

# VC210 Notes

Dzsyang

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Prof. Milias Liu

UM-SJTU Joint Institute

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# **1 Fundamentals**

## **2 Atomic Theory**

### **3 Basic Quantum Mechanics**

## **4 Molecular Shapes, VSEPR, VB and MO Theory**

## **5 Chemical Bonds**



## 6 Gases

### 6.1 The Nature of Gases

Eleven elements are gases under normal conditions: H, He, N, O, F, Ne, Cl, Ar, Kr, Xe, Rn. Low molar mass compounds such as carbon dioxide, hydrogen chloride are also gases.

### 6.2 The Unit of Pressure

$$1\text{Pa} = 1\text{kg} \cdot \text{m}^{-1} \cdot \text{s}^{-2}. \quad 10^5\text{Pa} = 1\text{bar}.$$
$$760\text{mmHg} = 760\text{Torr} = 1\text{atm} = 1.013 \times 10^5\text{Pa}.$$

### 6.3 The Gas Laws

**Boyle's Pressure Experiment**  $PV = \text{Const.}$

**Charles' Law**  $V/T = \text{Const.}$

No real gas has zero volume. Lowest possible temperature:  $-273.15^\circ\text{C}$ .

### 6.4 Avogadro's Principle

All gases occupy the same volume under the same conditions of temperature and pressures. The molar volume of all gases is close to  $22.4\text{L} \cdot \text{mol}^{-1}$  at  $0^\circ\text{C}$  and 1 atm.

### 6.5 Standard Conditions

#### Standard Ambient Temperature and Pressure (SATP)

SATP means exactly  $25^\circ\text{C}$  (298.15 K) and exactly 1 bar. The molar volume of an ideal gas is  $24.79\text{L} \cdot \text{mol}^{-1}$ .

#### Standard Temperature and Pressure (STP)

STP means  $0^\circ\text{C}$  (273.15 K) and 1 atm (both exactly). The molar volume of an ideal gas is  $22.41\text{L} \cdot \text{mol}^{-1}$ .

### 6.6 The Ideal Gas Law

$$pV = nRT$$

The constant  $R = 8.314\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ .

The ideal gas law is a limiting law, valid only as  $p \rightarrow 0$ .

The differences between ideal gases and real gases are significant at high pressures and low temperatures.

## 6.7 Combined Gas Law

$$\frac{p_1 V_1}{n_1 T_1} = \frac{p_2 V_2}{n_2 T_2}$$

## 6.8 Change n for The Ideal Gas Law

**Molar Concentration**  $M = \frac{p}{RT}$ .

**Gas Density**  $d = \frac{Mp}{RT}$ .

## 6.9 Mixtures of Gases

A mixture of gases behaves like a single pure gas.

### Dalton's Law of Partial Pressures

Dalton concluded that the total pressure is the sum of the individual pressures of each gas.

$$\chi_A = \frac{n_A}{n_A + n_B + \dots}, p_A = \chi_A p_T$$

## 6.10 The Kinetic Model of Gases

The kinetic model (KMT) of a gas allows us to derive the quantitative relation between pressure and the speeds of the molecules.

**Root Mean Square Speed**  $v_{rms} = \sqrt{\frac{3RT}{M}}$ .

**Most Possible Speed**  $v_{rms} = \sqrt{\frac{2RT}{M}}$ .

**Effusion** In effusion, molecules escape through a small hole in a barrier into a region of low pressure. And we can find  $\bar{v} \propto \frac{1}{\sqrt{m}}$ .

**The Maxwell Distribution of Speeds**  $f(v) = 4\pi \left(\frac{M}{2\pi RT}\right)^{\frac{3}{2}} v^2 e^{-Mv^2/2RT}$ .

For the same temperature, the greater the molar mass, the lower the speed.

For the same molar mass, the higher the temperature, the higher the average speed and the broader the spread of speeds.

## 6.11 Deviations from Ideality

Gases can be condensed to liquids when cooled or compressed.

A measurement of the compression factor  $Z = \frac{V_{m,real}}{V_{m,ideal}}$ .

At low pressures the attractive forces are dominant and  $Z < 1$ .

At high pressures, repulsive forces become dominant and  $Z > 1$  for all gases.

## 6.12 van der Waals Equation

$$(p + a \frac{n^2}{V^2})(V - nb) = nRT.$$

Parameter “a” represents the attraction between molecules; the value is large for strongly attracting molecules. Parameter “b” represents the role of repulsions; it can be thought of as representing the volume.

