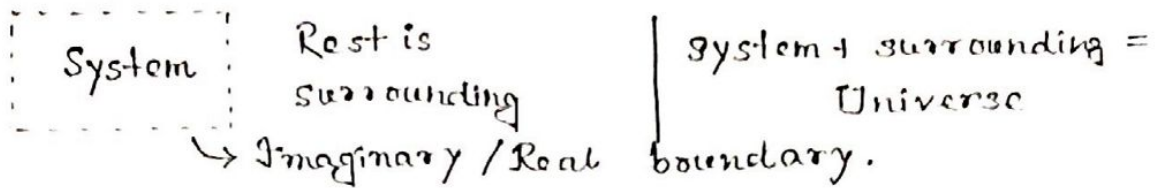




Handwritten Notes  
On  
Chemical Thermodynamics

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The Zeroth Law of Thermodynamics: When two systems are in thermal equilibrium, then both have the same temperature.

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The First Law of Thermodynamics:  $dU = \delta Q + \delta W$   
 ( $d \rightarrow$  total differential,  $\delta \rightarrow$  partial differential).  
 In practical,  $\Delta U = Q + W$ . [ $U$  is internal energy,  $Q \rightarrow$  heat,  $W \rightarrow$  work] [Statement of Conservation of Energy].

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Some basics:

• Isolated system: exchanging neither matter nor energy with surrounding.

• Closed: exchanging only energy. ( $U$ )

• Open: exchanging both (matter & energy).

• Homogeneous & Heterogeneous System  
 (Same or different phase).

• Heat: When delivered to system - positive, otherwise negative.

• Work: When done on system - positive, otherwise negative.

• Intensive & Extensive Thermodynamic quantities -  
 Intensive are those whose value do not change when system is divided into sub-systems.  
 Extensive are those whose value is proportional to the amount of substance.  
 (at const.  $T$  &  $P$ ).

• Reversible & Irreversible process:

Reversible, when at equilibrium at every point, direction of the process may be reversed by even a very slight change of initial condition. An ideal process, not real.

Name of Process	Constant Quantity	Symbol
Isothermal	Temperature	[T]
Isobaric	Pressure	[P]
Isochoric	Volume	[V]
Adiabatic	Heat	[ad]
Isentropic	Entropy	[S]
Isenthalpic	Enthalpy	[H]
Polytropic	Heat capacity	

continued -

\*  $dU = dQ - pdV$  [exchanges reversible volume]

If isochoric,  $\Delta U = Q$

\* It follows from the 1st law, it's impossible to construct perpetual motion machine, of first type.

\* Second Law of Thermodynamics:  $ds = \frac{\delta Q}{T}$  (reversible)  
 [S → Entropy] for irreversible,  
 unit J/K  $ds > \frac{\delta Q}{T}$

If in reversible process, then can be used. It follows from the law, it's impossible to construct perpetual machine, 2nd type, gains heat & converts into work without loss.



\* Entropy is the degree of disorder in the movement of molecules.

\* The Third Law of Thermodynamics:  $\lim_{T \rightarrow 0} S = 0$ .

It implies 0K cannot be attained by any process. Theoretically, at a temperature tending to 0K, the entropy is zero.

\* Enthalpy:  $H$  is a state function, (unit J).  $H = U + pV$

If system exchanges only heat & reversible volume work,  $dH = \delta Q + p \delta V$

If isobaric,  $dH = \delta Q$  |  $\Delta H = Q$

$$\Delta H = \Delta U + nR\Delta T$$

\* Helmholtz energy:  $F$ , state function (unit J)  $F = U - TS$ .

during reversible isothermal process,  $\Delta F = W$

For isothermal,

$$\Delta F = \Delta U - T\Delta S$$

For non-isothermal,

$$\Delta F = \Delta U - T_2 S_2 + T_1 S_1$$

\* Gibbs Energy:  $G$ , state function,  $G = H - TS$ .

$$(unit J) \quad G = H - TS = U + pV - TS = F + pV$$

$$\Rightarrow \Delta G = \Delta F + \Delta(pV) = \Delta F + p_2 V_2 - p_1 V_1$$

$$\Delta G = W + p\Delta V \quad [T, p, \text{reversible}]$$

\* Heat Capacities:  $c = \left(\frac{\delta Q}{\delta T}\right)_{\text{process}}$ .

