§9-3 Molecular substances; intermolecular force
(分子物質) (分子分子間作用力)

(§9-4 Network covalent; ionic; metallic solids)

TABLE 9.5 Structures and Properties of Types of Substances OHT

Type	Structural Particles	Forces Within Particles	Forces Between Particles	Properties	Examples
Molecular	Molecules (a) nonpolar	Covalent bond	Dispersion	Low mp, bp; often gas or liquid at 25°C; nonconductors; insoluble in water, soluble in organic solvents	H_2 CCl_4
	(b) polar	Covalent bond	Dispersion, dipole, H bond	Similar to nonpolar but generally higher mp and bp, more likely to be water-soluble	HCl NH_3
Network covalent	Atoms	—	Covalent bond	Hard, very high-melting solids; nonconductors; insoluble in common solvents	C SiO_2
Ionic	Ions	—	Ionic bond	High mp; conductors in molten state or water solution; often soluble in water, insoluble in organic solvents	NaCl MgO $CaCO_3$
Metallic	Cations, mobile electrons	—	Metallic bond	Variable mp; good conductors in solid; insoluble in common solvents	Na Fe

Molecules (分子化合物); 大多數為 gas or liquid , 少數為 solid；有以下特性:

1. 純物質不具導電性，但具極性分子之水溶液 or melt 狀態可導電.

2. 不溶於水(一般為低極性化合物)；但可溶於非極性溶劑中(如：CCl_4、C_6H_6).
   例外：具極性之 C_2H_5OH 等可溶於水
   極溶極 非極溶非極.
   Molecular substance 多為非極性物質.

3. 具低熔點、低沸點.
   大多數分子物質之 m.p.; b.p.＜300℃
   Intermolecular force↑ ⇒ b.p.↑

Intermolecular force 分子分子間作用力分為:

1. Dispersion (London) forces 倫敦分散力
2. dipole force 偶極力
3. hydrogen bonds

§1. Dispersion (London) forces

Found in all molecular substances.

It is basically electrical in nature，involving an attraction between temporary or induced dipoles in adjacent molecules.

由於電子之密度變動所造成，存在於所有的分子物質中.

Dispersion forces 強弱取決於：

1). 分子之組成原子的電子數多寡⇒MM↑ dispersion force↑

2). 生成短暫偶極之難易

⇒ MM↑ dispersion force↑⇒b.p.↑ Table 9-2

§2. Dipole force 偶極力

Nonpolar molecules: 分子間作用力: dispersion force

$\mu = 0$

Polar molecules: dispersion force + dipole force

$\mu \neq 0$

相同分子量之分子，polar molecule 之 b.p. ＞ nonpolar molecule 之 b.p.

Ex 9-4. Explain, in terms of intermolecular forces, why

(a). the boiling point of O_2 (-183℃) is higher than that of N_2 (-196℃).

(b). the boiling point of NO (-151℃) is higher than that of either O_2 or N_2.

Ans:

a) O_2、N_2 均 nonpolar molecule ∴MM↑⇒b.p.↑

MM：O_2: 32.00; N_2: 28.00 g/mol ∴O_2 之 b.p. ＞ N_2 之 b.p.

b) NO⇒polar molecule; N: EN=3.0; O: EN= 3.5

∴ NO 之 b.p. ＞ O_2 or N_2 之 b.p.

§3. Hydrogen bonds

存在於 H 原子(EN=2.2) 與其他分子中之非金屬原子之間，因 ΔEN(負電性標差值) ≠0 造成, ΔEN↑ H-bond strength↑

一般而言極性對沸點影響程度不大⇒MM↑ b.p.↑; 但氫鍵對沸點影響較大.

N(3.0)、O(3.5)、F(4.0)、Cl(3.2)、Br(3.0)、I(2.7)等原子之缺電性標高

⇓

NH_3 b.p. -33；H_2O b.p. 100；HF b.p. 19

⇓

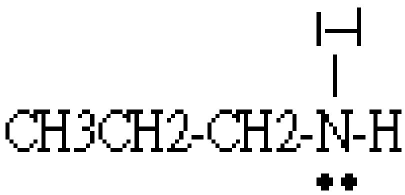
∵分子與分子之間生成 H-bond, ∴其沸點較相似分子量但無極性之分子高.

