

# **Chapter 8: Part B**

## **Equilibrium between phases or chemical species**

Zhi-Jie Tan  
Wuhan University

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# Purpose of the chapter

- **Beyond a single phase**
- **Beyond a single component**
- **Generally, beyond several species in several phases**
  
- **Phase equilibrium**
- **Chemical equilibrium**

# General equilibrium conditions

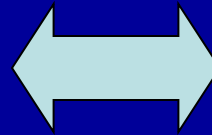
## 8.1 Isolated systems

Considering a thermally isolated system A, the system tends to achieve the larger entropy

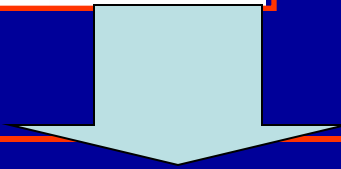
In statistical term , the system approaches to a situation of larger intrinsic probability

Direction:

$$\Delta S \geq 0$$



$\Omega$  increases

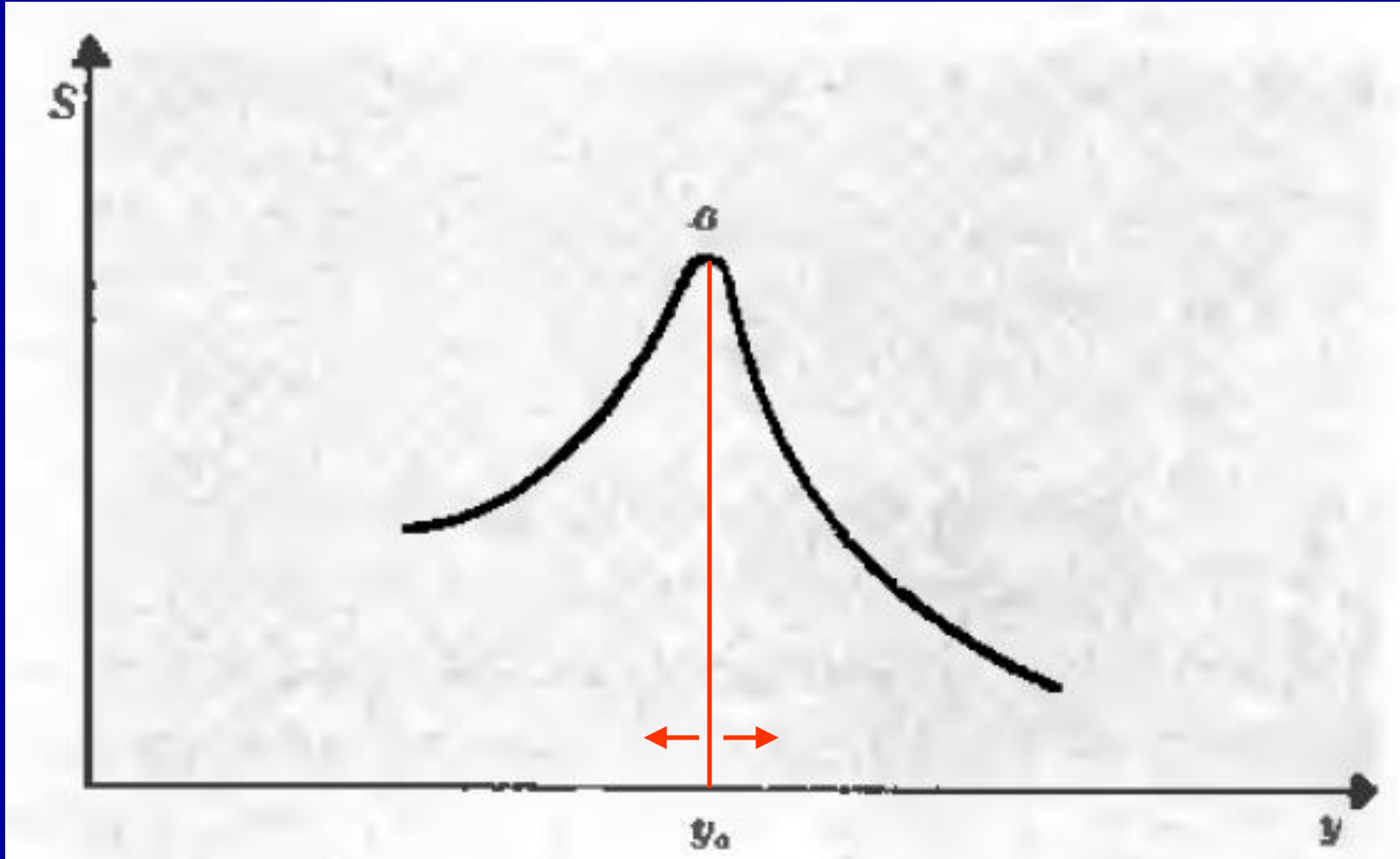


For a thermally isolated system, the stable equilibrium situation is characterized by the fact

$$S = \text{maximum}$$

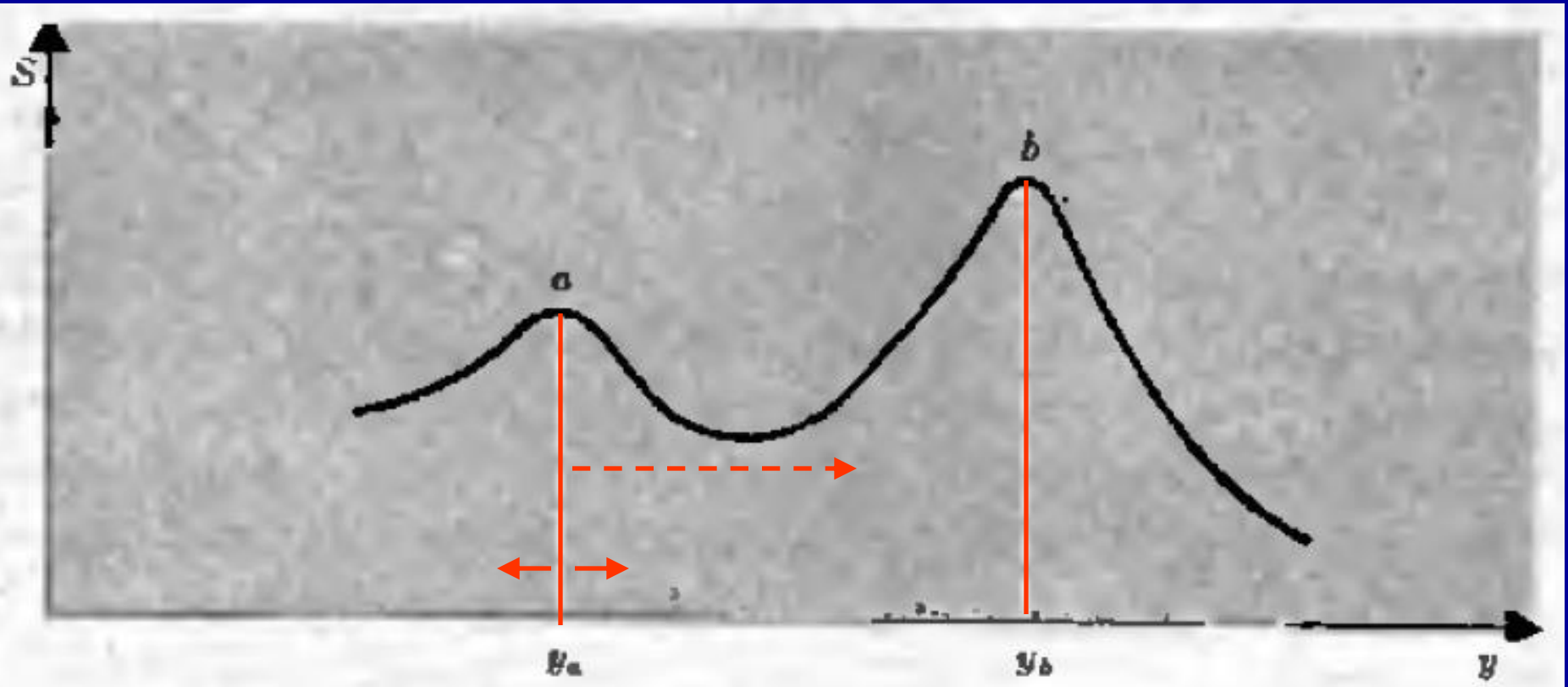
# General equilibrium conditions

## 8.1 Isolated systems



# General equilibrium conditions

## 8.1 Isolated systems



# General equilibrium conditions

## 8.1 Isolated systems

In a thermally isolated system

$$Q = 0 = W + \Delta \bar{E} \quad \longrightarrow \quad W = -\Delta \bar{E}$$

If the external parameters are kept fixed, then

$$\bar{E} = \text{constant}$$

$$S = \text{maximum}$$

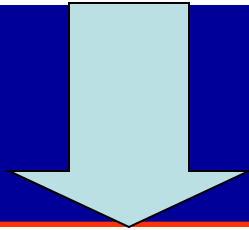
Can be discussed in statistical term

# General equilibrium conditions

## 8.1 Isolated systems

$\Omega(y)$  denotes the number of accessible states in  $[y, y+dy]$ ,  
the probability for  $y$  in  $[y, y+dy]$

$$P(y) \propto \Omega(y) = e^{S(y)/k}$$



$$\frac{P(y)}{P_{\max}} = e^{\Delta_m S/k}$$

$$\Delta_m S = S(y) - S_{\max}$$

Eqs. provide quantitative statements, and allow one to  
calculate the probability of occurrence of fluctuations  
where  $S \neq S_{\max}$

# General equilibrium conditions

## 8.1 Isolated systems: remarks

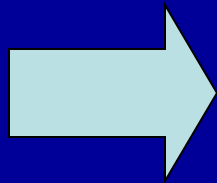
If  $S$  depends on a single  $y$ , then at  $y=y_m$  where  $S=S_m$

$$\frac{\partial S}{\partial y} = 0$$

The expansion gives

$< 0$

$$S(y) = S_{\max} + \frac{1}{2} \left( \frac{\partial^2 S}{\partial y^2} \right) (y - \tilde{y})^2 + \dots$$



$$P(y) \propto \exp \left[ - \frac{1}{2k} \left| \frac{\partial^2 S}{\partial y^2} \right| (y - \tilde{y})^2 \right]$$



# General equilibrium conditions

## 8.2 System in contact with a reservoir at constant T

Purpose: much expt. work is done under conditions of  $T_0$

For  $A^0$

$$\Delta S^{(0)} \geq 0$$

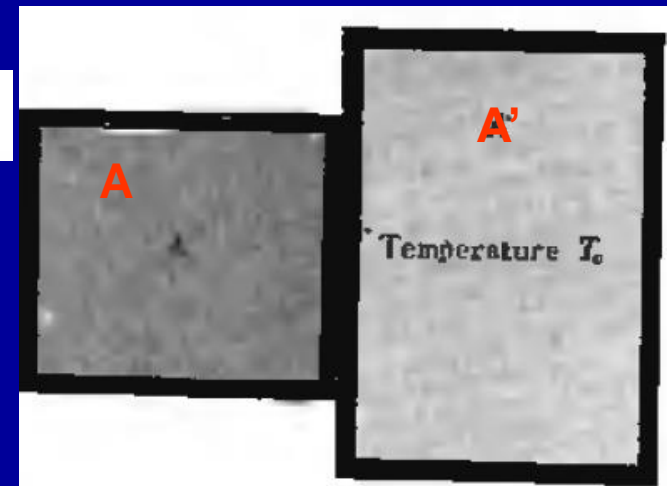
$$\Delta S^{(0)} = \Delta S + \Delta S'$$

If A absorbs Q heat from A',  
then A' absorbs  $-Q$  ( $T=T_0$ )

$$\Delta S' = \frac{(-Q)}{T_0}$$

1st law gives

$$Q = \Delta \bar{E} + W$$



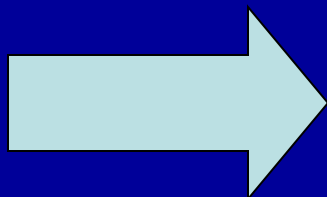
$A^0$



# General equilibrium conditions

## 8.2 System in contact with a reservoir at constant T

$$\begin{aligned}\Delta S^{(0)} &= \Delta S - \frac{Q}{T_0} \\ &= \frac{T_0 \Delta S - (\Delta \bar{E} + W)}{T_0} \\ &= \frac{\Delta(T_0 S - \bar{E}) - W}{T_0}\end{aligned}$$

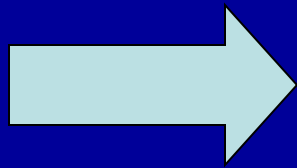


$$\Delta S^{(0)} = \frac{-\Delta F_0 - W}{T_0}$$

Helmholtz free energy  $F = \bar{E} - TS$

# General equilibrium conditions

## 8.2 System in contact with a reservoir at constant T

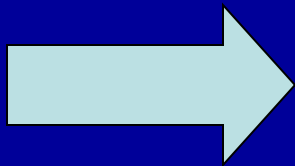


$$-\Delta F_0 \geq W$$

Means that maximum work which can be done by a system in contact with a heat reservoir is given by  $-\Delta F_0$

