

CHE201 IMPORTANT SUBJECTIVE SOLVED

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1) **Physical Chemistry**

Physical chemistry is the study of the underlying physical principles that govern the properties and behavior of chemical systems.

Chemical System

A chemical system can be studied from either a microscopic or a macroscopic viewpoint.

The microscopic viewpoint is based on the concept of molecules.

The macroscopic viewpoint studies large-scale properties of matter without explicit use of the molecule concept.

2) **Thermodynamics**

Thermodynamics: (Greek words for “thermo=heat” and “dynamics=power”) is the study of heat, work, energy, and the changes they produce in the states of systems. Thermodynamics studies the relationships between the macroscopic properties of a system

A key property in thermodynamics is temperature

Thermodynamics is sometimes defined as the study
of the relation of temperature to the
macroscopic properties of matter

Equilibrium Thermodynamics

It deals with systems in equilibrium

It is a macroscopic science and is independent of any theories of molecular structure Irreversible Thermodynamics

It deals with non-equilibrium systems and rate processes.

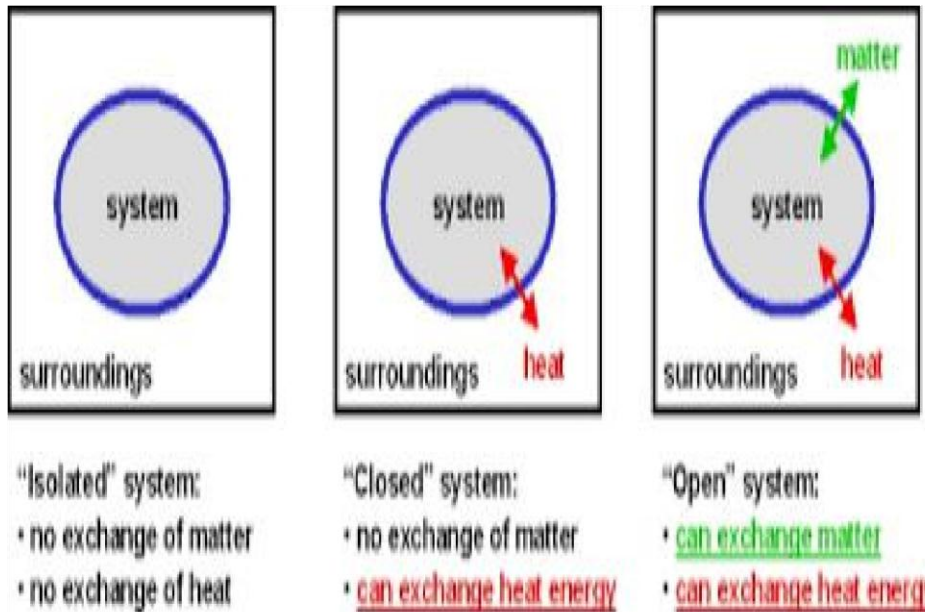
3) Thermodynamic Systems

The macroscopic part of the universe under study in thermodynamics is called the System

The parts of the universe that can interact with the system are called the surroundings. **Open system** is one where transfer of matter between system and surroundings can occur.

Closed system is one where no transfer of matter can occur between system and surroundings.

Isolated system is one that does not interact in any way with its surroundings. An isolated system is obviously a closed system, but not every closed system is isolated.



4) Equilibrium

Equilibrium thermodynamics deals with systems in equilibrium

An isolated system is in equilibrium when its macroscopic properties remain constant with time

A non-isolated system is in equilibrium when the following two conditions hold

- The system's macroscopic properties remain constant with time
- Removal of the system from contact with its surroundings causes no change in the properties of the system

If condition (A) holds but (B) does not hold, the system is in a steady state.

Mechanical Equilibrium:

No unbalanced forces act on or within the system;
hence the system undergoes no acceleration, and
there is no turbulence within the system.

Material Equilibrium:

No net chemical reactions are occurring in the system,
nor is there any net transfer of matter from one part of
the system to another or between the system and its
surroundings

Thermal Equilibrium between a system and its surroundings, there must be no change in the properties of the system or surroundings when they are separated by a thermally conducting wall.