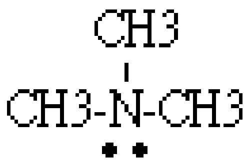
X-H---X-H   X = N、O、F、Cl、Br、I

H-bond 較一般 dipole force 爲強之原因:

1. △EN↑:介於 H 與 N, O, F, Cl, Br, I. 之間△EN 值高; H 原子受鄰近分子之吸引.
2. H 原子半徑小，可允許 N,O,F 上未鍵結電子對之接近，且 N,O,F 之半徑也小所以易接近 H 生成 H-bond.

生成之 H-bond 條件: N,O, F, Cl, Br, I.原子上須具備
1. 未共用電子對
2. 與氫原子相連





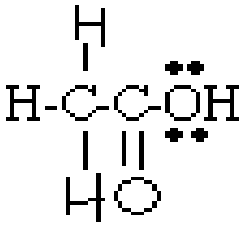
	丙胺	三甲胺
bp.	49℃	3℃
	→有氫鍵存在於分子與分子之間	→無氫鍵，因爲 N 旁未接任何 H

Ex 9-5. Would you expect to find hydrogen bonds in
(a) acetic acid? (b) diethyl ether? (c) hydrazine, N_2H_4?

Ans：

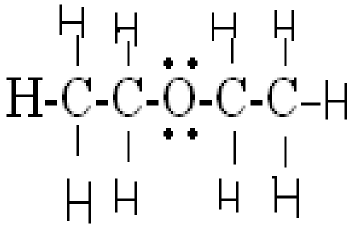
H-bond

(a). acetic acid



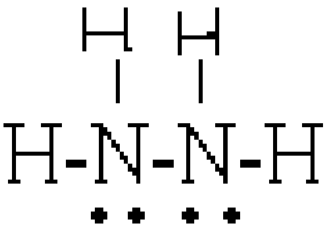
有

(b). diethyl ether



沒有

(c). hydrazine 聯胺



有

H_2O: many unusual properties.

⇒ b.p.: 100℃

specific heat: 4.18J/g.℃

heat of vaporization per gram: 2.26 kJ/g

(爲所有分子物質中最高)

冰: 0℃ d =0.917g/cm^3 水: 0℃ d =1.00 g/cm^3

⇒少見 (∵一般物質固態具有較液態大的密度)

Ex 9-6: What type of intermolecular forces are present in

(a)N_2 (b)$CHCl_3$ (c)CO_2 (d)NH_3

Ans:

a) N_2 nonpolar ∴dispersion force

b) $CHCl_3$ polar dispersion force + dipole force

c) CO_2 nonpolar ∴dispersion force

d) NH_3 polar dispersion force + dipole force + hydrogen bond

Intermolecular force < covalent bond strength (primary force)
2~10 kcal/mole >50 kcal/mole
∴ 叫做 secondary bond primary bond

§9-4 Network covalent solids 網狀共價固體; ionic solid and Metallic solid

在 STP 下(25℃，1atm) 所有 molecular substances 多為氣態或液態，而只有 1. network covalent solids (大多數為 3D 結構)
2. ionic solid
3. metallic solid
三者為固態⇒稱為 nonmolecular solid.

Network covalent solids 網狀共價固體:
原子以連續網狀共價鍵結，the entire crystal , consist of one huge molecule.

Ionic solid:
陰陽離子結合而成.

Metallic solid:
含陽離子(M^+，M^{2+}，M^{3+})及電子(e^-)所組成 see Fig 9-11.

§ Network covalent solids : 特性

1. High melting point: m.p.>1000℃.
2. Insoluble in all common solvents 3-D 立體結構.
3. Poor electrical conductors.

例 :
石墨 Graphite 2-D; sp^2 片狀結構 m.p>3500℃; 層與層間作用力量弱
d=2.26 g/cm^3.

鑽石 3-D; sp^3 四面體結構 m.p>3500℃; d=3.51 g/cm^3.

工業鑽石，利用石墨將 100,000 atm 及 2,000℃下製造.

§ Quartz 石英 SiO_2

網狀共價固體中結構最簡單之化合物

Si 以正四面體連接四個氧

O 連接兩個 Si → Fig9-14

§ Ionic solids 離子固體

金屬陽離子+非金屬陰離子，以電子之授與受生成鍵結.

