

# Ch.9 Liquids and Solids

## 9.1. Liquid-Vapor Equilibrium

1. Vapor Pressure
2. Vapor Pressure versus Temperature
3. Boiling Temperature
4. Critical Temperature and Pressure

## 9.2. Phase Diagram

1. Sublimation
2. Melting Point

## 9.3. Molecular Substances; Intermolecular Forces

1. Dispersion (London) Forces
2. Dipole Forces
3. Hydrogen Forces

## 9.4. Network Covalent; Ionic and Metallic Solids

1. Network Covalent Solids
2. Ionic Solids
3. Metals

## 9.5. Crystal Structures

1. Simple Cubic Cell (SC)
2. Face-centered Cubic Cell (FCC)
3. Body-centered Cubic Cell (BCC)

## Ch.9 Liquids and solids

Liquid and solid 與 gas 之差異處：

1. Molecules are much closer to one another in liquids and solids.
2. Intermolecular forces (分子分子間作用力) ; which are essentially negligible with gases , but play a much important role in liquids and solids.

液體之表面張力 (surface tension)↑, wetting ability↓, 可加入 soap or detergent (界面活性劑)使其 surface tension ↓ ⇒ wetting ability↑

### §9-1 Liquid-vapor equilibrium

Vaporization 蒸發 : a liquid converts to a gas (vapor).

Open system : liquid 持續蒸發成 vapor 至全部 liquid 用盡

Closed system : liquid 蒸發至一定數量後  $liquid \leftrightarrow vapor$  dynamic equilibrium.

### § Vapor pressure

The pressure exerted by the vapor over the liquid remain constant.  
液體上之壓力保持一定.

↓

Vapor pressure: 一特定液體在一特定 T 之下有一特定之 vapor pressure 值. Ex : 25°C H<sub>2</sub>O 之 vapor pressure = 24 mmHg.

25°C ether 之 vapor pressure = 537 mmHg.

**T=C vapor pressure 較高者 ⇒ b.p 較低.**

容器大小與 vapor pressure 無關. ∴  $P = \frac{n}{v}RT$  v↑ n↑ n/v 固定.

Ex 9-1: A “cool-mist” vaporizer with capacity 2.00 L is used to add moisture to dry air in a room at 25°C. The room has dimensions 12 ft by 12 ft by 8 ft. The vapor pressure of water is 24 mm Hg. Take the density of water at 25°C to be 1.00 g/mL.

a). If the vaporizer runs until it is empty, what is the vapor pressure of

water in the room?

- b). How much water is required to completely saturate the air at 25°C ?  
c). A relative humidity of 33% is desirable in heated space on wintry days. What volume of water is left in the vaporizer when the room's relative humidity reaches that level? (Relative humidity =  $100 \times P/P^0$ , where P is the actual pressure and  $P^0$  is the vapor pressure at saturation.)

Ans:

$$(a) \quad V = (12 \times 12 \times 8) \text{ ft}^3 \times \frac{28.32 \text{ L}}{1 \text{ ft}^3} = 3.3 \times 10^4 \text{ L}$$

$$n_{H_2O} = 2.00 \text{ L} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{1.00 \text{ g}}{1 \text{ mL}} \times \frac{1 \text{ mol}}{18.02 \text{ g}} = 111 \text{ mol}$$

$$P = \frac{nRT}{V} = \frac{111 \times 0.0821 \times 298}{3.3 \times 10^4} = 0.082 \text{ atm} = 62 \text{ mm Hg}$$

It is impossible to have a vapor pressure larger than 24 mm Hg. Thus, the assumption that all the water is vaporized is wrong. **The pressure in the room is 24 mm Hg.**

$$(b) \quad n_{H_2O} = \frac{PV}{RT} = \frac{(24/760) \times (3.3 \times 10^4)}{0.0821 \times 298} = 43 \text{ mol}$$

$$m_{H_2O} = 43 \times 18.02 = 7.7 \times 10^2 \text{ g}$$

$$(c) \quad P = \frac{\text{relative humidity}}{100} \times P^0 = \frac{33}{100} \times 24 \text{ mm Hg} = 7.9 \text{ mm Hg}$$