## 7 Liquids and Solids

### 7.1 Different Types of Intermolecular Forces

Type of interaction	$E_p$ dependence	Interacting species
ion-ion	$1/r$	ions
ion-dipole	$1/r^2$	ions and polar molecules
dipole-dipole (stationary)	$1/r^3$	stationary polar molecules
dipole-dipole (rotating)	$1/r^6$	rotating polar molecules
hydrogen bonding		special case of dipole-dipole: N-H, O-H, F-H

### 7.2 London Forces

Attractive forces between nonpolar molecules are London forces.

Even nonpolar noble gases can be liquefied, as well as many nonpolar compounds.

**London interaction**  $E_p \propto \frac{\alpha_1 \alpha_2}{r^6}$ .

#### Influence

Size: As size increases (more shells)  $\Rightarrow$  polarizability increases  $\Rightarrow$  melting and boiling points increase.

Shape: Rod-like molecules have a greater surface area, more contact points for molecules to join together (high melting and boiling points); Ball or spherical shaped molecules have fewer contact points for molecules to join together (low melting and boiling points).

### 7.3 Hydrogen Bonding

Very strong interaction between molecules that is specific to molecules with certain types of atoms (the second strongest only to ion-ion interaction).

A hydrogen bond is denoted by a dotted line,  $X - H \dots X$ ,  $X = N, O, F$ .

### 7.4 Surface Tension

**Viscosity** is a liquid's resistance to flow: the higher the viscosity of the liquid, the more sluggish the flow.  $\uparrow$ Viscosity indicates,  $\uparrow$ intermolecular strength.

**Surface tension** is the reason that the surface of a liquid is smooth. Strong forces pull the molecules together, with a net inward pull.

The upward curved meniscus (concave) of water forms because both water and glass have comparable forces: Adhesion  $\approx$  Cohesion.

The downward meniscus (convex) of mercury forms because the cohesive forces in mercury is stronger than between mercury atoms and the glass: Cohesion  $>$  Adhesion.

## 7.5 Liquid Crystals

Liquid crystals are neither a solid nor a liquid, but an intermediate called a mesophase. Here molecules have the fluidity of a liquid and some of the order of a molecular solid. They are responsive to changes in temperature and electric fields.

Anisotropic materials depend on the direction of measurement. Isotropic materials do not depend on orientation: water's viscosity is the same in all directions.

### Three phases

Nematic phase: parallel molecules, staggered along their long axes.

Smectic phase: molecules are parallel and line up to form sheets.

Cholesteric phase: sheets of parallel molecules are rotated relative to their neighbors and form a helical structure.

**LCD (liquid-crystal display)** Light is polarized when a potential difference is applied. The molecules rotate until they are oriented with the electric field and become opaque, forming dark spots on a screen.

## 7.6 Solids Types

**Crystalline and Amorphous Solids** Crystalline solids have long-range order. Amorphous solids have short-range order.

**Molecular Solids** Molecular solids are held together by intermolecular forces.

**Network Solids** Atoms in network solids are joined to their neighbors by strong covalent bonds. Therefore, network solids are very hard, rigid materials with high melting and boiling points.

**Metallic Solids** Metals are cations bound tightly together by a sea of swirling electrons that the metals have lost. Many metallic structures are closed-packed (layer upon layer).

**Closed-packed Structures** ABABAB pattern: Hexagonal closed-pack (hcp); ABCABC pattern: Cubic closed-pack (ccp).

## 7.7 Unit Cells

The smallest region of the crystal lattice that repeats itself is referred to as the unit cell. The atoms in a unit cell can stack, or arrange themselves, into one of three types of cubic structures: 1. Primitive cubic; 2. Body-centered cubic; 3. Cubic closed-packed. (4. Face-centered close packed; 5. Hexagonal close packed)

## 8 The First Law of Thermodynamics

### 8.1 Historical Views on Heat

**Sadi Carnot** Heat flowed to produce work.

**James Joule** Energy can be transformed into heat and/or work.

### 8.2 System versus Surroundings

The system and the surroundings jointly make up the universe.

System to the surroundings: Open, Close, Isolate:

Open: Exchange both matter and energy;

Close: Exchange energy;

Isolate: No contact.

