Physical Chemistry

Chapter 1
Introduction to Physical Chemistry

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1.0 Introduction to Physical Chemistry

- Aims
  - To explain the underlying physicals principles that govern the properties and behavior of chemical systems
  - To explain and describe the four areas of physical chemistry: thermodynamics, quantum chemistry, statistical mechanics and kinetics of gases and their transport properties

- Expected Outcomes
  - Student able to explain the underlying physicals principles that govern the properties and behavior of chemical systems.
  - Student able to explain and describe the four areas of physical chemistry: thermodynamics, quantum chemistry, statistical mechanics and kinetics of gases and their transport properties

- References

  - P. Atkins and J. D. Paula, Elements of Physical Chemistry, 5th Ed. Freeman, Oxford.
  - P. Atkins and L. Jones CHEMISTRY Molecules, Matter, and Change, 3rd Ed Freeman, Oxford.
  - R.Chang, Chemistry, Mc Graw Hill.

Subtopics

1.1 Introduction to Physical Chemistry
1.2 Introduction to thermodynamics
1.3 Thermodynamics systems
1.4 Thermodynamics equilibrium
1.5 Thermodynamics properties
1.6 Temperature and Pressure
1.7 Ideal and Real Gases

1.1 INTRODUCTION TO PHYSICAL CHEMISTRY

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- Understanding the quantitative aspect of chemical phenomena.
- The study of underlying physical principles that govern the properties and behavior of chemical systems.

Physical chemistry can be divided into

1

Thermodynamics

- Quantum chemistry
- Statistical mechanics

2

Kinetics

Thermodynamics is:

- Science of energy
- Ways energy is stored within a body
- How energy transforms
- Involve heat and work (may take place)

1.2 INTRODUCTION TO THERMODYNAMICS

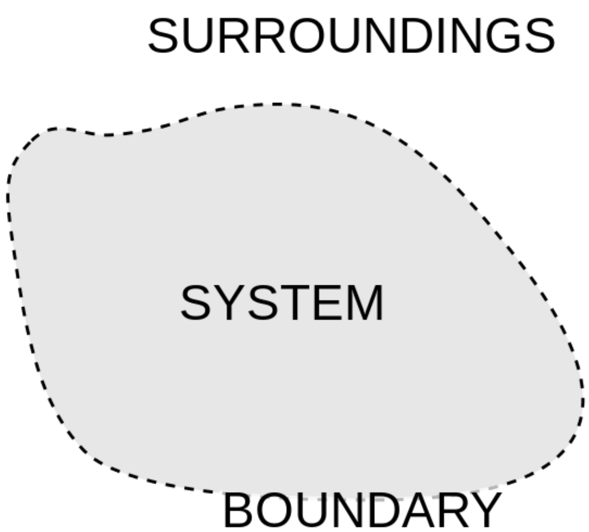
- Definition of Thermodynamic Boundary- the obvious separation between system and surroundings
- There three types of thermodynamic boundaries

Types of boundaries

1. Rigid or non-rigid (moveable)
2. Permeable (allow matter to pass through) or Impermeable
3. Adiabatic (thermal conducting) or non-adiabatic