離子固體特性:

1. Nonvolatile and high melting point (m.p : 600~2000℃).

2. Poor conductor for electric , because the charge ions are fixed.
   但 melt or 水溶液可導電.

3. Many (but not all) ionic solids are soluble in polar solvents.

Coulomb's law : the electrical energy of interaction between a cation and an anion in contact with one another.

$$E = k\, Q_1 Q_2 / d$$

$d=r_{cation} + r_{anion}$

|E|↑, 則鍵能↑, 則 m.p↑ ∴ E "-"

The strength of ionic bond depend on :

1. The charge of ions CaO m.p.=2927℃ (Q↑m.p↑)
   NaCl m.p.=801℃
   KBr m.p.=734℃

2. The size of the ions
   $E \propto 1 / d$
   d_{NaCl}=0.095+0.181=0.276nm
   d_{KBr}=0.133+0.195=0.328nm

§ Metals

Electron-sea model

The metallic crystal is pictured as an array of positive ions, for example Na^+ , Mg^{2+}.

特性 :

1. High electrical conductivity. 導電性 Ag>Cu>Au>Al
2. High thermal conductivity
3. Ductility and malleability 具延展性
4. Luster 光澤
5. Insolubility in water and other common solvents.

Hg 唯一液態金屬.

Amalgams : 汞合金 metal dissolve in mercury

m.p Hg = -39℃ W=3410℃ →所有元素最高

"+1"價金屬之 m.p. 均不高

Na: m.p.=98℃

K : m.p.=64℃

Ex 9-7. For each species in column A, choose the description in column B that best applies.

	A	B
j	(a). CO_2	(e). ionic , high-melting
e	(b). $CuSO_4$	(f). liquid metal , good conductor
i	(c). SiO_2	(g). polar molecule , soluble in water
f	(d). Hg	(h). ionic , insoluble in water
		(i). network covalent , high-melting
		(j). non polar molecule , gas at 25℃

§ 9-5 Crystal structures

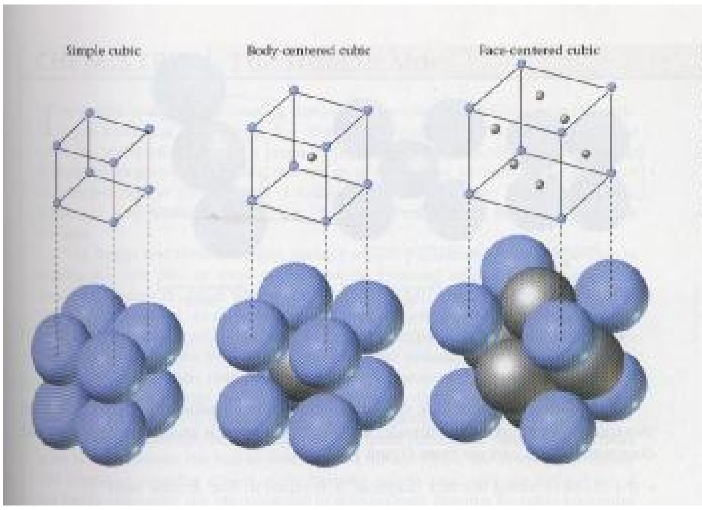
Unit cell 單位晶格; the smallest structural unit

共有十四種單位晶格

§ Metals:

Unit cell 可分爲三種:

1. Simple cubic cell 簡單立方晶系(SC)
2. Body- centered cubic cell 體心立方晶系(BCC)
3. Face-centered cubic cell 面心立方晶系(FCC)



	SC 簡單立方	BCC 體心	FCC 面心
單位晶格內原子數	8 · 1/8 = 1	(8 · 1/8)+1=2	(8 · 1/8)+(6 · 1/2)=4
晶格邊長(s)與 r 的關係	s= 2r	$\sqrt{3}$ s = 4r	$\sqrt{2}$ s = 4r
APF=	$\frac{1\cdot\frac{4}{3}pr^3}{s^3}=\frac{\frac{4}{3}\cdot p\cdot(\frac{1}{2}s)^3}{s^3}$ = 0.52	0.68	0.74

Ex 9-8: Silver is a metal commonly used in jewelry and photography. It crystallizes with a face-centered cubic (FCC) unit cell 0.407 nm on an edge.

