°(T) + RT\, ln(P_j/P°)$ for pure substance of an ideal gas -

We consider the pressure dependence of gas of pure substance (single-component).

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

Note that up to here ideal gas is not assumed.

Here, we assume ideal gas. Then, using $\left(\frac{\partial V}{\partial n}\right)_{T,p} = \frac{RT}{P}$

$$d\mu = RT\frac{dP}{P} \qquad \textbf{(const.-T)}$$

Taking the integral from the standard pressure ($P° = 1\ bar$) to an arbitrary pressure P,

$$\mu - \mu° = RT \ln \frac{P}{P°}$$

$$\mu(T,P) = \mu°(T) + RT \ln(P/P°)$$

Be careful that chemical potential μ is molar Gibbs energy for pure substance, but it is not the case when multiple substances are mixed.

3.1. Chemical equilibrium for gases
-Difference between $\left(\frac{\partial G}{\partial n_A}\right)_{T,P,n_B,n_Y,n_Z}$ and $\left(\frac{\partial G}{\partial n}\right)_{T,P}$ -

- ✓ These two partial derivative are both definitions of chemical potential, but for different conditions: $\left(\frac{\partial G}{\partial n_Y}\right)_{T,P,n_Z,n_A,n_B}$ is for a mixture (A,B,Y,Z) and $\left(\frac{\partial G}{\partial n}\right)_{T,P}$ for pure substance.
  - ✓ For example, $\left(\frac{\partial G}{\partial n}\right)_{T,P}$ is the change in Gibbs energy for the pure gas Y when an infinitesimal amount of gas Y (dn) is added keeping other parameters constant. In this case, $\left(\frac{\partial G}{\partial n_Y}\right)_{T,P} = \frac{G}{n_Y}$, because this process only change the amount of Y with fixing other thermodynamical conditions. Thus, chemical potential is equal to molar Gibbs energy (const.-T and const.-P) for pure substance.
  - ✓ $\left(\frac{\partial G}{\partial n_Y}\right)_{T,P,n_Z,n_A,n_B}$ is the change in Gibbs energy for the gas mixture when an infinitesimal amount of gas Y (dn_Y) is added keeping other parameters constant. The chemical potential is equal to partial molar Gibbs energy (const.-T and const.-P [total P]) for a mixture.

3.1. Chemical equilibrium for gases

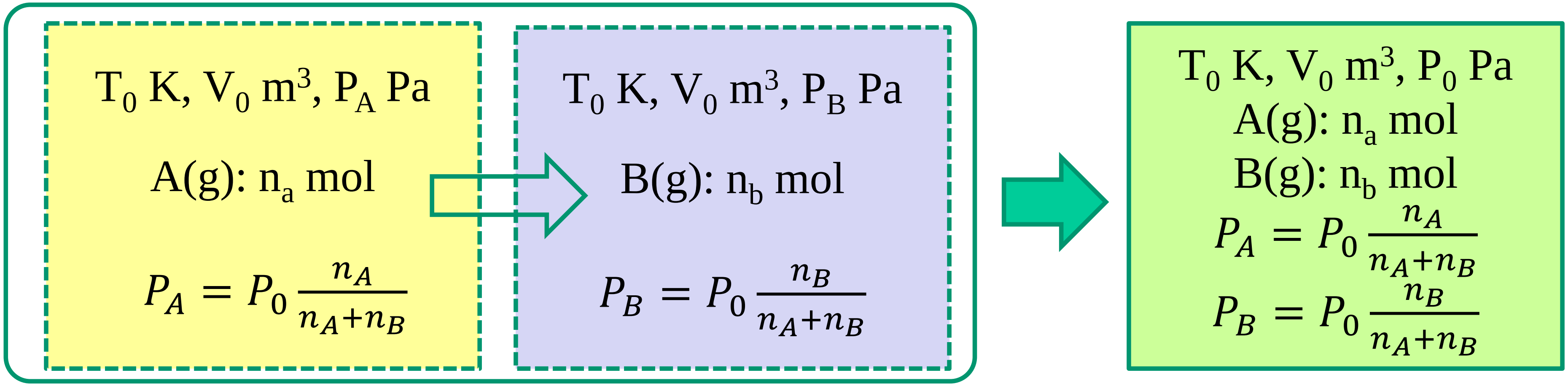
-Difference between $\left(\frac{\partial G}{\partial n_A}\right)_{T,P,n_B,n_Y,n_Z}$ and $\left(\frac{\partial G}{\partial n}\right)_{T,P}$-

