CHEM2100J Chapter 05&06 RC

Zeng Haoxuan

UM-SJTU Joint Institute
zenghaoxuan@sjtu.edu.cn

October 17, 2023

Table of Contents

Units of Pressure

- SI Unit
  - pascal(Pa): 1 Pa $= 1$ kg$\cdot$m$^{-1}\cdot$s^{-2}
- Alternative Units
  - 1 atm $= 1.01325\times10^5$ Pa
  - 1 bar $= 10^5$ Pa
  - 1 mmHg $\approx$ 1 torr $= \frac{1}{760}$ atm

Ideal Gas Law

- Ideal Gas Law
  - pV=nRT
  - R=8.314 J·K^{-1}·mol^{-1}
- Molar Volume and Gas Density
  - $V_m = \frac{V}{n} = \frac{RT}{P}$
  - $\rho = \frac{m}{V} = \frac{PM}{RT}$
- Remark
  - Ideal gas - no molecule volume, no intermolecular forces
  - Ideal gas law is a limiting law - reliable at low pressures and high temperatures

Standard Conditions

- Standard Ambient Temperature and Pressure(SATP)
  - 25 °C (298.15 K), 1 bar, V_m=24.79 L·mol^{-1}
- Standard Temperature and Pressure(STP)
  - 0 °C (273.15 K), 1 atm, V_m=22.41 L·mol^{-1}

Mixtures of Gases

- Dalton's Law of Partial Pressures
  - mole fraction - $x_i = \frac{n_i}{n_1+n_2+\ldots+n_N}$
  - partial pressure - $p_i = x_i p_{total}$
- Remark
  - The partial pressure of an ideal gas is the pressure that it would exert if alone in the container
  - The total pressure of a mixture of gases is the sum of the partial pressures

Kinetic Model of Gases

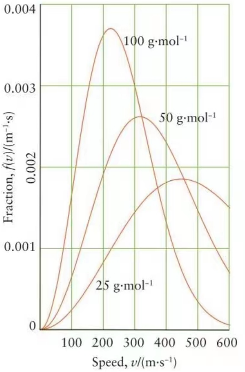
- Assumptions
  - A gas is in continuous random motion
  - Gas molecules are infinitesimally small
  - Molecules move in straight line until collision
  - Molecules do not influence one another except during collisions
  - The collisions are elastic
- Root Mean Square Speed
  - $v_{rms} = \sqrt{\frac{3RT}{M}}$
  - $\langle E_k \rangle = \frac{1}{2} m \langle v^2 \rangle = \frac{1}{2} m v_{rms}^2$ - average kinetic energy of molecules is proportional to v_{rms}^2

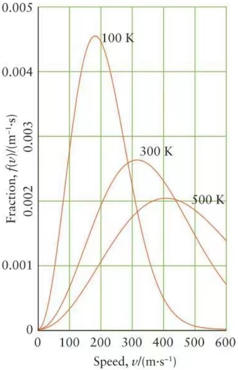
Diffusion & Effusion

- Diffusion
  - The gradual dispersal of one substance through another substance
- Effusion
  - The escape of a gas through a small hole into a vacuum region of lower pressure
- Graham's Law of Effusion
  - Rate of effusion $\propto \sqrt{\frac{T}{M}}$

Maxwell Distribution of Speeds

- $\Delta N = Nf(v)\Delta v$ with $f(v) = 4\pi(\frac{M}{2\pi RT})^{\frac{3}{2}} v^2 e^{-\frac{Mv^2}{2RT}}$
- Most probable speed: $v_p = \sqrt{\frac{2RT}{M}}$
- Root mean square speed $v_{rms} = \sqrt{\frac{3RT}{M}}$





Real Gases

Compression factor

$$Z = \frac{V_m^{real}}{V_m^{ideal}}$$

- At high pressures, repulsions are dominant, $Z > 1$
- At low pressures, attractions are dominant, $Z < 1$

van der Waals Equation

$$(P + \frac{an^2}{V^2})(V - nb) = nRT$$

- a: attractions between gas molecules; intermolecular force$\uparrow \Rightarrow$ a$\uparrow$
- b: volumes of gas molecules; molecular size$\uparrow \Rightarrow$ b$\uparrow$

Intermolecular Interactions

- Origin of Intermolecular Forces
  - Coulomb interaction $E_p = \frac{q_1 q_2}{4\pi\epsilon_0 r}$
- Classifications
  - Chemical bonds(ionic bonds, covalent bonds)
  - Hydrogen bonding(H−X···H,X=N,O,F)
  - Ion-dipole(hydration)
  - wan der Waals forces(dipole-dipole, dipole-induced-dipole, London)
- Strength Order
  - Chemical bonds > hydrogen bonding > ion-dipole > wan der Waals forces

Some Pattern

- London Interactions
  - Size$\uparrow$ $\Rightarrow$ polarisability$\uparrow$ $\Rightarrow$ London forces$\uparrow$
  - Contact points$\uparrow$ $\Rightarrow$ London forces$\uparrow$(Rod-like $>$ Spherical shaped)
- Intermolecular forces$\uparrow$ $\Rightarrow$ melting and boiling point$\uparrow$
  - All types of intermolecular interactions needs to be considered for the total intermolecular force.

