

VC210

Final Review

Part II. Chapter 5-11

UM-SJTU Joint Institute

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2018 Fall

- Gas
- Thermodynamic
- Equilibrium

Ideal gas law



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$$PV=nRT$$

$R=8.314$ if Pa & m^3

$R=0.08206$ if atm & L



Partial pressure



$$P_T = \frac{n_T RT}{V} = (n_A + n_B + \dots) \frac{RT}{V} \quad \text{and} \quad P_A V = n_A RT$$

Rearrange to get
$$P_A = \frac{n_A}{(n_A + n_B + \dots)} P_T$$

Define molar fraction

$$\chi_A = \frac{n_A}{n_A + n_B + \dots}$$

Note that: $\chi_A + \chi_B + \dots + \chi_N = 1$

We have $P_A = \chi_A P$

$$E_k = \frac{1}{2} M v_{rms}^2 = \frac{3}{2} RT$$

$$v_{rms}^2 = \frac{3RT}{M}$$

PAT ATTENTION TO UNIT!

The Maxwell Distribution of Speeds

$$\Delta N = N f(v) \Delta v \quad \text{with } f(v) = 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} v^2 e^{-Mv^2/2RT}$$

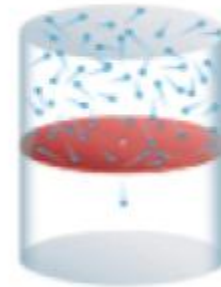
Most possible speed

$$v_{\text{mps}} = \sqrt{\frac{2RT}{M}}$$

- *Definition:* **Effusion** is the escape of a gas through a tiny hole (a balloon will deflate over time due to effusion).

Two gases with molar masses m_1 and m_2 , the relative **rate** of effusion is given by

$$\frac{v_1}{v_2} = \sqrt{\frac{m_2}{m_1}}$$



Diffusion and Mean Free Path

- *Definition:* Diffusion of a gas is the spread of the gas through space.
- Diffusion is significantly slower than rms speed.
- Diffusion is slowed by gas molecules colliding with each other.
- Average distance of a gas molecule between collisions is called **mean free path**.
- The mean free path of gas is **about $5 \times 10^{-8} \text{m}$** .

From the ideal gas equation, we have **compression factor**

$$Z = \frac{PV}{nRT}$$

For ideal gas, $Z=1$ for all pressures.

In a real gas, Z varies from 1 significantly.

The van der Waals Equation

$$\left(P + a \frac{n^2}{V^2} \right) (V - nb) = nRT$$

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

Relation between a, b and Z?

$$Z = \frac{V}{V - nb} - \frac{an}{RTV}$$

Intermolecular Interactions



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Type of interaction	Typical energy (kJ·mol ⁻¹)	distance dependence
Ion-Ion	250	1/r
ion-dipole	15	1/r ²
*dipole-dipole (stationary- solids/liquids)	2	1/r ³
dipole-dipole (rotating-gases)	0.3	1/r ⁶
dipole-induced-dipole	2	1/r ⁶
London or induced (or dispersion)	2	1/r ⁶

Intermolecular Interactions



Match the following properties of liquids to what they indicate about the relative strength of the intermolecular forces in that liquid.

Strong intermolecular forces

high boiling point

high surface tension

high viscosity

Weak intermolecular forces

high vapor pressure

Intermolecular Interactions



Rank these compounds by boiling point.

Highest Boiling Point

hexane

pentane

neopentane

Lowest Boiling Point

pentane: $\text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$

neopentane: $\begin{array}{c} \text{CH}_3 \\ | \\ \text{H}_3\text{C}-\text{C}-\text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$

hexane: $\text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$

Summary: how to compare the strength of intermolecular interactions?

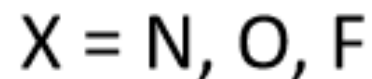
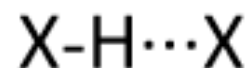
1. Boiling point
2. Surface tension
3. Viscosity
4. Vapor pressure (inverse proportion)
5. Surface area

Hydrogen bond



- Specific molecules with hydrogen attached to a strong electronegative atoms **N, O, or F**, form bridging hydrogen bonds to electron lone pairs on **N, O, or F** atoms.

