

Gas-Liq-Solids Three-laws-Thermo

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Outline

- 1 States of Matter
 - Gas, Liquid, and Solid
 - Intermolecular Forces
- 2 Thermodynamics
 - Introduction
 - Examples
- 3 Conclusions
 - As for States of Matter
 - As for Thermodynamics

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General Notice

- unit: Kelvin(K) & $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$

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- formula transformation: molarity & density

Gas

$$pV = nRT$$

How to understand ideal gas equation?

Gas

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How to understand ideal gas equation?

- empirical law?

Why do we study kinetic molecular theory?

Gas

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How to understand ideal gas equation?

- empirical law?

$$v_{\text{rms}} = \sqrt{3RT/M}$$

Why do we study kinetic molecular theory?

- Graham's law of effusion?

Understanding from A New Point of View

Here we will discuss the **ideal gas equation** from a new point of view, *i.e.*, **kinetic molecular theory**(KMT).

Understanding from A New Point of View

First we should get aware of the **prerequisite** of KMT.

¹Sun, Ting, *CHEM2100J-FA21-Ch5-6*, pp. 35.

Understanding from A New Point of View

First we should get aware of the **prerequisite** of KMT.
Recall what has been taught in lectures.

1. A gas is in continuous random motion
2. Gas molecules are infinitesimally small
3. They move in straight lines until collision
4. Gas molecules do not influence one another except during collisions
5. The collisions are elastic

Prerequisites of KMT shown in slides¹

¹Sun, Ting, *CHEM2100J-FA21-Ch5-6*, pp. 35.

Understanding from A New Point of View

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- A gas is in continuous random motion and evenly distributed throughout the container. Irregular molecular movement does not do work.

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- Gas molecules do not influence one another except during collisions.
- The collisions are elastic.

Understanding from A New Point of View

Example

For a model satisfying KMT, suppose there exists N gas molecules in a cubic box with length L . Each molecule has the mass of m , and the speed of u .

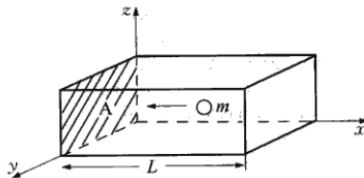


Figure 1.7 An elastic collision of molecule with a wall.

Understanding from A New Point of View

- (1) Calculate the average kinetic energy of each molecule \bar{E}_k .
- (2) If the relationship between average molecule and the temperature is

$$\bar{E}_k = \frac{3}{2}kT$$

where k denotes the Boltzmann constant and satisfies $k = \frac{R}{N_A}$, what familiar formula will derived?

Understanding from A New Point of View

Solution

We may assume there are $\frac{N}{3}$ molecules moving along the x -axis direction since there are N molecules and only three directions in total.

Apparently, the momentum of these molecules is mu . For a whole collision process (we can also refer this process as *bouncing*), the distance the molecule travels is $2L$ and the change of momentum is $2mu$.

Understanding from A New Point of View

(Continued)

Hence for each molecule the change of momentum in a unit time is

$$\frac{2mu}{2L/u} = \frac{mu^2}{L} \quad (1)$$

For $\frac{N}{3}$ molecules, apply the theorem of momentum

$$F = \frac{N}{3} \cdot \frac{mu^2}{L} \quad (2)$$

Then we get the pressure

$$p = \frac{F}{A} = \frac{F}{L^2} = \frac{N}{3} \frac{mu^2}{V} \quad (3)$$

Understanding from A New Point of View

Hence

$$u^2 = \frac{3pV}{Nm} \quad (4)$$

Finally, the average kinetic energy

$$\bar{E}_k = \frac{1}{2}m\bar{u}^2 = \frac{3pV}{2N} \quad (5)$$

Understanding from A New Point of View

Plug in the information

$$\frac{3}{2}kT = \frac{3pV}{2N} \quad (6)$$

$$\Rightarrow pV = NkT \quad (7)$$

where $k = \frac{R}{N_A}$ Hence we get

$$pV = NkT = \frac{N}{N_A}RT = nRT \quad (8)$$

More about KMT

FYI, we can also derive an interesting fact from Eq.(4)

$$u^2 = \frac{3pV}{Nm} = \frac{3nRT}{Nm} = \frac{3RT}{Nm} \quad (9)$$

One thing worth noticing is that there are actually N molecules, we thus get the expression of the whole system

$$\bar{u}^2 = \frac{3RT}{M} \quad (10)$$

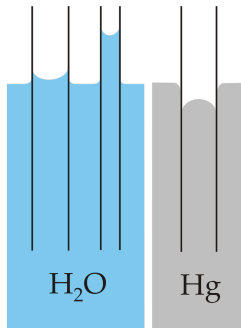
Looks familiar, right?