For thermodynamic equilibrium, all three kinds of equilibrium must be present.

5) Thermodynamic Properties

An extensive thermodynamic property is one whose value is equal to the sum of its values for the parts of the system. Thus, if we divide a system into parts, the mass of the system is the sum of the masses of the parts; mass is an extensive property. So is volume.

What properties does thermodynamics use to characterize a system in equilibrium? Clearly, the composition must be specified. This can be done by stating the mass of each chemical species that is present in each phase. The volume V is a property of the system. The pressure P is another thermodynamic variable. Pressure is defined as the magnitude of the perpendicular force per unit area exerted by the system on its surroundings:

Intensive thermodynamic property is one whose value does not depend on the size of the system, provided the system remains of macroscopic size—recall nanoscopic systems

Density and pressure are examples of intensive properties.

If each intensive macroscopic property is constant throughout a system, the system is homogeneous.

If a system is not **homogeneous**, it may consist of a number of homogeneous parts. A homogeneous part of a system is called a **phase**. A system composed of two or more phases is heterogeneous

Suppose that the value of every thermodynamic property in a certain thermodynamic system equals the value of the corresponding property in a second system. The systems are then said to be in the same **thermodynamic state**

6) Temperature

Suppose two systems separated by a movable wall are in mechanical equilibrium with each other

Because we have mechanical equilibrium, no unbalanced forces act and each system exerts an equal and opposite force on the separating wall.

- Systems in mechanical equilibrium with each other have the same pressure.
- Just as systems in *mechanical* equilibrium have a common *pressure*, it seems plausible that there is some thermodynamic property common to systems in *thermal* equilibrium.
- This property is what we *define* as the **temperature**, symbolized by θ (theta).

By definition,

Two systems in thermal equilibrium with each other have the same temperature; two systems not in thermal equilibrium have different temperatures.

7) Pressure

Pressure is defined as the magnitude of the perpendicular force per unit area exerted by the system on its surroundings:

$$P = F/A$$

For a system in mechanical equilibrium, the pressure throughout the system is uniform and equal to the pressure of the surroundings.

If external electric or magnetic fields act on the system, the field strengths are thermodynamic variables; we won't consider systems with such fields

8) Mole

The ratio of the average mass of an atom of an element to the mass of some chosen standard is called the atomic weight or relative atomic mass A_r

(the r stands for "relative")

The standard used since 1961 is $1/12$ times the mass of the isotope ^{12}C

The ratio of the average mass of a molecule of a substance to $1/12$ times the mass of a ^{12}C atom is called the molecular weight or relative molecular mass M_r of that substance.

The number of ^{12}C atoms in exactly 12 g of ^{12}C is called Avogadro's number. The average mass of an atom or molecule is called the atomic mass or the molecular mass.

Molecular masses are commonly expressed in units of atomic mass units (amu) where 1 amu is one-twelfth the mass of a ^{12}C atom

A mole of some substance is defined as an amount of that substance which contains Avogadro's number of elementary entities

9) Ideal Gas vs. Real Gases No gas is ideal.

Most gases behave ideally (almost) at pressures of approximately 1 atm or lower, when the temperature is approximately 0°C or higher.

When we do calculations, we will assume our gases are behaving as ideal gases

Ideal Gas Equation

$PV = nRT$

Pressure, Volume, No. of moles, Universal Gas Constant, Temperature

$R = 0.0821 \text{ atm L / mol K}$
 $R = 8.314 \text{ kPa L / mol K}$

Water: Chemistry: A Molecular Approach, 1999, page 466

Gas Laws

A large number of experiments have determined that 4 variables are sufficient to define the physical condition (or state) of a gas: the gas laws.

Boyle's Law, Charles' Law,
Avogadro's hypothesis

10 Boyle's Law

Robert Boyle: (1627-1691) the first modern chemist, known as the father of chemistry.

His 1661 book *The Sceptical Chymist* marks the introduction of the scientific method, a definition of elements and compounds and a

refutation of alchemy and magic potions.