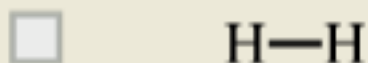
Hydrogen Bonds



Hydrogen bond



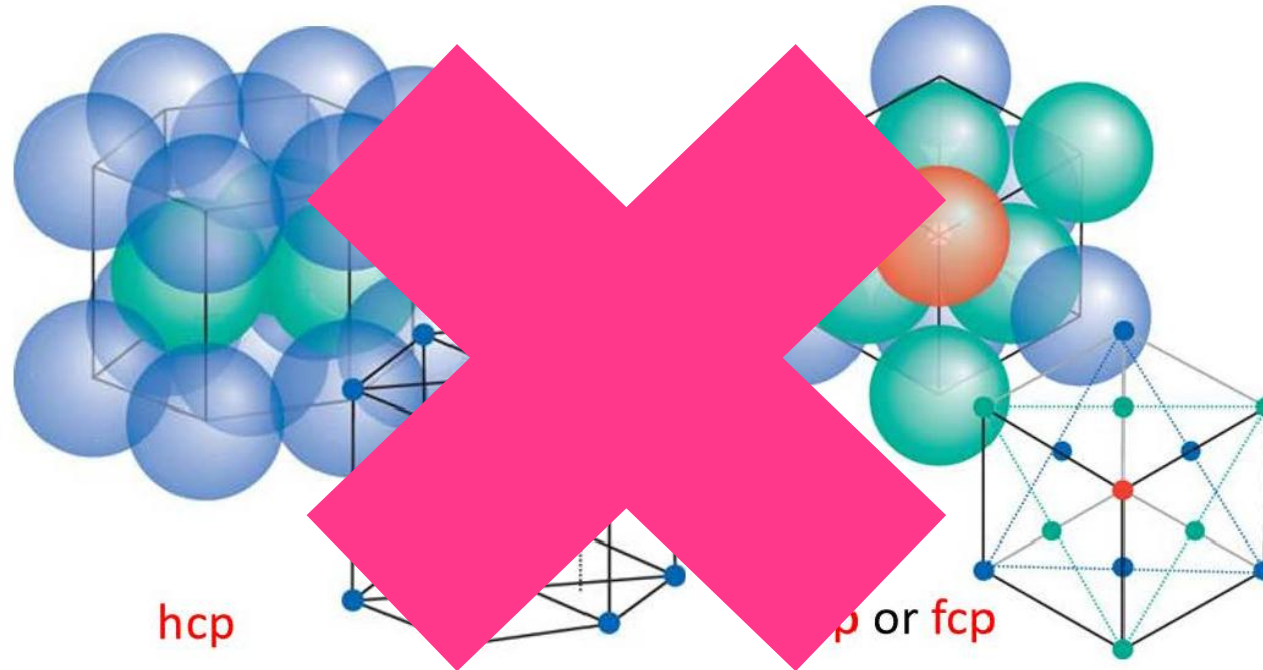
If a solid line represents a covalent bond and a dotted line represents intermolecular attraction, which of these choices shows a hydrogen bond? Check all that apply.



Definition:

The smallest region of the crystal lattice that repeats itself, is referred to as the unit cell.

Count atoms: **corner** atom counts as $1/8$
 face atom contributes $1/2$
 body atom counts as 1



Important: fcc, bcc and corners
How to calculate their volumes

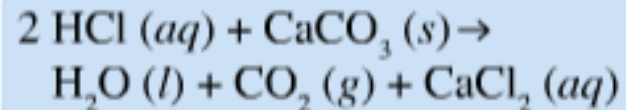
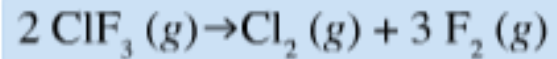
Expansion work



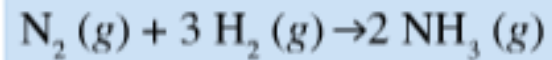
$$W_{\text{exp}} = -P\Delta V$$

For each of the following reactions at constant pressure, determine whether the system does work on the surroundings, the surroundings does work on the system, or essentially no work is performed.

