Thermodyamics

1. First law $\Delta U = q + w$

2. Heat (q) :

Heat capacity (c) — JK^{-1}, $cal\,K^{-1}$

Specific Heat capacity ($\bar{c}$) — $JK^{-1}g^{-1}$, $cal\,K^{-1}g^{-1}$

Molar Heat capacity (C_m) — $JK^{-1}mol^{-1}$, $cal\,K^{-1}mol^{-1}$

$q = c\,\Delta T = c\,(T_2 - T_1)$

$q = \bar{c}\,\Delta T \times m = m\bar{c}\,(T_2 - T_1)$

$q = C_m\,\Delta T \times n = n C_m\,(T_2 - T_1)$

3. Work (w) :

$w = -P_{ext}\,(V_2 - V_1)$

1 atm = 101·3 J = 24·3 cal

1 bar = 100 J

- Isothermal Reversible process

$$w = -2.303\,nRT \log_{10}\left(\frac{V_2}{V_1}\right)$$

$$= -2.303\,PV \log_{10}\left(\frac{V_2}{V_1}\right)$$

$$w = -2.303\,nRT \log_{10}\left(\frac{P_1}{P_2}\right)$$

4. Internal energy (U) :

① $\Delta U = q + w$

② $\Delta U = nC_v\Delta T$ — C_v – molar heat capacity at constant volume.

③ Isothermal process (Ideal gas)

$\Delta T = 0$

$\Delta U = 0$

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5. Enthalpy (H):

① $H = U + PV$

② $\Delta H = \Delta U + \Delta(PV)$ — (i) $\Delta H = \Delta U + \Delta nRT$

at constant pressure.

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

③ $\Delta H = nC_p\Delta T$ C_p - molar Heat capacity at constant pressure.

④ In isothermal process (Ideal gas)

$\Delta H = 0$

6. For a chemical Reaction:

$\Delta H = \Delta U + \Delta nRT$

$\omega = -\Delta nRT$

7. Entropy (S): JK^{-1} $calK^{-1}$

① $\Delta S = \frac{q_{rev}}{T}$

② $(\Delta S)_{system} = nC_v \ln\left(\frac{T_2}{T_1}\right) + nR\ln\left(\frac{V_2}{V_1}\right)$

or

$(\Delta S)_{system} = nC_p \ln\left(\frac{T_2}{T_1}\right) + nR\ln\left(\frac{P_1}{P_2}\right)$

③ In Isothermal process, $\Delta S = nR\ln\left(\frac{V_2}{V_1}\right) = nR\ln\left(\frac{P_1}{P_2}\right)$

④ For isochoric and isobaric process, $\Delta S = nC_v\ln\left(\frac{T_2}{T_1}\right) \pm nC_p\ln\left(\frac{T_2}{T_1}\right)$

Respectively.

- Adiabatic reversible process, $\Delta S = 0$
  irreversible process, $\Delta S \neq 0$

- Reversible process
  $(\Delta S)_{sys} + (\Delta S)_{surr} = 0$

  Irreversible process
  $(\Delta S)_{system} + (\Delta S)_{surr} > 0$

⑤ $(\Delta S)_{surr} = \frac{q_{surr}}{T}$

⑥ At equilibrium $\Delta S = \frac{\Delta H}{T}$

8. Gibb's Free energy :

① $G = H - TS$

② $\Delta G = \Delta H - \Delta(TS)$

at constant temp.

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

③ At equilibrium $\Delta G = 0$

$\Delta H = T\Delta S$

$\Delta S = \frac{\Delta H}{T}$ $\quad T = \frac{\Delta H}{\Delta S}$

④ $\Delta G < 0$ spontaneous

$\Delta G > 0$ non-spontaneous

$\Delta G = 0$ equilibrium

⑤

ΔH	ΔS	ΔG
−	+	− always spontaneous
+	−	+ always non spontaneous
+	+	spontaneous at high temperature
−	−	spontaneous at low temperature

⑥ $\Delta G = \Delta G^\circ + RT\ln(Q)$

At eq. $\Delta G = 0$

$Q = K$

$\Delta G^\circ = -RT\ln(K)$ $\quad \Delta G^\circ = -2.303\, RT \log(K)$

Thermochemistry

- If Formation enthalpies given in problem,

$$\Delta H = \Sigma (\Delta f H)_P - \Sigma (\Delta f H)_R$$

- If enthalpy of combustion are given,

$$\Delta H = \Sigma (\Delta c H)_R - \Sigma (\Delta c H)_P$$

- If data is given in term of B.E then (gases),

$$\Delta H = \Sigma (B.E)_R - \Sigma (B.E)_P$$

- Hess law :

a) Rxn Reverse ΔH ka sign Badal jata hain.

b) Rxn multiply ΔH ko bhi multiply karna.

c) Rxn ko add ΔH ko bhi add karna.