$$(Unit J/K). \text{ isochoric } c_v = \left(\frac{\delta Q}{\delta T}\right)_{\text{isochoric}} = \left(\frac{\delta U}{\delta T}\right)_v$$

$$\text{isobaric } c_p = \left(\frac{\delta Q}{\delta T}\right)_{\text{isobaric}} = \left(\frac{\delta U}{\delta T}\right)_p$$

$$c_{pm} = \frac{c_p}{n}, \quad c_{vm} = \frac{c_v}{n} \quad [\text{intensive now, molar heat capacity}]$$

\* State functions give exact differential, that can be integrated over limits.

$$\int_a^b dU = U_b - U_a \quad \text{but} \quad \int_a^b dW = W, \quad \text{because}$$

$W$  depends on the path followed.

\* For reversible expansion,  $P_{\text{ext}} = P_{\text{int}}$

$$W_{\text{rev}} = - \int_{V_1}^{V_2} P_{\text{ext}} dV = - \int_{V_1}^{V_2} P_{\text{int}} dV = - 2.303 nRT \log \frac{V_2}{V_1}$$

\* For irreversible expansion,  $W_{\text{irr}} = - \int_{V_1}^{V_2} P_{\text{ext}} dV$ .

$$W_{\text{rev}} > W_{\text{irr}} \quad = - P_{\text{ext}} (V_2 - V_1)$$

\* Work in different processes.

i) Isobaric -  $W = - P_{\text{ext}} \Delta V = - nR (T_2 - T_1)$ .

ii) mass lifting or falling -  $W = - mgh = - p \Delta V$   
 $W = mgh = - p \Delta V$ .

iii) Isothermal reversible -  $W = - 2.303 nRT \log \frac{P_1}{P_2}$   
 $= - 2.303 nRT \log \frac{V_2}{V_1}$ .

$$\Delta U = 0, \quad \Delta H = 0, \quad q = -W = 2.303 nRT \log \frac{P_1}{P_2}$$

iv) Isothermal irreversible -  $W_{\text{irr}} = - nRT \left[ 1 - \frac{P_2}{P_1} \right]$ .

$$q = nRT \left[ 1 - \frac{P_2}{P_1} \right]$$

v) Isochoric -  $W = 0, \quad q = \Delta U$ .

vi) Adiabatic -  $q = 0, \quad W = \Delta U = nC_V \Delta T$ .

$$W = \frac{nR}{\gamma - 1} (T_2 - T_1) \quad [\text{reversible adiabatic}]$$

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

\* Energy changes:

$$\Delta U = q_V$$

$$\Delta H = q_P$$

$q_V \rightarrow$  heat exchange at const. vol.

$q_P \rightarrow$  " " " " at " " press.



c.

\*  $\Delta H = \Delta U + \Delta n_g RT$

\* Heat capacity,  $C = \frac{\Delta Q}{\Delta T}$ ,  $C_v = \left(\frac{\delta U}{\delta T}\right)_v$ ,  $C_p = \left(\frac{\delta H}{\delta T}\right)_p$ .

\* Extensive Properties: Volume, Number of moles, mass, free energy (G), Entropy (S), Enthalpy (H), Internal energy (U), Heat Capacity.

\* Intensive Properties: Molar volume, density, refractive index, surface tension, viscosity, free energy/mole, specific heat, pressure, temperature, BP, FP.

\* Exothermic reaction -  $\sum H(\text{product}) < \sum H(\text{reactant})$

Endothermic reaction -  $\sum H(\text{product}) > \sum H(\text{reactant})$

\* Hess's Law - Total enthalpy change is equal to the sum of sequence reaction's enthalpy change.

$$\Delta H^\circ = \sum \Delta H_f^\circ (\text{products}) - \sum \Delta H_f^\circ (\text{reactants})$$

(standard state - 1 atm, 101.325 kPa & 298 K is assigned a zero value).

\* Kirchhoff's eqn's:  $\Delta C_p = \frac{\Delta H_2 - \Delta H_1}{T_2 - T_1}$

$$\Delta C_v = \frac{\Delta U_2 - \Delta U_1}{T_2 - T_1}$$

\* Trouton's Rule: Entropy of vaporisation of non-associated or non-dissociated liquid is constant & may be taken as 87.3 J/mol K

\* Average bond energy:  $\frac{\Delta H_f \text{ of molecules}}{\text{no. of bonds}}$

BE is an additive property.