- ✓ These two partial derivative are both definitions of chemical potential, but for different conditions: $\left(\frac{\partial G}{\partial n_Y}\right)_{T,P,n_Z,n_A,n_B}$ is for a mixture (A,B,Y,Z) and $\left(\frac{\partial G}{\partial n}\right)_{T,P}$ for pure substance.
  - ✓ (1) For example, if [T= 300 K and P= 1 atm, n=1 mol], "$\left(\frac{\partial G}{\partial n}\right)_{T,P} dn$" corresponds to the Gibbs energy change by increasing dn mol of the substance.
  - ✓ (2) On the other hand, if [T= 300 K, P= 1 atm, n=1 mol], "$\left(\frac{\partial G}{\partial n_Y}\right)_{T,P,n_Z,n_A,n_B} dn_Y$" corresponds to the Gibbs energy change by increasing dn_Y mol of Y. In this case, the partial pressure of the gas is not 1 atm, but $\frac{n_Y}{n_Y+n_Z+n_A+n_B}$ atm. As the Gibbs energy of gas largely depends on the partial pressure, the Gibbs energy change should be different from that of (1).

How can we define Gibbs energy of gas mixture?

3.1. Chemical equilibrium for gases

-Gibbs energy in gas mixture (ideal gas)-



T_0 K, V_0 m^3, P_A Pa

A(g): n_a mol

$$P_A = P_0 \frac{n_A}{n_A+n_B}$$

T_0 K, V_0 m^3, P_B Pa

B(g): n_b mol

$$P_B = P_0 \frac{n_B}{n_A+n_B}$$

T_0 K, V_0 m^3, P_0 Pa

A(g): n_a mol

B(g): n_b mol

$$P_A = P_0 \frac{n_A}{n_A+n_B}$$

$$P_B = P_0 \frac{n_B}{n_A+n_B}$$

The 1st law: $dU = PdV - TdS$

As const.-T const.-V condition, $\Delta U = -T\Delta S$

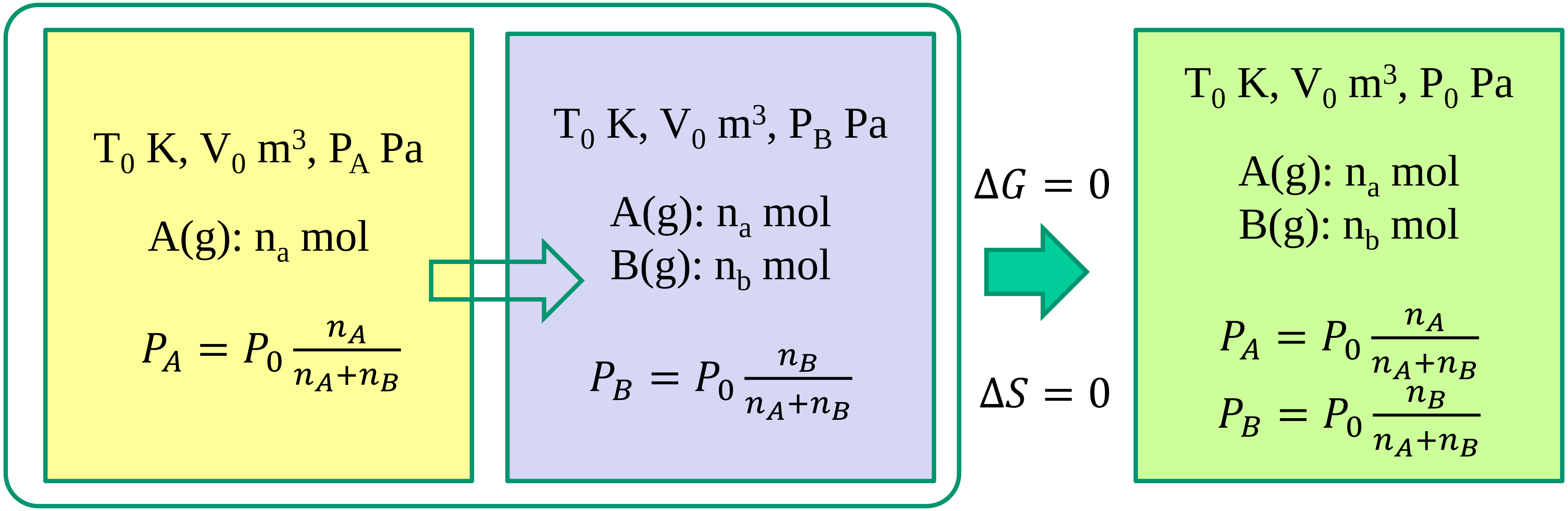
If the gases are ideal gases, because const.-T is assumed, $\Delta U = \Delta U(T) = 0$, hence, $\Delta S = 0$.