1.3 THERMODYNAMICS SYSTEM

1.2.1 Thermodynamics systems consist of:



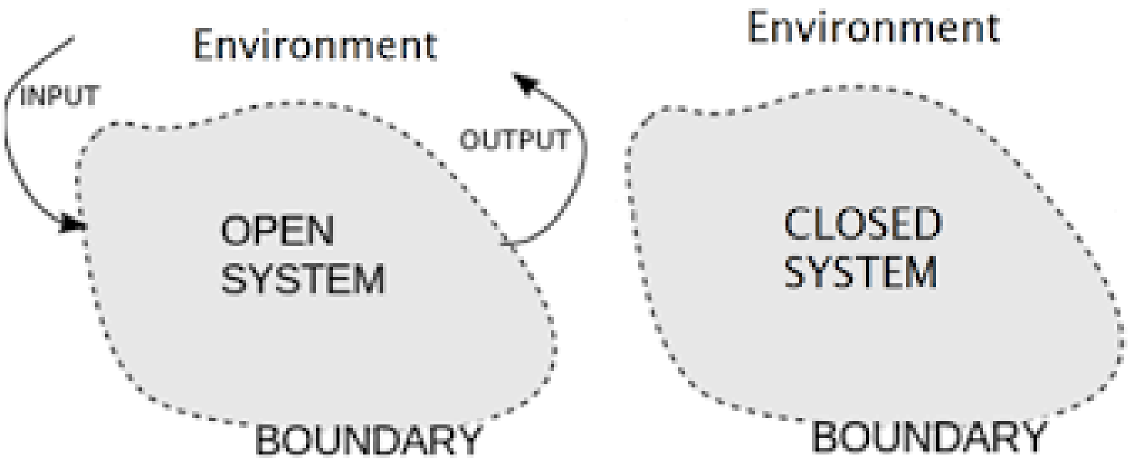
(Source: https://en.wikipedia.org/wiki/File:System_boundary2.svg)

System:
Quantity of matter or region in space chosen for study

Surrounding:
Mass or region outside the system

Boundary:
Surface separate system from surrounding

1.2.2 Types of thermodynamics systems



(Source: http://keywordsuggest.org/gallery/16039.html)

- **Opened system**
  - Have mass and energy flow across their boundries.
- **Closed system**
  - Closed system does not have mass flow across the boundary.
  - Only energy

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- **Isolated system**
  - No interaction between system and surrounding
  - Neither matter nor energy can be transferred between system and surrounding.

1.4 THERMODYNAMICS EQUILIBRIUM

Definition:

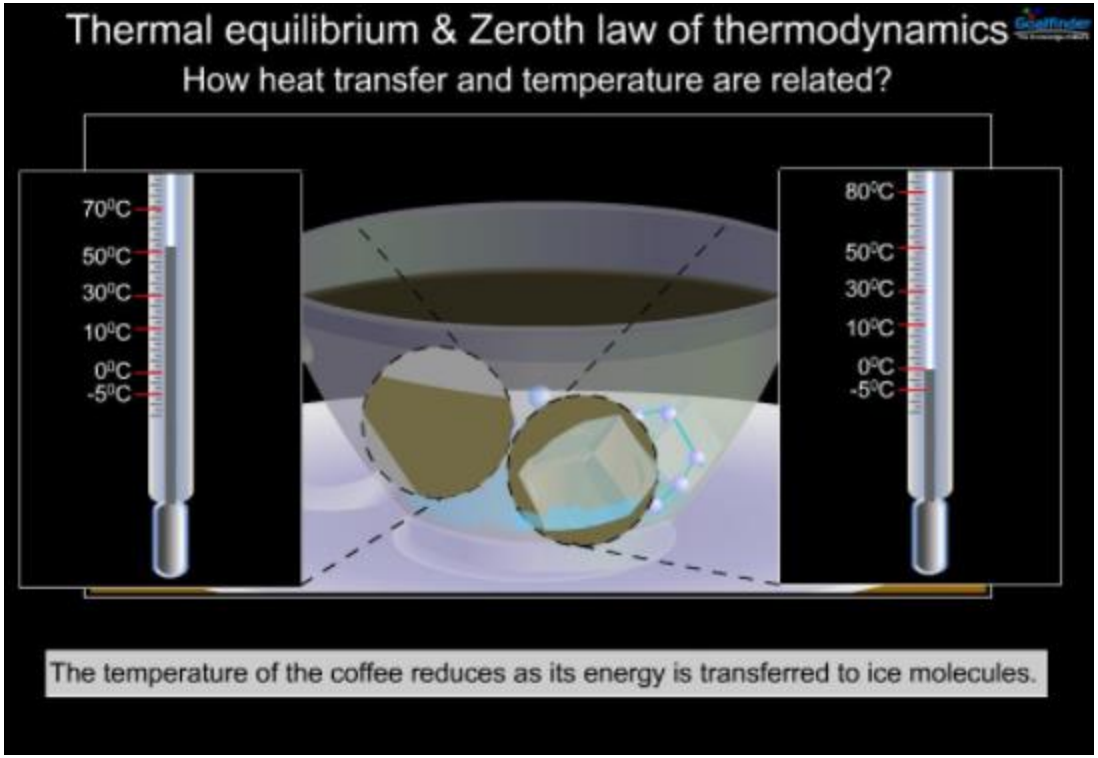
- no changes, macroscopic properties remain constant with time.

