16 Liquids and solids

Study of matter in different states

Condensed state

g, *l*, *s*

larger difference

smaller difference, such as density

Ex. *P* (atm)	H_2O	density (g/mL)
--	*s*	very little change
1	*l*	0.99707
1065	*l*	1.046
1	*g*	3.26×10^{-4}
242	*g*	0.157

Compressibilities are different

※ Intermolecular forces

◎ Dipole-dipole forces

Some molecules exhibit dipole moment

Dipole-dipole attraction: distance dependent

In gas state: not important

Dipole-dipole repulsion

◎ Hydrogen bonding

a special dipole-dipole forces

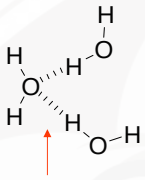
Highly polarized bonds

F—H

O—H

N—H

Elements with high electronegativity



Strong interaction

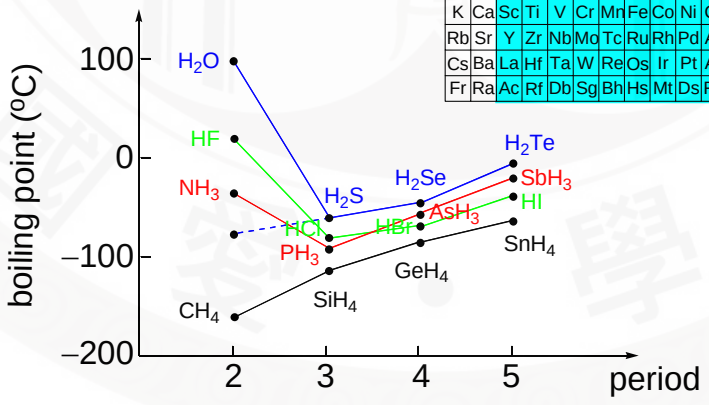
1A													3A	4A	5A	6A	7A	8A
H	2A																	He
Li	Be												B	C	N	O	F	Ne
Na	Mg												Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn		Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd		In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg		Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn		Unt	Fl	Uup	Lv	Uus	Uuo

Another reason for the strong interaction:

small sizes of H, F, O, N

→ intermolecular distance is smaller

1A													3A	4A	5A	6A	7A	8A
H	2A																	He
Li	Be												B	C	N	O	F	Ne
Na	Mg												Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn		Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd		In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg		Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn		Unt	Fl	Uup	Lv	Uus	Uuo



◎ London dispersion forces

Weak attraction forces among nonpolar molecules
noble gas atoms

Derived from instant dipole

H–H no polarization

δ^- H–H δ^+ with instant polarization

Higher MW
→ more e⁻s
→ more polarizable

MW ↑ London dispersion forces ↑ bp ↑

◎ Van der Waals forces { dipole–dipole
dipole-induced dipole
London dispersion forces

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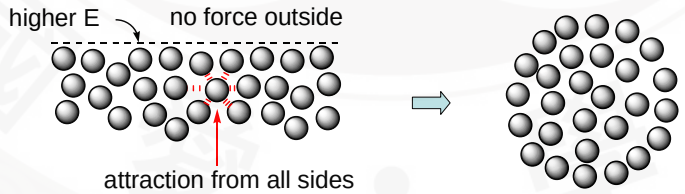
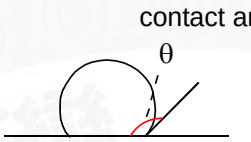
※ The liquid state

High density
Low compressibility
Mobile: viscosity is a measurement of mobility

✓Surface tension
derived from intermolecular attraction forces

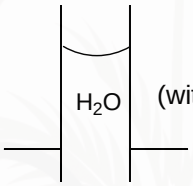


Keep minimum surface
to lower the E



✓Capillary action

Seeking a balance of adhesive forces (attraction with the wall)
and cohesive forces (intermolecular attraction)



In general:
easier to build structural model for gas and solid
but more difficult for liquid

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※ Types of solids

Solid: rigid (vibrates), highly ordered, close distance

- Amorphous – random (glass): super cooled liquid
- Crystalline – highly ordered
  may be anisotropic: different properties in different direction

✓Types of crystalline solids

- Ionic solids
- Molecular solids
- Atomic solids (ex. metals, diamond)

Three dimensional crystal structure – crystal lattice
composed of unit cell

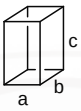
Unit cell: the smallest repeating unit

✓ 7 crystal systems

Cubic (立方晶系)

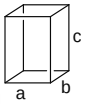
a = b = c; 90 °∠

Tetragonal (四方晶系)



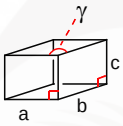
a = b ≠ c; 90 °∠

Orthorhombic (斜方晶系)



a ≠ b ≠ c; 90 °∠

Monoclinic (單斜晶系)