Exercise

Compare the melting and boiling point of the following molecules:

$$H_2, \text{Ne}, \text{CO}, \text{HF}$$

Exercise

Experiment has shown that F-H-F hydrogen bond is much stronger than O-H-O hydrogen bond. But at 0 °C water is solid while HF is liquid. Explain the seemingly contradictory phenomenon.

Summary

TABLE 3F.1 The Interactions Between Ions and Molecules*

Type of interaction	E_p dependence	Typical energy $E_p/(\mathrm{kJ \cdot mol^{-1}})$	Interacting species
ion–ion	$-\|z\|^2/r$	250	ions
ion–dipole	$-\|z\|\mu/r^2$	15	ions and polar molecules
dipole–dipole	$-\mu_1\mu_2/r^3$	2	stationary polar molecules
	$-\mu_1\mu_2/r^6$	0.3	rotating polar molecules
dipole–induced-dipole	$-\mu_1{}^2\alpha_2/r^6$	2	molecules, at least one must be polar
London (dispersion)†	$-\alpha_1\alpha_2/r^6$	2	all types of molecules and ions
hydrogen bonding‡		20	molecules containing an N—H, O—H, or F—H bond

Viscosity & Surface Tension

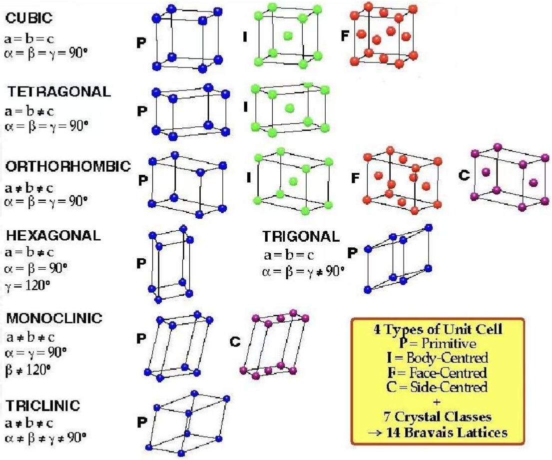
- Viscosity
  - The viscosity of a liquid is its resistance to flow
  - Molecular interaction$\uparrow$ $\Rightarrow$ viscosity$\uparrow$ $\Rightarrow$ more sluggish it flows
- Surface Tension
  - The surface tension is a net inward pull
  - Adhesion: forces that bind a substance to a surface
  - Cohesion: forces that bind the molecules of a substance together
  - Concave: adhesion $>$ cohesion; Convex: cohesion $>$ adhesion

Classification

- Crystalline Solids & Amorphous Solids
    - Crystalline solids: long-range order; fixed melting point
    - Amorphous solids: short-range order; non-fixed melting point
- Classifications of Crystalline Solids
    - Molecular solids - van der Waals forces
    - Network solids - covalent bonds
    - Metallic solids - metallic bonds
    - Ionic solids - ionic bonds

Unit Cells

- All crystal structure are derived form the 14 Bravais lattices
- The atoms in a unit cell are counted by determining what fraction of each atom resides within the cell

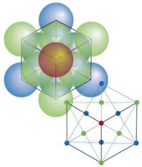


Coordinate Number

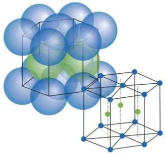
- Metallic Solids
  - The number of nearest neighbors of each atom
- Ionic Solids
  - For A_xB_y, $x \cdot n_a = y \cdot n_b$
  - n_a - the number of the closest cations to a anion.
  - n_b - the number of the closest anions to a cation.

Closed-Packed Structure

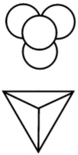
- In closed-packed structure, octahedral hole : tetrahedral hole= 1 : 2



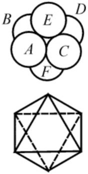
ccp



hcp



Tetrahedral hole

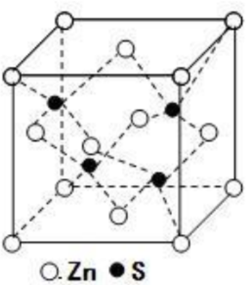


Octahedral hole

Solid

Exercise

The unit cell of ZnS is given as follows. Find the coordination numbers of S and Zn. Also, what type of holes does S^{2-} ions fit in?



Reference

- Atkins, P. (2016) *Chemical principles: The quest for insight*. New York: W H Freeman.
- Prof. Milias Liu, Lecture Slides. 23FA VC210
- ZHOU Jieshen, RC Slides, 22FA VC210
- SU Zixun, RC Slides, 22FA VC210

Thanks!