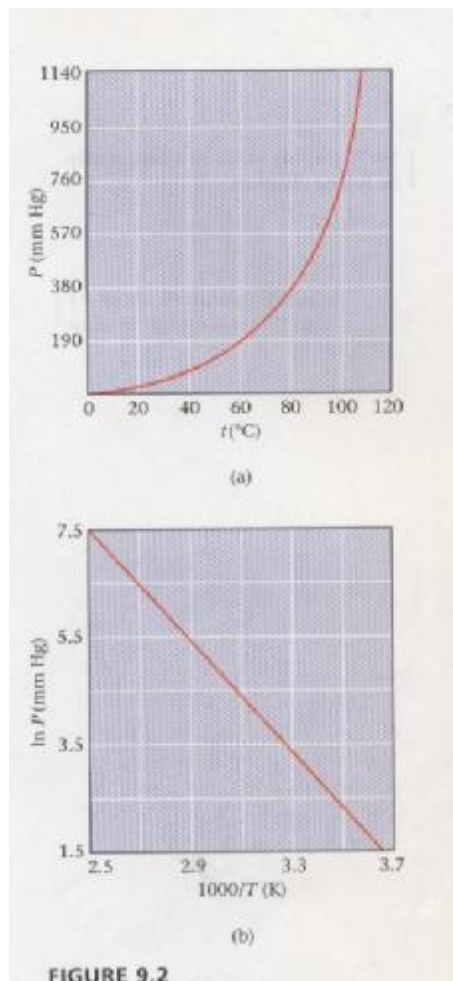
$$n_{H_2O} = \frac{PV}{RT} = \frac{(7.9/760) \times (3.3 \times 10^4)}{0.0821 \times 298} = 14 \text{ mol}$$

$$m_{H_2O} = 14 \times 18.02 = 2.5 \times 10^2 \text{ g} = 0.25 \text{ L}$$

The volume of water left in the vaporizer is:

$$2.00 - 0.25 = 1.75 \text{ L}$$

## § Vapor pressure versus T



Vapor pressure of water:  $25^{\circ}\text{C}$  24 mm Hg  
 $50^{\circ}\text{C}$  92 mm Hg  
 $100^{\circ}\text{C}$  760 mm Hg

(a) 
$$P = a \cdot e^{-\Delta H_{vap} / RT}$$

$\ln P$  vs.  $1/T$  呈 linear  $\Rightarrow$  Fig 9-2 b.

$$y = mx + b$$

$$\ln P = \frac{-\Delta H_{vap}}{RT} + \ln a$$

Clausius – Clapeyron equation:

$$\ln \frac{P_2}{P_1} = -\frac{\Delta H_{vap}}{R} \left[ \frac{1}{T_2} - \frac{1}{T_1} \right]$$

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_{\text{vap}}}{R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right] \quad \Delta H_{\text{vap}} : \text{J/mol}$$

$$R = 8.314 \text{ J/mol} \cdot \text{K}$$

Ex 9-2: Benzene has a vapor pressure of 183 mm Hg at 40°C. Taking its heat of vaporization to be 30.8 kJ/mol, calculate its vapor pressure at 25°C.

Ans :  $P_1 = 183 \text{ mm Hg}$ ;  $T_1 = 313 \text{ K}$

$P_2 = ?$ ;  $T_2 = 298 \text{ K}$ ;  $\Delta H_{\text{vap}} = 30.8 \text{ kJ/mol}$

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_{\text{vap}}}{R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\ln \frac{P_2}{183} = \frac{30.8 \times 10^3}{8.31} \left[ \frac{1}{40 + 273} - \frac{1}{25 + 273} \right]$$

$$= 3.71 \times 10^3 \cdot (-1.61 \times 10^{-4})$$

$$\ln \frac{P_2}{183} = -0.596$$

$$\frac{P_2}{183} = 0.551$$

$$P_2 = 101 \text{ mm Hg}$$

### § Boiling point (b.p.): $T_b$

A liquid boils at a temperature at which its vapor pressure is equal to the pressure above its surface.