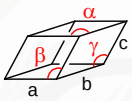


a ≠ b ≠ c

Hexagonal (六方晶系)

a = b ≠ c
γ = 120 °

Rhombohedral (trigonal; 菱形晶系)

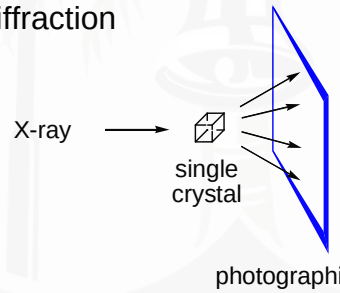


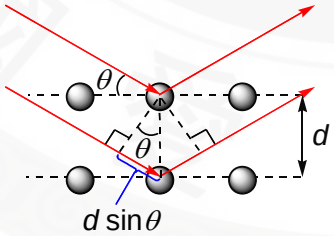
a = b = c
α = β = γ

Triclinic (三斜晶系)

a ≠ b ≠ c
α ≠ β ≠ γ

✓ Method for determination of crystal structures
X-ray diffraction





wavelength

Bragg equation: $2d\sin\theta = n\lambda$

integer:
reinforce each other

※ Structure and bonding in metals

◎ The unit cells

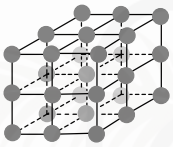
Simple cubic

Body-centered cubic (BCC)

Face-centered cubic (FCC)

a primitive unit cell
→ atoms only at corner

The closest packing for cubic unit cell



← Lattice from simple cubic

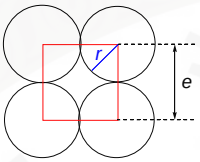
◎ Packing efficiency

$$\frac{\text{Volume of spherical atoms}}{\text{Volume of unit cell}}$$

Corner atom: $\frac{1}{8}$ V each
Face atom: $\frac{1}{2}$ V each
Center atom: 1 V each

Simple cubic: $8 \times \frac{1}{8}\ V = V$
Body-centered: $8 \times \frac{1}{8}\ V + 1\ V = 2\ V$
Face-centered: $8 \times \frac{1}{8}\ V + 6 \times \frac{1}{2}\ V = 4\ V$

✓ Simple cubic

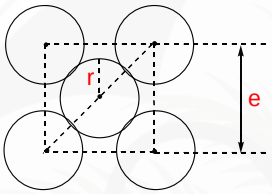


$e = 2r$

radius of the atom

$$\frac{V_{sphere}}{V_{cell}} = \frac{\frac{4}{3}\pi r^3}{(2r)^3} = 52.4\%$$

✓ Face-centered cubic



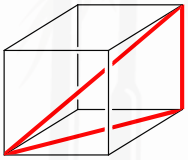
$(4r)^2 = e^2 + e^2$

⇨ $e^2 = 8r^2$

⇨ $e = 2\sqrt{2}\, r$

$$\frac{V_{sphere}}{V_{cell}} = \frac{4 \times \frac{4}{3}\pi r^3}{(2\sqrt{2}\, r)^3} = 74.0\%$$

✓ Body-centered cubic



$(4r)^2 = e^2 + 2e^2$

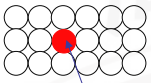
⇨ $e = \frac{4}{\sqrt{3}} r$

$$\frac{V_{sphere}}{V_{cell}} = \frac{2 \times \frac{4}{3}\pi r^3}{\left(\frac{4}{\sqrt{3}} r\right)^3} = 68.0\%$$

◎ Structure in metals

Possible packing

✓ Simple cubic

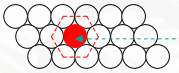


Square packing

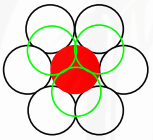
4 neighbors → total = 6 (above and below)

✓ BCC: 8 neighbors

✓ HCP (hexagonal closest packed)



6 neighbors
→ total 12 (3 above and 3 below)
→ close packing or closest packing



ABAB

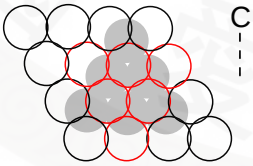
⇨ hcp

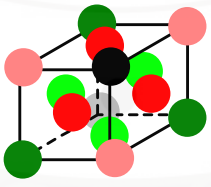
ABCABC

⇨ Cubic closest packed (ccp)

≡

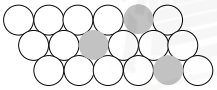
fcc





◎ Metal alloys

✓ Substitutional alloy

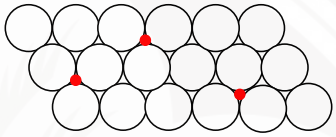


Brass: $^{1}/_{3}$ Zn, $^{2}/_{3}$ Cu

Similar size

✓ Interstitial alloy

Mild steel:
0.2% C in Fe → soft



Forms covalent bond with Fe

Higher carbon steel:
0.6-1.5% C in Fe → hard

◎ Bonding in metals

Properties of metals: malleability
metallic luster
conducting heat and electricity
(directionless)