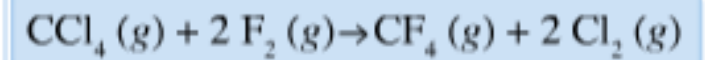
Work done by the system



Work done on the system



No work done



$$C = q / \Delta T$$

At constant volume, the heat of combustion of a particular compound, compound A, is -3701.0 kJ/mol . When 1.127 g of compound A (molar mass = 116.13 g/mol) was burned in a bomb calorimeter, the temperature of the calorimeter (including its contents) rose by $6.423 \text{ }^{\circ}\text{C}$.

Using this data, what is the heat capacity (calorimeter constant) of the calorimeter?

Number

$\text{kJ} / ^{\circ}\text{C}$

Suppose a 3.083 g sample of a second compound, compound B, was combusted in the same calorimeter, and the temperature rose from $23.89 \text{ }^{\circ}\text{C}$ to $27.20 \text{ }^{\circ}\text{C}$.

What is the heat of combustion per gram of compound B?

Number

kJ / g

The change of internal energy is related to work and heat:

$$\Delta U = q + w$$

The internal energy of an **isolated** system is **constant**:

$$\Delta U = 0$$

At constant V and non-expansion work, the change of internal energy is

$$\Delta U = q$$

$$\text{Isothermal: } w = -nRT \ln\left(\frac{V_{\text{final}}}{V_{\text{initial}}}\right)$$

$$\text{Isobaric: } w = p(V_{\text{final}} - V_{\text{initial}})$$

$$H=U+PV$$

If pressure is constant, $\Delta H=q$

And we know $C_v=\Delta U/\Delta T$

From this, we deduce that:

$$C_p=C_v+nR$$

Normally speaking, $n=1$ since we'd like to take molar heat capacity.

	Monoatomic	Linear	Nonlinear
$C_{v,m}$	$\frac{3}{2}R$	$\frac{5}{2}R$	$3R$
$C_{p,m}$	$\frac{5}{2}R$	$\frac{7}{2}R$	$4R$

Standard Enthalpies of Formation



The standard enthalpy of formation, ΔH_f° , of a substance is the standard reaction enthalpy **per mole** of formula units **for the formation of a substance from its elements in their most stable form**, as in the reaction.

Combining standard enthalpies of formation to calculate a **standard reaction enthalpy**.

Substance	Formula	ΔH_f°	Substance	Formula	ΔH_f°
Inorganic compounds			Organic compounds		
ammonia	$\text{NH}_3(\text{g})$	-46.11	benzene	$\text{C}_6\text{H}_6(\text{l})$	+49.0
carbon dioxide	$\text{CO}_2(\text{g})$	-393.51	ethanol	$\text{C}_2\text{H}_5\text{OH}(\text{l})$	-277.69
carbon monoxide	$\text{CO}(\text{g})$	-110.53	ethyne	$\text{C}_2\text{H}_2(\text{g})$	+226.73
dinitrogen tetroxide	$\text{N}_2\text{O}_4(\text{g})$	+9.16	(acetylene)		
hydrogen chloride	$\text{HCl}(\text{g})$	-92.31	glucose	$\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$	-1268
hydrogen fluoride	$\text{HF}(\text{g})$	-271.1	methane	$\text{CH}_4(\text{g})$	-74.81
nitrogen dioxide	$\text{NO}_2(\text{g})$	+33.18			
nitric oxide	$\text{NO}(\text{g})$	+90.25			

In an isolated system the disorder measured by **Entropy** increases in the course of any spontaneous change.

Entropy and second law



Disorder is measured by a state function – **Entropy**, S. Entropy.

Low entropy means little disorder;

High entropy means great disorder.

A entropy is a state function. Its change can be calculated in a reversible process:

$$\Delta S = \frac{q_{\text{rev}}}{T} \longrightarrow \Delta S = \frac{\Delta H}{T}$$

q is energy transferred, “rev” means energy must be transferred reversibly, T is the absolute temperature, and typical units for entropy are **J·K⁻¹**

T constant?

We have

$$\Delta S = \frac{q_{\text{rev}}}{T} = nR \ln \frac{V_2}{V_1}$$

As volume increases, the entropy increases.

Can be easily rewrite as:

$$\Delta S = nR \ln \frac{P_1}{P_2}$$

Entropy and second law



V constant?

If C is constant:

$$\Delta S = \int_{T_1}^{T_2} \frac{C dT}{T}$$

$$\Delta S = c_{v,m} \ln \frac{T_2}{T_1}$$

How to judge the value of entropy by inspection?