Types of equilibrium:

- Thermal
- Mechanical
- Phase
- Chemical/ material

1.4 THERMODYNAMICS EQUILIBRIUM (CONT..)

1. Thermal equilibrium



(Source: https://www.flickr.com/photos/goalfinder/6806035586)

1.4 THERMODYNAMICS EQUILIBRIUM (CONT..)

2. Mechanical equilibrium

- Related to pressure
- There is no change in pressure at any point of the system with time.
- Whenever the net force on an object is zero, the object is in mechanical equilibrium

1.4 THERMODYNAMICS EQUILIBRIUM (CONT..)

3. Phase equilibrium

- If a system involves two phases, it is in phase equilibrium when the mass of each phase reaches an equilibrium level and stays there

1.4 THERMODYNAMICS EQUILIBRIUM (CONT..)

3. Chemical equilibrium

- Chemical composition does not change with time
- No chemical reactions occur

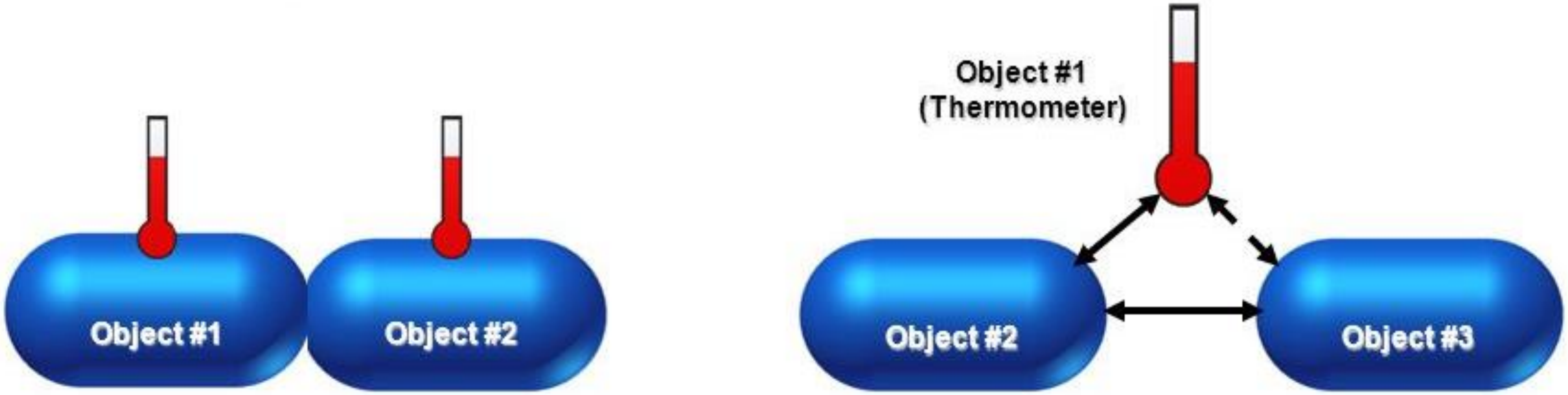
1.5 THERMODYNAMICS PROPERTIES

- **Intensive variable**
  - ✓Independent of the amount of mass of the system
    - Pressure (P),
    - Temperature (T)
    - Specific volume
    - Density (ρ)

- **Extensive variable**
  - ✓Depend on the size of the system
    - Total volume (V_t)
    - mass (m)

1.6 TEMPERATURE AND PRESSURE

Zeroth Law of Thermodynamics: If two systems are separately found to be in thermal equilibrium with a third system, the first two systems are in thermal equilibrium with each other.