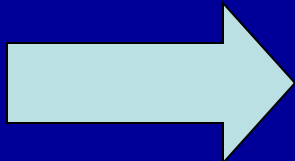
If the external para. Is kept fixed

$$W = 0$$



$$\Delta F_0 \leq 0$$

In a system whose para is fixed, is in thermal contact with a heat reservoir, the stable equilibrium condition is



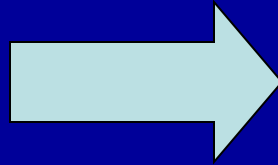
$$F_0 = \text{minimum}$$

# General equilibrium conditions

## 8.2 System in contact with a reservoir at constant T

$$W = 0$$

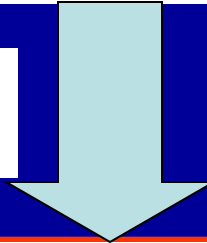
$$\Delta S^{(0)} = \frac{-\Delta F_0 - W}{T_0}$$



$$\Delta S^{(0)} = -\frac{\Delta F_0}{T_0}$$

$$S^{(0)}(y) = S^{(0)}(y_1) - \frac{\Delta F_0}{T_0} = S^{(0)}(y_1) - \frac{F_0(y) - F_0(y_1)}{T_0}$$

$$P(y) \propto \Omega^{(0)}(y) = e^{S^{(0)}(y)/k}$$



$$P(y) \propto e^{-F_0(y)/kT_0}$$


# General equilibrium conditions

## 8.2 System in contact with a reservoir at constant T: remarks

For canonical ensemble

$$P(y) \propto \sum_r e^{-\beta_0 E_r}, \quad \beta_0 = (kT_0)^{-1}$$

The sum is over all states for which  $y$  is in  $[y, y+dy]$


$$P(y) \propto \sum_E \Omega(E; y) e^{-\beta_0 E}$$

Only  $E=\bar{E}$  (mean)  
contributes to the  
sum



S

$$P(y) \propto \Omega(\bar{E}; y) e^{-\beta_0 \bar{E}(y)} = e^{S(y)/k - \beta_0 \bar{E}(y)} = e^{-\beta_0 F_0(y)}$$

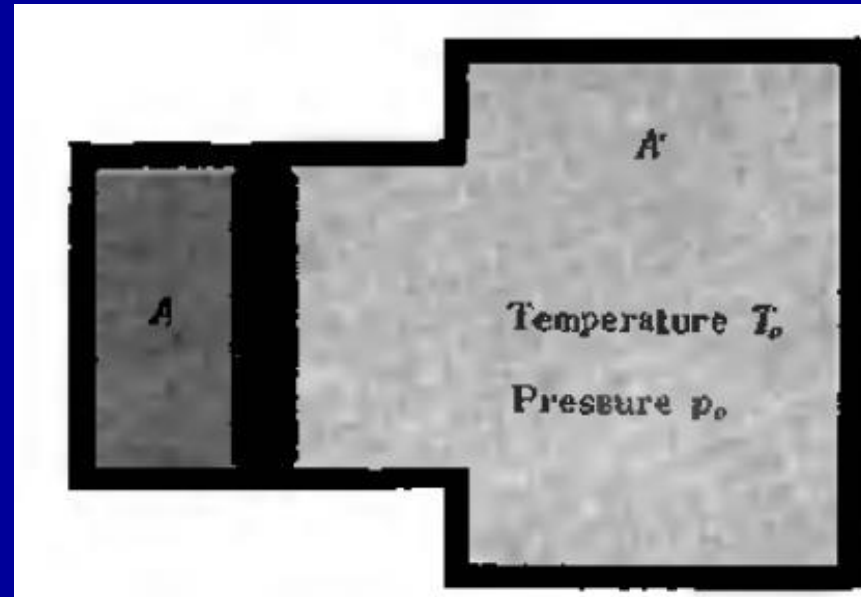
# General equilibrium conditions

## 8.3 System in contact with a reservoir at constant T and pressure

$$\Delta S^{(0)} = \Delta S + \Delta S' \geq 0$$

If A absorbs Q heat from A',

$$\Delta S' = -Q/T_0$$



1st law gives

$$Q = \Delta \bar{E} + p_0 \Delta V + W^*$$

$$A^{(0)} = A + A'$$

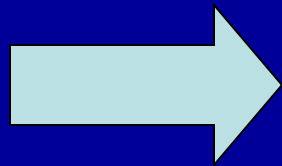
By pressure other work

$$\begin{aligned} \Delta S^{(0)} &= \Delta S - \frac{Q}{T_0} = \frac{1}{T_0} [T_0 \Delta S - Q] \\ &= \frac{1}{T_0} [T_0 \Delta S - (\Delta \bar{E} + p_0 \Delta V + W^*)] \end{aligned}$$

# General equilibrium conditions

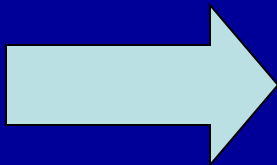
## 8.3 System in contact with a reservoir at constant T and pressure

$$\begin{aligned}\Delta S^{(0)} &= \Delta S - \frac{Q}{T_0} = \frac{1}{T_0} [T_0 \Delta S - Q] \\ &= \frac{1}{T_0} [T_0 \Delta S - (\Delta \bar{E} + p_0 \Delta V + W^*)] \\ &= \frac{1}{T_0} [\Delta(T_0 S - \bar{E} - p_0 V) - W^*]\end{aligned}$$



$$\Delta S^{(0)} = \frac{-\Delta G_0 - W^*}{T_0}$$

Gibbs free energy  $G = \bar{E} - TS + pV$



$$-\Delta G_0 \geq W^*$$

# General equilibrium conditions

## 8.3 System in contact with a reservoir at constant T and pressure

If external paras except for V are kept fixed

$$W^* = 0$$



$$\Delta G_0 \leq 0$$

In a system whose para is fixed except for V, is in thermal contact with a heat reservoir, the stable equilibrium condition is

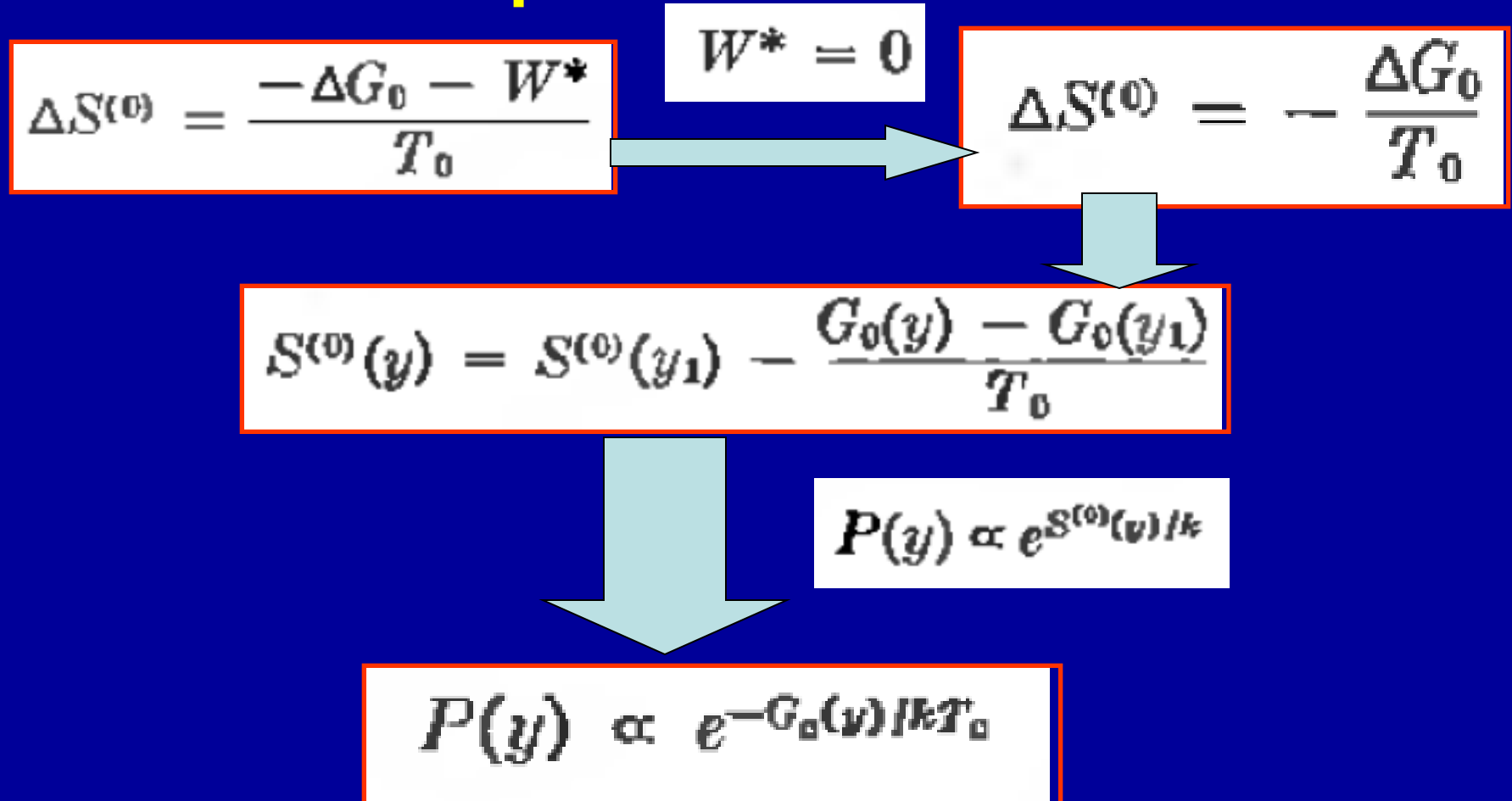


$$G_0 = \text{minimum}$$



# General equilibrium conditions

## 8.3 System in contact with a reservoir at constant T and pressure



# General equilibrium conditions

## 8.4 stability conditions for a homogeneous substance

The small part is relatively small  
And the rest is like a reservoir with  $T_0$  and  $p_0$ , then stable equil. Condi.



$$G_0 \equiv \bar{E} - T_0 S + p_0 V = \text{minimum}$$

\* Stability against T variation

Expanding

$$\Delta_m G_0 = G_0 - G_{\min}$$

$$= \left( \frac{\partial G_0}{\partial T} \right)_V \Delta T + \frac{1}{2} \left( \frac{\partial^2 G_0}{\partial T^2} \right)_V (\Delta T)^2 + \dots$$

$$T = \tilde{T} \text{ when } G_0 = G_{\min}$$

$$\Delta T \equiv T - \tilde{T}$$

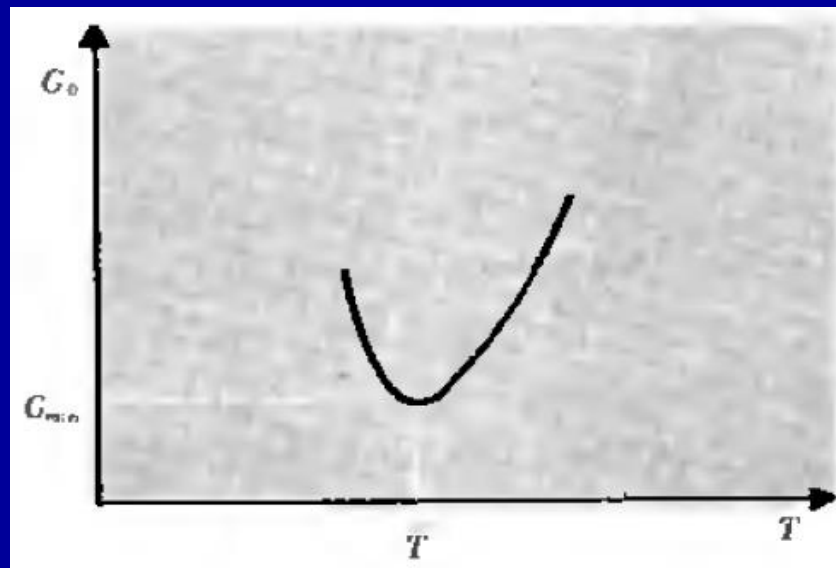
# General equilibrium conditions

## 8.4 stability conditions for a homogeneous substance

$$\Delta_m G_0 = G_0 - G_{\min} \\ = \left( \frac{\partial G_0}{\partial T} \right)_v \Delta T + \frac{1}{2} \left( \frac{\partial^2 G_0}{\partial T^2} \right)_v (\Delta T)^2 + \dots$$

$$\left( \frac{\partial G_0}{\partial T} \right)_v = 0 \quad \text{for } T = \tilde{T}$$

$$\left( \frac{\partial^2 G_0}{\partial T^2} \right)_v \geq 0 \quad \text{for } T = \tilde{T}$$