Liquid

■ viscosity

Liquid

- viscosity
- surface tension



Solid

- crystalline & amorphous

Solid

- crystalline & amorphous
- Molecular Solids & Network Solids & Metallic Solids

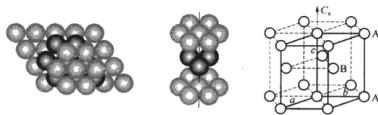


Figure 8.17 Hexagonal closest packing (ABAB ...).

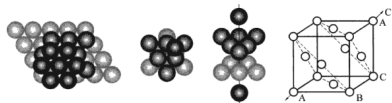


Figure 8.20 Cubic closest packing (ABCABC...).

How to understand packed structures?

What is packed structures/closed-packed structures?

What does A , B , C mean?

How to calculate the occupied rate?

Intermolecular Forces

The key to understanding intermolecular forces is to understand the way to form chemical bonds.

Several ways to consider

- polarity

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Several ways to consider

- polarity
- spacial geometries
- chemical elements

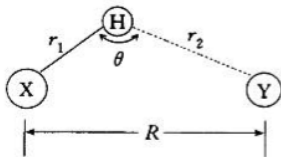
Intermolecular Forces

	Ion-Ion	Ion-Dipole	Dipole-Dipole
E_p dependence	$\frac{1}{r}$	$\frac{1}{r^2}$	$\frac{1}{r^3}$

	Dipole-Dipole (induced)	London	Hydrogen Bonding
E_p dependence	$\frac{1}{r^6}$	$\frac{1}{r^6}$	/

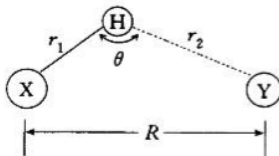
Remarks: In daily life, Total Price = Unit Price \times Amount.
So is chemistry.

Hydrogen Bonding



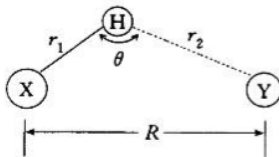
- Tend to be formed and can be formed easily.

Hydrogen Bonding



- Tend to be formed and can be formed easily.
- Both intermolecular or intramolecular.

Hydrogen Bonding



- Tend to be formed and can be formed easily.
- Both intermolecular or intramolecular.
- Depends on the geometry, the environment, and the nature of the specific donor and acceptor atoms, varying between a large range.

Hydrogen Bonding

Examples of hydrogen bond

- The density of water and ice.

Hydrogen Bonding

Examples of hydrogen bond

- The density of water and ice.
- The acidity of HF.

Hydrogen Bonding

Examples of hydrogen bond

- The density of water and ice.
- The acidity of HF.
- Alcohol solution

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Introduction

**The key to understanding
thermodynamics is to design
thermodynamic cycle.**

Key Concepts

- system & surrounding

Key Concepts

- system & surrounding
- work & heat & energy

The First Law $\Delta U = q + w$

Key Concepts

- system & surrounding
- work & heat & energy

The First Law $\Delta U = q + w$

- expansion work

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The First Law $\Delta U = q + w$

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- state function

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The First Law $\Delta U = q + w$

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The First Law $\Delta U = q + w$

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The First Law $\Delta U = q + w$

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 - constant pressure
 - constant volume

Key Concepts

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The First Law $\Delta U = q + w$

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- state function
- heat capacity
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 - constant pressure
 - constant volume
- heating curve

Key Concepts

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The First Law $\Delta U = q + w$

- expansion work
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- Hess's Law

Key Concepts

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 - expansion work
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- Hess's Law
- The Born-Haber Cycle