In addition, for ideal gas, $\Delta H = \Delta H(T) = 0$. Hence, $\Delta G = \Delta(H - TS) = 0$.

This result means that the Gibbs energy of mixed gas can be defined as the summation of Gibbs energies of constituent pure gasses holding corresponding partial pressure (for ideal gas).

$$\underbrace{\mu_A = \left(\frac{\partial G}{\partial n_A}\right)_{T,P,n_B}}_{\text{Mixture}} = \underbrace{\left(\frac{\partial G}{\partial n_A}\right)_{T,P_A} = \mu°_A(T) + RT\ln(P_A/P°)}_{\text{Pure substance}}$$

3.1. Chemical equilibrium for gases
-Gibbs energy in gas mixture (ideal gas)-



T_0 K, V_0 m^3, P_A Pa

A(g): n_a mol

$$P_A = P_0 \frac{n_A}{n_A+n_B}$$

T_0 K, V_0 m^3, P_B Pa

A(g): n_a mol
B(g): n_b mol

$$P_B = P_0 \frac{n_B}{n_A+n_B}$$

$\Delta G = 0$

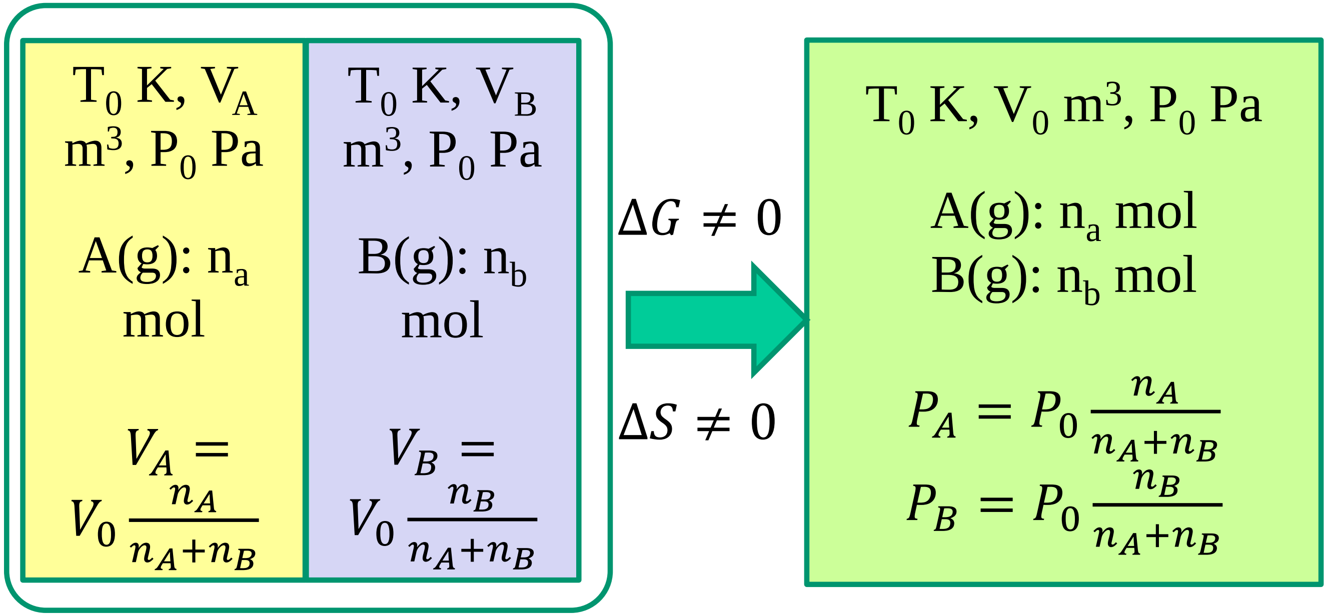
$\Delta S = 0$

T_0 K, V_0 m^3, P_0 Pa

A(g): n_a mol
B(g): n_b mol

$$P_A = P_0 \frac{n_A}{n_A+n_B}$$
$$P_B = P_0 \frac{n_B}{n_A+n_B}$$

- ✓ In this case, we need to consider the entropy of mixing.
- ✓ Indeed, the entropy of mixing is related to entropy change due to volume change.



T_0 K, V_A m^3, P_0 Pa

A(g): n_a mol

$$V_A = V_0 \frac{n_A}{n_A+n_B}$$

T_0 K, V_B m^3, P_0 Pa

B(g): n_b mol

$$V_B = V_0 \frac{n_B}{n_A+n_B}$$

$\Delta G \neq 0$

$\Delta S \neq 0$

T_0 K, V_0 m^3, P_0 Pa

A(g): n_a mol
B(g): n_b mol

$$P_A = P_0 \frac{n_A}{n_A+n_B}$$
$$P_B = P_0 \frac{n_B}{n_A+n_B}$$

3.1. Chemical equilibrium for gases

-review-

- ✓ Regarding the pressure effect, it is largely different between gas phase and condensed phases (solid, liquid)

	Solid	**Liquid**	**Gas**
Effect of pressure on Gibbs energy	✓ Negligible (< GPa level)	✓ Negligible (< GPa level)	✓ Important (comparable with temperature effect) ✓ Depending on partial pressure