\*  $\Delta S = \frac{q_{rev}}{T}$  [  $q_{rev}$  heat supplied isothermally & reversibly ].

\* for reversible cycle,  $\frac{q_1}{T_1} + \frac{q_2}{T_2} = 0$

for irreversible engine,  $\frac{q_1}{T_1} + \frac{q_2}{T_2} < 0$ .

\*  $\Delta S = nC_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$

\* Isochoric heating/cooling:  $\Delta U = nC_v \Delta T$

$$\Delta H = nC_p \Delta T = q_p$$

$$\Delta S = nC_p \ln \frac{T_2}{T_1}$$

\* Isochoric heating/cooling:  $\Delta U = C_v \Delta T = q_v$

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

$$\Delta S = nC_v \ln \left( \frac{T_2}{T_1} \right)$$

\* Adiabatic:  $\Delta U = C_v \Delta T$ ,  $\Delta H = C_p \Delta T$

$$\Delta S = nC_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} \text{ (irreversible)}$$

$$\Delta S = 0 \text{ (reversible)}$$

\*  $\Delta G_r^\circ = \sum \Delta G_f^\circ (\text{products}) - \sum \Delta G_f^\circ (\text{reactants})$

$$\Delta G^\circ = -2.303 RT \log K_{eq}$$

$\Delta G^\circ = W_{max}$  (for reversible change [P][T]).

$$\Delta G = -nFE_{cell}$$

\*  $\log \frac{P_2}{P_1} = \frac{\Delta H}{2.303R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$  [liquid  $\leftrightarrow$  gas equilibrium, Clausius Clapeyron's eqn]

$P_1, P_2$  vapour pressure at  $T_1, T_2$ .

\*  $\Delta S^\circ = \sum S^\circ (\text{products}) - \sum S^\circ (\text{reactants})$



# Thermodynamics.

## Formula Sheet

\* Work done for reversible process:  $W_{rev} = -pdV$

$$* \bar{W}_{isothermal} = -nRT \ln \frac{V_2}{V_1} = -nRT \ln \frac{P_1}{P_2}$$

$$W_{isobaric} = -P \Delta V \quad ; \quad W_{isochoric} = 0.$$

$$W_{adiabatic} = \frac{1}{\gamma - 1} (P_2 V_2 - P_1 V_1) = \frac{nR}{\gamma - 1} (T_2 - T_1).$$

$$* dU = \delta Q + \delta W$$

$$* Q = cm \Delta T \quad ; \quad Q = n C_m \Delta T$$

$$C_v = \frac{1}{n} \frac{\Delta U}{\Delta T} \quad ; \quad C_p = \frac{1}{n} \frac{\Delta H}{\Delta T}, \quad \Delta H = n C_p \Delta T.$$

$$\Delta U = n C_v \Delta T \quad ; \quad \Delta U = n C_p \Delta T - n R \Delta T.$$

\* for Bomb Calorimeter,  $\Delta U_{sys} + Q_{water} = 0$

$$n C_v \Delta T_{sys} = -m C_{water} \Delta T_{water}$$

\* for Adiabatic Process,  $PV^\gamma = \text{const.}$      $TV^{\gamma-1} = \text{const.}$   
 $T^\gamma P^{1-\gamma} = \text{const.}$

$$* \Delta H = \Delta U + P \Delta V \quad | \quad Q_p = \Delta U + P \Delta V$$

$$\Delta H = \Delta U + (\Delta n_g) RT$$

$$* S = \int \frac{dq_{rev}}{T} \quad ; \quad \Delta S = n C_v \ln \frac{T_2}{T_1} + n R \ln \frac{V_2}{V_1}$$

$$\Delta S = n C_p \ln \frac{T_2}{T_1} + n R \ln \frac{P_1}{P_2}.$$

$$* \Delta G_{sys} = \Delta H_{sys} - T \Delta S_{sys}.$$

\*  $dG = V dp - S dT$  (reversible change in pressure & temperature).

$$dG = nRT \ln \frac{V_1}{V_2} = nRT \ln \frac{P_2}{P_1} \quad (\text{for isothermal process}).$$