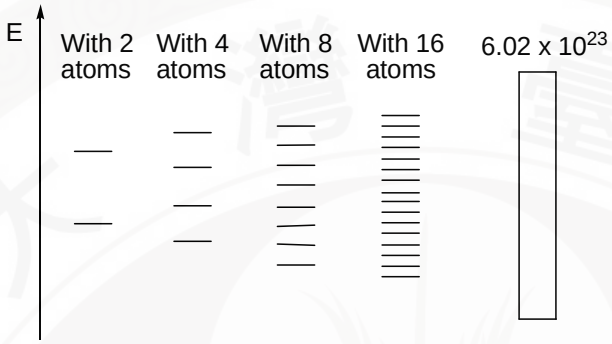
✓ The electron sea model

Delocalized e^{-}s in-between

Explains malleability and conduction but not metallic luster

When mixed with covalent bonding:
hardened (ex. C in Fe)

✓ The band model (MO view)



As more atoms are involved the energy spacing decreases

A continuous band of energy is formed eventually

- ✓ Electron moves freely from one end to the other (when partially filled)
- ✓ Also transmit thermal energy
- ✓ Accepts photons and releases again easily (explains the metallic luster)

Ex. Mg: $3s^2$

3*s* and 3*p* merged at the bonding level: partially filled band

※ Carbon and silicon

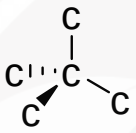
Network atomic solids: involving directional covalent bond

Properties:

Brittle

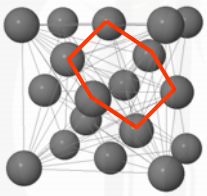
Do not efficiently conduct heat or electricity

Ex. Diamond



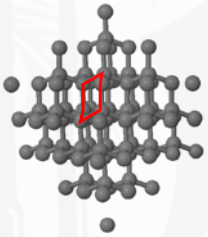
Extending and forms a network ⇨

hard and insulator



Unit cell

an fcc arrangement of atoms plus more atoms in half of the tetrahedral holes

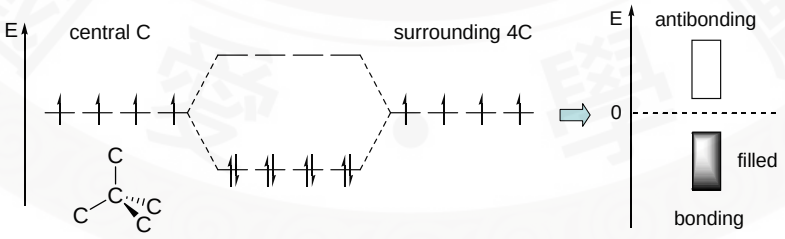


8 unit cells

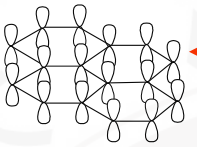
Bonding

Each C (4 AOs) is surrounded by 4 Cs (4 AOs)

With 8 e⁻s (4 bonds) in 8 MO → bonding MOs are filled



Ex. Graphite: layered structure
with weak dispersion forces between layers
(distance between layers: 3.35 Å)



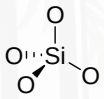
Overlapping *p* orbitals
with π type bonding

Bonding (π) and
antibonding (π*)
band merged

Forms a half-filled band:
Good conductor

✓ Silica: With empirical formula of SiO_2 (O:Si = 2:1)

Forms a network of SiO_4



Silicates: SiO_4^{4-}, $Si_2O_7^{6-}$,···· (O:Si > 2:1)

Cf. CO_2 is a gas

O=C=O ← π from $2p_C$ and $2p_O$

O=Si=O ← π from $3p_{Si}$ and $2p_O$ is too weak

Silica $\xrightarrow{1600\ ^oC}$ $\xrightarrow{\text{cooled rapidly}}$ Glass ← Homogeneous noncrystalline

Addition of B_2O_3 → borosilicate glass
(Pyrex)
heat resistant

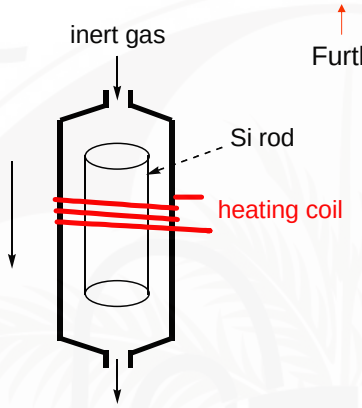
Purification of silicon

$SiO_2(l) + 2C(s) \rightarrow Si(l) + 2CO(g)$

$Si(s) + 2Cl_2(g) \rightarrow SiCl_4(g)$ ← Purified by fractional distillation

$SiCl_4(g) + 2H_2(g) \rightarrow Si(s) + 4HCl(g)$

↑ Further purified by zone refining



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※ Ceramics

A class of nonmetallic materials
Strong, brittle, and resistant to heat and chemicals