# General equilibrium conditions

## 8.4 stability conditions for a homogeneous substance

$$G_0 \equiv \bar{E} - T_0 S + p_0 V$$

$$\left( \frac{\partial G_0}{\partial T} \right)_V = \left( \frac{\partial \bar{E}}{\partial T} \right)_V - T_0 \left( \frac{\partial S}{\partial T} \right)_V = 0$$

$$T dS = d\bar{E} + \bar{p} dV$$

$$T \left( \frac{\partial S}{\partial T} \right)_V = \left( \frac{\partial \bar{E}}{\partial T} \right)_V$$

$$\left( \frac{\partial G}{\partial T} \right)_V = \left( 1 - \frac{T_0}{T} \right) \left( \frac{\partial \bar{E}}{\partial T} \right)_V = 0$$



$$\tilde{T} = T_0$$

# General equilibrium conditions

## 8.4 stability conditions for a homogeneous substance

$$G_0 \equiv \bar{E} - T_0 S + p_0 V$$

$$\left(\frac{\partial^2 G_0}{\partial T^2}\right)_V = \frac{T_0}{T^2} \left(\frac{\partial \bar{E}}{\partial T}\right)_V + \left(1 - \frac{T_0}{T}\right) \left(\frac{\partial^2 \bar{E}}{\partial T^2}\right)_V \geq 0$$

$= 0$



$$\left(\frac{\partial \bar{E}}{\partial T}\right)_V \geq 0$$



$$C_V \geq 0$$

# General equilibrium conditions

## 8.4 stability conditions for a homogeneous substance

- Stability against volume fluctuation expansion gives

fixed at  $T = T_0$

$$\Delta V \equiv V - \tilde{V}$$

$$\Delta_m G_0 \equiv G_0 - G_{\min} = \left( \frac{\partial G_0}{\partial V} \right)_T \Delta V + \frac{1}{2} \left( \frac{\partial^2 G_0}{\partial V^2} \right)_T (\Delta V)^2 + \dots$$

$$\left( \frac{\partial G_0}{\partial V} \right)_T = \left( \frac{\partial \bar{E}}{\partial V} \right)_T - T_0 \left( \frac{\partial S}{\partial V} \right)_T + p_0 \quad \left\{ \begin{array}{l} G_0 \equiv \bar{E} - T_0 S + p_0 V \end{array} \right.$$

$$T dS = d\bar{E} + \bar{p} dV \quad \longrightarrow \quad T \left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial \bar{E}}{\partial V} \right)_T + \bar{p}$$

$$\left( \frac{\partial G_0}{\partial V} \right)_T = T \left( \frac{\partial S}{\partial V} \right)_T - \bar{p} - T_0 \left( \frac{\partial S}{\partial V} \right)_T + p_0$$

# General equilibrium conditions

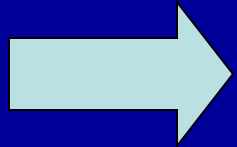
## 8.4 stability conditions for a homogeneous substance

### • Stability against volume fluctuation

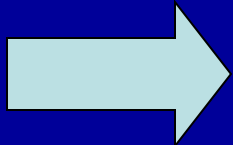
fixed at  $T = T_0$

$$\Delta V \equiv V - \tilde{V}$$

$$\left(\frac{\partial G_0}{\partial V}\right)_T = T \left(\frac{\partial S}{\partial V}\right)_T - \bar{p} - T_0 \left(\frac{\partial S}{\partial V}\right)_T + p_0$$



$$\left(\frac{\partial G_0}{\partial V}\right)_T = -\bar{p} + p_0 = 0$$



$$\bar{p} = p_0$$

# General equilibrium conditions

## 8.4 stability conditions for a homogeneous substance

### • Stability against volume fluctuation

fixed at  $T = T_0$

$$\Delta V \equiv V - \tilde{V}$$

$$\left( \frac{\partial^2 G_0}{\partial V^2} \right)_T = - \left( \frac{\partial \bar{p}}{\partial V} \right)_T \geq 0$$

$$G_0 \equiv \bar{E} - T_0 S + p_0 V$$

$$\kappa \equiv - \frac{1}{V} \left( \frac{\partial V}{\partial \bar{p}} \right)_T$$

$$\kappa \geq 0$$



# General equilibrium conditions

## 8.4 stability conditions for a homogeneous substance

- density fluctuation  
equilibrium

$$G_0(\tilde{V}) = G_{\min.}$$

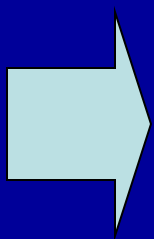
$$V = \tilde{V}$$

$P(v)dV$  is the probability for  $V$  in  $[V, dV]$

$$\mathcal{P}(V) dV \propto e^{-G_0(V)/kT} dV$$

$\Delta V$  is small, then

$$G_0(V) = G_{\min} - \frac{1}{2} \left( \frac{\partial^2 \bar{p}}{\partial V^2} \right)_T (\Delta V)^2 = G_{\min} + \frac{(\Delta V)^2}{2\tilde{V}_\kappa}$$



$$\mathcal{P}(V) dV = B \exp \left[ - \frac{(V - \tilde{V})^2}{2kT_0 \tilde{V}_\kappa} \right] dV$$

# General equilibrium conditions

## 8.4 stability conditions for a homogeneous substance

- density fluctuation  
equilibrium

$$G_0(\tilde{V}) = G_{\min.}$$

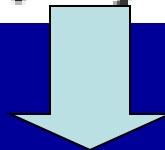
$$V = \tilde{V}$$



$$\overline{(\Delta V)^2} \equiv \overline{(V - \tilde{V})^2} = kT_0 \tilde{V} \kappa$$

$$\tilde{n} = N / \tilde{V}$$

$$\Delta n = - (N / \tilde{V}^2) \Delta V = - (\tilde{n} / \tilde{V}) \Delta V.$$



$$\overline{(\Delta n)^2} = \left( \frac{\tilde{n}}{\tilde{V}} \right)^2 \overline{(\Delta V)^2} = \tilde{n}^2 \left( \frac{kT_0}{\tilde{V}} \kappa \right)$$

# General equilibrium conditions

## Discussions:

$$\Delta_m G_0 = G_0 - G_{\min}$$
$$= \left( \frac{\partial G_0}{\partial T} \right)_V \Delta T + \frac{1}{2} \left( \frac{\partial^2 G_0}{\partial T^2} \right)_V (\Delta T)^2 + \dots$$

$$\Delta_m G_0 \equiv G_0 - G_{\min} = \left( \frac{\partial G_0}{\partial V} \right)_T \Delta V + \frac{1}{2} \left( \frac{\partial^2 G_0}{\partial V^2} \right)_T (\Delta V)^2 + \dots$$

### Le Châtelier's principle

If a system is in *stable* equilibrium, then any spontaneous change of its parameters must bring about processes which tend to restore the system to equilibrium.

# Equilibrium between phases

## 8.5 equilibrium conditions and Clausius-Clapeyron equation

Consider a single component system consisting of two phases 1 and 2. Suppose that it is in equilibrium with a reservoir with **constant  $T$  and mean  $p$**

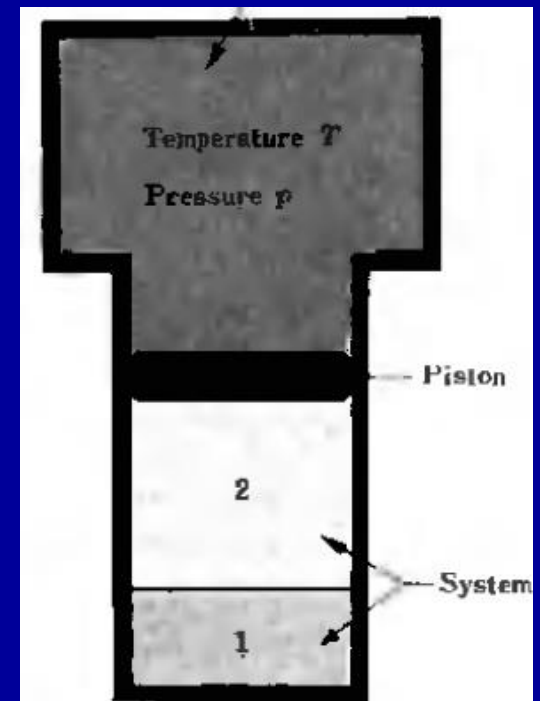
Finding the conditions for equilibrium between 1 and 2.  
Previous condition gives

$$G = E - TS + pV = \text{minimum}$$

$\nu_i$  is number of moles of phase  $i$ ;

$g_i(T,p)$ : Gibbs free energy/mole at  $(T,p)$

$$G = \nu_1 g_1 + \nu_2 g_2$$



# Equilibrium between phases

## 8.5 equilibrium conditions and Clausius-Clapeyron equation

Conservation of matter gives

$$\nu_1 + \nu_2 = \nu = \text{constant}$$

In equilibrium,  $G$  must be stationary, then

$$dG = g_1 d\nu_1 + g_2 d\nu_2 = 0$$


$$(g_1 - g_2) d\nu_1 = 0$$

$$d\nu_2 = -d\nu_1$$


$$g_1 = g_2$$

# Equilibrium between phases

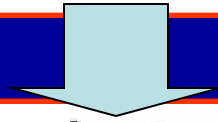
## 8.5 equilibrium conditions and Clausius-Clapeyron equation

Conservation of matter gives

$$\nu_1 + \nu_2 = \nu = \text{constant}$$

In equilibrium,  $G$  must be stationary, then

$$dG = g_1 d\nu_1 + g_2 d\nu_2 = 0$$



$$(g_1 - g_2) d\nu_1 = 0$$

$$d\nu_2 = -d\nu_1$$



$$g_1 = g_2$$

$$g_1(T, p) = g_2(T, p)$$

# Equilibrium between phases

## 8.5 equilibrium conditions and Clausius-Clapeyron equation

In equilibrium,

$$g_1(T, p) = g_2(T, p)$$

- If  $(T, p)$  are such that  $g_1 < g_2$ , the minimum  $G$  is achieved if all substance is transformed to phase 1 so that  $G = \nu g_1$ ;
- If  $(T, p)$  are such that  $g_1 > g_2$ , the minimum  $G$  is achieved if all substance is transformed to phase 2 so that  $G = \nu g_2$ ;
- If  $(T, p)$  are such that  $g_1 = g_2$ , any amount of phase 1 can coexist with phase 2 with amount  $\nu_2 = \nu - \nu_1$ .
- $(T, p)$  satisfying the condition represents the “**phase-equilibrium line**” along which two phases can coexist in equilibrium

# Equilibrium between phases

## 8.5 equilibrium conditions and Clausius-Clapeyron equation

$$g_1(T, p) = g_2(T, p)$$

It is possible to characterize the “phase-equilibrium line” by differential equation. For the system

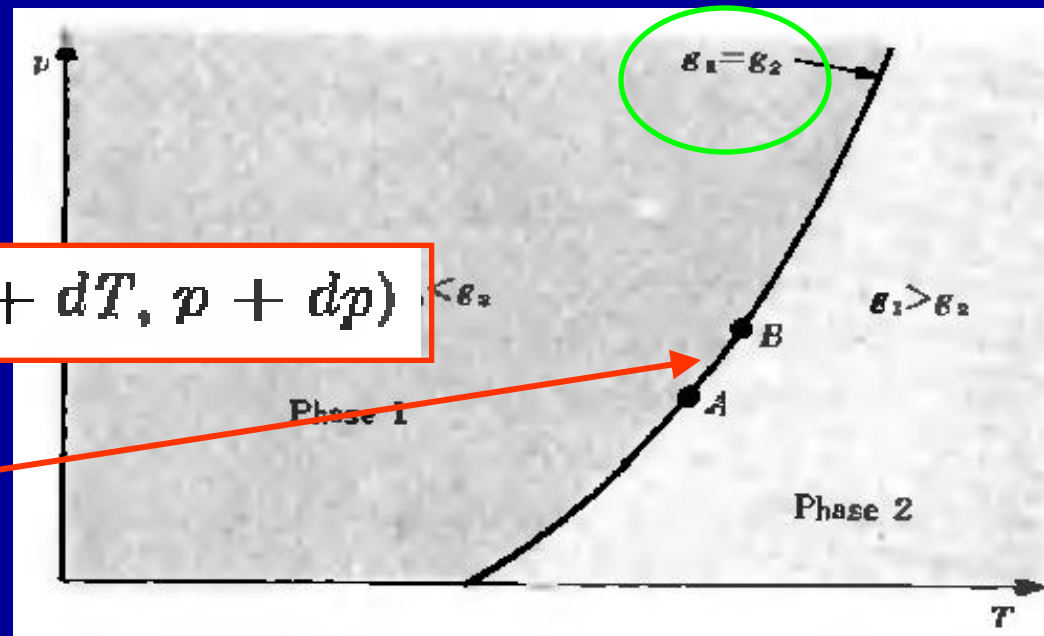
$$g_1(T, p) = g_2(T, p)$$

B point on the line

$$g_1(T + dT, p + dp) = g_2(T + dT, p + dp)$$

$$dg_1 = dg_2$$

$$dg_i = \left( \frac{\partial g_i}{\partial T} \right)_p dT + \left( \frac{\partial g_i}{\partial p} \right)_T dp$$





