THERMODYNAMICS

ISHITA KANODIA

1. Thermodynamics deals with macroscopic models but not with microscopic models.
2. Universe = system + surroundings

→ boundaries - 1) diathermic ⇒ conducting
2) adiabatic ⇒ non-conducting

3. Types of systems -
1) Open system ⇒ system can exchange matter and energy with surroundings.
2) Closed system ⇒ only energy can be exchanged (not matter)
3) Isolated system ⇒ neither matter nor energy can be exchanged.

4. State function ⇒ variables which depend only on initial and final state of system and do not depend on path/mechanism followed.
Eg - E, H, S, G, T, etc.
Path function ⇒ properties which depend on initial and final state of system and the path/mechanism followed.
Eg - Work done (w), heat (q).

5. Intensive Properties ⇒ properties which are independent of quantity (size/mass).
Eg - molar volume, molar mass, temperature, pressure, Specific heat, concentration terms, density, pH.
Extensive Properties ⇒ dependent on quantity (size / mass)
Eg - volume, mass, number of moles, G, H, S, U, C (C = heat capacity).

→ ratio of two extensive properties = intensive property
Eg - $d = \frac{m}{V}$.

→ Extensive property can be converted into intensive property when it is defined for unit amount of the substance.
→ Intensive properties are non-additive.
Extensive properties are additive.

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Most stable element for STP

C graphite P_4 (white) Br_2 (l)
S_8 (rhombic) O_2(g) H_2(g) M(s) [Hg (l)]

6. **Heat (q)**

Heat given to the system = +ve
Heat taken out from the system = -ve

7. $W = -P(\Delta V)$ $(\Delta V = V_2 - V_1)$

Expansion ⇒ w = -ve ⇒ work done by the system
Compression ⇒ W = +ve ⇒ work done on the system.

8. **Internal Energy (U/E)** ⇒ depends only on temperature.

9. $\boxed{\Delta U = q + w}$ ⇒ FLOT. (Robert Mayer and Helmholtz).

Isobaric (P = constant)

$\boxed{q_p = \Delta H}$ ⇒ heat becomes a state function

$\boxed{\Delta H = \Delta U + P\Delta V}$

Isochoric ($\Delta V = 0$)

$\boxed{W = 0}$

$\boxed{q_V = \Delta U}$

Irreversible Process (P_{ext} = constant)

$\boxed{W = -P_{ext}(\Delta V)}$

Isothermal (T = constant)

$\Delta T = 0 \Rightarrow \boxed{\Delta U = 0}$

$\boxed{q_T = -w}$

Adiabatic ($q = 0$)

$\boxed{\Delta U = W}$

Cyclic Process

all state function = constant.
$\Delta U, \Delta P, \Delta T, \Delta V = 0$
$\therefore W = 0$
$\therefore q = 0.$

Reversible Process ⇒ Maximum work is obtained.
⇒ Completed in infinite no. of steps.

For Isothermal reversible process -

$$W = -\int_{V_1}^{V_2} P\,dV = -\int_{V_1}^{V_2} \frac{nRT}{V}\,dV = -nRT \ln \frac{V_2}{V_1}.$$

$PV = nRT$
$\therefore P = \frac{nRT}{V}$

$$\boxed{W = -2.303\, nRT \log \frac{V_2}{V_1} = -2.303\, nRT \log \frac{P_1}{P_2}}$$

9a. Heat Capacity (C) ⇒ amount of heat required to raise the temp. of the substance by 1°C. $\boxed{C = \frac{q}{\Delta T}}$

Molar Heat Capacity (c) ⇒ amount of heat required to raise the temp. of one mole of substance by 1°C. $c = \frac{q}{n\Delta T}$.

$C_p = \frac{q_p}{n\Delta T} = \frac{\Delta H}{n\Delta T}$ $\quad C_v = \frac{q_v}{n\Delta T} = \frac{\Delta U}{n\Delta T}$.

$\therefore \boxed{\Delta H = n C_p \Delta T}$
$\boxed{\Delta U = n C_v \Delta T.}$

→ For physical process – $\boxed{C_p = C_v + R}$ ⇒ Mayer's formula. $\boxed{C_p = C_v + nR}$

For chemical reaction –

$P\Delta V = \Delta n_g RT = -W.$

$\therefore \boxed{\Delta H = \Delta U + \Delta n_g RT} \Rightarrow \boxed{q_p = q_v + \Delta n_g RT}$.

→ $\boxed{\gamma = \frac{C_p}{C_v}}$ ⇒ Poisson's ratio.

II: Work done in different processes

Isobaric $\quad W = -P_{ext}(\Delta V)$

Isochoric $\quad W = 0.$

Isothermal (Reversible)

$W = -2.303\, nRT \log \frac{V_2}{V_1}$

$= -2.303\, nRT \log \frac{P_1}{P_2}$.

Free expansion ($\Delta V = 0$)

$\therefore W = 0.$

Adiabatic process ($\Delta U = W$) ⇒ $nC_v\Delta T = W.$

$\boxed{C_p = \frac{R\gamma}{\gamma - 1}}$ $\quad \boxed{C_v = \frac{R}{\gamma - 1}}$ $\quad \therefore \boxed{W = \frac{nR(T_2 - T_1)}{\gamma - 1}}$

$\boxed{W = \frac{P_2V_2 - P_1V_1}{\gamma - 1}}$

12. $\boxed{\Delta S = \frac{q_{rev}}{T}}$ ⇒ for reversible isothermal reaction.

