Thermodynamics Processes

System

Open   Closed   Isolated

Earth   Universe

Macroscopic System

System with Large number of particle

Thermodynamic process

Isothermal process — Temperature remains constant, dT = 0

Isobaric process — Pressure remains constant, dP = 0

Isochoric process — Volume remains constant, dV = 0

Adiabatic process — Heat absorption or emission = 0, dQ = 0
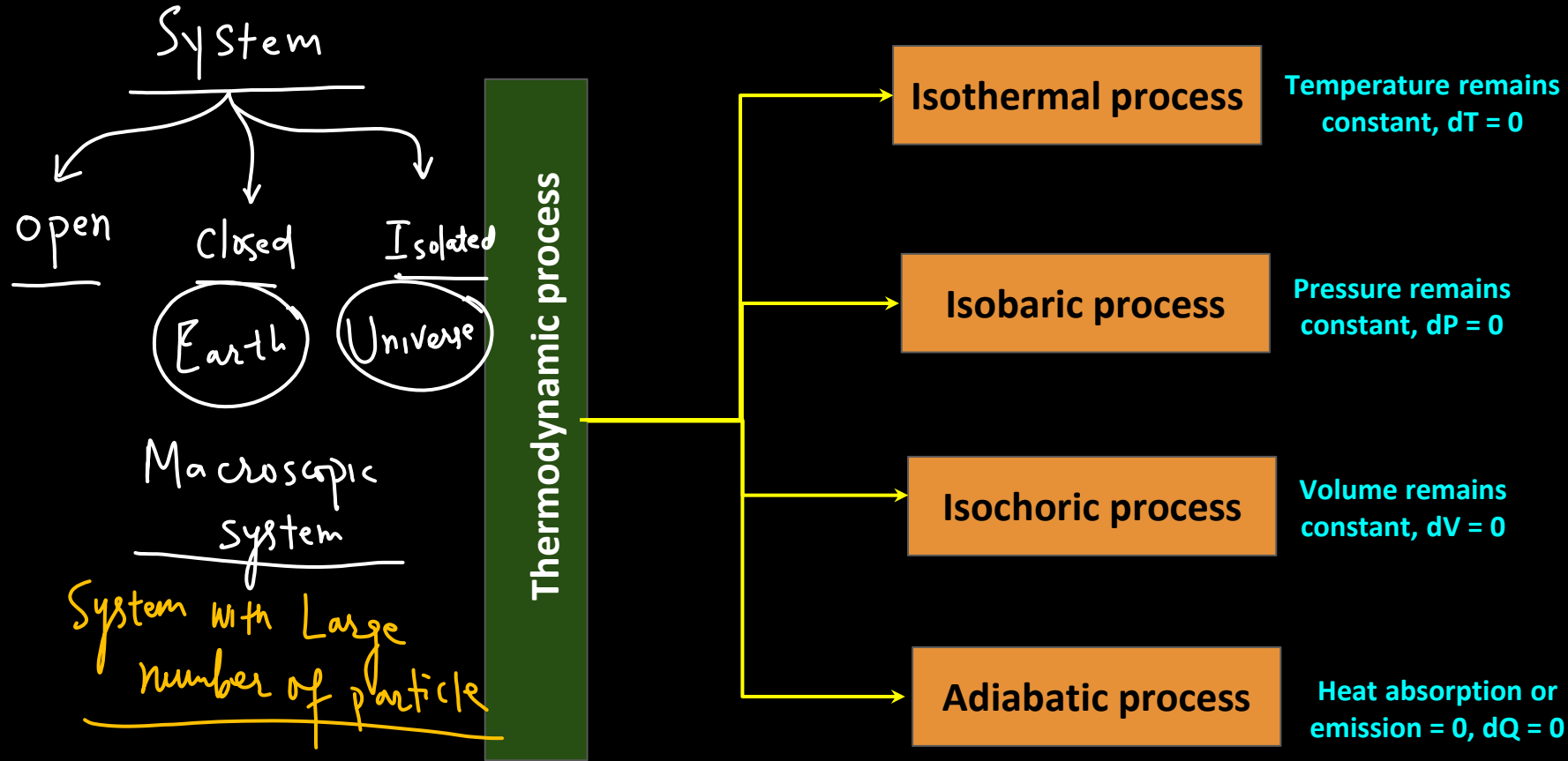
Intensive property
(Independent of mass of the system)

1. Pressure
2. Temperature
3. Density
4. Concentration
5. Surface tension
6. Viscosity, etc

Extensive property
(depends on mass of the system)

1. mass
2. Volume
3. Internal energy
4. Heat capacity
5. Enthalpy
6. Entropy
7. Gibbs energy, etc

ΔH_m
ΔG_m
ΔS_m

$* \dfrac{Energy}{mole}$

$*$ All types of Concentration

$$Intensive = \dfrac{Extensive}{Extensive}$$

$\dfrac{C_m}{Intensive}$

Heat Capacity

extensive

Specific Heat Capacity

Heat Capacity per unit volume

KFC

must be
defined at each
point of the System

ΔH_m

ΔG_m

ΔS_m

ΔP

ΔV

ΔT

State function:

If the value of a physical quantity depends only upon the state of the system and does not depend upon the path by which this state has been attained.