If the total pressure is 1 bar…	✓ Any solid phase feels 1 bar.	✓ Any liquid phase feels 1 bar	✓ Total gas pressure is 1 bar, but partial pressures are changeable.

*Note there is no "partial pressure" for solid and liquid.

- ✓ For pure substance, the chemical potential, which is molar Gibbs energy for pure substance, is as follows, where "°" denotes the standard state

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

  - ✓ For example, "$RT\ln(P/P^{\circ})$" term at 300 K becomes -1.72 kJ/mol for $0.5\text{x}10^5$ Pa, -28.7 kJ/mol for 1 Pa, -57.4 kJ/mol for $1\text{x}10^{-5}$ Pa.
  - ✓ However, the contribution to Gibbs energy of the system (μn , not μ) is not so large because n is very small for a low pressure.

3.1. Chemical equilibrium for gases

-review-

✓ The following equation is for pure substance:

$$\mu(T,P)=\left(\frac{\partial G}{\partial n}\right)_{T,P}=\frac{G}{n}=\mu^{\circ}(T)+RT\ln(P/P^{\circ})$$

Now we want to know the related equation for mixture.

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

<(system-1) Mixture>
T_0 K, P_0 Pa
A(g): n_A mol, B(g): n_B mol
Y(g): n_Y mol, Z(g): n_Z mol

<(system-2) Pure A substance>
T_0 K, P_0 Pa
A(g): n_A mol

✓ For each system, if we add Δn_A of A with keeping other quantities fixed (T_0 and P_0, and n_B, n_Y and n_Z for system-1), Gibbs energy of the system should be also changed, ΔG. However, because the composition of the system different, $\Delta G_{sys-1}\neq\Delta G_{sys-2}$. And

$$\lim_{\Delta n_A\to 0}\frac{\Delta G_{sys-1}}{\Delta n_A}=\left(\frac{\partial G}{\partial n_A}\right)_{T,P,n_B,n_Y,n_Z}=\mu_A\neq\frac{G}{n_A}$$

$$\lim_{\Delta n_A\to 0}\frac{\Delta G_{sys-2}}{\Delta n_A}=\left(\frac{\partial G}{\partial n_A}\right)_{T,P}=\mu_A=\frac{G}{n_A}$$

*Note both are definitions of chemical potential, but for different systems.