# Equilibrium between phases

## 8.5 equilibrium conditions and Clausius-Clapeyron equation

For each phase,  $dg$  can be obtained by fundamental thermodynamic relation

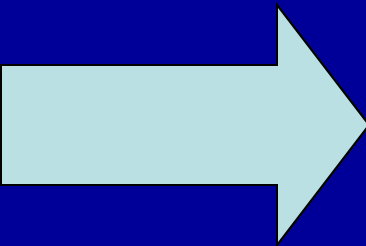
$$d\epsilon = T ds - p dv$$


$$dg \equiv d(\epsilon - Ts + pv) = -s dT + v dp$$

Equilibrium:

$$-s_1 dT + v_1 dp = -s_2 dT + v_2 dp$$

$$(s_2 - s_1) dT = (v_2 - v_1) dp$$


$$\frac{dp}{dT} = \frac{\Delta s}{\Delta v}$$

**Clausius-Clapeyron equation**

# Equilibrium between phases

## 8.5 equilibrium conditions and Clausius-Clapeyron equation

$$\frac{dp}{dT} = \frac{\Delta s}{\Delta v}$$

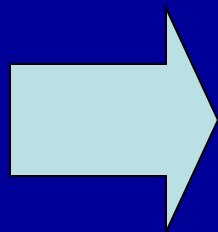
Clausius-Clapeyron equation

Entropy change      volume change

Since entropy change associated with phase transition, heat must be adsorbed

$$\Delta S = S_2 - S_1 = \frac{L_{12}}{T}$$

Heat adsorbed when phase 1 is transitioned to 2



$$\frac{dp}{dT} = \frac{\Delta S}{\Delta V} = \frac{L_{12}}{T \Delta V}$$

molar volume/ heat per mole  
gram volume/ heat gram

# Equilibrium between phases

## 8.5 equilibrium conditions and Clausius-Clapeyron equation

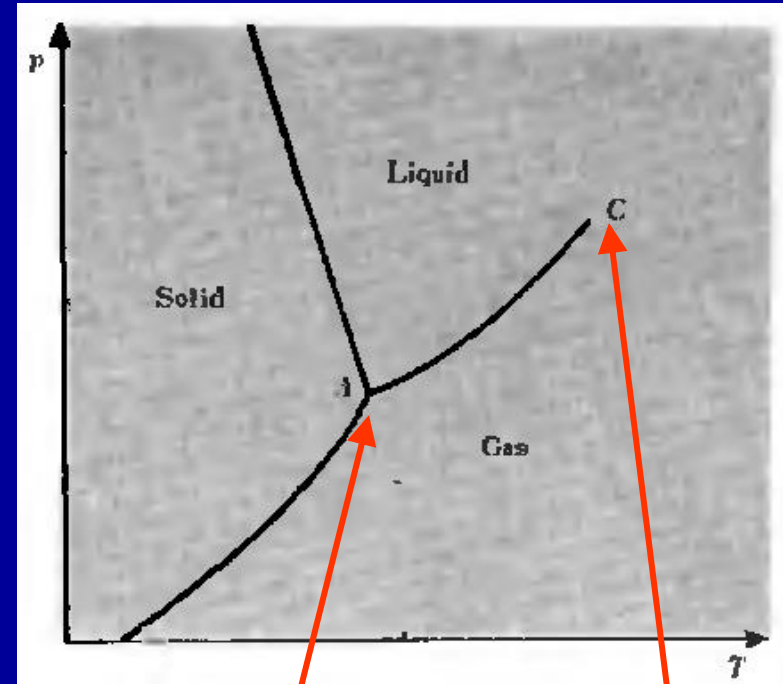
Phase transformation of a simple substance

Generally, there are three phases: gas, liquid, solid

➤ From solid to liquid, the entropy almost always increases,  $L_{sl} > 0$ , and in most cases,  $\Delta V > 0$ , then the slope  $> 0$ ;

➤ For substance like water,  $\Delta V < 0$ , then the slope  $< 0$ .

$$\frac{dp}{dT} = \frac{\Delta s}{\Delta v}$$



**Triple  
point**

**critical  
point**

# Equilibrium between phases

## 8.5 equilibrium conditions and Clausius-Clapeyron equation

Approximate calculation of the vapor pressure

C-C equation can be used to derive an approx. expression for vapor pressure (gas in equilibrium with solid/liquid)

$$\frac{dp}{dT} = \frac{l}{T \Delta v}$$

1 stands for solid/liquid, and 2 for gas, then

$$\Delta v = v_2 - v_1 \approx v_2$$

Gas is approximated as ideal gas

$$pv_2 = RT$$

# Equilibrium between phases

## 8.5 equilibrium conditions and Clausius-Clapeyron equation

Approximate calculation of the vapor pressure

$$pv_2 = RT$$

$$\Delta v = v_2 - v_1 \approx v_2$$

$$\Delta v = RT/p$$

$$\frac{dp}{dT} = \frac{l}{T \Delta v}$$

$$\frac{1}{p} \frac{dp}{dT} = \frac{l}{RT^2}$$

$$p = p_0 e^{-l/RT}$$

$$\ln p = -\frac{l}{RT} + \text{constant}$$

# Equilibrium between phases

## 8.6 Phase transformations & equation of state

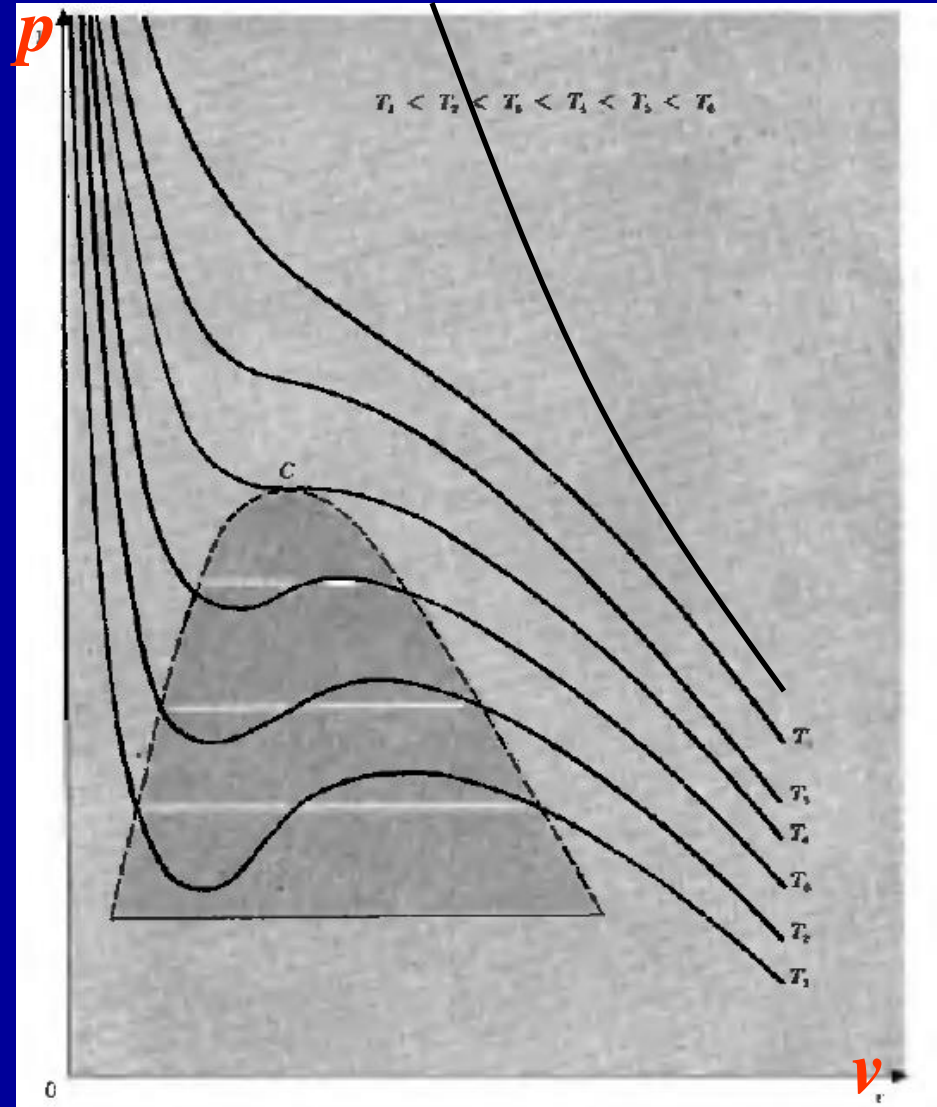
Considering a single-component system with state of equation

$$p = p(v, T)$$

For van der Waals gas

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT$$

The equation of state can be illustrated in 2D with T's

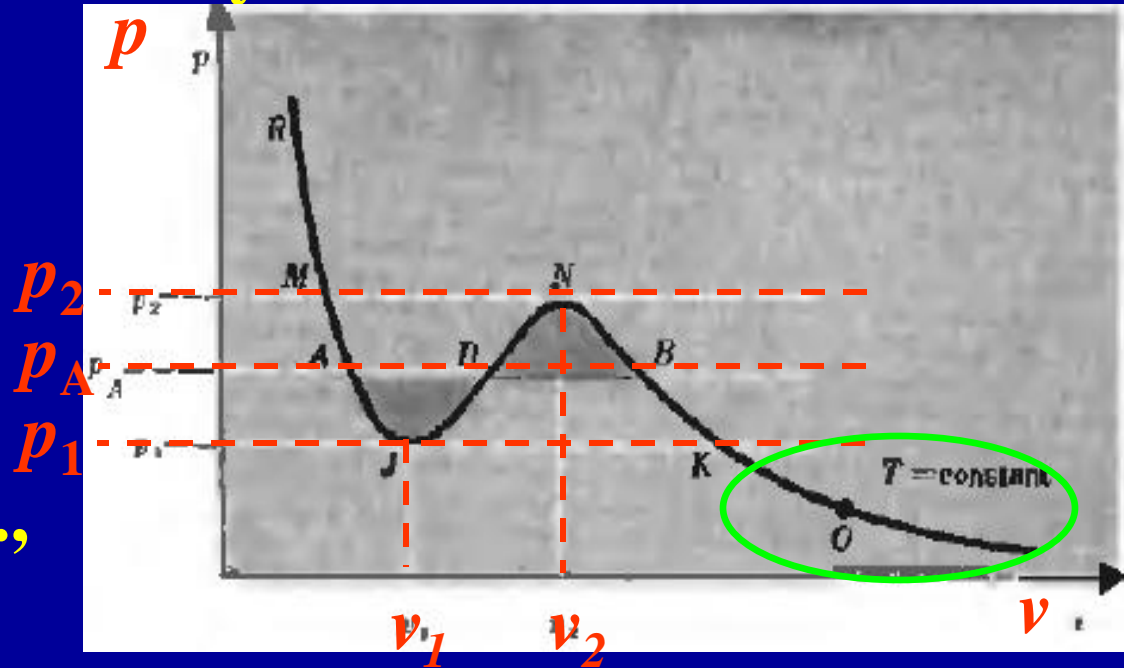


# Equilibrium between phases

## 8.6 Phase transformations & equation of state

One curve can be illustrated by

1, If at a given  $T$ ,  $p$  is very low so that  $p < p_1$ , there is only a single phase and  $dp/dv \leq 0$ , and  $|dp/dv|$  is small, i.e., the compressibility is large, corresponding to gas phase

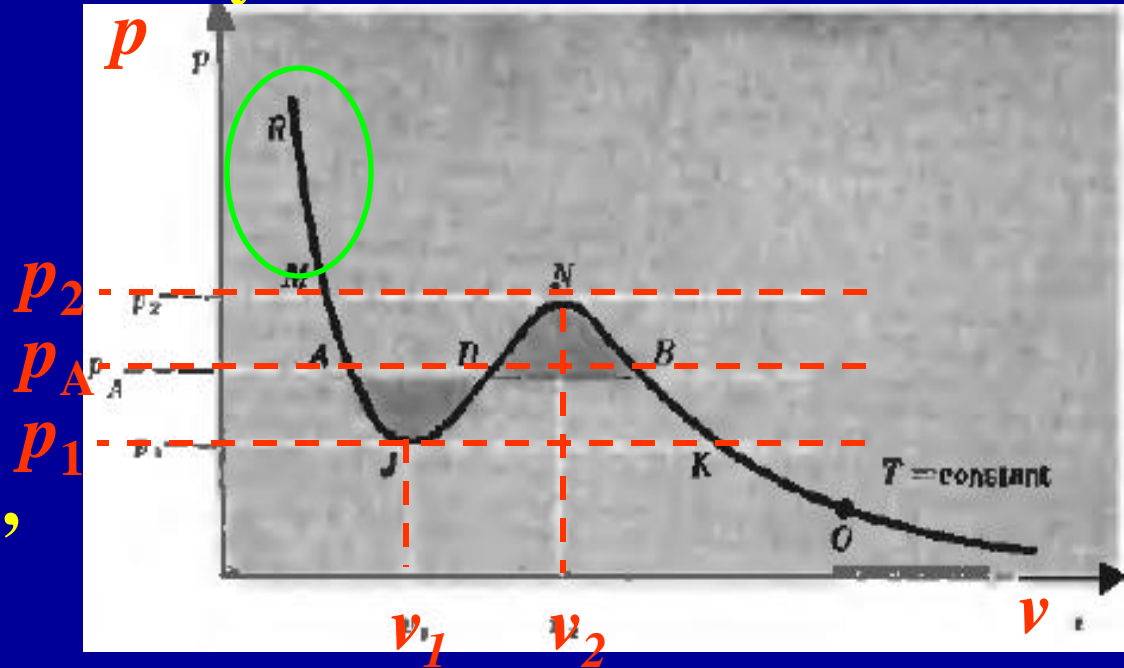


# Equilibrium between phases

## 8.6 Phase transformations & equation of state

One curve can be illustrated by

2, If at a given  $T$ ,  $p$  is very high so that  $p > p_2$ , there is only a single phase and  $dp/dv < 0$ , and  $|dp/dv|$  is large, i.e., the compressibility is small, corresponding to liquid phase