Boyle investigated the variation of the volume occupied by a gas as the pressure exerted upon it was altered and noted that the volume of a fixed quantity of gas, at constant temperature is inversely proportional to the pressure

1

$$V \propto \frac{1}{p} \text{ or } PV = \text{constant}$$

Where 'k' is constant

Boyle's law is understandable from the picture of a gas as consisting of a huge number of molecules moving essentially independently of one another. The pressure exerted by the gas is due to the impacts of the molecules on the walls. A decrease in volume causes the molecules to hit the walls more often thereby increasing the pressure.

In actuality, the molecules of a gas exert forces on one another, so Boyle's law does not hold exactly.

In the limit of zero density (reached as the pressure goes to zero or as the temperature goes to infinity), the gas molecules are infinitely far apart from one another, forces between molecules become zero, and Boyle's law is obeyed exactly. We say the gas becomes ideal in the zero-density limit.

11) Charles' Law

A French scientist, Jacques Charles discovered volume of a fixed amount of gas, as constant is proportional to the absolute temperature.

$$V_2/T_2$$

Charles' law is obeyed most accurately in the limit of zero pressure

But even in this limit, gases still show small deviations

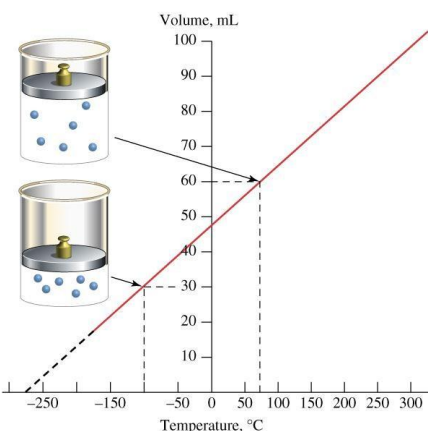
These deviations are due to small differences between the thermal expansion behavior of ideal gases

12 Avogadro's Hypothesis

In 1811 Avogadro stated that,

At constant temperature and pressure, the volume of a gas is directly related to the number of moles.

$$V = K n$$



$$V_1 / n_1 = V_2 / n_2$$

K is constant

N is number of moles of gas

Equal volumes of gases at the same temperature and pressure contain equal numbers of molecules

Since the number of molecules is proportional to the number of moles, Avogadro's hypothesis states that equal volumes of different gases at the same T and P have equal numbers of moles.

This Equation incorporates Boyle's law, Charles' law and Avogadro's hypothesis. definition of T), and Avogadro's hypothesis.

An ideal gas is a gas that obeys $PV = nRT$. Real gases obey this law only in the limit of zero density, where intermolecular forces are negligible.

Using $M = m/n$ to introduce the molar mass M of the gas, we can write the ideal-gas law as

$$PV = nRT/M \quad \text{ideal gas}$$

Ideal Gas Equation

$PV = nRT$

Pressure (P), Volume (V), No. of moles (n), Universal Gas Constant (R), Temperature (T)

$R = 0.0821 \text{ atm L / mol K}$
 $R = 8.314 \text{ kPa L / mol K}$

Kaler, Carr, Scott: Chemistry: A World of Choices, 1999, page 566

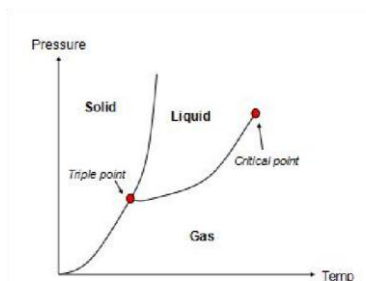
13) Equations of state

How are states represented

Mathematically

Using equations of state we relate state variables to

describe property of matter Examples of state variables



- Pressure
- Volume
- Temperature

Equations of state are mainly used to describe fluids

- Liquids
- Gases

Particular emphasis on gases

- ABCs of gas equations
- Avogadro's Hypothesis
- Boyle's Law
- Charles' Law

Combining all 3 laws...

Thus we get the ideal gas equation: $pV = nRT$

For the Ideal Gas it is assumed that...