Metal oxides $\xrightarrow[-H_2O]{\text{High T}}$ Ceramics

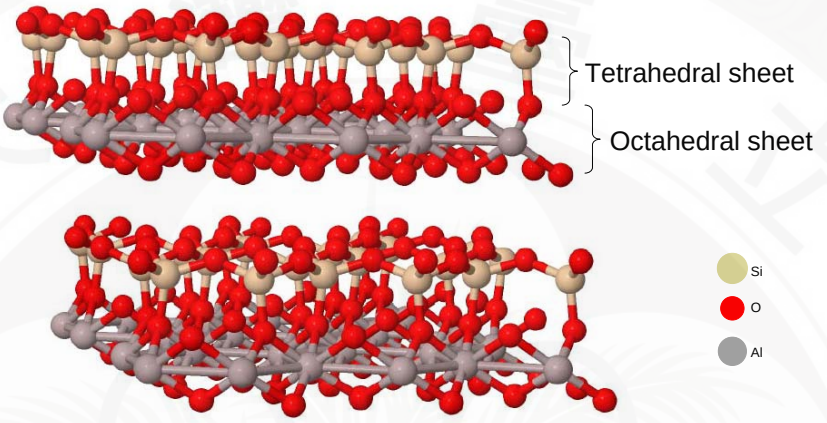
↑ Such as clay (oxides of Na, K, Al, Si)

↑ With network-like structure
Hard and brittle

Ex. Kaolinite: $Al_2Si_2O_5(OH)_4$ (高嶺石): a clay mineral

Roughly hexagonal, platy crystals

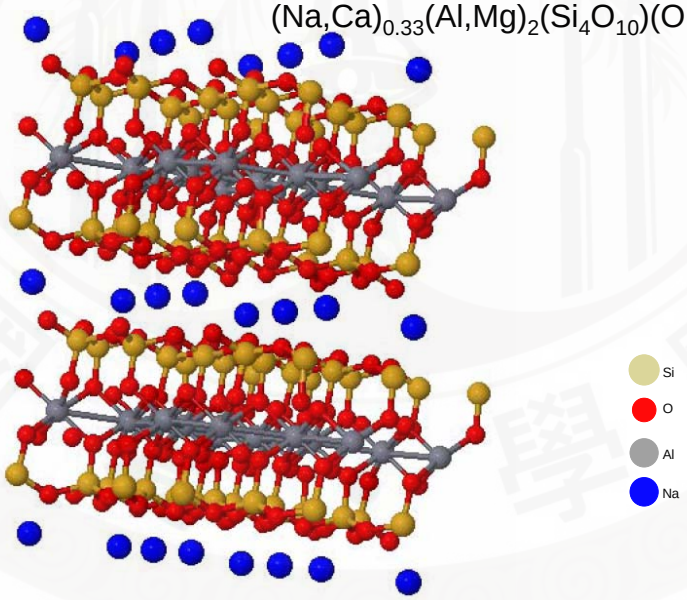
about 0.1 μm–10 μm or even larger



With H_2O in the range of 20–35% ⇨ becomes plastic

Montmorillonite (蒙脫石): a clay mineral

$(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$

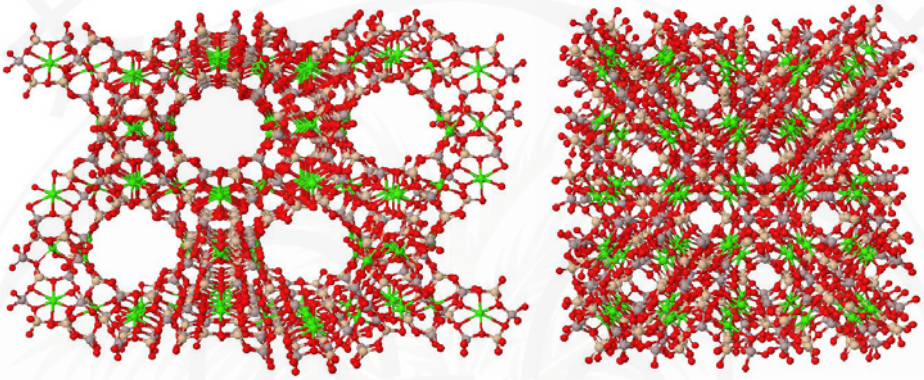


Zeolites (沸石): hydrated aluminosilicate minerals

Framework structure encloses interconnected cavities occupied by large M^{n+} and H_2O