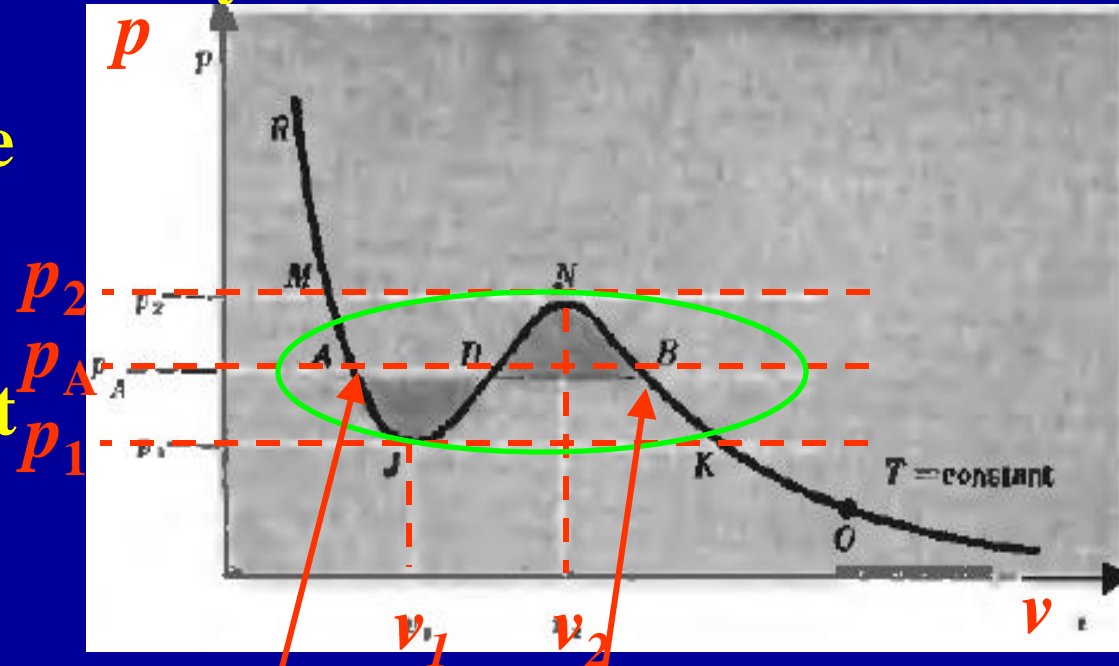


# Equilibrium between phases

## 8.6 Phase transformations & equation of state

One curve can be illustrated by

3, for  $p_2 > p > p_1$ , there are three  $v$  values for each  $p$ . Then which one corresponds to the most stable situation???



For  $v_2 > v > v_1$ ,  $dp/dv \leq 0$  is violated, i.e., slope is positive---intrinsic unstable situation;

Then there still leaves two possible values  $v_A$  and  $v_B$ .

Relative magnitude:

$$g_A(T, p) \text{ and } g_B(T, p) \quad ???$$

# Equilibrium between phases

## 8.6 Phase transformations & equation of state

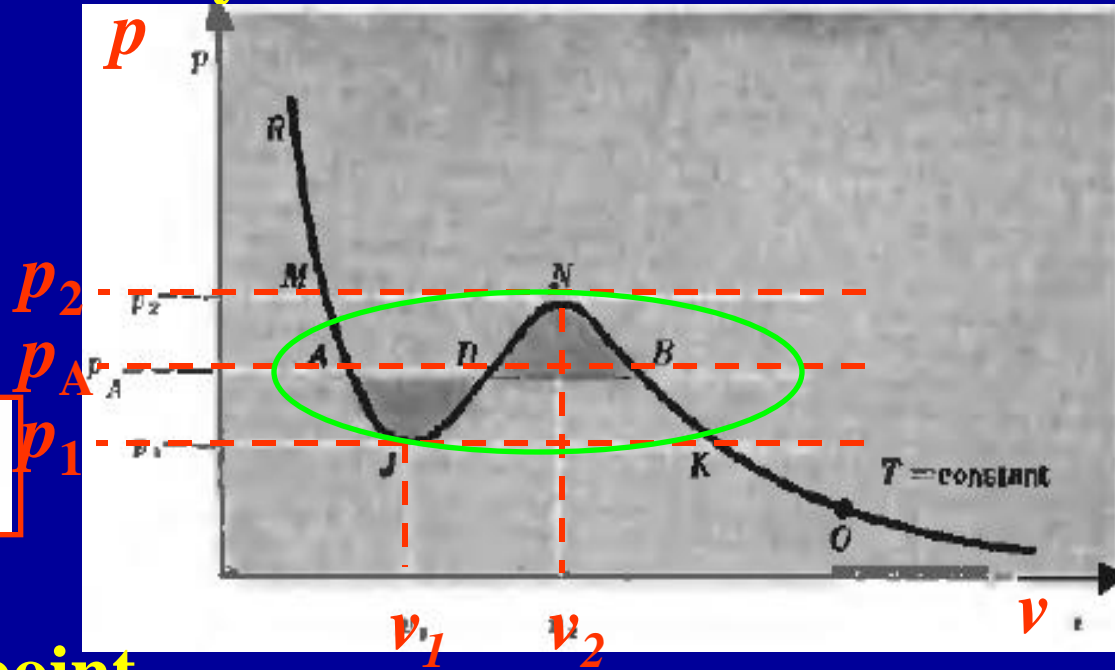
One curve can be illustrated by

3, for  $p_2 > p > p_1$ ,

$$T ds = d\epsilon + p dv$$

Constant T

$$dg = d(\epsilon - Ts + pv) = v dp$$



Select O at an standard point

$$g - g_0 = \int_{p_0}^p v dp$$

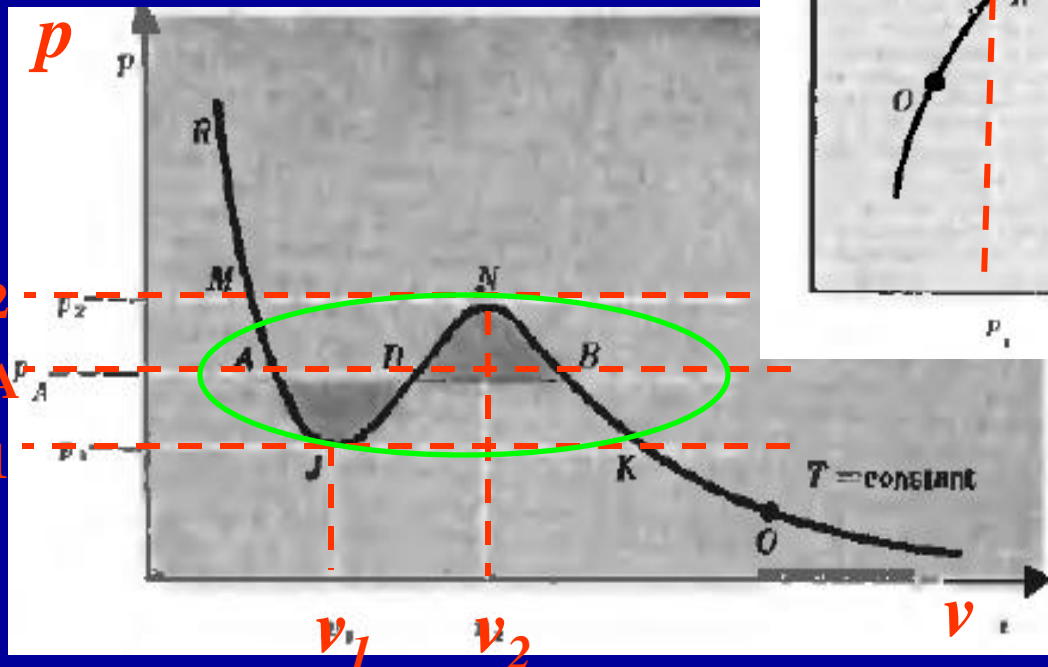
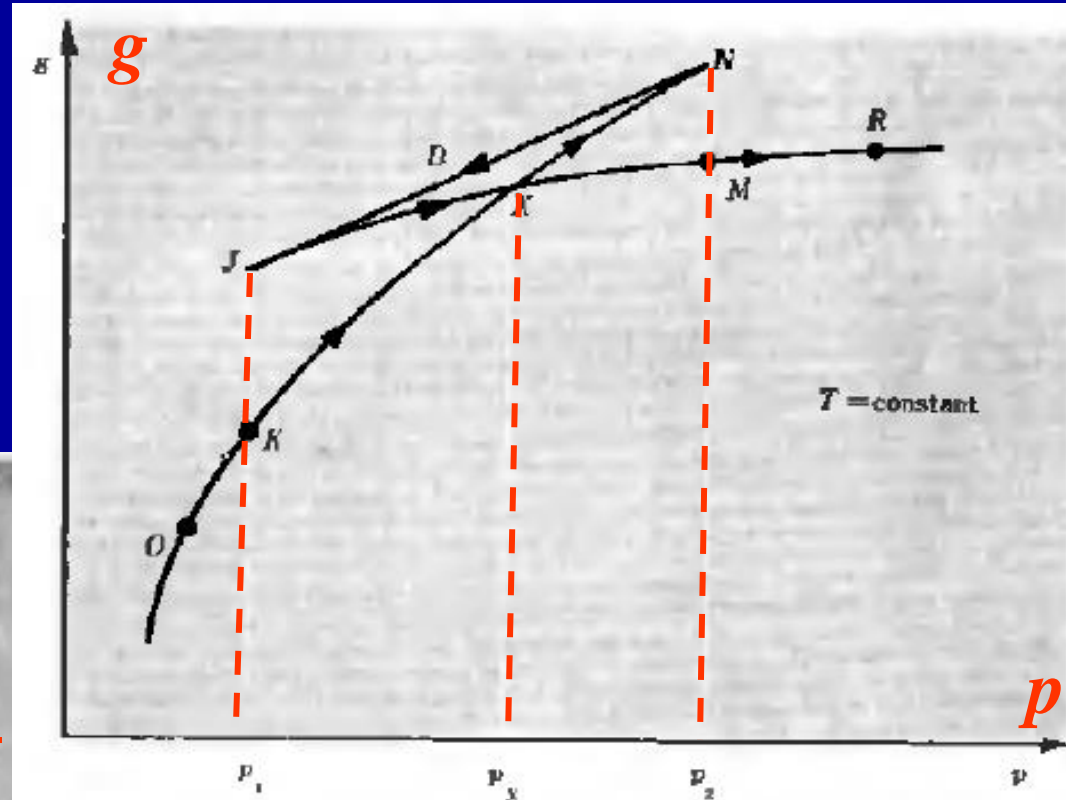
Corresponds to the area between the curve and the p axis

# Equilibrium between phases

## 8.6 Phase transformations & equation of state

One curve can be illustrated by

3, for  $p_2 > p > p_1$ ,



# Equilibrium between phases

## 8.6 Phase transformations & equation of state

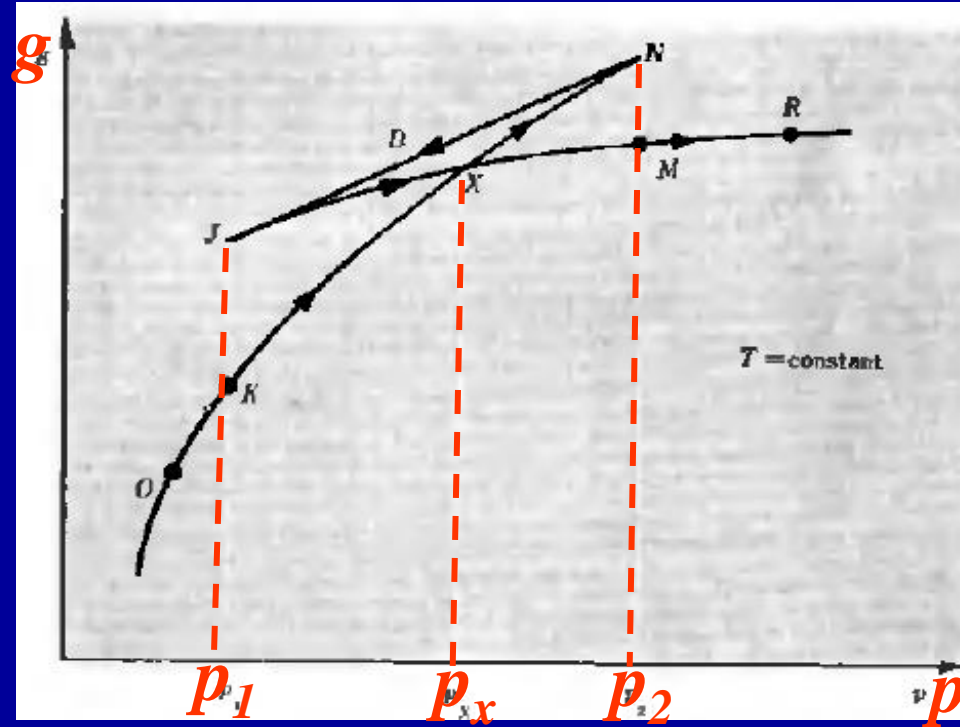
One curve can be illustrated by

3, for  $p_2 > p > p_1$ , there are three values of  $g$

a, the value of  $g$  along OKXN corresponds to large  $v(>v_2)$  with high compressibility.  $\rightarrow$  gas