→ $\boxed{\Delta S = nC_V \ln\frac{T_2}{T_1} + nR\ln\frac{V_2}{V_1} = nC_p \ln\frac{T_2}{T_1} + nR\ln\frac{P_1}{P_2}}$

Isothermal · $\Delta S = nR\ln\frac{V_2}{V_1}$ Isobaric - $\Delta S = nC_p \ln\frac{T_2}{T_1}$

Isochoric $\Delta S = nC_V \ln\frac{T_2}{T_1}$

Entropy of the universe is constantly increasing SLOT

→ $\Delta n_g = +ve \Rightarrow \Delta S = +ve \Rightarrow$ spontaneous
$\Delta n_g = -ve \Rightarrow \Delta S = -ve \Rightarrow$ non-spontaneous
$\Delta n_g = 0 \Rightarrow \Delta S = 0 \Rightarrow$ equilibrium.

→ In adiabatic process - $q_V = 0 \Rightarrow \Delta S = 0$
∴ isoentropic process.

13. Gibbs Free Energy (G) - $\boxed{\Delta G = \Delta H - T\Delta S}$.

→ $\Delta H = +ve \Rightarrow$ endothermic
$\Delta H = -ve \Rightarrow$ exothermic.

$\Delta G = -ve \Rightarrow$ spontaneous
$\Delta G = +ve \Rightarrow$ non-spontaneous
$\Delta G = 0 \Rightarrow$ equilibrium.

→ $W_{useful} = -\Delta G$.
$\Delta G_{system} = -T\Delta S_{Total}$.

→ $\boxed{\Delta G = \Delta G^\circ + RT\ln Q}$ (ΔG° = standard gibbs free energy).

At equilibrium - $\Delta G = 0$ $Q = K_c$.
⇒ $\boxed{\Delta G^\circ = -RT\ln K_c}$

$\boxed{K_{eqm} = e^{-\Delta G^\circ/RT}}$. $\boxed{\Delta G^\circ = -nFE^\circ}$

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Third Law of Thermodynamics

→ At absolute zero (0K) temp., entropy of perfectly crystalline substances becomes 0. That means all kinds of molecular movement ceases.
(but no substance is perfectly crystaline).

Thermochemistry

1. $\Delta H_R = \Sigma H_p - \Sigma H_R$. // $\Delta H = +ve \Rightarrow$ endo
$\Delta H = -ve \Rightarrow$ exo.

Different Types of Heat of Reaction (ΔH_R)

① **Heat of Formation (ΔH_f)** → one mole of product is formed from its constituent elements (in the most stable form).

$\Delta H_f = {}_p\Sigma H_f - {}_r\Sigma H_f$.

lesser the $\Delta H_f \Rightarrow$ greater stability of the compound.

② **Heat of combustion (ΔH_c)** ⇒ amount of heat released when one mole of substance is burnt completely.

Calorific value (CV) = $\frac{\Delta H_c}{\text{molecular mass}}$

↑ CV ⇒ ↑ efficiency of fuel.

③ **Heat of Neutralisation (ΔH_n)** ⇒ amount of energy released when one equivalent of acid completely neutralises one eq. of base.

For 1 eq. of SA – SB $\boxed{\Delta H_n = -13.7 \text{ Kcal/eq.}} = -57.2 \text{ KJ/eq.}$

Except – When HF reacts with any strong base.

$|\Delta H_n| > 13.7$ ⇒ due to high hydration energy of F^-.

$\Delta H_n = -16.7$ Kcal/eq.

④ **Heat of Fusion (ΔH_{fus})** ⇒ amount of heat absorbed when one mole of solid completely converts into liquid.

⑤ **Heat of Vaporisation (ΔH_{vap})** ⇒ amount of heat absorbed when 1 mole of liquid completely converts into gas.

(6) Heat of Sublimation (ΔH_{sub}) ⇒ amount of heat absorbed when 1 mole of solid completely converts to gas.

$$\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap.}$$ ⇒ Hess law

(7) Heat of Hydrogenation (HOH) ⇒ amount of heat released when one mole of unsaturated compound converts into saturated compound.

(8) Heat of Crystallisation / Hydration (ΔH_{hyd}) ⇒ amount of energy released when 1 mole of anhydrous salt converts into crystal (hydrated).

(9) Heat of solution (ΔH_{sol}) ⇒ amount of energy released when 1 mole of salt is completely dissolved in the solvent until there is no change in heat.

(10) Heat of Atomisation (ΔH_{atom}) ⇒ amount of heat required to dissociate 1 mole of gaseous molecules into atoms.

(11) Bond Dissociation Energy (BDE) ⇒ amount of energy required to break one mole of bonds.

$$BDE = \sum_{R} BDE - \sum_{P} BDE.$$

Heat of formation of pure element in its most stable form = 0.

→ Laplace and Lavoisier Law ⇒
Enthalpy of formation of compound is numerically equal to the enthalpy of decomposition of that compound with opposite sign.