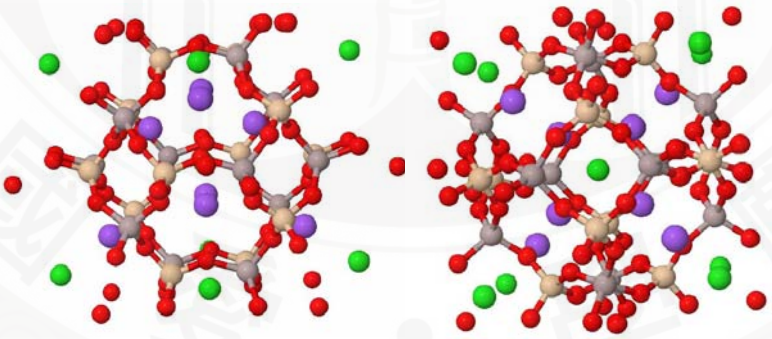
In petroleum industry: catalyst for cracking and isomerization

Ex. Faujasite (八面沸石)



Ex. Sodalite (方鈉石； $Na_4Al_3Si_3O_{12}Cl$)

A common structural unit in zeolites constructed from 4- and 6-membered rings



※ Semiconductors

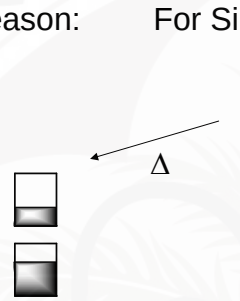
Conductivity

insulator < semiconductor < metal

For metal: T ↑ conductivity ↓

Semiconductor: T ↑ conductivity ↑

Reason: For Si



Band gap: C 502 kJ/mol
Si 100
Ge 67

Now conducts

◎ Doping

✓ n-Type: Si doped with As (P, Sb, Bi)

n for negative

One more valence e^- than Si

B	C	N
Al	Si	P
Ga	Ge	As
In	Sn	Sb
Tl	Pb	Bi

MO

Can be viewed as

✓ p-Type: Si doped with B (Al, Ga, In)

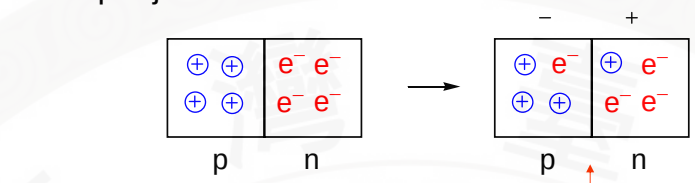
p for positive

One less valence e^- than Si

MO:

Now with holes (partially filled)
Also conducts better

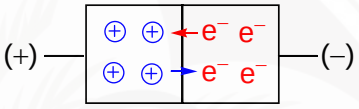
✓ The p-n junction



Creates potential against e^- flow

no e^- flow
no current

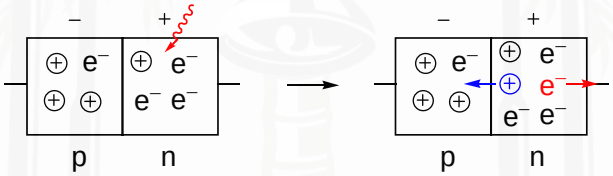
Reverse bias
prevents e^- flow



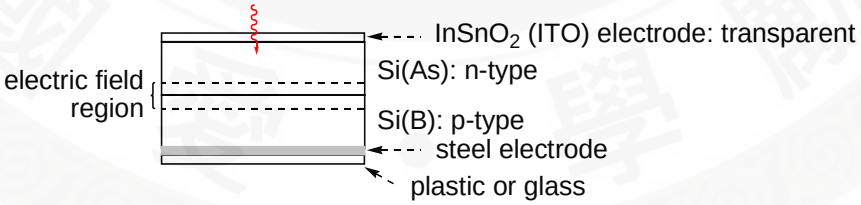
Forward bias
e^- flows readily

Used as rectifier

✓ Photovoltaic cell



Ex.



~ 0.077 W/m^2

◎ Perovskites – future solar cell material?

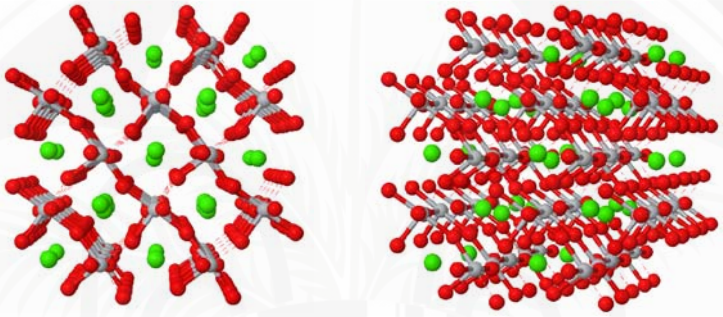
With a general formula of ABX_3

Ex. $CH_3NH_3PbI_3$

Easily prepared from CH_3NH_3I and PbI_2

Efficiency up to 16% in 2 yrs from a few percent

Ex. $CaTiO_3$-perovskite structure:



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※ Molecular solids

van der Walls forces between molecules

- Dipole-dipole forces
- London forces – attraction between instant dipoles

Usually good insulators

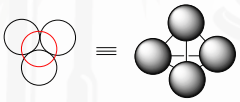
※ Ionic solids

Electrostatic forces between cations and anions

For binary solids:
usually large anions in closest packing
with smaller cations in the holes

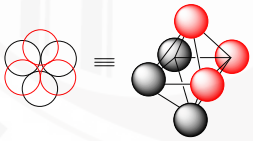
✓ Holes

Tetrahedral holes



Coordination #: 4

Octahedral holes



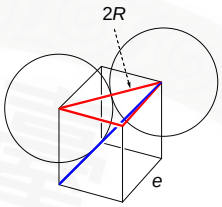
Coordination #: 6

Cubic holes

Coordination #: 8

✓ Hole size

△ Tetrahedral holes



$(2R)^2 = e^2 + e^2$

⇨ $e = \sqrt{2}R$

hole radius

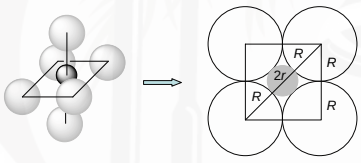
$(2R)^2 + e^2 = [2(R + r)]^2$

⇨ $(2R)^2 + (\sqrt{2}R)^2 = [2(R + r)]^2$

⇨ $6R^2 = [2(R + r)]^2$ ⇨ $\sqrt{\frac{3}{2}}R = R + r$

$r = 0.225R$

△ Octahedral holes



$(2R)^2 + (2R)^2 = [2(R + r)]^2$

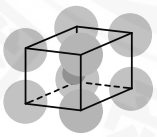
⇨ $8R^2 = 4(R + r)^2$

⇨ $2R^2 = (R + r)^2$

⇨ $\sqrt{2}R = R + r$

⇨ $r = (\sqrt{2} - 1)R = 0.414R$

△ Cubic holes



$(2R)^2 + (2R)^2 + (2R)^2 = [2(R + r)]^2$

⇨ $12R^2 = 4(R + r)^2$

⇨ $3R^2 = (R + r)^2$

⇨ $\sqrt{3}R = R + r$

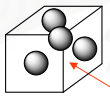
⇨ $r = (\sqrt{3} - 1)R = 0.732R$

Overall

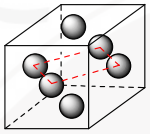
cubic holes > octahedral holes > tetrahedral holes

$r = 0.732R$ $r = 0.414R$ $r = 0.225R$

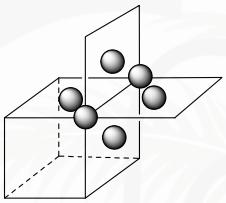
Ex. ccp



Corner: tetrahedral hole
Total: 8
Per unit cell: 4 atoms ⇨ $\frac{\text{hole}}{\text{atom}} = \frac{2}{1}$



Center: one octahedral hole



Side: ¼ octahedral hole
Total: 12 × ¼ = 3

Total octahedral hole = 4 ⇨ $\frac{\text{hole}}{\text{atom}} = \frac{1}{1}$

△ Guidelines

For ionic solids

– usually with large anions and small cations

$0.225\ R^- < r^+ < 0.414\ R^-$

tetra octa

Fill in tetrahedral hole to avoid R^- repulsions

$0.414\ R^- < r^+ < 0.732\ R^-$ < r^+

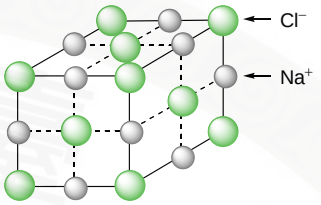
octa cubic

Fill in octahedral hole

Fill in cubic hole

Ex. NaCl: $r_{Na^+} = 0.66\ R_{Cl^-}$

In octahedral holes



Rock salt structure

$Na^+ : Cl^- = 1:1$

Cl^- arranged in distorted ccp (expanded)

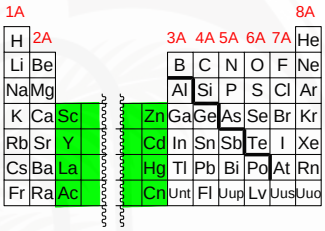
Ex. CsF: large Cs^+, small F^-

⇨ similar as rock salt structure

Ex. CsCl: Cs^+, Cl^- – of similar size

In cubic holes

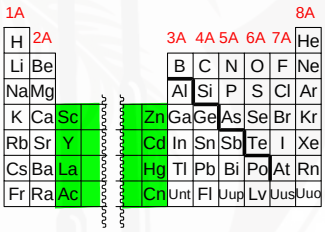
Simple cubic



Ex. CaF_2: the fluorite structure

ccp In tetrahedral hole large Ca^{2+}, small F^-

$$\frac{\text{hole}\,(F^-)}{\text{atom}\,(Ca^{2+})} = \frac{2}{1}$$



Ex. Li_2O: the antifluorite structure

– reverse of the fluorite structure

small large

Ex. ZnS: the zinc blende structure

ccp $r_{Zn^{2+}} \sim 0.35\ R_{S^{2-}}$

Occupies only half of the tetrahedral holes

◎ Lattice defects

✓ Point defects

△ Vacancy (Schottky defects)

ex. $YBa_2Cu_3O_{7-x}$

(nonstoichiometric due to the absence of O)