3.1. Chemical equilibrium for gases

-review-

✓ Indeed, if we assume ideal gases, the chemical potential for a gas mixture can be replaced with the chemical potential for a pure gas substance with the corresponding partial pressure.

<System of mixture>

T_0 K, V_0 m^3, **P_0** Pa
A(g): n_A mol
B(g): n_B mol

$$P_A = P_0 \frac{n_A}{n_A+n_B}$$

$$P_B = P_0 \frac{n_B}{n_A+n_B}$$

<System of pure A >

T_0 K, V_0 m^3, **P_A** Pa
A(g): n_A mol

$$P_A = P_0 \frac{n_A}{n_A+n_B}$$

<System of pure B >

T_0 K, V_0 m^3, **P_B** Pa
B(g): n_B mol

$$P_B = P_0 \frac{n_B}{n_A+n_B}$$

where $G_{sys-mix} = G_{pure-A} + G_{pure-B}$ [for ideal gas].

✓ This idea can be extended to more than binary systems, then we can evaluate the pressure dependence of chemical potential of mixture as:

$$\underbrace{\mu_A = \left(\frac{\partial G}{\partial n_A}\right)_{T,P,n_B}}_{\text{Mixture}} \underbrace{= \left(\frac{\partial G}{\partial n_A}\right)_{T,P_A} = \mu^\circ{}_A(T) + RT\ln(P_A/P^\circ)}_{\text{Pure substance}}$$

3.1. Chemical equilibrium for gases

-review-

- ✓ Using the obtained pressure dependence of Gibbs energy of gas phase in a mixture, we can further write down “$\mathrm{dG} = \sum_i \mu_i dn_i$” to find $\mathrm{dG} = 0$ condition, which is the condition for equilibrium state.
- ✓ Then, as a result, following chemical equilibrium equations are obtained.
  - ✓ Again, please recall that these equations give us the condition where the Gibbs energy of the system is minimized. So, we can get the same result if we directly evaluate the Gibbs energy of the system and find the condition with which it is minimized.

For “ν_AA(g) + ν_BB(g) ⇌ ν_YY(g) + ν_ZZ(g)”

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

$$\Delta_r G^\circ = \nu_Y \mu^\circ{}_Y(T) + \nu_Z \mu^\circ{}_Z(T) - \nu_A \mu^\circ{}_A(T) - \nu_B \mu^\circ{}_B(T)$$

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

$$P^\circ = 1\ bar$$

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

$$K_P(T) = exp\left(-\frac{\Delta_r G^\circ}{RT}\right)$$

Quiz

(Quiz-1) Please determine the equilibrium constant for the following reaction at 1000 K: $\mathrm{H_2(g) + CO_2(g) \rightleftharpoons CO(g) + H_2O(g)}$

(Quiz-2) Suppose that we have a mixture of the gases H_2(g), CO_2(g), CO(g) and H_2O(g) at 1000 K at 1 bar, with $P_{H_2} = 0.200\ bar$, $P_{CO_2} = 0.200\ bar$, $P_{CO} = 0.300\ bar$, and $P_{H_2O} = 0.300\ bar$. Is the reaction described by the equation "$\mathrm{H_2(g) + CO_2(g) \rightleftharpoons CO(g) + H_2O(g)}$" at equilibrium? If not, in what direction (left or right) will the reaction proceed to attain equilibrium for const.-T cons.t-P condition?

(Quiz-3) Please determine the equilibrium partial pressures at 1000 K at 1 bar.