1. Gas>Liquid>Solid
2. More **complex** the molecule, more chaotic the substance is.
3. **Heavier** atom has more energy
4. **Polar** molecules have **less** entropy

$$S = k \ln W$$

Boltzmann formula is called **statistical entropy**.

An **absolute scale of entropy** at any temperature.

$$k = 1.381 \times 10^{-23} \text{ J} \cdot \text{K}^{-1} \quad (R = k N_A)$$

W is the **microstates** (**W**).

The number of positions atoms or molecules can be arranged and yet give rise to the same total energy

Each arrangement is a microstate, W is the number different microstates corresponding to the same energy.

Vapor Pressure



For liquids, which of the following factors affect vapor pressure? Check all that apply.

- ☒ intermolecular forces
- ☒ temperature
- ☐ surface area
- ☐ humidity
- ☐ volume

$$\ln \frac{P_2}{P_1} = -\frac{\Delta H_{\text{vap}}^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

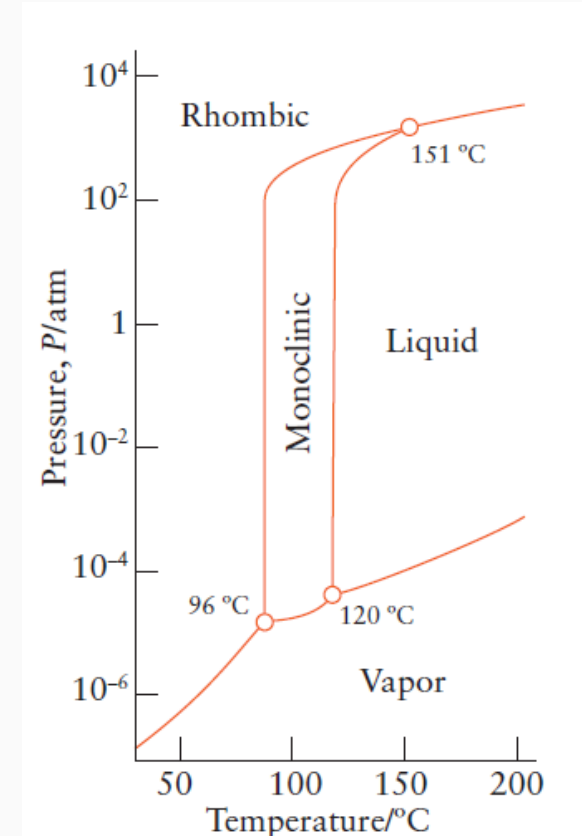
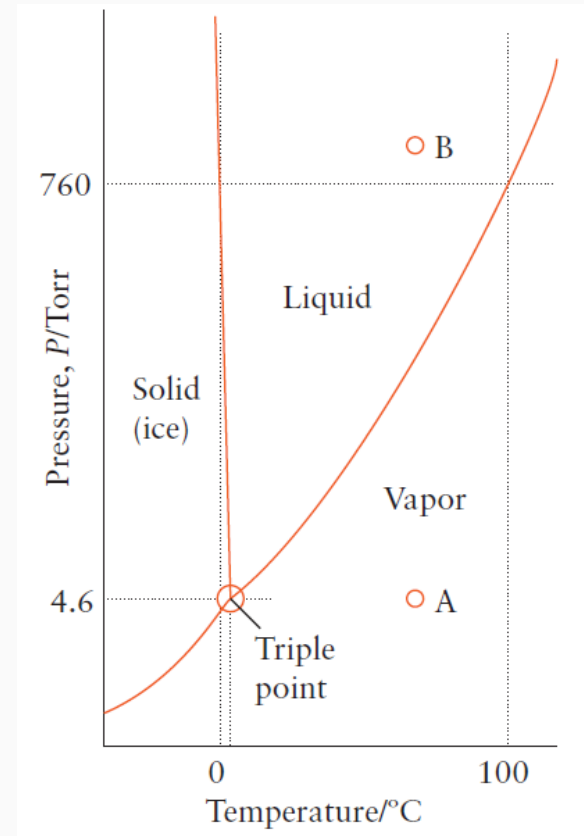
$$\ln \left(\frac{P}{P_0} \right) = -\frac{\Delta H_{\text{vap}}^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

- **Normal boiling point, T_b :**
- a liquid boils when the external pressure is **1 atm**.
- Boiling occurs when the **vapor pressure of a liquid is equal to the external (atmospheric) pressure**.
- Strong intermolecular forces usually lead to high normal boiling points.