Ideal gas particles occupy negligible volume

Ideal gas has negligible intermolecular interactions

But sadly assumptions fail...Nothing is ideal in this world... Real gas particles do occupy finite volume

Real gas has considerable intermolecular interactions

Ideal gas equation shows deviations from

Avogadro's Hypothesis

Boyle's Law

Charles' Law

So its called

Failures of ideal gas equation

14) Van der Waals Equation for real gases

As the ideal gas equation deviates from gas laws

So van der Waals in 1873 modified the ideal-gas equation to give the van der Waals equation for real gases

Van der Waals

Modified from ideal gas equation Accounts for:

- Non-zero volumes of gas particles (repulsive effect)
- Attractive forces between gas particles (attractive effect)

Attractive effect

- Pressure = Force per unit area of container exerted by gas molecules ➤ Dependent on:
 1. Frequency of collision
 2. Force of each collision
- Both factors affected by attractive force
- Each factor dependent on concentration (n/V)
- Hence pressure changed proportional to $(n/V)^2$
- Letting a be the constant relating p and (n/V)
- Pressure term, p , in ideal gas equation becomes
- $[p + a(n/V)^2]$

Repulsive effect

- Gas molecules behave like small, impenetrable sphere
- Actual volume available for gas smaller than volume of container, V
- Reduction in volume proportional to

$$\text{amount of gas, } n \propto n^2 \propto \frac{1}{V^2}$$

- $\frac{p}{n^2} + \frac{a}{V^2} = \frac{nRT}{V-nb}$ amount of $\frac{p}{n^2} + \frac{a}{V^2} = \frac{nRT}{V-nb}$

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

- Volume term in ideal gas equation, V , OR becomes $(V-nb)$

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

Combining both derivations... $\left(\frac{p}{n^2} + \frac{a}{V^2}\right) = \frac{nRT}{V-nb}$

We get the Van der Waals Equation

15) Van der Waal's corrections

Sir Johannes Diderik van Der Waals in 1873, modified the Ideal Gas Equation

He proposed the ideal gas equation with

“Van der Waal's corrections”

By adding the necessary Constants

Critical Constants

A. For intermolecular attractions (weak forces)

B. The volume occupied by the gas particles (themselves)

Volume correction

At higher pressure, the volume is much reduced and at this state the volume of gas molecules

Becomes “no more negligible” in comparison with the total volume V occupied by the gas.

The “no more negligible” volume is generally denoted by “ b ” called effective volume. Therefore the total (actual) volume available in which the molecules are free to move will be

= Total volume (V) — Effective volume (b). i.e., Correct Volume
($V - b$)

Pressure correction:

The pressure of a gas is due to the hits of the molecules on the walls of the container.

The weak attractive force (Van Der Waals's forces) between the molecules comes into play

when the molecules are brought close (under high pressure) together during compression of the gas,

therefore an extra inward pull is observed on the molecules Towards the center of the gas, which ultimately decreases the total pressure.

Therefore the ideal pressure (P_i)

will be equal to (total) observed pressure (P) plus a pressure correction (P_a).

P_a depending upon the inwards pull (attractive forces) among the gas molecules.

I.e. $P(\text{Ideal}) = P + P_a$

After adding necessary corrections, the Ideal gas Equation can be used for the real gases as well.

It is known as Van Der Waals Equation

This equation explains the behavior of real gases with great accuracy and also describes the deviations of gas law from ideal behavior.

Ideal gas equation is

$$PV=nRT$$

After adding the necessary corrections by calculating critical constants for additional pressure and subtracted volume. For 1 mole of a substance $(P+a/V^2)(V-b)=RT$

For “n” mole of a substance

Critical Constants

The Critical Volume: The volume occupied by a unit mass of a gas or vapors in its critical states.

The Critical Pressure: The pressure required to liquefy a gas at its critical temperature

The Critical Temperature

The temperature at and above which vapors of the substance cannot be liquefied, no matter how much pressure is applied. For Van Der Waal's critical constants,

the pressure required to liquefy the gas at critical temperature is called critical pressure and the volume occupied by 1 mole of a gas under critical conditions is called the critical volume.

The relationship between critical constants of the gases and their Van der Waal constants is as follows:

$$V_c = 3b, P_c = a/27b^2, T_c = 8a/27Rb$$

Here, P_c , V_c , and T_c are the critical values for pressure, molar volume, and temperature, and Z_c is the compressibility which is equal to $P V / RT$, at the critical points.