△ Interstitial atoms or ions (Frenkel defects)

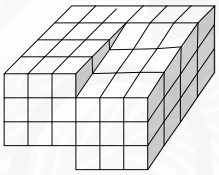
△ Impurity

ex. Ruby Al_2O_3

Al^{3+} replaced by Cr^{3+}

✓ Line defects

Ex. Dislocation of rows



✓ Planar defects

Ex. ABCAABC・・・

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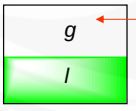
※ Vapor pressure and changes of state

liquid ⟶ gas (vaporization)

gas ⟶ liquid (condensation)

ΔH^o_{vap} molar heat of vaporization

A close system



Pressure of gas: vapor pressure

At dynamic equilibrium

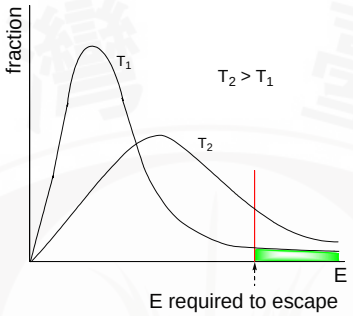
Liquid with high P_{vap} : volatile

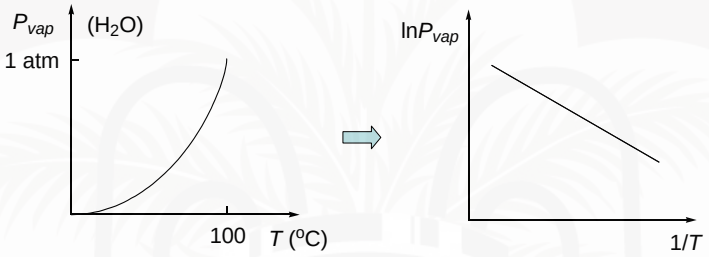
The higher the intermolecular forces

→ the lower the P_{vap}

Qualitatively: T ↑ P_{vap} ↑

Reason:





liquid ⟶ gas ΔH^o_{vap}

$\Delta G^o = \Delta H^o - T\Delta S^o = -RT\ln K$

At equilibrium: $K = P_{vap}$

→ $\Delta H^o_{vap} - T\Delta S^o_{vap} = -RT\ln P_{vap}$

$$\ln P_{vap} = -\frac{\Delta H^o_{vap}}{RT} + \frac{\Delta S^o_{vap}}{R}$$

$$= (-\frac{\Delta H^o_{vap}}{R})(\frac{1}{T}) + \frac{\Delta S^o_{vap}}{R}$$

$\ln P_{vap}$ / $\frac{1}{T}$ ⇨ A straight line with slope = $-\frac{\Delta H^o_{vap}}{R}$

intercept = $\frac{\Delta S^o_{vap}}{R}$

At two different temperatures: T_1 and T_2

Clausius-Clapeyron equation:

$$\ln P_{vap}^{T_1} - \ln P_{vap}^{T_2} = \frac{\Delta H^o{}_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) = \ln \frac{P_{vap}^{T_1}}{P_{vap}^{T_2}}$$

Similarly:

solid $\xrightarrow[\text{sublimation}]{}$ gas $\quad \Delta H^o{}_{sub}$

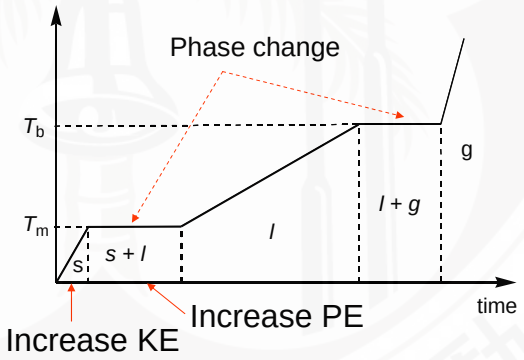
solid $\xrightarrow[\text{melting}]{}$ liquid $\quad \Delta H^o{}_{fusion}$

liquid $\xrightarrow[\text{freezing}]{}$ solid $\quad \Delta H^o{}_{crystallization}$