$T_b(\text{b.p.}) \text{ a } P$

### Normal boiling point: 正常沸點

vapor pressure of a liquid = 760 mm Hg

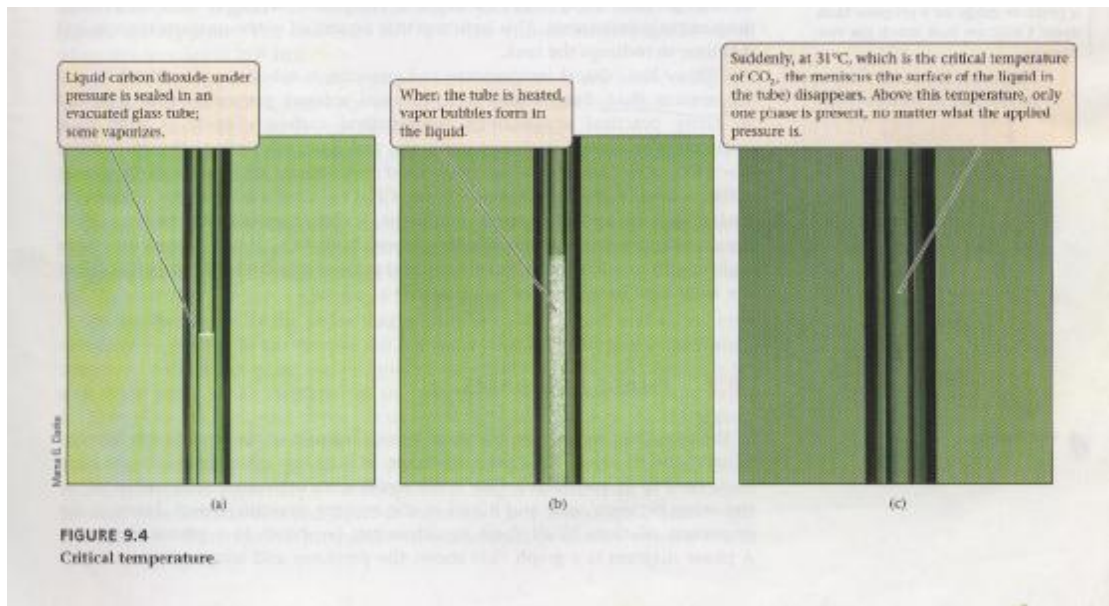
water 之 normal boiling point = 100°C

∴ at 24mmHg 水之 b.p. = 25°C

### § Critical temperature and pressure:

$\text{CO}_{2(l)}$	0°C	vapor pressure	34 atm
	10°C		44 atm
	20°C		56 atm
	31°C		73 atm

$T > 31^\circ\text{C} \Rightarrow$  the tube contains only one phase  $\Rightarrow$  vapor



When  $T > 31^\circ\text{C}$ , no matter how much pressure is applied, it is **impossible** to have liquid CO<sub>2</sub>.  
 $\therefore$  即使  $P = 1000\text{atm}$ ,  $35^\circ\text{C}$  or  $40^\circ\text{C}$  之溫度均無法使 CO<sub>2</sub> 液化.

**Critical temperature** : 臨界溫度

The temperature above which the liquid phase of a pure substance cannot exist.

The pressure that must be applied to cause condensation at that temperature is called the **critical pressure**.



Critical pressure is the vapor pressure of the liquid at the critical temperature.

$\therefore$  CO<sub>2</sub> 之  $T_c = 31^\circ\text{C}$   $P_c = 73\text{ atm}$

TABLE 9.1 Critical Temperatures (°C)					
Permanent Gases		Condensable Gases		Liquids	
Helium	-268	Carbon dioxide	31	Ethyl ether	194
Hydrogen	-240	Ethane	32	Ethyl alcohol	243
Nitrogen	-147	Propane	97	Benzene	289
Argon	-122	Ammonia	132	Bromine	311
Oxygen	-119	Chlorine	144	Water	374
Methane	-82	Sulfur dioxide	158		



$T_c < 25^\circ\text{C}$

§ **Supercritical fluid 超臨界流體** :

超過臨界溫度及壓力之物質 have unusual solvent properties.

例 : Supercritical CO<sub>2</sub> 萃取 coffee 中之 caffeine.