	$\Delta_f \boldsymbol{G}°$ (kJ/mol) @ 1000 K
H_2(g)	0
CO_2(g)	-394.9
CO(g)	-155.4
H_2O(g)	-192.6

Quiz-answer

(Quiz-1) Please determine the equilibrium constant for the following reaction at 1000 K: $\mathrm{H_2(g) + CO_2(g) \rightleftharpoons CO(g) + H_2O(g)}$

	$\Delta_f \boldsymbol{G}°$ (kJ/mol) @ 1000 K
H_2(g)	0
CO_2(g)	-395.9
CO(g)	-200.3
H_2O(g)	-192.6

$$\Delta_r G° = \nu_Y \mu°_Y(T) + \nu_Z \mu°_Z(T) - \nu_A \mu°_A(T) - \nu_B \mu°_B(T)$$
$$= \mu°_{CO}(T) + \mu°_{H2O}(T) - \mu°_{H2}(T) - \mu°_{CO2}(T)$$
$$= (-200.3) + (-192.6) - (0) - (395.9) = 3\ \text{kJ/mol}$$

$$K_P(T) = exp\left(-\frac{\Delta_r G°}{RT}\right) = exp\left(-\frac{3 \times 10^3}{8.31 \times 1000}\right) = 0.697$$

Quiz answer

(Quiz-2) Suppose that we have a mixture of the gases H_2(g), CO_2(g), CO(g) and H_2O(g) at 1000 K at 1 bar, with $P_{H_2} = 0.200\ bar$, $P_{CO_2} = 0.200\ bar$, $P_{CO} = 0.300\ bar$, and $P_{H_2O} = 0.300\ bar$. Is the reaction described by the equation "$\mathrm{H_2(g) + CO_2(g)} \rightleftharpoons \mathrm{CO(g) + H_2O(g)}$" at equilibrium? If not, in what direction (left or right) will the reaction proceed to attain equilibrium for const.-T cons.t-P condition?

We need to use an equation like:

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

First, we evaluate "*reaction quotient" using the following equation:*

$$Q = \left[\frac{(P_Y/P°)^{\nu_Y}\,(P_Z/P°)^{\nu_Z}}{(P_A/P°)^{\nu_A}\,(P_B/P°)^{\nu_B}}\right] = \frac{0.300 \times 0.300}{0.200 \times 0.200} = 2.25$$

*Be careful that Q is not identical to Q_{eq}. $Q = Q_{eq} = K_P(T)$ is achieved when the system (thus partial pressures) are of equilibrium state.

Because this value is larger than $K_P(= 0.697)$, the system should evolve to decrease Q (non-equilibrium state now). Thus, partial pressure of reactants will increase, which means the reaction will proceed from the right to the left.

Quiz answer

(Quiz-3) Please determine the equilibrium partial pressures at 1000 K at 1 bar.

If we define the extent of reaction with ξ, the partial pressures at equilibrium state is given as follows (ξ becomes ξ_{eq}):

$$P_{H_2} = (0.200 - \xi_{eq})\ bar \qquad P_{CO_2} = (0.200 - \xi_{eq})\ bar$$

$$P_{CO} = (0.300 + \xi_{eq})\ bar \qquad P_{H_2O} = (0.300 + \xi_{eq})\ bar$$

Then,

$$K_P(T) = Q_{eq} = \left[\frac{(P_Y/P^\circ)^{\nu_Y}\,(P_Z/P^\circ)^{\nu_Z}}{(P_A/P^\circ)^{\nu_A}\,(P_B/P^\circ)^{\nu_B}}\right]_{eq} = \left[\frac{(0.300 + \xi_{eq})(0.300 + \xi_{eq})}{(0.200 - \xi_{eq})(0.200 - \xi_{eq})}\right]_{eq} = 0.697$$

$$\left(0.300 + \xi_{eq}\right) = \sqrt{0.697}\left(0.200 - \xi_{eq}\right)$$

$$\xi_{eq} = -0.0725$$

Applying this value to the partial pressure expressions, we can obtain the following equilibrium partial pressures.

$$P_{H_2} = P_{CO_2} = 0.273\ bar \qquad P_{CO} = P_{H_2O} = 0.227\ bar$$

3.1. Chemical equilibrium for gases

-an example-

(Problem) Initially, we have 1 mol of CH_4(g) and 1 mol of H_2O(g) in the system and keep const.-T (1000 K) const.-P (1 bar) condition. When the system arrived at the equilibrium state, we found CH_4(g), H_2O(g), CO(g), H_2(g), C_2H_2(g). Please determine the equilibrium amounts of these species.