Phase diagram



- Phase boundaries
- Triple point
- Critical temperature



- **The Vapor Pressure of Mixtures**
- **Raoult's law:**
the vapor pressure of a liquid is proportional to its mole fraction.
- **Ideal solution / Real solution:**
Obey Raoult's law at all concentrations?
- **Binary Liquid Mixtures**

$$P = P_A + P_B = x_A(l)P_A^* + x_B(l)P_B^*$$

Raoult's law



When two volatile liquids (X and Y) are mixed, the solution process involves

1. breaking the intermolecular X---X and Y---Y attractions, and
2. forming new X---Y attractions.

Complete this table describing how the relative strengths of these attractive forces affect vapor pressure and enthalpy of solution.

Strength of the attractive forces	Raoult's law deviations	ΔH_{soln}	
X---X, Y---Y, and X---Y are equal	zero	zero	positive
X---Y is strongest	negative	negative	negative
X---Y is weakest	positive	positive	zero

Colligative properties of solution



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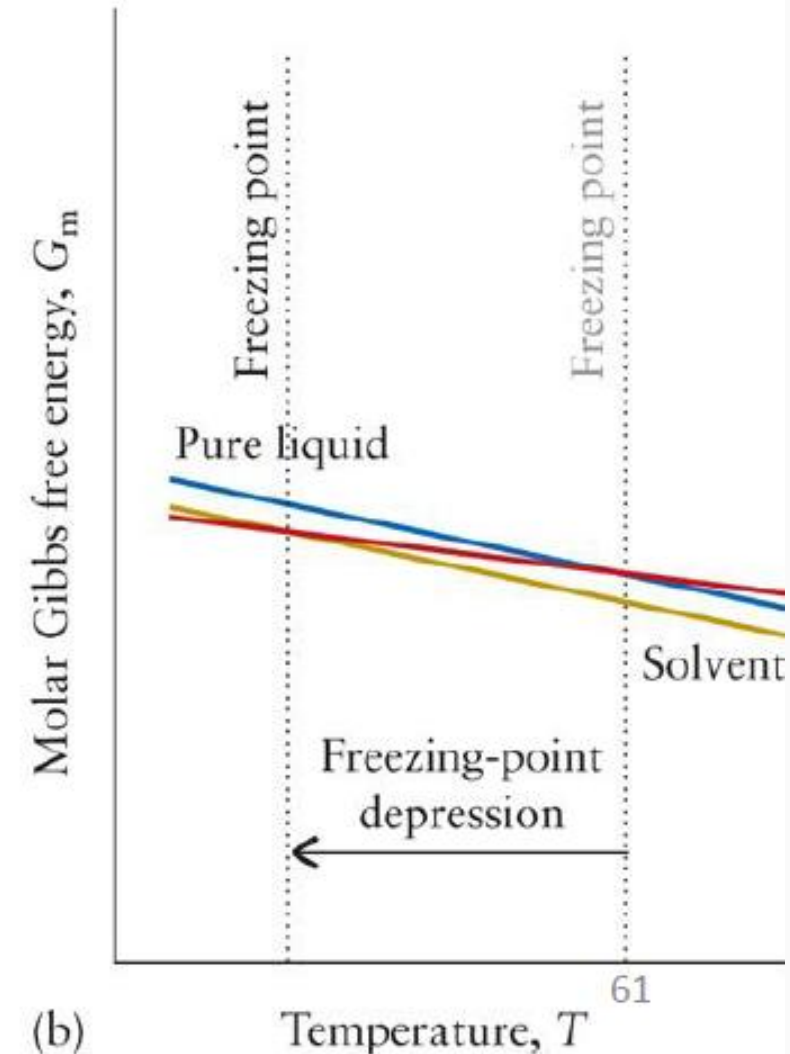
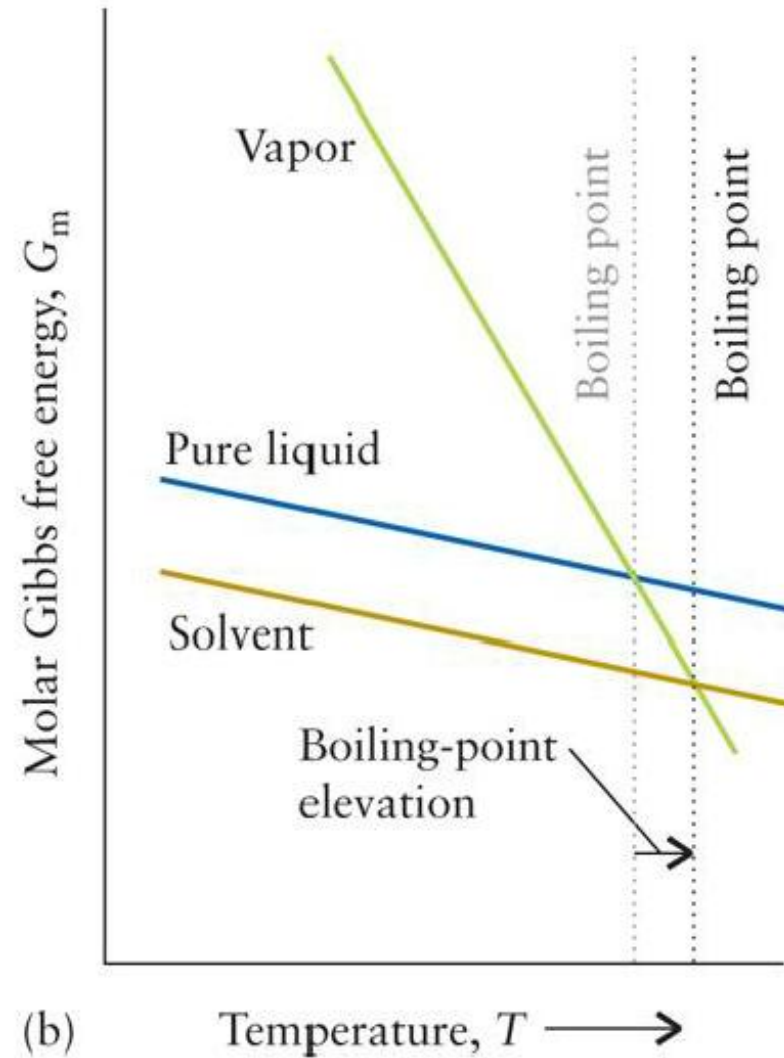
- Vapor-pressure Lowering
- Freezing point depression
- Boiling point elevation
- Osmosis