### 8.3 Formula

$$\Delta U = Q + W. \text{ i.e., } Q = \Delta U + p\Delta V.$$

### 8.4 Internal Energy U

In thermodynamics, the capacity of a system to do work is called its internal energy U. Absolute internal energy is not measurable because it includes the energies of all the atoms, their electrons, and the components of their nuclei.

Internal energy is energy stored in a system as kinetic energy and potential energy.

The internal energy of an isolated system is constant.

### 8.5 Work

**Expansion work** is a change in volume of a system.  $W = -p\Delta V$ .

Two forms:

Isobar (Constant pressure);

Isothermal (Constant temperature)  $W = -nRT \ln \frac{V_{final}}{V_{initial}}$ .

Expansion against zero pressure is called free expansion.

**Nonexpansion work** can be the flow of electrical current.

### 8.6 Heat Capacity

Specific heat capacity:  $Q = mC_s\Delta T$  (for water  $4.18 J \cdot K^{-1} \cdot g^{-1}$ );

Molar heat capacity:  $Q = nC_m\Delta T$  (for water  $75 J \cdot K^{-1} \cdot mol^{-1}$ ).

## 8.7 State Functions

A property that depends only on the current state of the system and is independent of how that state was prepared is called a state function.

Such as pressure, volume, temperature, mass, altitude and internal energy.

## 8.8 The Origin of Internal Energy

The **equipartition theorem** (not derived here) states the average value of each quadratic contribution at a temperature  $T$  is equal to  $\frac{1}{2}kT$ .

For monoatomic molecules: Total  $E_{kin}$ :  $\frac{3}{2}RT = 3.72kJ \cdot mol^{-1}$ ;

For linear molecules: Total  $E_{kin}$ :  $\frac{5}{2}RT = 6.02kJ \cdot mol^{-1}$ ;

For nonlinear molecules: Total  $E_{kin}$ :  $\frac{6}{2}RT = 7.44kJ \cdot mol^{-1}$ .

## 8.9 Enthalpy

$$H = U + pV. \text{ i.e., } \Delta H = \Delta U + p\Delta V = Q + (p - p_{ex})\Delta V.$$

For a chemical reaction open to the atmosphere, or at constant pressure, the heat released or required is the enthalpy of the system.  $\Delta H = Q$ . Therefore,  $\Delta H < 0$  for exothermic reactions, "-";  $\Delta H > 0$  for endothermic reactions, "+".

**Vaporisation**  $\Delta H_{vap,m} = H_m(vapor) - H_m(liquid)$ , where  $\Delta H_m$  is the molar heat.

**Fusion**  $\Delta H_{fus,m} = H_m(liquid) - H_m(solid)$ .

**Freezing**  $\Delta H_{fre,m} = -\Delta H_{vap,m}$ . **Condensation**  $\Delta H_{con,m} = -\Delta H_{fus,m}$ .

**Sublimation**  $\Delta H_{sub,m} = H_m(vapor) - H_m(solid)$ . **Deposition**  $\Delta H_{dep,m} = -\Delta H_{sub,m}$ .

## 8.10 The Relation between H and U

At constant volume, the heat transfer is  $\Delta U$ ;  $C_{V,m} = \frac{\Delta U}{\Delta T}$ .

At constant pressure, it is  $\Delta H$ ;  $C_{p,m} = C_{V,m} + R$ .

## 8.11 Hess's Law

The overall reaction enthalpy is the sum of the reaction enthalpies of each step.

## 8.12 The Born-Haber Cycle

In a Born-Haber cycle, we

- break apart the bulk elements into atoms,
- ionize the atoms,
- combine the gaseous ions to form the ionic solid,
- then form the elements again from the ionic solid.

## 9 The Second and Third Laws of Thermodynamics

### 9.1 Entropy and Disorder

Entropy,  $S$ , is a measure of disorder.

Low entropy means little disorder. High entropy means great disorder.

In an isolated system the entropy increases in the course of any spontaneous change.

The natural progression of a system and its surroundings is from order to disorder, from lower to higher entropy.

An entropy change in a system is calculated as:  $\Delta S = \frac{q_{rev}}{T}$ .

Entropy can predict the natural direction of a reaction.

### 9.2 Deriving a Change in Entropy

Changes in temperature:  $\Delta S = C \ln \frac{T_2}{T_1}$ .

Changes in volume:  $\Delta S = nR \ln \frac{V_2}{V_1}$ .