(Source: https://www.slideshare.net/gunabalans/02-part1-thermo-laws-zeroth-law)

1.6 TEMPERATURE AND PRESSURE

1.6.1 Temperature Scale

Ice point

Temperature equilibrium between pure ice and liquid water with air saturated with vapor

0^oC at 1 atm

Steam point

Temperature equilibrium between pure liquid water and water vapor

100^oC at 1 atm

Celcius scale (SI) and Fahrenheit scale (English)

1.6 TEMPERATURE AND PRESSURE

Conversion Unit

$$T\,K = T\,^{\circ}\mathrm{C} + 273.15$$

$$T\,R = T\,^{\circ}\mathrm{F} + 459.67$$

$$T\,R = 1.8\,T\,K$$

$$T^{\circ}F = \frac{9}{5}T^{\circ}C + 32$$

1.6 TEMPERATURE AND PRESSURE

Pressure

$$P = \frac{Force}{Area} = \frac{F}{A}$$

$$1\,kPa = 10^3\,\frac{N}{m^2}$$

$$1\,MPa = 10^6\,\frac{N}{m^2} = 10^3\,kPa$$

1.7 IDEAL AND REAL GASES

1.7.1 Ideal Gas/Perfect gas

At low pressure and high temperature, the density of the gases decrease and the gas behave as an ideal gas.

$$PV = nRT$$

$$PV = mRT / M$$

$$Pm = \rho RT$$

1.7 IDEAL AND REAL GASES (CONT..)

Values of the gas constant, R

Values of the Universal Gas Constant R			
Values of R	**Units**	**Values of R**	**Units**
8.314472	$J \cdot K^{-1} \cdot mol^{-1}$	83.14472	$L \cdot mbar \cdot K^{-1} \cdot mol^{-1}$
0.082057	$L \cdot atm \cdot K^{-1} \cdot mol^{-1}$	8.314472×10^{-5}	$m^3 \cdot bar \cdot K^{-1} \cdot mol^{-1}$
8.205745×10^{-5}	$m^3 \cdot atm \cdot K^{-1} \cdot mol^{-1}$	10.73159	$ft^3 \cdot psi \cdot °R^{-1} \cdot lb\text{-}mol^{-1}$
8.314472	$L \cdot kPa \cdot K^{-1} \cdot mol^{-1}$	0.73024	$ft^3 \cdot atm \cdot °R^{-1} \cdot lb\text{-}mol^{-1}$
8.314472	$m^3 \cdot Pa \cdot K^{-1} \cdot mol^{-1}$	1.98588	$Btu \cdot °R^{-1} \cdot lb\text{-}mol^{-1}$
82.05745	$cm^3 \cdot atm \cdot K^{-1} \cdot mol^{-1}$	62.36367	$L \cdot torr \cdot K^{-1} \cdot mol^{-1}$

(Source: https://chemengineering.wikispaces.com/file/view/Gas_Constant.png/242836283/Gas_Constant.png)

1.7 IDEAL AND REAL GASES (CONT..)

1.7.1 **Ideal Gas Laws**

✓Boyle's Law

➢*The pressure of a fixed amount of gas at constant temperature is inversely proportional to the volume* (n and *T* constant)

$$p \alpha \frac{1}{V} \quad or \quad V \alpha \frac{1}{p}$$

1.7 IDEAL AND REAL GASES (CONT..)

✓Charles' Law

- *The volume of a fixed amount of gas in a container at constant P and n is directly proportional to the absolutely temperature.*

- *The pressure of a fixed amount of gas in a container at constant volume is proportional to the absolute temperature*

$$V \alpha T(Kelvin) \quad or \quad P \alpha T(Kelvin)$$

1.7 IDEAL AND REAL GASES (CONT..)

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- ✓Avogadro's Principle
  - ➢Volume of any gas is directly proportional to the particles number at constant T and *P*

$$V \alpha\ n$$

1.7 IDEAL AND REAL GASES (CONT..)

1.7.2 Ideal Gas Mixtures

✓ Dalton's Law

Total pressure *of an ideal gas mixture is* ***equal*** *to the* ***sum of the partial pressure of the individual gases***

$$P = P_A + P_B + \dots$$

$$P = \frac{n_A RT}{V} + \frac{n_B RT}{V} + \dots = (n_A + n_B + \dots)\frac{RT}{V}$$