→ 7 State

Examples :
Pressure, volume, temperature, internal energy, entropy, free energy.

Enthalpy

Path Function:

Quantities which are dependent on the path/way the system has achieved a particular state

Examples :
Heat, work, Heat capacities(Molar heat capacities, specific heat capacities etc
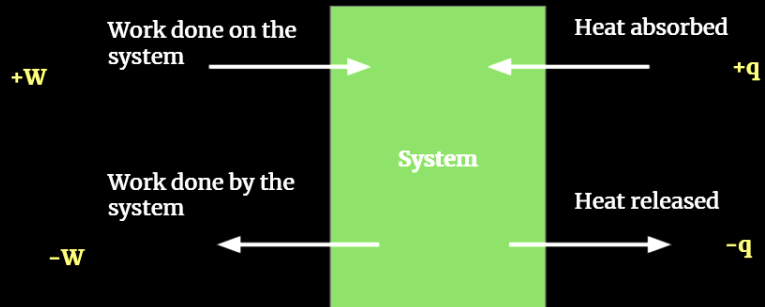
$\Delta q, \Delta w$
Δc

q, W, c

$$W = - \int_{V_1}^{V_2} P_{ext} \, dV$$

$$\Downarrow$$

$$W_{exp} = -ve$$

$$W_{comp} = +ve$$

Sign Convention

❑ **Heat supplied to the system is +ve i.e, q > 0**

❑ **Heat given out by the system is -ve i.e, q < 0**

❑ **Work done on the system (compression) is +ve i.e, W > 0**

❑ **Work done by the system (expansion) is -ve i.e, W < 0**

Work done on the system   Heat absorbed

+W   +q

System

Work done by the system   Heat released

-W   -q

$$\Delta U = Q + w$$

Calculate of heat (q) :

Total heat capacity :

$$C_T = \frac{\Delta q}{\Delta T} = \frac{dq}{dT} = J/^\circ C$$
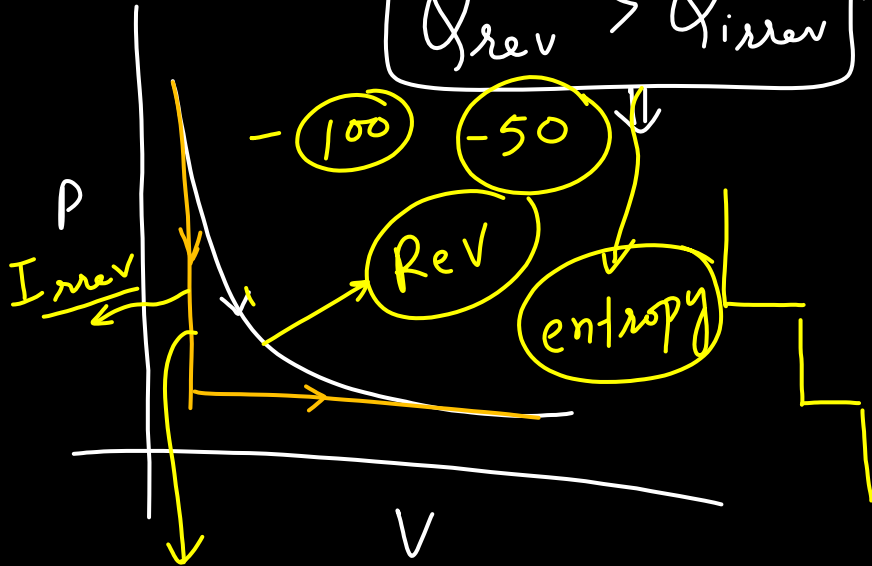
Molar heat capacity :

$$C = \frac{\Delta q}{n\Delta T} = \frac{dq}{ndT} = J mole^{-1} K^{-1}$$

$$C_p = \frac{\gamma R}{\gamma - 1} \qquad C_V = \frac{R}{\gamma - 1}$$

Specific heat capacity (s) :

$$S = \frac{\Delta q}{m\Delta T} = \frac{dq}{mdT} = J\ gm^{-1} K^{-1}$$

KFi

$$W_{rev} < W_{irrev}$$

$$Q_{rev} > Q_{irrev}$$

-100 -50

Rev

entropy

P

Irrev

V

Sudden chye in P $\rightarrow$ Sudden in V

First law of thermodynamics

➢ **Energy can neither be created nor be destroyed , it can simply be converted from one form to another.**

