

# Thermodynamics

## Thermodynamic terms

**Intensive:** These do not depend upon quantity of matter. e.g.,  $T, P$ .

**Extensive:** These depend upon quantity of matter. e.g., mass, volume, energy.

## Thermodynamic laws

**Properties of system:** Physical quantities which are used to define the system.

**Thermodynamic processes**

- If  $dq = 0$ , process is adiabatic.
- If  $dT = 0$  and  $dE = 0$ , the process is isothermal.
- If  $dV = 0$ , process is isochoric.
- If  $dP = 0$ , process is isobaric.

**Heat ( $q$ ) and heat capacity ( $C$ )**

- Heat capacity,  $C = dq/dT$
- $C_v = \left(\frac{\partial U}{\partial T}\right)_V$ ;  $C_p = \left(\frac{\partial H}{\partial T}\right)_P$
- When  $n_1$  moles of gas A and  $n_2$  moles of gas B are mixed.

$$(C_v)_{\text{mix}} = \frac{n_1 C_{v1} + n_2 C_{v2}}{n_1 + n_2}$$

- $C_p - C_v = nR$

**Work ( $W$ )**

- $W = -P_{\text{ext}} \Delta V$   
[irreversible isothermal expansion]
- $W = -2.303nRT \log(P_1/P_2)$
- $W = -2.303nRT \log(V_2/V_1)$   
[reversible isothermal expansion]
- $W = nC_v dT = \frac{nR}{\gamma - 1} (T_2 - T_1)$   
[reversible adiabatic expansion]  
where,  $\gamma = C_p/C_v$
- $W = -P_{\text{ext}} R \left( \frac{T_2 P_1 - T_1 P_2}{P_1 P_2} \right)$   
[irreversible adiabatic expansion]

**Bond enthalpy**  
It is the enthalpy change accompanying the breaking of one mole of covalent bonds.  
Bond enthalpy =  
 $\sum$  Bond enthalpies of reactants  
-  $\sum$  Bond enthalpies of products

**Enthalpy ( $H$ )**  
Total heat of the system

- $H = U + PV$
- $\Delta H = \Delta U + P\Delta V = C_p \Delta T = \Delta U + \Delta n_g RT$  (at constant pressure)
- $\Delta H = \sum H_{\text{product}} - \sum H_{\text{reactant}}$   
= -ve (exothermic)  
= +ve (endothermic)

**Gibbs Free Energy ( $G$ )**  
Useful work done by the system

- $G = H - TS$
- $\Delta G = \Delta H - T\Delta S$   
(Gibbs - Helmholtz equation)
- $\Delta G^\circ = \sum G_f^\circ(\text{product}) - \sum G_f^\circ(\text{reactant})$
- $\Delta G^\circ = -2.303 RT \log K_{\text{eq}}$
- If  $\Delta G = +ve$  (Non-spontaneous)
- If  $\Delta G = -ve$  (Spontaneous)

**Enthalpy of combustion,  $\Delta_c H$**   
It is the enthalpy change when 1 mole of a substance burnt completely in air.

**Hess's law of constant heat summation**  
 $\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$

**Enthalpy change of a reaction**  
It is the enthalpy change when a given reactant reacts completely.

**Enthalpy of formation**  
It is the enthalpy change occurring during the formation of 1 mole of a substance from its elements.

**Enthalpy of solution**  
 $\Delta_{\text{sol}} H = \Delta_{\text{ionise}} H + \Delta H_{\text{hyd}}$   
where,  $\Delta_{\text{ionise}} H = S + I + \frac{1}{2} D - \Delta_f H + E.A.$

**Zeroth law:** System in thermal equilibrium with each other have same temperature.

**First law:** The total energy of the universe remains constant although it may undergo transformation from one form to the other.  
 $\Delta U = q + w$  ( $\Delta U$  = internal energy)

**Second law:** In a spontaneous process total energy of the universe increases.  
 $\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0$

**Entropy ( $S$ )**  
Measure of randomness or disorder

- $\Delta S = \frac{q_{\text{rev}}}{T}$  (reversible process)
- $\Delta S = 2.303n C_v \log\left(\frac{T_2}{T_1}\right) + 2.303nR \log\left(\frac{V_2}{V_1}\right)$
- $\Delta S = 2.303n C_p \log\left(\frac{T_2}{T_1}\right) + 2.303nR \log\left(\frac{P_1}{P_2}\right)$
- $\Delta S = 2.303nR \log\left(\frac{V_2}{V_1}\right)$  } isothermal
- $\Delta S = 2.303nR \log\left(\frac{P_1}{P_2}\right)$  }
- $\Delta S = 2.303n C_p \log\left(\frac{T_2}{T_1}\right)$  [isobaric]

**Third law**

- Entropy of all pure crystals is zero at the absolute zero temperature.
- $\lim_{T \rightarrow 0} S = 0$
- Residual Entropy  
 $S_R = k \ln W$   
( $W$  = thermodynamic probability)

# Engineering Chemistry Notes Chemical Thermodynamics

**C. J. Armstrong**



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