Thermodynamics

⇒ Properties :

State function : depends on initial & final stage Ex: U, S, H, G

path function : depends only on path Ex: W, Q

Intensive property : Independent on quantity of matter.

Ex: Molar properties, P, M.P, B.P, sp heat, etc.

Extensive property : dependent on quantity of matter.

Ex: Heat capacity, U, S, H, G.

Internal energy (U) : All energies except gravitational energies.

$\Delta U = U_2 - U_1 = C_v = Q_v = \sum (\Delta U_{products} - \Delta U_{reactants})$

↓ Can be measured — Cannot be measured

$\Delta U = nC_v dT = Q_v$

$dU = nC_{vm}(T_2 - T_1)$

Enthalpy : $\Delta H = \Delta U + P\Delta V \Rightarrow \Delta H = \Delta U + \Delta n_{(g)} RT$

for expansion $W = -P_{ext} \times \Delta V$ $\Delta H = nC_p dT = Q_p$,

for compression $W = +P_{ext} \times \Delta V$,

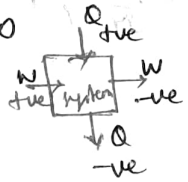
$C_p - C_V = R$

⇒ Thermodynamic process :

① Isothermal $dT = 0$ ② Isobaric $dP = 0$ ③ Isochoric $dV = 0$ ④ Adiabatic $dq = 0$ Polytropic $pV^n = \text{const}$

cyclic process $dU = 0$

⇒ Sign convention →



⇒ Laws –

i) Zeroth law – 2 system are eq with 3rd then all are eq with each other

ii) First law – $\Delta U = q + W$

$$\frac{\Delta H_{T_2} - \Delta H_{T_1}}{T_2 - T_1} = \Delta C_p$$

$$\frac{\Delta E_{T_2} - \Delta E_{T_1}}{T_2 - T_1} = \Delta C_v$$

Work calculation

Isochoric for ② ⇒ $\Delta U = q_v + W = q_v$ $dV = 0 \Rightarrow W = 0$

Isobaric for ② ⇒ $W = -P_{ext}\Delta V$, $\Delta H = Q_p$

Isothermal for ① ⇒ $dT = 0$, $dU = 0 \Rightarrow 0 = q + W \Rightarrow -W = q$

Reversible $W = -nRT\ln\left(\frac{V_2}{V_1}\right) = -nRT\ln\left(\frac{P_1}{P_2}\right)$

irreversible $W = -P_{ext}\left(\frac{nRT}{P_2} - \frac{nRT}{P_1}\right)$

for ④ adiabatic $q = 0$

$\Delta U = w = nC_v(\Delta T)$ $\quad \gamma = \frac{C_p}{C_v}$

$TV^{\gamma-1} = PV^{\gamma} = T^{\gamma}P^{1-\gamma} = \text{const}$

Reversible work: $W = \frac{P_2V_2 - P_1V_1}{\gamma - 1} = \frac{nR(T_2 - T_1)}{\gamma - 1}$

Irreversible: $W = nC_v\Delta T = -P_{ext}\Delta V$

Cyclic process

Work done = Area enclosed by P-V graph

clockwise = -ve, anticlockwise = +ve

Heat capacity (C)

$C = \frac{dq}{dt}$, $q_v = \Delta U$, $C_v = \left(\frac{q_v}{T_2 - T_1}\right) = \left(\frac{\partial U}{\partial T}\right)_V$, $C_p = \left(\frac{\partial H}{\partial T}\right)_P$

$C = J/°C$

iii) 2nd law: ① No cyclic process can convert all energy into work

② In an irreversible process, entropy of universe (sys + surr) ↑ but it remains const.

for reversible process: $\Delta S_{sys} + \Delta S_{surr} = 0$ i.e., $\Delta S_{total} > 0$

in general $\Delta S_{sys} + \Delta S_{surr} \geq 0$

$S_{(g)} > S_{(l)} > S_{(s)}$

Entropy (S) –

$\Delta S = \frac{-Q_{reversible}}{T}$

$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr}$

$\Delta S_{sys} = nC_v \ln\left(\frac{T_2}{T_1}\right) + nR \ln\left(\frac{V_2}{V_1}\right) = nC_p \ln\left(\frac{T_2}{T_1}\right) + nR \ln\left(\frac{P_1}{P_2}\right)$

$\Delta S = \int \frac{dq}{T} \Rightarrow \Delta S_{sys} = \frac{q_{sys}}{T_{sys}}$ $\quad (q_{sys} = -q_{surr})$

$\Delta S_{surr} = \frac{q_{surr}}{T_{surr}} = \frac{-q_{sys}}{T_{surr}}$

Gibbs energy (G): state, extensive

for pure solids, liquids, gases $P^\circ = 1$ bar, for ion conc. $C^\circ = 1M$

ΔG = +ve (non spontaneous), ΔG = -ve (spontaneous), $\Delta G = 0$ (eq)

$\Delta G = \Delta H - T\Delta S$ $\quad \Delta G$ = -ve with ↑ in temp.