1.7 IDEAL AND REAL GASES (CONT..)

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✓Real gas

- exhibit properties that cannot be explained entirely using the **ideal gas** law
- Gases tend to behave ideally in two different situations
  - High Temperature
  - Low Pressure

- Intermolecular forces;
- Attractive: dipole-dipole forces, H-bonds, dispersion forces
- Repulsive: repulsion of electrons

- Measure;
- Compressibility factor, Z
- Virial equations
- Van Der Waals equation

1.7 IDEAL AND REAL GASES (CONT..)

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✓Compressibility Factor, Z

One way to measure the deviation from ideal behaviour is to define a compressibility factor, Z as:

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

Where *V* the molar volume of the gas, V/n

1.7 IDEAL AND REAL GASES (CONT..)

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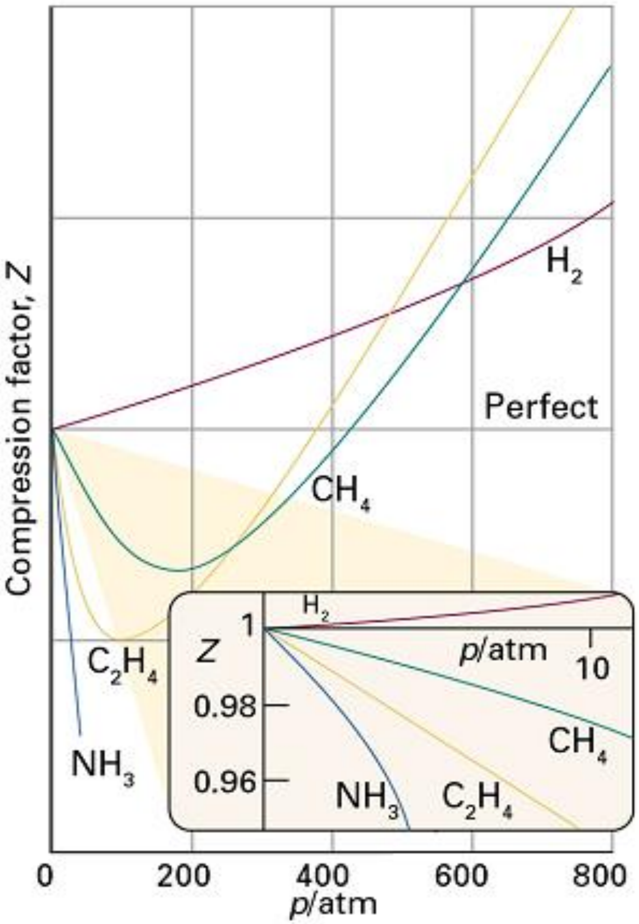

(Source: http://faculty.chem.queensu.ca/people/faculty/mombourquette/Chem221/1_Gases/Index.asp

For an ideal gas Z=1

Departure from Z = 1

- A gas is not behaving as an ideal gas

Intermediate Pressure: Z < 1

- Compression is favoured, due to dominance of attractive forces

High Pressure: Z > 1

- Expansion is favoured, as repulsive forces come into play

Conclusion of Introduction to Physical Chemistry

- Conclusion
  - Physical chemistry is the quantitative aspect of chemical phenomena.
  - Thermodynamics systems consist of surrounding, boundary and system and divided into opened system, closed system and isolated system.
  - Thermodynamics equilibrium consist of thermal, mechanical, phase and chemical/ material equilibrium
  - Thermodynamics properties included intensive variable and extensive variable
  - Zeroth Law state if two systems are separately found to be in thermal equilibrium with a third system, the first tow systems are in thermal equilibrium with each other.
  - Real gases exhibit properties that cannot be explained entirely using the **ideal gas** law

Author Information

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