The First Law

$$\Delta U = q + w$$

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$$\Delta U = q + w$$

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- sign

Expansion Work

$$\delta W = -pdV$$

- free expansion

Expansion Work

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- expansion at constant pressure

Expansion Work

$$\delta W = -pdV$$

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- expansion at constant pressure
- expansion at constant temperature

Expansion Work

$$\delta W = -pdV$$

- free expansion
- expansion at constant pressure
- expansion at constant temperature
- reversible expansion

Heat Capacity

■ Definition: $C = \frac{q}{\Delta T}$

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 - specific heat capacity: $C_s = \frac{C}{m}$

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- Definition: $C = \frac{q}{\Delta T}$
 - specific heat capacity: $C_s = \frac{C}{m}$
 - molar heat capacity: $C_m = \frac{C}{n}$

Enthalpy

■ definition

Enthalpy

- definition
- origin

Enthalpy

- definition
- origin
- constant pressure and constant volume

Enthalpy

- definition
- origin
- constant pressure and constant volume
- relationship between heat capacity

Expansion

Example

10 mol ideal gas expands at 300 K, with initial volume $V_1 = 25 \text{ dm}^3$, final volume $V_2 = 100 \text{ dm}^3$, experiencing the following four paths:

- (1) free expansion;
- (2) expands at final pressure when it is 100 dm^3 ;
- (3) first expands at the initial pressure until it is 50 dm^3 , then expands at the final pressure until final state;
- (4) reversible expansion.

Expansion

Solution

(1) By definition, $W = 0$.

$$(2) W = - \int_{25}^{100} p_2 dV = -p_2(V_2 - V_1) = -18.7 \text{ kJ}$$

$$(3) p'_2 V_2 = nRT$$

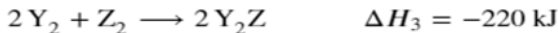
$$W = W_1 + W_2 = -24.9 \text{ kJ}$$

$$(4) W = -nRT \ln \frac{V_2}{V_1} = -34.6 \text{ kJ}$$

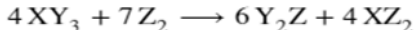
Hess's Law

Example

Given the thermochemical equations



Calculate the change in enthalpy for the reaction.



Hess's Law

Solution

Consider an ionic compound, MX_2 , composed of generic metal M and generic, gaseous halogen X.

- The enthalpy of formation of MX_2 is $\Delta H_f^\circ = -819 \text{ kJ/mol}$.
- The enthalpy of sublimation of M is $\Delta H_{\text{sub}} = 159 \text{ kJ/mol}$.
- The first and second ionization energies of M are $\text{IE}_1 = 693 \text{ kJ/mol}$ and $\text{IE}_2 = 1415 \text{ kJ/mol}$.
- The electron affinity of X is $\Delta H_{\text{EA}} = -335 \text{ kJ/mol}$. (Refer to the hint).
- The bond energy of X_2 is $\text{BE} = 209 \text{ kJ/mol}$.

Determine the lattice energy of MX_2 .

The Born-Haber Cycle

Example

At p^\ominus and 298.15 K, mix 1 mol CH_4 and 4 mol O_2 and fire them to make them explode under constant pressure. Suppose this reaction happens in an instantaneous moment. Calculate the higher temperature this system may achieve.

Data:

$$\Delta_f H_m^\ominus (\text{CO}_2, \text{g}) = -393.51 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_f H_m^\ominus (\text{H}_2\text{O}, \text{g}) = -241.82 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_r H_m^\ominus (\text{CH}_4, \text{g}) = -74.81 \text{ kJ} \cdot \text{mol}^{-1}$$

The Born-Haber Cycle

Solution

Refer to RC notes. No needs to handle well since there is little possibility that this kind of question will occur in your exam. Here is just for helping you have a better understanding.

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- Understanding is always more important than just using.

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- Process: constant pressure, constant volume, adiabatic

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- Example: vaporation, fusion, freezing, condensation, sublimation, deposition, expansion

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- Process: constant pressure, constant volume, adiabatic
- Example: vaporation, fusion, freezing, condensation, sublimation, deposition, expansion
- Know the concepts and design your cycle smartly.