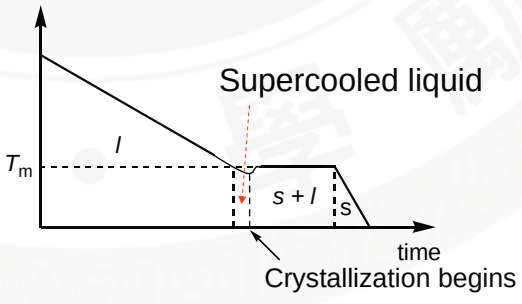
◎ Change of states

Heating curve

Slope is related to heat capacity

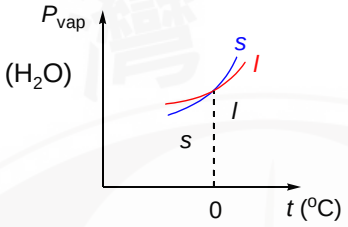


Cooling curve



◎ Normal melting point

the point at which $_{(s)}P_{vap} = {}_{(l)}P_{vap}$ at 1 atm total pressure



◎ Normal boiling point

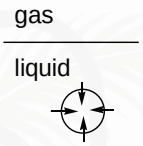
the point at which $_{(l)}P_{vap}$ = 1 atm

Superheated liquid: with T > bp

bumping occurs

To avoid → keep a good stirring

(Ex. add boiling chips)



◎ Applications

✓ Distillation : a good way to purify and separate a liquid

✓ Steam distillation

distillation of two immiscible liquids

Ex. Mixture of bromobenzene and H_2O

P_{vap} at 95 ^{o}C: 120 640 mmHg

Total = 760 mmHg

⇨ Boils at 95 ^{o}C

In the vapor phase

MW of bromobenzene

$$\frac{Wt_{(bb)}}{Wt_{(water)}} = \frac{120 \times 157}{640 \times 18} = \frac{1.63}{1.00}$$

MW of H_2O

Requirements of steam distillation

1. The substance to be distilled has P_{vap} > 5 mmHg
2. Does not destroy by H_2O

Advantage

1. Distillation at low T
2. Water is cheap
3. Water has a small MW

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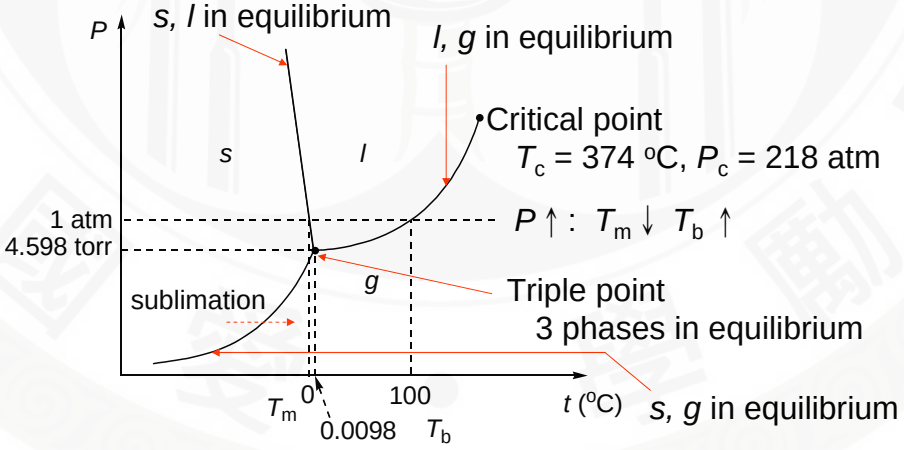
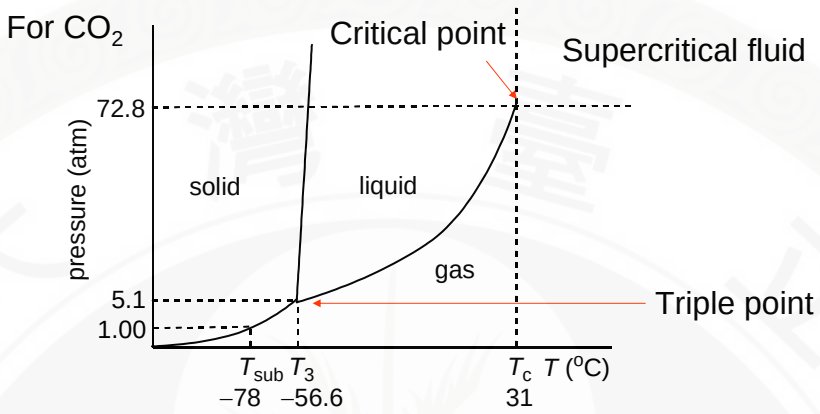
※ Phase diagram

For H_2O



Above T_c : gas can not be liquefied



Supercritical fluid

- Retain dissolving ability of liquid
- High penetration ability
- Low viscosity
- Adjustable dielectric constant (through change of *P*)
- Low surface tension

✓ liq-gas equilibria

heat + liquid ⇆ gas

✓ solid-liq equilibria

heat + solid ⇆ liquid

P ↑ : favor higher density

✓ solid-gas equilibria: sublimation

heat + solid ⇆ gas

✓ More than one solid phase is possible – polymorphic with different crystal structure