Changes in pressure:  $\Delta S = nR \ln \frac{p_1}{p_2}$ .

### 9.3 A Molecular Interpretation of Entropy

The entropies of all perfect crystals approach zero as the absolute temperature approaches zero.

The entropy of any substance to be greater than zero above  $T = 0$ .

### 9.4 Boltzmann Formula - Statistical Entropy

$S = k \ln W$ , where  $k = 1.381 \times 10^{-23} J \cdot K^{-1}$ ,  $W$  is the number of positions atoms or molecules can arrange into and are called microstates.

$W = \Pi$  orientations of each molecule.

### 9.5 Standard Molar Entropies

$$\Delta S^\circ = \frac{\Delta H^\circ}{T}$$

Complex molecules have greater entropy values. Heavier molecules have greater entropy values.



## 9.6 Global Changes in Entropy: Total

$$\Delta S(\text{total}) = \Delta S(\text{system}) - \Delta S(\text{surroundings}).$$

$$\Delta S(\text{system}) = \sum n S_m(\text{products}) - \sum n S_m(\text{reactants}).$$

$$\Delta S(\text{surroundings}) = -\frac{\Delta H}{T}.$$

If  $\Delta S(\text{total})$  is positive (an increase), the process is spontaneous.

If  $\Delta S(\text{total})$  is negative (a decrease), the reverse process is spontaneous.

If  $\Delta S(\text{total}) = 0$ , the process has no tendency to proceed in either direction (phase changes are the most common examples of when  $\Delta S(\text{total}) = 0$ ).

**Clausius inequality** In an isolated system  $q = 0$  so  $\Delta S \geq 0$ , meaning the entropy cannot decrease in an isolated system, or in other words, the entropy of the universe is steadily increasing.

## 9.7 Equilibrium

A system at equilibrium has no tendency to change in either direction (forward or reverse). The equilibrium state is a dynamic equilibrium, where the forward and reverse processes are continually at matching rates.

## 9.8 Gibbs Free Energy

Gibbs free energy accomplishes the same task more simply, and it also tells us how much nonexpansion work (work under free expansion when  $W$  usually = 0) we can get from the system.

Gibbs free energy is a measure of the energy free to do nonexpansion work.

$$G = H - TS. \text{ i.e., } \Delta G = \Delta H - T\Delta S.$$

When  $\Delta G$  is large "-" the process is spontaneous.

### Labile versus inert

If  $\Delta G_f^\circ < 0$ , then elements are poised to change spontaneously into the compound.

If  $\Delta G_f^\circ > 0$ , then the compound is poised to change spontaneously into the pure elements (unstable).

**The crossover point** is where  $\Delta G_f^\circ$  goes from "+" to "-".

$$\text{Therefore, we can take } \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \text{ set it to 0, i.e., } T = \frac{\Delta H^\circ}{\Delta S^\circ}.$$

## 10 Physical Equilibrium

### 10.1 Phases and Phase Transitions

Matter exists in a single phase such as a solid, liquid, or gas. A phase change occurs when converting one phase into another.

Carbon has three distinct solid phases: diamond, graphite, and Buckminsterfullerenes (C<sub>60</sub>). Helium is only known to exist as a gas and liquid.

### 10.2 Vapour Pressure

Evaporation takes place at the surface because molecules are bound to fewer neighbors. A dynamic equilibrium is when the rate of escaping matches the rate of returning.

Solids and gases aside, liquids with weak intermolecular forces have the highest vapour pressure; Liquids with strong intermolecular forces, ones capable of forming hydrogen bonds, have the lowest vapour pressure.

### 10.3 Clausius - Clapeyron Equation

$$\ln \frac{p_2}{p_1} = \frac{\Delta H_{\text{vap}}^\circ}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right).$$

### 10.4 Water is Unusual

Most substances are more dense in the solid phase than liquid, water being an exception. Water is highly unusual, at 0.0°C,  $\text{density}_{\text{liquid}} > \text{density}_{\text{solid}}$ .

Solid water hydrogen bonds hold the molecules apart at low temperatures. As ice melts, the hydrogen bonds collapse, allowing water molecules to pack more closely.

### 10.5 Phase Diagram

A phase diagram is a map showing phases at different pressures and temperatures.

**For water**, a triple point is the temperature and pressure at which water exists as a solid, liquid, and vapour. The slope of the solid–liquid boundary depends on the relative density and for liquid water it is more dense than its solid.