b, the value of  $g$  along JXMR corresponds to small  $v(<v_1)$  with low compressibility.  $\rightarrow$  liquid

c, JDN corresponds to the unstably intrinsic range



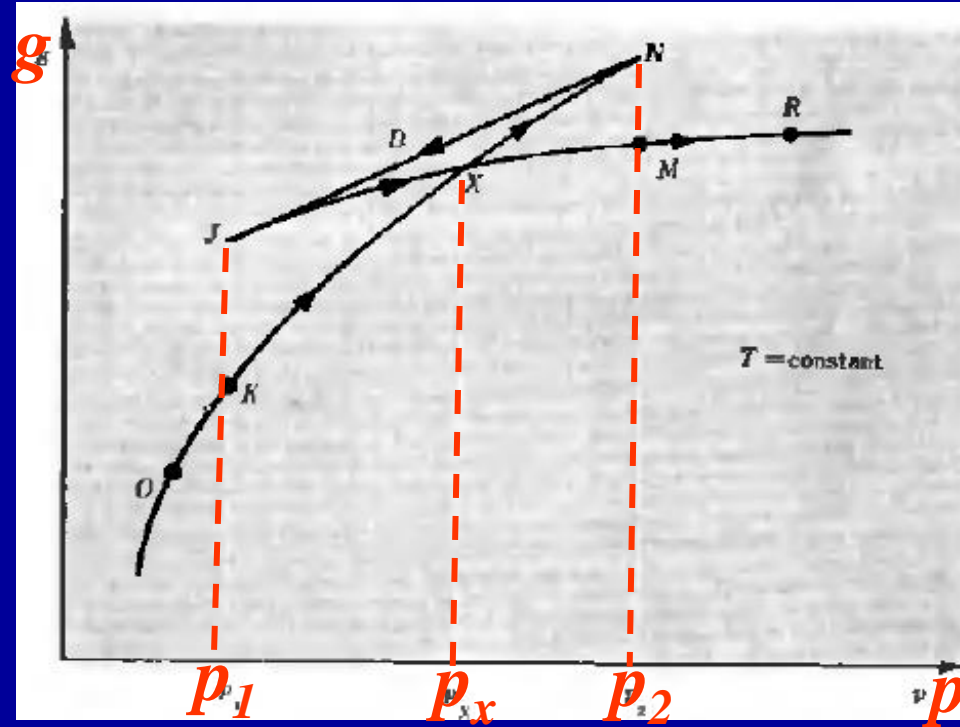
# Equilibrium between phases

## 8.6 Phase transformations & equation of state

One curve can be illustrated by

3, for  $p_2 > p > p_1$ , there are three values of  $g$

d, At X point,  $g$ 's of liquid and gas are equal  $\rightarrow$  equilibrium point;  
 $p_X \rightarrow$  equilibrium pressure



# Equilibrium between phases

## 8.6 Phase transformations & equation of state

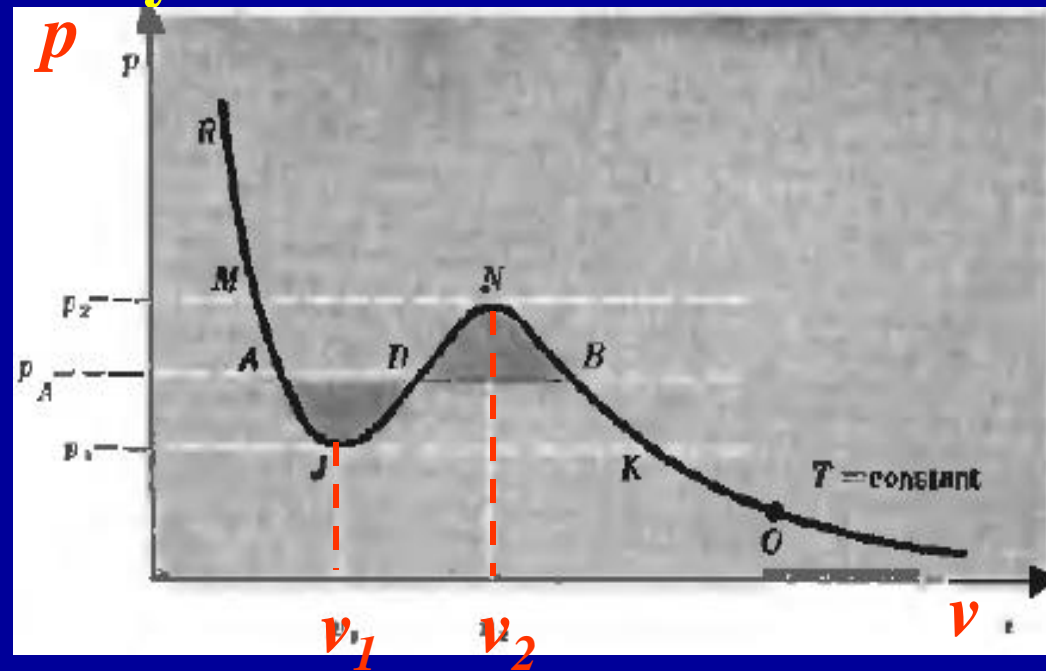
One curve can be illustrated by  
3, for  $p_2 > p > p_1$ ,

Assuming  $p_A = p_X$ , and  $\zeta$   
of mole substance is in  
gas state, then the total  
mole volume

$$v_{\text{tot}} = \xi v_B + (1 - \xi) v_A$$

Molar  
volume  
of gas

Molar  
volume of  
liquid



Equilibrium gives

$$g_B = g_A$$

# Equilibrium between phases

## 8.6 Phase transformations & equation of state

One curve can be illustrated by  
3, for  $p_2 > p > p_1$ ,

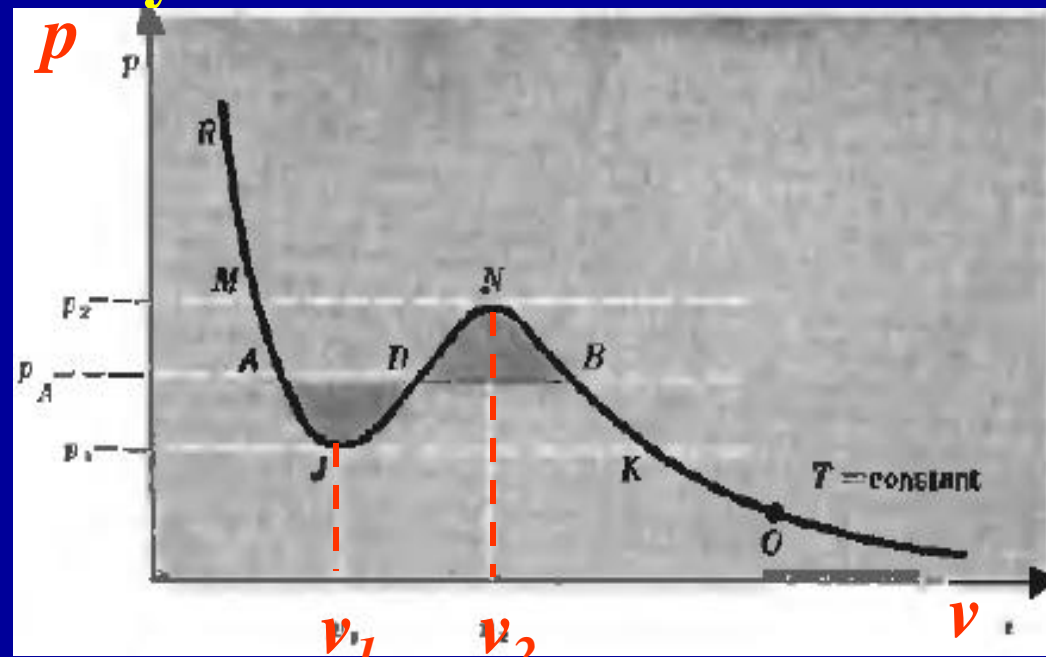
$$g_B = g_A$$

$$\int_{BNDJA} v dp = 0$$

$$\int_B^N v dp + \int_N^D v dp + \int_D^J v dp + \int_J^A v dp = 0$$

$$\text{area}(DNB) - \text{area}(AJD) = 0$$

$$\text{area}(AJD) = \text{area}(DNB)$$





# Equilibrium between phases

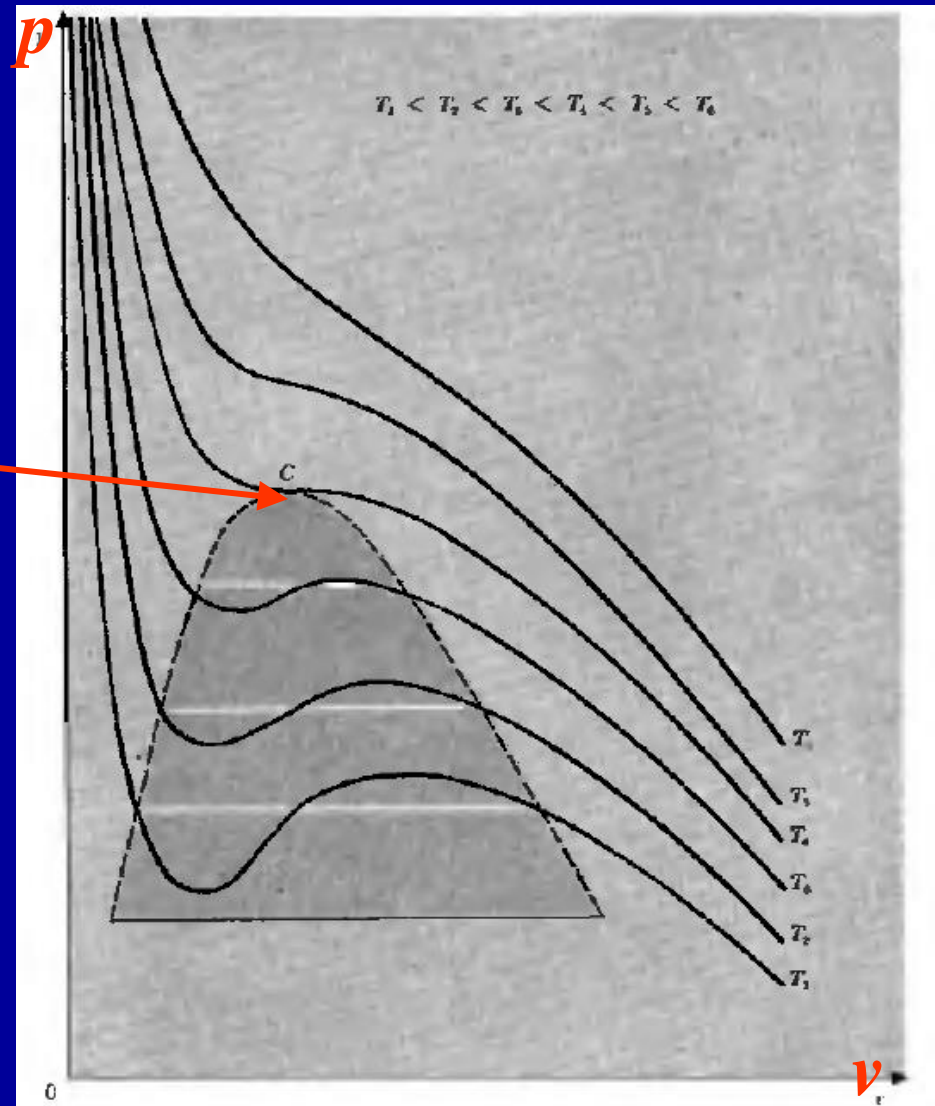
## 8.6 Phase transformations & equation of state

At a certain high  $T$ ,  $v_1$  and  $v_2$  move closer together. Then

$$\begin{cases} (\partial p / \partial v)_T = 0 \\ (\partial^2 p / \partial v^2)_T = 0 \end{cases}$$

Critical point

At higher  $T$ ,  $(\partial p / \partial v) < 0$   
Everywhere, and there is no phase transition





# Equilibrium between phases

## 8.6 Phase transformations & equation of state

$$(\partial p / \partial v)_T = 0$$

$$(\partial^2 p / \partial v^2)_T = 0$$



$$\left( \frac{\partial p}{\partial v} \right)_T = - \frac{RT}{(v-b)^2} + \frac{2a}{v^3} = 0,$$
$$\left( \frac{\partial^2 p}{\partial v^2} \right)_T = \frac{2RT}{(v-b)^3} - \frac{6a}{v^4} = 0,$$



$$v_c = 3b,$$
$$p_c = \frac{a}{27b^2},$$
$$RT_c = \frac{8a}{27b}.$$

$$\left( p + \frac{a}{v^2} \right) (v - b) = RT$$



实际上,从(5.6.18)的三个

$$\frac{RT_c}{p_c v_c} = \left( \frac{8a}{27b} \right) / \left[ \frac{a}{27b^2} \cdot 3b \right] = \frac{8}{3} = 2.667$$

# Equilibrium between phases

## 8.6 Phase transformations & equation of state

$$\frac{RT_c}{p_c v_c} = \left( \frac{8a}{27b} \right) / \left[ \frac{a}{27b^2} \cdot 3b \right] = \frac{8}{3} = 2.667,$$

表 3.6.1 几种气体  $RT_c/(p_c v_c)$  的实验值

气体	He	H <sub>2</sub>	Ne	N <sub>2</sub>	Ar	O <sub>2</sub>	CO <sub>2</sub>	NH <sub>3</sub>	H <sub>2</sub> O
$\frac{RT_c}{p_c v_c}$	3.28	3.27	3.25	3.43	3.42	3.42	3.65	4.11	4.37

Ideal gas,

$$\frac{RT}{pv} = 1$$

# Equilibrium between phases

## 8.6 Phase transformations & equation of state

Above the critical point there exists a state of matter that is continuously connected with (can be transformed without phase transition into) both the liquid and the gaseous state. It is called supercritical fluid.