§9-2 Phase diagram: P vs. T

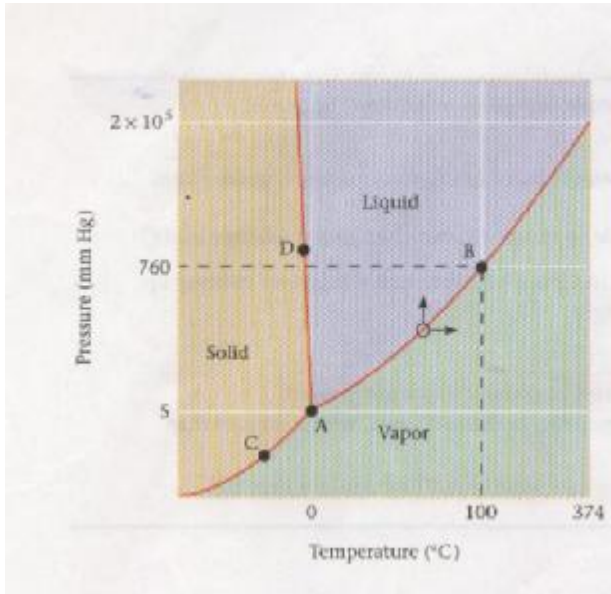


Fig 9-5 : Phase diagram of H<sub>2</sub>O

AB : liquid-vapor equilibrium line

AC : vapor-solid equilibrium line

AD : liquid-solid equilibrium line

A: triple point 三相點; for H<sub>2</sub>O 0.01°C, 4.56 mm Hg

↓

(l)(s)(g) 三相共存

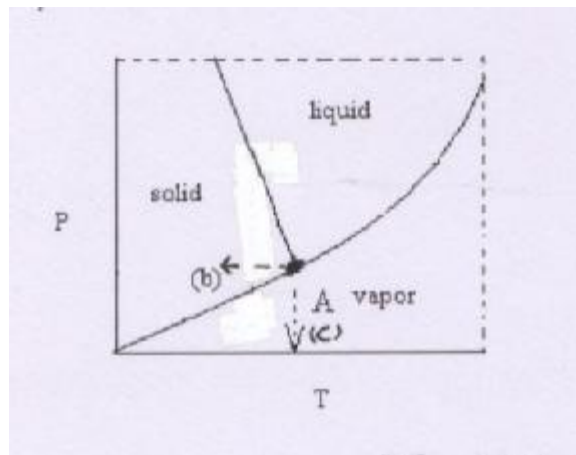
Ex 9-3: Consider a sample of H<sub>2</sub>O at point A in Figure 9-5.

- what phase(s) is (are) present ?
- If the temperature of the sample were reduced at constant pressure, what would happen ?
- How would you convert the sample to vapor without changing the temperature ?

Ans :

- A 為 triple point ∴同時呈現 gas、liquid 及 solid 三相.

b.



⇒ 成爲 solid (ice).

c.  $T=C$  使成爲 vapor ⇒ P 下降,  $P < 4.56 \text{ mm Hg}$

### § Sublimation 昇華

Solid changes directly to vapor without passing through the liquid phase. ∴ 一固體要發生昇華  $T < T_{\text{三相點}}$  才可

若  $T > T_{\text{三相點}}$  固體會融化成爲 liquid.

※ ∴ 昇華：先將  $T < T_{\text{三相點}}$ ，再逐步降壓至 Fig. 9.5 中 s-g 平衡線 (AC) 以下即可發生昇華。

↓  
碘、奈丸

### § Melting point 熔點 $s \rightarrow l$

Identical to freezing point (凝固點) ⇒  $l \rightarrow s$ .

The temperature at which solid and liquid phase are in equilibrium.  
⇒ for most substance, **the melting point at 1atm is virtually identical with the triple point temp.**

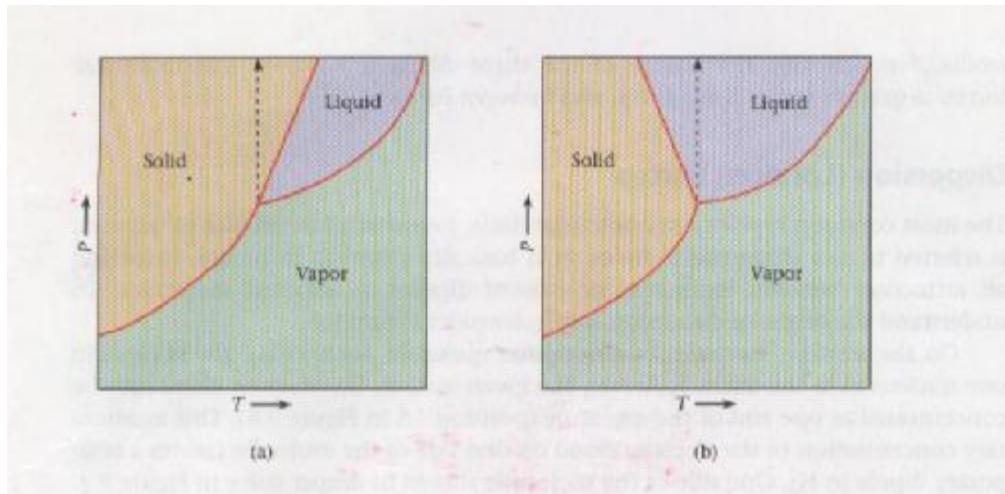
H<sub>2</sub>O: melting point 0.00°C

triple point 0.01°C

差 0.01°C



§ P 對 m.p.之影響：



1. 如 Fig 9-7(a): (s)-(l) 之平衡線向右傾 $\Rightarrow$ 固態更具凝相 $\Rightarrow$ 佔絕大多數;  $P\uparrow\Rightarrow m.p.\uparrow$  一般化合物多屬此種
2. 如 Fig 9-7(b): (s)-(l) 之平衡線向左傾 $\Rightarrow$ 液態更具凝相 $\Rightarrow$ 佔少數;  $P\uparrow\Rightarrow m.p.\downarrow$  如：水. 壓力增加 134 atm, melting point 下降低  $1^{\circ}\text{C}$ .