3.1. Chemical equilibrium for gases

-an example-

(Problem) Initially, we have 1 mol of $CH_4(g)$ and 1 mol of $H_2O(g)$ in the system and keep const.-T (1000 K) const.-P (1 bar) condition. When the system arrived at the equilibrium state, we found $CH_4(g)$, $H_2O(g)$, $CO(g)$, $H_2(g)$, $C_2H_2(g)$. Please determine the equilibrium amounts of these species.

$$CH_4(g) + H_2O(g) \rightarrow$$
$$n_{CH4}\, CH_4(g) + n_{H2O}\, H_2O(g) + n_{CO}\, CO(g) + n_{H2}\, H_2(g) + n_{C2H2}\, C_2H_2(g)$$

- ✓ For mass conservation, we have 3 conditions.
  - ✓ [H] $4+2=4\, n_{CH4} + 2\, n_{H2O} + 2\, n_{H2} + 2\, n_{C2H2}$
  - ✓ [C] $1= n_{CH4} + n_{CO} + 2n_{C2H2}$
  - ✓ [O] $1= n_{H2O} + n_{CO}$
- ✓ We need 2 additional equations to determine 5 parameters. At equilibrium states, any balance reactions should be of equilibrium states. Then, we consider 2 of them.
  - ✓ [eq.1] $CH_4(g) + H_2O(g) \rightleftharpoons 3H_2(g) + CO(g)$
  - ✓ [eq.2] $CH_4(g) + CO(g) \rightleftharpoons C_2H_2(g) + H_2O(g)$

- ✓ Now we have 5 equations for 5 unknown variables, then we can determine the 5 variables.

3.1. Chemical equilibrium for gases

-an example -

(Problem) Initially, we have 1 mol of CH_4(g) and 1 mol of H_2O(g) in the system and keep const.-T (1000 K) const.-P (1 bar) condition. When the system arrived at the equilibrium state, we found CH_4(g), H_2O(g), CO(g), H_2(g), C_2H_2(g). Please determine the equilibrium amounts of these species.

[eq.1] $CH_4(g) + H_2O(g) \rightleftharpoons 3H_2(g) + CO(g)$

$$K_{P,1}(T) = exp\left(-\frac{\Delta_r G°_1}{RT}\right) = \left(\frac{P_{H2}^3 P_{CO}}{P_{CH4} P_{H2O}}\right)$$

[eq.2] $CH_4(g) + CO(g) \rightleftharpoons C_2H_2(g) + H_2O(g)$

$$K_{P,2}(T) = exp\left(-\frac{\Delta_r G°_2}{RT}\right) = \left(\frac{P_{C2H2} P_{H2O}}{P_{CH4} P_{CO}}\right)$$

where partial pressures are proportional to molar fractions.

- ✓ For example, if the balance reaction given in [eq.1] is not of equilibrium state, some reaction (to right or to left) should happen to decrease the Gibbs energy of the system.
- ✓ Hence, any kind of balance reaction between constituent gases should achieve equilibrium conditions.

Quiz

(Quiz-1) Please determine the equilibrium constant for the following reaction at 1000 K: $\mathrm{H_2(g) + CO_2(g) \rightleftharpoons CO(g) + H_2O(g)}$

(Quiz-2) Suppose that we have a mixture of the gases H_2(g), CO_2(g), CO(g) and H_2O(g) at 1000 K at 1 bar, with $P_{H_2} = 0.200\ bar$, $P_{CO_2} = 0.200\ bar$, $P_{CO} = 0.300\ bar$, and $P_{H_2O} = 0.300\ bar$. Is the reaction described by the equation "$\mathrm{H_2(g) + CO_2(g) \rightleftharpoons CO(g) + H_2O(g)}$" at equilibrium? If not, in what direction (left or right) will the reaction proceed to attain equilibrium for const.-T cons.t-P condition?

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-an example-

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