$\Delta G = -2.303RT \log_{10} K_{eq}$

Degree of freedom → $DF = f_t + f_v + f_R = 3N$ (N = atomicity)

Type of gas	f_t	f_v	f_R
Monoatomic Ex: He, Ne, Ar	3	0	0
Diatomic Ex: O_2, CO, etc	3	2	3n-5
Non-linear Ex: SO_2, O_3, etc	3	3	3n-6

$U = \frac{f_t}{2}(nRT) + \frac{f_R}{2}(nRT) + \frac{f_v}{2}(nRT) + C$

$Q = m\Delta T = C\Delta T = nC_m\Delta T$

Units of pressure

1 atm = 1.013×10^5 Pa = 760 mm Hg = 76 cm Hg

1 atm = 760 torr

1 atm lit = 1.013×10^5 N/m² × 10^{-3} m³

= 101.3 Nm = 101.3 J

1 bar lit = 100 J

Enthalpy (H) case (I): If $\Delta n_{(g)} > 0$ i.e, +ve

$\Delta H > \Delta U$ (or) $\Delta H > \Delta E$

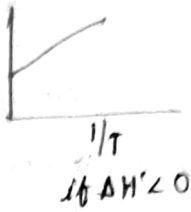
case (II): If $\Delta n_{(g)} < 0$ i.e, −ve case (III): If $\Delta n_{(g)} = 0$, $\Delta H = \Delta E$

$\Delta H < \Delta U$ (or) $\Delta H < \Delta E$

Effect of temperature : Vant Hoff eqn

ⓐ $\frac{d(\ln k)}{dT} = \frac{\Delta H^\circ}{RT^2}$ ⓑ $\frac{d(\ln k)}{d(1/T)} = \frac{-\Delta H^\circ}{R}$, $\ln K = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$

$\ln\left(\frac{K_2}{K_1}\right) = \frac{-\Delta H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$



if $\Delta H' < 0$

IV) Third law of thermodynamics: at absolute 0 temp., the entropy of a perfectly crystalline is zero.

$$\int dS_T = \int \frac{\Delta_r C_{p,m} \cdot dT}{T}$$

$$\Delta_r S_{T_2} - \Delta_r S_{T_1} = \Delta_r C_{p,m} \ln \frac{T_2}{T_1}$$

Diathermic wall: Heat change occurs to maintain const. temp

Thermo chemistry

$\Delta H^\circ = H^\circ_{m,2} - H^\circ_{m,1} = C_p \Delta T$ → $\Delta H_{com} = -\Delta H_{formation}$

→ If $\Delta H_p > \Delta H_R$ then rxn is endothermic, if $\Delta H_p < \Delta H_{rc}$ then rxn will be exothermic.

→ $\Delta H_{reaction} = \sum \Delta H_{products} - \sum \Delta H_{reactants}$ = +ve − endo; = −ve − exo

→ $\Delta H_2^\circ = \Delta H_1^\circ + \Delta C_p (T_2 - T_1)$

$\Delta C_p = C_p(\text{products}) - C_p(\text{reactants})$

$\Delta E_2^\circ = \Delta G^\circ + \int \Delta C_v \, dT$

$\Delta_f H^\circ = \sum \Delta H_p^\circ - \sum \Delta H_R^\circ$

$\Delta H = \Delta H_{ion} + \Delta H_{neu}$

$\Delta H_{neu} = -13.7 \text{ kcal/eq} = -57.1 \text{ kJ/eq}$

SA & SB

SB with HF > 13.7 k cal

Enthalpy for bond dissociation $\Delta H = \Delta H_{react} - \Delta H_{prod}$

Resonance energy $\Delta H^\circ_{resonance} = \Delta H_{experimental} - \Delta H^\circ_{calculated}$

if Bomb calorimeter used then $\Delta E = \frac{(W+m)(T_2 - T_1)}{W_1} \times M$, $\Delta H = \Delta E + \Delta n_g RT$