Vapor-pressure Lowering



$$P = \chi_{\text{solvent}} P_{\text{pure}}$$

Freezing and boiling point



Freezing and boiling point



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

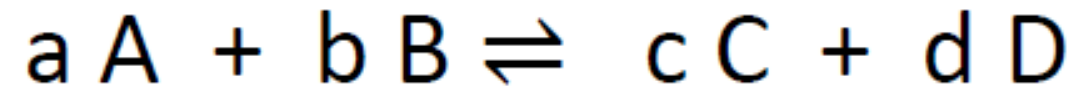
Boiling-point elevation = $k_b \times \text{molality}$, temp. increases.

- **General equation:** $\Delta T = i \times k \times m$

- **Definition:** Osmosis is the flow of solvent through a membrane into a more concentrated solution.

$$\Pi = iRTc$$

For a reaction



$$K = \frac{(a_c)^c (a_d)^d}{(a_A)^a (a_B)^b}$$

Thermodynamic interpretation



At equilibrium , $\Delta G = 0$. This leads to,

$$\Delta G_r^\circ = - RT \ln K$$

Very important!!!

This links the thermodynamic tables ΔG° to K .

$$K = e^{-\frac{\Delta G_r^\circ}{RT}}$$

$$K = e^{-\Delta H_r^\circ/RT + \Delta S_r^\circ/R} = e^{-\Delta H_r^\circ/RT} e^{\Delta S_r^\circ/R}$$

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1. Chemical principal
2. Guo Linyun, VC210 FA2017 RC4-6
3. Zhu keyue, VC210 FA2017 RC5&7
4. Sun Huai, VC210 FA2017 Chapter 10 & 11
5. Sapling learning



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THANKS