(a) What is the atomic radius of silver in cm? (1 nm = 10^{-7} cm)

(b) What is the volume of a single silver atom? (The volume of a spherical ball of radius is $V = \frac{4}{3}pr^3$)

(c) What is the density of a single silver atom?

Ans:

(*a*) $4r = \sqrt{2}s$

$$r = \frac{\sqrt{2}s}{4} = \frac{\sqrt{2}\cdot 0.407}{4} = 0.144 \text{ nm} \times \frac{10^{-7}\text{ cm}}{1\text{ nm}} = 1.44\times 10^{-8}\text{ cm}$$

(b) $V = \frac{4}{3}pr^3 = \frac{4}{3}\,p\,(1.44\times 10^{-8}\text{ cm})^3 = 1.25\times 10^{-23}\text{ cm}^3$

(*c*) $MM_{Ag} = 107.9$ g/mol

$$m_{Ag\text{ atom}} = \frac{107.9\text{ g}}{1\text{ mol}} \times \frac{1\text{ mol}}{6.022\times 10^{23}\text{ atoms}} = 1.792\times 10^{-22}\text{ g/atom}$$

$$d_{Ag\text{ atom}} = \frac{1.792\times 10^{-22}\text{ g/atom}}{1.25\times 10^{-23}\text{ cm}^3} = 14.3\text{ g/cm}^3\cdot atom$$

§ Ionic crystals

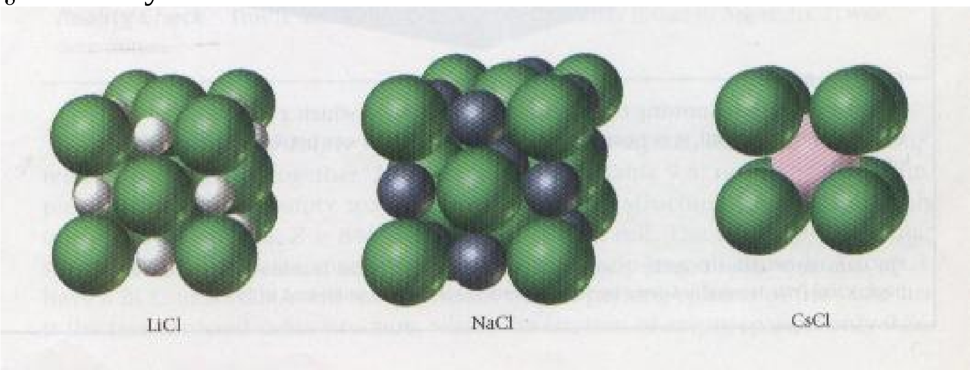


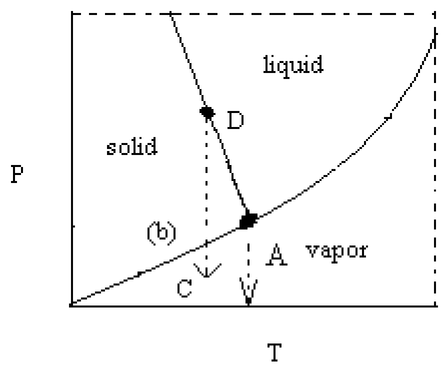
Fig. 9-18.

Ex 9-9. Consider Figure 9-18. The length of an edge of a cubic cell, s, is the distance between the center of an atom or ion at the "top" of the cell and the center of the atom or ion at the "bottom". Taking the ionic radii of Li^+, Na^+, and Cl^- to be 0.060 nm, 0.095 nm, and 0.181 nm, respectively, determine s for (a) NaCl (b) LiCl.

Ans: 搭配 Fig 9-18

a) NaCl: $s = 2\cdot[(r_{Na}{}^{+}) + (r_{Cl}{}^{-})]$
$= 2\cdot[(0.095)+(0.181)]$
$= 0.552\text{nm}$

b) LiCl: $\sqrt{2}\, s = 4\cdot(r_{Cl}{}^{-})$
$\sqrt{2}\, s = 4\cdot(0.181)$
$s = 0.512\text{nm}$


liquid
D
solid
P
(b)
A
vapor
C
T