The common textbook knowledge that all distinction between liquid and vapor disappears beyond the critical point.

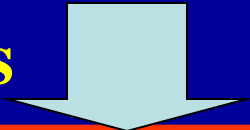
# System with several components

## 8.7 General relations for system with multiple components

Consider a homogenous system with energy  $E$  and of volume  $V$ , consisting of  $m$  different kinds molecules.  $N_i$  is the number of molecule  $i$ , then

$$S = S(E, V, N_1, N_2, \dots, N_m)$$

In quasi-static process


$$dS = \left( \frac{\partial S}{\partial E} \right)_{V,N} dE + \left( \frac{\partial S}{\partial V} \right)_{E,N} dV + \sum_{i=1}^m \left( \frac{\partial S}{\partial N_i} \right)_{E,V,N} dN_i$$

2nd law and  $N_i$  is kept fixed

$$dS = \frac{dQ}{T} = \frac{dE + p dV}{T}$$

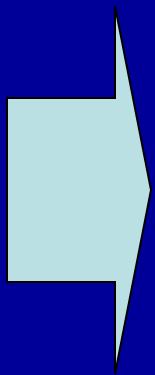
# System with several components

## 8.7 General relations for system with multiple components

$$dS = \left( \frac{\partial S}{\partial E} \right)_{V,N} dE + \left( \frac{\partial S}{\partial V} \right)_{E,N} dV + \sum_{i=1}^m \left( \frac{\partial S}{\partial N_i} \right)_{E,V,N} dN_i$$

$$dS = \frac{dQ}{T} = \frac{dE + p dV}{T}$$

If  $N_i$  are kept fixed, i.e.,  $dN_i = 0$



$$\left( \frac{\partial S}{\partial E} \right)_{V,N} = \frac{1}{T}$$

$$\left( \frac{\partial S}{\partial V} \right)_{E,N} = \frac{p}{T}$$

# System with several components

## 8.7 General relations for system with multiple components

$$dS = \left( \frac{\partial S}{\partial E} \right)_{V,N} dE + \left( \frac{\partial S}{\partial V} \right)_{E,N} dV + \sum_{i=1}^m \left( \frac{\partial S}{\partial N_i} \right)_{E,V,N} dN_i$$

Introducing a abbreviation

$$\mu_j \equiv -T \left( \frac{\partial S}{\partial N_j} \right)_{E,V,N}$$

Chemical potential per molecule of  $j$  chemical species and has the dimension of energy

$$dS = \frac{1}{T} dE + \frac{p}{T} dV - \sum \frac{\mu_i}{T} dN_i$$

$$dE = T dS - p dV + \sum_{i=1}^m \mu_i dN_i$$

Generalization of fundamental relation  $dE = T dS - p dV$  for case where numbers of particles are allowed to vary

# System with several components

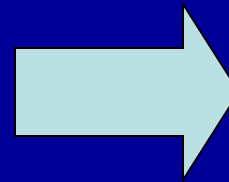
## 8.7 General relations for system with multiple components

$$\mu_j \equiv -T \left( \frac{\partial S}{\partial N_j} \right)_{E,V,N}$$

Chemical potential can be written in many forms equivalent to

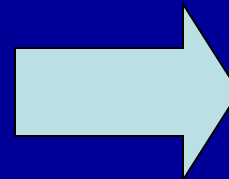
All variables other than  $N_j$  are kept fixed

$$dE = T dS - p dV + \sum_{i=1}^m \mu_i dN_i$$



$$\mu_j = \left( \frac{\partial E}{\partial N_j} \right)_{S,V,N}$$

$$d(E - TS) = dF = -S dT - p dV + \sum_i \mu_i dN_i$$



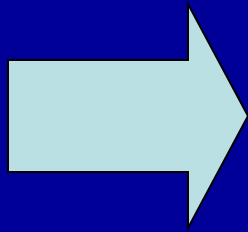
$$\mu_j = \left( \frac{\partial F}{\partial N_j} \right)_{T,V,N}$$

# System with several components

## 8.7 General relations for system with multiple components

Chemical potential can be written in many forms equivalently

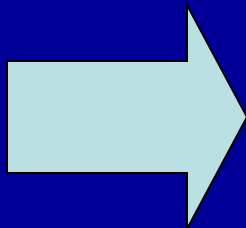
$$d(E - TS + pV) = dG = -S dT + V dp + \sum_i \mu_i dN_i$$



$$\mu_j = \left( \frac{\partial G}{\partial N_j} \right)_{T,p,N}$$

If only one species

$$G = G(T, p, N_j)$$



$$G(T, p, N_j) = N_j g'(T, p)$$

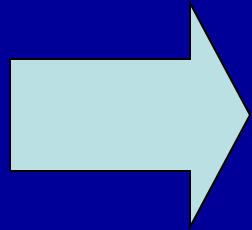
Independent on  $N_j$



# System with several components

## 8.7 General relations for system with multiple components

Chemical potential can be written in many forms equivalently



$$G(T, p, N_j) = N_j g'(T, p)$$

$$\mu_j = \left( \frac{\partial G}{\partial N_j} \right)_{T, p} = g'(T, p)$$

When several components are present,

$G = G(T, p, N_1, \dots, N_m)$  , generally

$$\mu_j = \left( \frac{\partial G}{\partial N_j} \right)_{T, p, N} \neq \frac{G}{N_j}$$

# System with several components

## 8.8 Alternative discussion of equilibrium between phases

Considering the total system is isolated.  $N$  molecules form a substance consisting of two phases 1 and 2.

Then

$$\left. \begin{aligned} E_1 + E_2 &= E = \text{constant} \\ V_1 + V_2 &= V = \text{constant} \\ N_1 + N_2 &= N = \text{constant} \end{aligned} \right\}$$

Entropy is the function of the parameters and the stable equilibrium gives

$$S = S(E_1, V_1, N_1; E_2, V_2, N_2) = \text{maximum}$$

Total entropy is given by

$$S = S_1(E_1, V_1, N_1) + S_2(E_2, V_2, N_2)$$

# System with several components

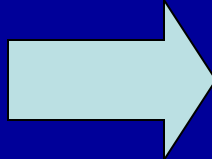
## 8.8 Alternative discussion of equilibrium between phases

Maximum condition gives

$$dS = dS_1 + dS_2 = 0$$

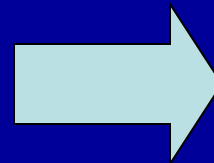
and

$$\left. \begin{aligned} E_1 + E_2 &= E = \text{constant} \\ V_1 + V_2 &= V = \text{constant} \\ N_1 + N_2 &= N = \text{constant} \end{aligned} \right\}$$



$$\left. \begin{aligned} dE_1 + dE_2 &= 0 \\ dV_1 + dV_2 &= 0 \\ dN_1 + dN_2 &= 0 \end{aligned} \right\}$$

$$\begin{aligned} dS &= \left( \frac{1}{T_1} dE_1 + \frac{p_1}{T_1} dV_1 - \frac{\mu_1}{T_1} dN_1 \right) \\ &+ \left( \frac{1}{T_2} dE_2 + \frac{p_2}{T_2} dV_2 - \frac{\mu_2}{T_2} dN_2 \right) = 0 \end{aligned}$$

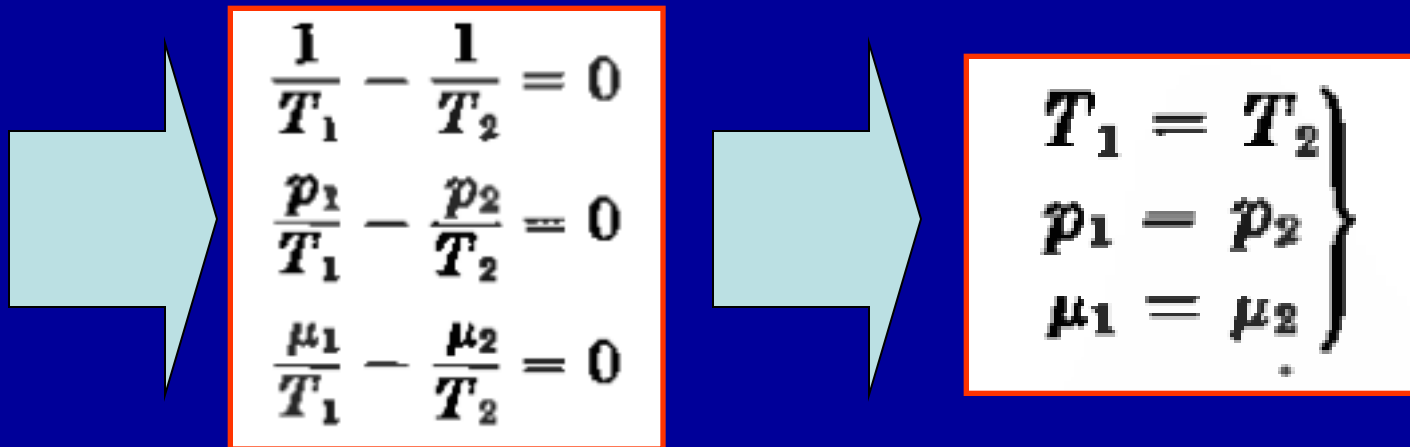


# System with several components

## 8.8 Alternative discussion of equilibrium between phases

Maximum condition gives

$$dS = \left( \frac{1}{T_1} - \frac{1}{T_2} \right) dE_1 + \left( \frac{p_1}{T_1} - \frac{p_2}{T_2} \right) dV_1 - \left( \frac{\mu_1}{T_1} - \frac{\mu_2}{T_2} \right) dN_1 = 0$$


$$\begin{array}{l} \frac{1}{T_1} - \frac{1}{T_2} = 0 \\ \frac{p_1}{T_1} - \frac{p_2}{T_2} = 0 \\ \frac{\mu_1}{T_1} - \frac{\mu_2}{T_2} = 0 \end{array} \quad \Rightarrow \quad \left. \begin{array}{l} T_1 = T_2 \\ p_1 = p_2 \\ \mu_1 = \mu_2 \end{array} \right\}$$

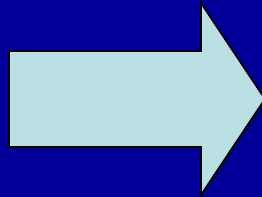
Necessary conditions for equilibrium between two phases  $\rightarrow$  reflects respective conservation conditions

# System with several components

## 8.8 Alternative discussion of equilibrium between phases

Since each phase consists only one component, then

$$\mu_1 = g_1'$$



$$g_1' = g_2'$$

One can take the above equilibrium condition, and write it in form

$$\mu_1(T, p) = \mu_2(T, p)$$

can be solved to find  $p$  as a function of  $T$

# System with several components

## 8.9 General condition for chemical equilibrium

Consider a homogeneous system (one phase) which contains  $m$  different kinds of molecules, denoted by  $B_1, B_2, \dots, B_m$ . There exists chemical reaction for transformation, and obeys conservation for atom number. For example,



$$-2\text{H}_2 - \text{O}_2 + 2\text{H}_2\text{O} = 0$$

More generally,

$$\sum_{i=1}^m b_i B_i = 0$$

Chemical reaction

$N_i$  is the number of  $B_i$  molecules, then

# System with several components

## 8.9 General condition for chemical equilibrium



The changes in  $N_i$  must be proportional to number in reaction equation

$$dN_i = \lambda b_i \quad \text{for all } i$$

For example:

$$dN_{\text{H}_2\text{O}} : dN_{\text{H}_2} : dN_{\text{O}_2} = 2 : -2 : -1$$

The equilibrium condition gives

$$S = S(E, V, N_1, \dots, N_m) = \text{maximum}$$

$$dS = 0$$

# System with several components

## 8.9 General condition for chemical equilibrium

$$dS = \frac{1}{T} dE + \frac{p}{T} dV - \sum \frac{\mu_i}{T} dN_i$$

Under assumed conditions of constant E and V

$$\sum_{i=1}^m \mu_i dN_i = 0$$

$$\sum_{i=1}^m b_i \mu_i = 0$$

Chemical potential is a function of variables describing system. For example,

$$\mu_i = \mu_i(E, V, N_1, \dots, N_m)$$

$$\mu_i = \mu_i(T, V, N_1, \dots, N_m)$$



# System with several components

## 8.9 chemical equilibrium between ideal gases

Consider chemical reaction can occur between  $m$  different types of molecules, and the system is at  $T$  and in  $V$ , then what is the relationship between the mean numbers of molecules at equilibrium??