On putting above values

$$Z_c = P_c V_c / RT_c$$

17) Zeroth Law of Thermodynamics

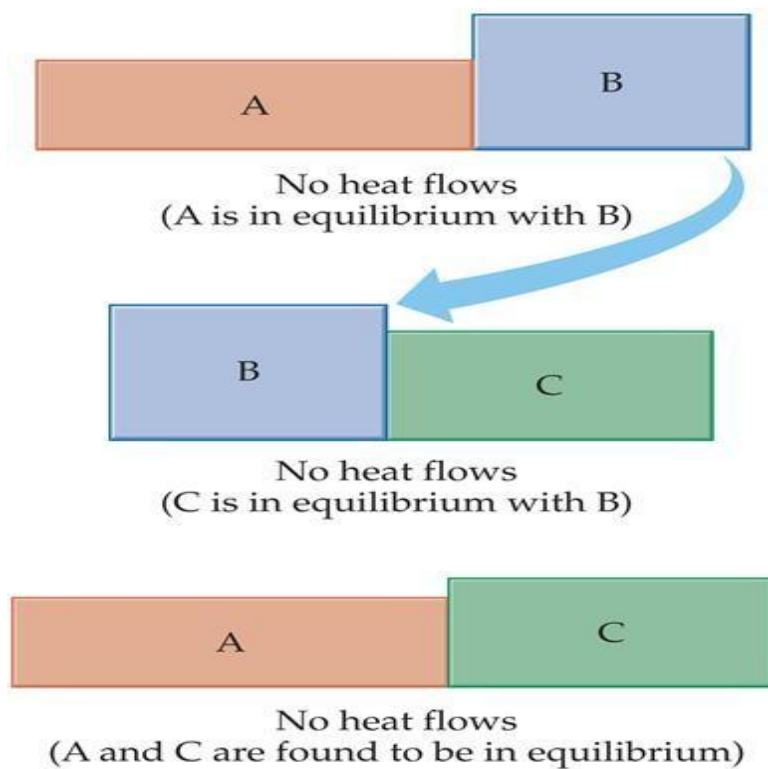
Two systems that are each found to be in thermal equilibrium with a third system will be found to be in thermal equilibrium with each other.

This generalization from experience is the Zeroth law of thermodynamics

It is so called because only after the first, second, and third laws of thermodynamics had been formulated was it realized that the Zeroth law is needed for the development of thermodynamics.

Statement of the Zeroth law logically precedes the other three laws of thermodynamics

The Zeroth law allows us to assert the existence of temperature as a state function.



18) First Law of Thermodynamics

The first law of thermodynamics is a statement of the conservation of energy

It is also called the Law of Conservation of Energy

Energy can be changed from one form to another, but it cannot be created or destroyed. The total amount of energy and matter in the Universe remains constant, merely changing from one form to another.

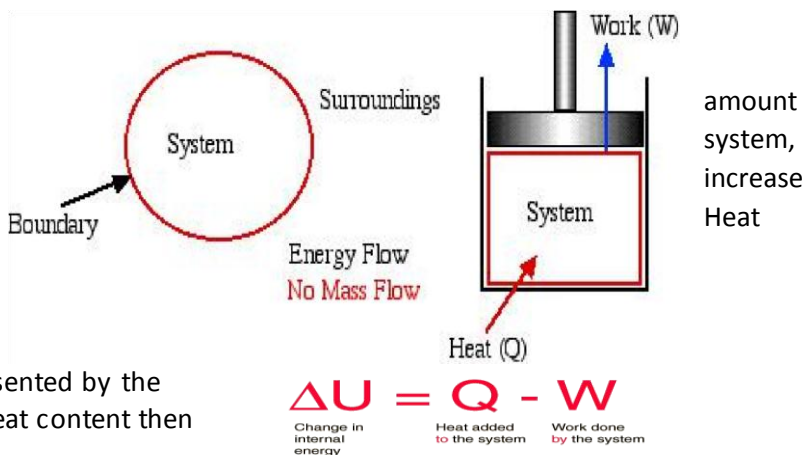
Heat and work changes

The energy of a system will change if heat is transferred to or from the system or work is done by the system

