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Physical chemistry

Lecture 7

The Conservation of Energy

By

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2.1 First Law of Thermodynamics
2.2 Energy

Terminology	Definition
2.1 First Law of Thermodynamics	Thermodynamics contributes the law of conservation of energy, which energy cannot be created or destroyed during a process; it can only change from one form to another
2.2 Energy	Energy is capacity to do work. Unit : J (1 J= 1 kgm_2s^{-2}) In thermodynamics analysis, forms of energy can be divided into two groups; macroscopic and microscopic energy. **TWO form of energies: (a) Microscopic and(b) macroscopic**
2.2 (a) Microscopic energy	The forms of energy are those related to the molecular structure of a system and the molecular activity › The sum of all the microscopic forms of energy is called the internal energy of a system and is denoted by U.
2.2 (b) Macroscopic energy	The macroscopic energy of a system is related to motion and the influence of some external effects such as gravity, magnetism, electricity and surface tension. Magnetism, electricity and surface tension are usually ignored. Consider **1- Kinetic energy** **2- Potential energy**

2.2 Energy

Terminology	Definition
2.2 (b) Kinetic energy ***(Macroscopic energy)***	The energy that a system possesses as a result of its motion is called kinetic energy (KE). $KE = m\frac{V^2}{2}\ (kJ)$
2.2 (b) Potential Energy ***(Macroscopic energy)***	The energy that a system possesses as a result of its elevation in a gravitational field is called potential energy (PE) g is the gravitational acceleration, 9.81 m/s2 z is the elevation $PE = mgz\ (kJ)$
Combination of energies	The total energy of a system consists of the kinetic, potential, and internal energies and is expressed as $\boldsymbol{E = U + KE + PE = U + m\frac{V^2}{2} + mgz \quad (kJ)}$
Static energy	The total energy of a system, can be contained or stored in a system, and thus can be viewed as the static forms of energy.
Dynamic energy	The forms of energy not stored in a system can be viewed as the dynamic forms. The only two modes of transfer energy interactions associated with a closed system are work and heat transfer.

2.3 Work

Terminology	Definition
2.3 Work	Work is the energy transfer associated with a force acting through a distance or work is performed when the object moves some distance z due to the application of a force, F e.g. Chemical reaction to work $Zn + 2HCl \longrightarrow ZnCl2 + H2$ The gas produced drives out the piston and raise the weight. Work is done on a system is reported as positive quantity (energy is transferred to the system by doing work)
2.3(a) Expansion Work	1. Maximum work is obtained when the external pressure is only infinitesimally less than the pressure of the gas in the system. 2. System that remains in mechanical equilibrium with its surroundings at all stages of the expansion does maximum expansion work. 3. When a system is in a state of mechanical equilibrium, an infinitesimal change in pressure results in opposite directions of change. In this case is said reversible process.

2.4 Heat Transfer

Terminology	Definition
2.4 Heat Transfer	- Energy can cross the boundary of a closed system in two distinct forms; *heat* and *work*. - Heat – forms of energy that is transferred between 2 system by temperature difference. - No heat transfer between two systems that are at the same temperature - **3 modes of energy transfer : conduction, convection and radiation**
(a) Exothermic	A process in a system that heats release to the surrounding
(b) Endothermic	A process in a system that is heated by the surrounding
(c) Diathermic	Walls that permit heating for heat transfer
(d) Adiabatic	Walls that do not permit heating for heat transfer

2.5 Internal Energy

Definition

- Total energy of a system denoted as *U*
- KE + PE = *U*
- the change in internal energy of a system is

$$dU = dq + dw_{\exp} + dw_{e}$$

w_{exp} = expansion work

w_e = work in addition to the expansion work (e.g electrical work)

- If system kept at constant volume, $w_{exp} = 0$
- When the system release energy to surrounding, the internal energy of the system decrease, (-ve sign)
- Works done by the system
- Heat loses during heating process
- When the internal energy increase, (+ve sign)
- Work done on the system
- The system absorb heat from surrounding

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2.6 Enthalpy

- Enthalpy, H (J) is **extensive property**, while molar enthalpy, H_m (H/n; J/mol) is **intensive property**
- Enthalpy of a system is defined as

$$H = U + PV$$

- A change in enthalpy arises from a change in the internal energy and a change in the product PV.

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

- If the changes takes place at constant pressure,

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

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2.6 Enthalpy

- Molar enthalpy, $H_m = U_m + PV_m$
- For perfect gas, $PV_m = RT$

Where,

$$H_m = U_m + RT$$

Molar Enthalpy, $H_m = H / n$

Molar volume, $V_m = V / n$

2.6 Enthalpy

- At constant pressure, no non-expansion work:

$$\Delta H = q_P$$

- Endothermic reaction; $q > 0$, $\Delta H > 0$
- Exothermic reaction; $q < 0$, $\Delta H < 0$

2.6 Enthalpy

- Three properties of enthalpy:
  - Heat supplied at constant pressure

$$\Delta H = q_p$$

  - Enthalpy change

$$\Delta H = H_f - H_i$$

  - Specific heat at constant pressure

$$C_p = \Delta H / \Delta T$$

2.7 Measurement of Heat and Specific Heat

- Specific Heats

$$C_V = \left(\frac{\partial u}{\partial T}\right)_v \quad and \quad C_P = \left(\frac{\partial h}{\partial T}\right)_P$$

C_V = the change in internal energy with temperature at constant volume

C_p = the change in enthalpy with temperature at constant pressure

2.7 Measurement of Heat and Specific Heat

Internal energy of a system rises as the temperature increased. The same as enthalpy, which also rises when temperature is increased.

Constant-volume heat capacity, Cv shows the temperature dependence of the internal energy at constant volume.

Constant-pressure heat capacity, Cp shows the enthalpy of a system changes as its temperature is raised at constant pressure.

2.7 Measurement of Heat and Specific Heat

- For a perfect gas,

$$C_{P,m} - C_{V,m} = R$$

- Molar heat capacity of a perfect gas is greater at constant pressure than at constant volume. Why?

At **constant volume,** all energy supplied as heat to the system **remains inside**.

At **constant pressure,** the energy supplied as heat **escapes back** to surrounding when the system expands and does work.

2.8 Thermochemistry

- Thermochemistry is the **study of heat change in chemical reactions.**
- The application of enthalpy in chemistry.
- The thermochemistry processes contributing enthalpies are as follows:
  1. Phase changes
  2. Chemical changes (combustion, formation and reaction)

- **Enthalpy in phase changes**
  - Vaporization
  - Fusion
  - Freezing
  - Sublimation


Thank you