$$d(E - TS) = dF = -S dT - p dV + \sum_i \mu_i dN_i$$

Free energy:

$$F = F(T, V, N_1, \dots, N_m)$$

$b_i$  molecules are produced from reaction, and the free energy change is given by

$$\Delta F = \sum_i \left( \frac{\partial F}{\partial N_i} \right)_{T,V,N} b_i = \sum_i \mu_i b_i$$

$$\mu_i = \left( \frac{\partial F}{\partial N_i} \right)_{T,V,N}$$

In equilibrium

$$\Delta F = \sum_i b_i \mu_i = 0$$

$\mu_i$  –remains unsolved

# System with several components

## 8.9 chemical equilibrium between ideal gases

### Calculating chemical potential

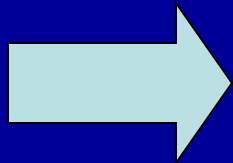
Label possible states of  $k$ th molecules by  $s_k$ , and the energy is  $\epsilon_k$ , and the interactions are negligible. Total energy in one state can be given by

$$E = \epsilon_1(s_1) + \epsilon_2(s_2) + \epsilon_3(s_3) + \dots$$

Partition function becomes

$$Z' = \sum_{s_1, s_2, s_3} e^{-\beta[\epsilon_1(s_1) + \epsilon_2(s_2) + \dots]}$$

Sum over all the states of each molecule

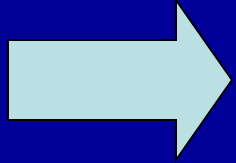


$$Z' = \left( \sum_{s_1} e^{-\beta \epsilon_1(s_1)} \right) \left( \sum_{s_2} e^{-\beta \epsilon_2(s_2)} \right) \dots$$

# System with several components

## 8.9 chemical equilibrium between ideal gases

### Calculating chemical potential



$$Z' = \left( \sum_{s_1} e^{-\beta \epsilon(s_1)} \right) \left( \sum_{s_2} e^{-\beta \epsilon(s_2)} \right) \cdot \dots$$

Then there will be  $N_i$  equal factors for  $i$ -th type molecules, and each of the factors being equal to

$$\zeta_i \equiv \sum_s e^{-\beta \epsilon(s)}$$

Then partition function is

$$Z' = \zeta_1^{N_1} \zeta_2^{N_2} \dots \zeta_m^{N_m}$$

Since molecules of  $i$  type are indistinguishable, then

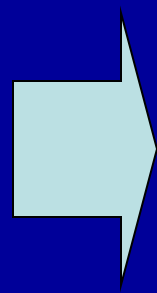
$$Z = \frac{\zeta_1^{N_1} \zeta_2^{N_2} \dots \zeta_m^{N_m}}{N_1! N_2! \dots N_m!}$$

# System with several components

## 8.9 chemical equilibrium between ideal gases

### Calculating chemical potential

$$Z = \frac{\zeta_1^{N_1} \zeta_2^{N_2} \cdots \zeta_m^{N_m}}{N_1! N_2! \cdots N_m!}$$



$$Z = Z_1 Z_2 \cdots Z_m$$

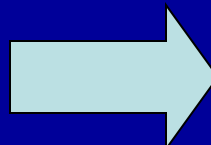
$$Z_i = \frac{\zeta_i^{N_i}}{N_i!}$$

Partition function of a gas of  $N_i$  molecules in  $V$  by itself in the absence of all other gases

$$\ln Z = \sum_i \ln Z_i$$

Thermodynamic functions are additive ← ignoring the interactions

$$\bar{E} = (-\partial \ln Z / \partial \beta)$$



$$\bar{E}(T, V) = \sum_i \bar{E}_i(T, V)$$

# System with several components

## 8.9 chemical equilibrium between ideal gases

### Calculating chemical potential

$$\bar{p} = \beta^{-1}(\partial \ln Z / \partial V), \quad \longrightarrow \quad \bar{p} = \sum_i \bar{p}_i$$

$\bar{p}_i$  is the mean pressure by  $i$ th gas in  $V$  by itself, and is called the partial pressure of  $i$ th gas.

For  $i$ th gas

$$\bar{p}_i = n_i k T, \quad n_i \equiv \frac{N_i}{V}$$

Hence, for gas mixture

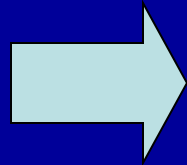
$$\bar{p} = n k T, \quad \text{where } n \equiv \sum_{i=1}^m n_i$$

# System with several components

## 8.9 chemical equilibrium between ideal gases

### Calculating chemical potential

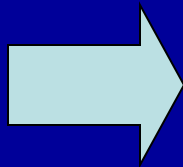
$$\ln Z = \sum_i \ln Z_i$$



$$F(T, V) = \sum_i F_i(T, V)$$

Since

$$F = \bar{E} - TS,$$



$$S(T, V) = \sum_i S_i(T, V)$$

Going to calculating chemical potential

$$\ln Z_i = N_i \ln \xi_i - \ln N_i!$$

$$\xi_i = \xi_i(T, V)$$

Partition function  
for single molecule

# System with several components

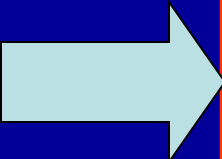
## 8.9 chemical equilibrium between ideal gases

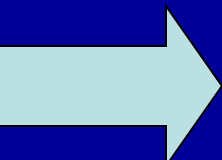
### Calculating chemical potential

$$F = -kT \ln Z = -kT \sum_i (N_i \ln \xi_i - \ln N_i!)$$

$$F = -kT \sum_i N_i (\ln \xi_i - \ln N_i + 1)$$

$$\ln N! = N \ln N - N.$$


$$\mu_j = \left( \frac{\partial F}{\partial N_j} \right)_{T,V,N} = -kT (\ln \xi_j - \ln N_j)$$


$$\mu_j = -kT \ln \frac{\xi_j}{N_j}$$

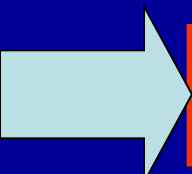
# System with several components

## 8.9 chemical equilibrium between ideal gases

### Law of mass action

$$\Delta F = \sum_i b_i \mu_i = 0$$

$$\mu_j = -kT \ln \frac{\xi_j}{N_j}$$


$$\Delta F = -kT \sum_i b_i (\ln \xi_i - \ln N_i) = \Delta F_0 + kT \sum_i b_i \ln N_i$$

$$\Delta F_0 \equiv -kT \sum_i b_i \ln \xi_i$$

Standard free energy change,  
Depending only on T and V


$$\Delta F = \Delta F_0 + kT \sum_i b_i \ln N_i = 0$$



# System with several components

## 8.9 chemical equilibrium between ideal gases

### Law of mass action

$$\Delta F_0 \equiv -kT \sum_i b_i \ln \zeta_i$$

$$\Delta F = \Delta F_0 + kT \sum_i b_i \ln N_i = 0$$

$$\sum_i \ln N_i^{b_i} = \ln (N_1^{b_1} N_2^{b_2} \cdots N_m^{b_m}) = -\frac{\Delta F_0}{kT}$$

$$N_1^{b_1} N_2^{b_2} \cdots N_m^{b_m} = K_N(T, V)$$

Law of mass action

$$K_N(T, V) \equiv e^{-\Delta F_0/kT} = \zeta_1^{b_1} \zeta_2^{b_2} \cdots \zeta_m^{b_m}$$

$K_N$  is independent of numbers of molecules, and is called as equilibrium constant.

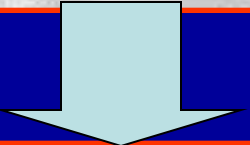
# System with several components

## 8.9 chemical equilibrium between ideal gases

Law of mass action: **example**



Law of mass action gives

$$N_{\text{H}_2}^{-2} N_{\text{O}_2}^{-1} N_{\text{H}_2\text{O}}^2 = K_N$$


$$\frac{N_{\text{H}_2\text{O}}^2}{N_{\text{H}_2}^2 N_{\text{O}_2}} = K_N(T, V)$$

# System with several components

## 8.9 chemical equilibrium between ideal gases

### Law of mass action

In fact,  $\zeta_i(V, T)$  is proportional to  $V$

$$\zeta_i \propto \int d^3\mathbf{r} \int d^3\mathbf{p} e^{-\beta p^2/2m} \sum_{\alpha} e^{-\beta \epsilon_{\alpha}^{(int)}}$$

Non-monatomic molecule

Only consider center motion

$$\zeta_i(V, T) = V \zeta_i'(T)$$

$$\mu_j = -kT \ln \frac{\zeta_j}{N_j}$$

$$\mu_j = -kT \ln \frac{\zeta_j'}{n_j}$$



$$n_j = N_j/V$$

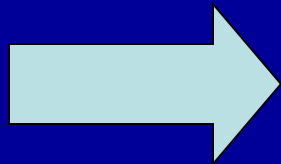
# System with several components

## 8.9 chemical equilibrium between ideal gases

### Law of mass action

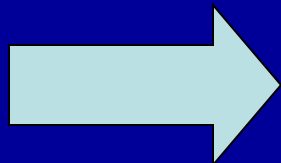
The fundamental equilibrium condition can be written by

$$\sum_i b_i \ln n_i = \sum_i b_i \ln \xi_i'$$



$$n_1^{b_1} n_2^{b_2} \cdots n_m^{b_m} = K_n(T)$$

$$K_n(T) = \xi_1'^{b_1} \xi_2'^{b_2} \cdots \xi_m'^{b_m}$$



$$K_N(T, V) = V^b K_n(T), \quad \text{where } b \equiv \sum_{i=1}^m b_i$$

# System with several components

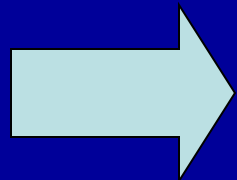
## 8.9 chemical equilibrium between ideal gases

### T-dependence of equilibrium constant

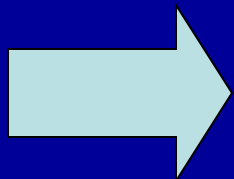
The fundamental equilibrium condition can be written by

$$\ln K_N(T, V) = - \frac{\Delta F_0}{kT}$$

$$\Delta F = \Delta F_0 + kT \sum_i b_i \ln N_i = 0$$



$$\left( \frac{\partial \ln K_N}{\partial T} \right)_V = - \left( \frac{\partial}{\partial T} \right)_V \left( \frac{\Delta F_0}{kT} \right) = - \left( \frac{\partial}{\partial T} \right)_{V, N} \frac{\Delta F}{kT}$$



$$\left( \frac{\partial \ln K_N}{\partial T} \right)_V = \frac{1}{kT^2} \Delta F - \frac{1}{kT} \left( \frac{\partial \Delta F}{\partial T} \right)_{V, N}$$

# System with several components

## 8.9 chemical equilibrium between ideal gases

### T-dependence of equilibrium constant

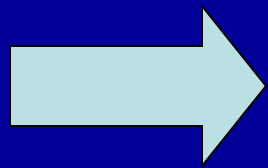
But

$$-\left(\frac{\partial}{\partial T}\right) \Delta F = -\sum_i \left(\frac{\partial}{\partial T}\right) \left(\frac{\partial F}{\partial N_i}\right) b_i$$

$$\left(\frac{\partial F}{\partial T}\right)_{V,N} = -S$$

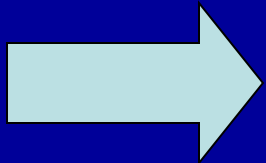
$$= -\sum_i \left(\frac{\partial}{\partial N_i}\right) \left(\frac{\partial F}{\partial T}\right) b_i = \sum_i \frac{\partial S}{\partial N_i} b_i \equiv \Delta S$$

$\Delta S$  is the entropy change for  $b_i$  molecules transformed



$$\left(\frac{\partial \ln K_N}{\partial T}\right)_V = \frac{1}{kT^2} (\Delta F + T \Delta S) = \frac{\Delta E}{kT^2}$$

Since  $K_n$  differs from  $K_N$  only by a factor involving  $V$ ,

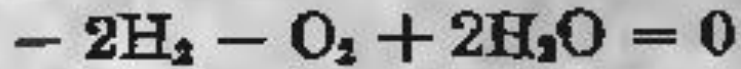


$$\frac{d \ln K_n}{dT} = \frac{\Delta E}{kT^2}$$

# System with several components

## 8.9 chemical equilibrium between ideal gases

For



Law of mass action gives

$$\frac{N_{\text{H}_2\text{O}}^2}{N_{\text{H}_2}^2 N_{\text{O}_2}} = K_N(T, V)$$

How to calculate  $K_N$  ?

$$K_N(T, V) \equiv e^{-\Delta F_0/kT} = \zeta_1^{b_1} \zeta_2^{b_2} \cdot \cdot \cdot \zeta_m^{b_m}$$

9th chapter

# Class-work

P 328 8.14



# Homework

8.12, 8.15, 8.16, 8.17

# Homework