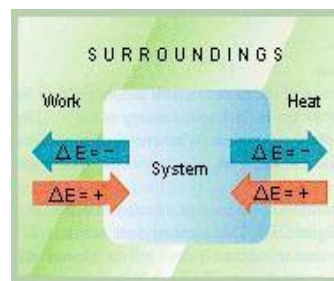
1st law stated that, if some of heat (Q) is added into the it must either do work or the total energy of the system and work changes

19) Enthalpy

If the capacity to do work is represented by the symbol “W” and “H” stands for heat content then the 1st law can be expressed as:



q (heat)	+ system gain thermal energy	- System loses thermal energy
w (work)	+ work done on the system	- Work done by the system
ΔU (change in internal energy)	+ energy flows into the system	- Energy flows out of the system



The energy change associated with a chemical reaction is called the enthalpy of reaction and abbreviated ΔH .

$$H = E + PV$$

- E = energy of the system
- P = pressure of the system ➤ V = volume of the system

Enthalpy = Heat Transferred

Recall our original definition of enthalpy:

$$H = E + PV$$

Then for a change in enthalpy:

$$\Delta H = \Delta E + \Delta (PV)$$

If we set P constant, then:

$$\Delta H = \Delta E + P \Delta V$$

Since

$$q_p = \Delta E + P \Delta V$$

Then

$$H = q_p$$

The change in enthalpy, ΔH , is then equal to the heat transferred at constant pressure, q_p .

Enthalpy is a “State Function”

A “state function” is a value that is a function only of the initial and final states of the system, not the path you take to get there!

Entropy

Entropy (S): Can be thought of as a measure of the disorder of a system

In general, greater disorder means greater entropy

Entropy is a state function just as enthalpy

$$\Delta S = S_{\text{final}} - S_{\text{initial}} \text{ Rewrite:}$$

$$\Delta S = k \ln W_{\text{final}} - k \ln W_{\text{initial}}$$

$W_f > W_i$ then $\Delta S > 0$ entropy increases

20) Second law of Thermodynamics

The first law of thermodynamics is simple, general, but does not constitute a complete theory because certain processes it permits do not occur in nature!

The problems arise from:

1. Classical thermodynamics is connected with states of equilibrium and various processes connecting them.
2. The exact process by which a system reaches the final state from its initial state is immaterial. i.e. the transition is independent of the particular path taken
3. The theory emphasizes reversible processes! Yet, real processes are irreversible! **Two**

statements of the second law of thermodynamics

- Clausius Statement: It is impossible to construct a device that operates in a cycle and whose sole effect is to transfer heat from a cooler body to a hotter body.

- **Kevin-Planck Statement:** It is impossible to construct a device that operates in a cycle and produces no other effects than the performance of work and the exchange of heat with a single reservoir.

Equivalence of the Two Statements

It can be shown that the violation of one statement leads to a violation of the other statement, i.e. they are equivalent.

The second law of thermodynamics states that the total entropy of an isolated system can only increase over time. It can remain constant in ideal cases where the system is in a steady state (equilibrium) or undergoing a reversible process. The increase in entropy accounts for the irreversibility of natural processes, and the asymmetry between future and past.

- Entropy of the universe increases in a spontaneous process and remains unchanged in an equilibrium process.
- Equilibrium process: caused to occur by adding or removing energy from a system that is at equilibrium

Mathematically speaking:

Spontaneous process:

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$$

Equilibrium process:

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = 0$$

21) Third Law of Thermodynamics

Entropy of a perfect crystalline substance is zero at absolute zero.

Importance of this law: it allows us to calculate absolute entropies for substances

“It is impossible to reach a temperature of absolute zero.”

On the Kelvin Temperature Scale,

$$T = 0 \text{ K}$$

is often referred to as “Absolute Zero”

The Third Law of Thermodynamics can mathematically be expressed as $\lim_{T \rightarrow 0} S = 0$

where S = entropy
(J/K)

T = absolute temperature (K)

Importance of Third law of Thermodynamics

- It helps in calculating the thermodynamic properties.
- It is helpful in measuring chemical affinity. Because of this it is known as Nernst theorem.
- It explains the behavior of solids at very low temperature.
- It helps in analyzing chemical and phase equilibrium.

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