#### Critical Properties

There is an end in the liquid–vapour phase boundary called the critical point.

The density of the vapour is so great that it is equal to the density of the liquid.

The surface boundary disappears into a single, uniform phase.

Here, the critical pressure and critical temperature mark the end of either liquid or vapour, and is now a supercritical fluid, a very dense fluid.

## 10.6 Raoult's Law

$p = \chi_{\text{solvent}} \cdot p_{\text{pure}}$ , where  $p$  is the vapour pressure of the solvent,  $\chi_{\text{solvent}}$  is the mole fraction of the solvent, and  $p_{\text{pure}}$  is the vapour pressure of the pure solvent.

$$\chi_{\text{solvent}} = \frac{n_{\text{solvent}}}{n_{\text{solute}} + n_{\text{solvent}}}$$

$$\chi_{A,\text{vapour}} = \frac{\chi_{A,\text{liquid}} \cdot p_{A,\text{pure}}}{\chi_{A,\text{liquid}} \cdot p_{A,\text{pure}} + \chi_{B,\text{liquid}} \cdot p_{B,\text{pure}}}$$

## 10.7 Distillation

The vapour pressure as well as the boiling point of the mixture will be intermediate between the two pure liquids.

**Fractional distillation** is a continuous re-distillation.

Higher BP (Boiling Point) vapour condenses and vapourizes over and over as it rises; the lower BP liquid drips back into the boiling mixture. Vapour becomes richer in the component with the lower boiling point. The final distillate is nearly pure (lower BP liquid), and the liquid in the pot is also nearly pure (higher BP liquid).

## 10.8 Pressure and Gas Solubility: Henry's Law

The solubility of a gas is directly proportional to its partial pressure:  $s = k_H p$ , where  $k_H$  is called Henry's constant.

## 10.9 Enthalpy of Solution

Measuring heat released or absorbed when a substance dissolves is called molar enthalpy of solution,  $\Delta H_{\text{sol}}$ .

The first step sublimes solid ions to gas ions. Highly endothermic, this is the lattice enthalpy,  $\Delta H_L$ ;

In the second step, gaseous ions plunge into water forming the final solution. This is the enthalpy of hydration,  $\Delta H_{\text{hyd}}$ ;

Combining these steps:  $\Delta H_{\text{sol}} = \Delta H_L + \Delta H_{\text{hyd}}$ .

High charge and small ionic radius contribute to high lattice enthalpy ( $\Delta H_L$ ). However, often these can be the same properties that relate to low enthalpy of hydration ( $\Delta H_{\text{hyd}}$ ). Therefore it is very difficult to make reliable predictions and instead rationalise what is observed.

## 10.10 Solubility

**Limits:** unsaturated and saturated solution.

**Like Dissolves Like:** polar-polar, nonpolar-nonpolar.

## 10.11 Colligative Properties

Properties that depend on the numbers of solute and solvent molecules and not on chemical identity are called colligative properties.

Four colligative properties of major importance are the:

1. lowering of the vapour pressure,
2. raising boiling points,
3. lowering of freezing points, and
4. osmosis.

Colligative properties are measured using either mole fraction ( $\chi_A = \frac{n_A}{n_A + n_B + \dots}$ )

or molality ( $\frac{n_{solute}(mol)}{m_{solvent}(kg)}$ ).

## 10.12 Boiling-Point Elevation and Freezing-Point Depression

A nonvolatile solute lowers the vapour pressure of the solvent, therefore increasing the boiling point and therefore it is called boiling-point elevation. The increased boiling temperature is usually quite small and is of little practical importance in science.

Freezing-point depression is more significant. An added solute lowers of the freezing point of a solvent. Melting point are also a method for determining the purity of a solid.

Boiling-point elevation =  $k_b \times \text{molality}$ , temperature increases.

Freezing-point depression =  $k_f \times \text{molality}$ , temperature decreases.

## 10.13 Van't Hoff $i$ Factor

The van't Hoff  $i$  factor, is determined experimentally.

In very dilute solution, where all ions are independent,  $i$  = number of ions.

## 10.14 Osmosis

**Osmotic pressure**,  $\Pi = iRTc$ , where  $c$  is molarity.

Osmometry is the technique used to determine the molar mass of a solute from osmotic pressure measurements.

## **11 Chemical Equilibrium**