

### STATE FUNCTION

Properties which depend only on initial and final state of system & do not depend on process or path  
e.g. U, H, S etc.

### PATH FUNCTION

Depends on path or process, as well as initial and final state of the system  
e.g. work, heat

### THERMODYNAMIC PROPERTIES

#### EXTENSIVE

Properties which are dependent of matter (size & mass) present in system  
e.g. Mass, volume, Internal energy, heat capacity, Entropy, Enthalpy etc.

#### INTENSIVE

Properties which are independent of matter (size & mass) present in system  
e.g. Pressure, temperature, Melting point, density, Specific heat, Surface tension etc.

### WORK

$\Delta W = P \Delta V = \Delta nRT$

$\Delta W = \text{Joule}$

$P \rightarrow \text{Pascal}$      $1 \text{ atm} = 1.01 \times 10^5 \text{ Pa}$   
 $V \rightarrow \text{m}^3$          $1 \text{ L atm} = 101 \text{ J}$

$\text{dm}^3 \text{ or L}$   
 $10^{-3} \text{ m}^3$   
 $10^{-6} \text{ m}^3$   
 $\text{cm}^3$

## FIRST LAW OF THERMODYNAMICS

(Based on Law of conservation of energy)

$$\Delta U = \Delta q + \Delta W$$

### SIGN CONVENTION

W(Compression)  $\rightarrow$  (+)ve

W(Expansion)  $\rightarrow$  (-)ve

q(Heating)  $\rightarrow$  (+)ve

q(Cooling)  $\rightarrow$  (-)ve

### FLOT

- Adiabatic process** -  $\Delta Q = 0$ ,  $\Delta U = \Delta W$
- Isothermal process** -  $\Delta T = 0$ ,  $\Delta U = 0$ ,  $\Delta Q + \Delta W = 0$ ,  $\Delta Q = -\Delta W$
- Isochoric process** -  $\Delta V = 0$ ,  $\Delta W = 0$ ,  $\Delta U = \Delta Q = nC_v \Delta T$
- Isobaric process** -  $\Delta W = P \Delta V$ ,  $\Delta U = \Delta Q + \Delta W$

**FREE EXPANSION**  $P_{\text{ext}} = 0, W = 0, \Delta U = 0, q = 0$

**ISOTHERMAL**  $dT = 0; \Delta U = 0; q = -W$

Reversible Isothermal	Irreversible Isothermal
$W_{\text{rev}} = nRT \ln \left( \frac{V_2}{V_1} \right)$	$W_{\text{ir}} = -P_{\text{ext}} \left[ \frac{nRT}{P_2} - \frac{nRT}{P_1} \right]$

### Spontaneity

#### ENTHALPY

$\Delta H = \Delta U + \Delta n_p RT$

$\Delta n_p = 0, \Delta H = \Delta U$

$\Delta n_p > 0, \Delta H > \Delta U$

$\Delta n_p < 0, \Delta H < \Delta U$

All exothermic process are spontaneous

#### ENTROPY

$S_{\text{gas}} > S_{\text{liquid}} > S_{\text{solid}}$

#### ENTROPY CHANGE

- Isothermal**  
 $\Delta S = nR \ln \frac{V_2}{V_1} = nR \ln \frac{P_1}{P_2}$
- Isochoric (P=const)**  
 $\Delta S = nC_v \ln \frac{T_2}{T_1} = nC_v \ln \frac{P_2}{P_1}$
- Isobaric**  
 $\Delta S = nC_p \ln \frac{T_2}{T_1} = nC_p \ln \frac{V_2}{V_1}$

$\Delta S_{\text{total}} > 0$ , Spontaneous

$\Delta S_{\text{total}} = 0$ , Equilibrium

$\Delta S_{\text{total}} < 0$ , Non-spontaneous

#### GIBBS FREE ENERGY

$\Delta G = \Delta H - T \Delta S$

$\Delta G < 0$  Or (-)ve, Spontaneous

$\Delta G > 0$  Or (+)ve, Non-spontaneous

$\Delta G = 0$ , Equilibrium

#### Equilibrium Temperature

$$T_e = \frac{\Delta H}{\Delta S}$$

$\Delta H$	$\Delta S$	$\Delta G = \Delta H - T \Delta S$	Spontaneity.
(-)	(+)	Always Negative	Spontaneous at all temp
(+)	(-)	Always Positive	Non-spontaneous at all temperature.
(+)	(+)	+ve @ low temp. -ve @ high temp.	Non spontaneous at low temperature Spontaneous at high temperature
(-)	(-)	-ve @ low temp. +ve @ high temp.	Spontaneous at low temperature, $T < T_e$ Non spontaneous at high temperature

# THERMODYNAMICS

## THERMOCHEMISTRY

- Heat of Reaction ( $\Delta H_{\text{rxn}}$ )**  
 $\Delta H_{\text{rxn}} = \Delta H_{\text{products}} - \Delta H_{\text{reactants}}$
- Heat of Formation**  
Heat Change in formation of 1 mole of substance at 298 K and 1 atm Pressure (standard enthalpy of formation)  
 $\frac{1}{2} \text{N}_2 + \frac{3}{2} \text{H}_2 \rightleftharpoons \text{NH}_3$   
 $A + B \rightleftharpoons C + D$   
 $a \quad b \quad c \quad d$   
 $\Delta H_{\text{reaction}} = \text{Heat of formation of products} - \text{Heat of formation of reactants}$   
 $= (c + d) - (a + b)$   
Standard enthalpy of formation (298 K, 1 atm) of element at its standard state is zero e.g.,  
 $\text{O}_2(\text{g}) = 0 \quad \text{Cl}_2(\text{g}) = 0 \quad \text{Br}(\text{g}) \neq 0 \quad \text{Br}_2(\text{l}) = 0$
- Enthalpy of Combustion (1 mole, 298 K)**  
(standard enthalpy of combustion)  
 $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} ; \Delta H_{\text{combustion}}$   
 $A + B \rightarrow C + D$   
Enthalpy of combustion:  
 $\Delta H_{\text{react}} = \text{Heat of combustion of reactants} - \text{Heat of combustion of products}$   
 $= (a + b) - (c + d)$
- Heat of Neutralisation ( $\Delta H = (-)ve$ )**  
 $\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O} ; \Delta H_{\text{neutralisation}}$   
 $S.A + S.B \rightarrow \Delta H = -13.7 \text{ k Cal} = -57 \text{ kJ}$   
 $S.A + S.B \rightarrow (S.A / S.B + W.A / W.B) \rightarrow W.A + W.B$  (Order of  $\Delta H$  neutralisation)



### BOND ENERGY

$A + B \rightarrow C + D$

Bond energy: a b c d

$\Delta H_{\text{reaction}} = \text{Bond energy of reactants} - \text{Bond energy of products}$   
 $= (a + b) - (c + d)$

$\text{NH}_3 \Rightarrow \text{B.E} = x$   
B.E of N-H =  $\frac{x}{3}$

$\text{CH}_4 \Rightarrow \text{B.E} = x$   
B.E of C-H =  $\frac{x}{4}$

- $A \rightarrow B ; \Delta H_1$   
 $B \rightarrow C ; \Delta H_2$   
 $A \rightarrow C ; \Delta H_3 = \Delta H_1 + \Delta H_2$
- $A \rightarrow B ; \Delta H = x$   
 $B \rightarrow A ; \Delta H = -x$
- $A \rightarrow B ; \Delta H = x$   
 $nA \rightarrow nB ; \Delta H = nx$

## HESS' LAW OF CONSTANT HEAT SUMMATION

$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$