➢ **Internal energy of system remains constant unless energy is transferred from surrounding in the form of heat or work.**

❏ $\Delta U = q + W$

$$\Delta H = \Delta(U + PV)$$

$$= \Delta U + \Delta(PV)$$

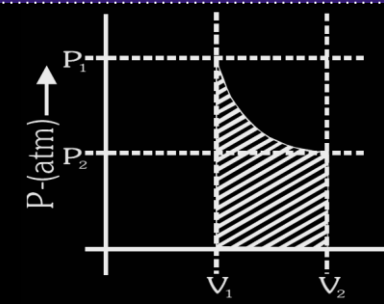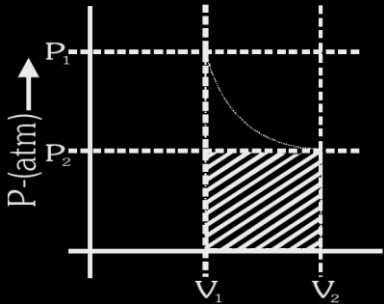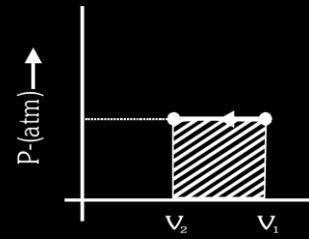Ideal

$$PV = nRT$$

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

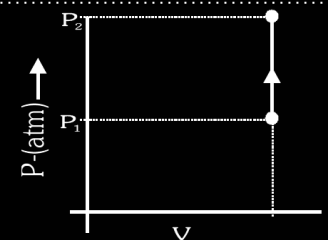$$\Delta H = \Delta U + \Delta n_g RT$$

Reaction

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

$\hookrightarrow$ one gas

Maha Misconcept~

$$\Delta H = n C_{pm} \Delta T$$

Real

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

- **Enthalpy of a system is defined as**

  H = U + PV

  $$\Delta U = n C_{vm} \Delta T$$

  So dH = dU + d(PV)

- **At constant pressure P, we have heat capacity**

  q_P = n $C_P\Delta T$

  This value is equal to the change in enthalpy, that is,

  q_P = n $C_P\Delta T$ = ΔH

- **Similarly, at constant volume V, we have**

  q_V = n $C_V\Delta T$

  This value is equal to the change in internal energy,

  q_V = n $C_V\Delta T$ = ΔU
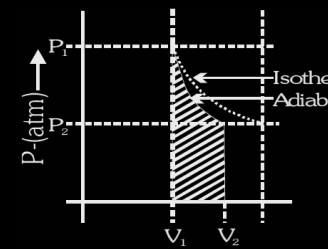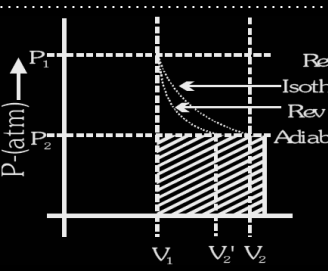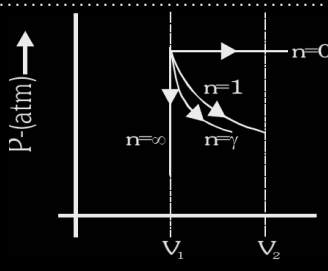
Graph ke
Qstn mein
Bahot
useful.

Process	Expansion for w	Expansion for q	ΔU	ΔH	Work on PV-graph
Reversible isothermal process	$w = -nRT \ln \dfrac{V_2}{V_1}$ $= -nRT \ln \dfrac{P_1}{P_2}$	$q = nRT \ln\left(\dfrac{V_2}{V_1}\right)$ $q = nRT \ln\left(\dfrac{P_1}{P_2}\right)$	0	0	
Irreversible isothermal process	$w = -P_{ext}(V_2 - V_1)$ $= -P_{ext}\left(\dfrac{nRT}{P_2} - \dfrac{nRT}{P_1}\right)$	$q = P_{ext}(V_2-V_1)$	0	0	
Isobaric process	$w = -P_{ext}(V_2-V_1)$ $= -nR\Delta T$	$q = \Delta H = nC_p\Delta T$	$\Delta U = nC_V\Delta T$	$\Delta H = nC_p\Delta T$	

Handwritten annotations:

$P_{ext} \cong P_{int}$

$P_{ext} = P_{int} \pm \boxed{dP}$

$P_{ext} \neq P_{int}$

$KFL \quad P_2 \cong P_{ext}$

Process	w	q	ΔU	ΔH	
Isochoric process	w = 0	q = ΔU = $nC_V\Delta T$	$\Delta U = nC_V\Delta T$	$\Delta H = nC_p\Delta T$	
Reversible adiabatic process	$w = nC_v(T_2 - T_1)$ $= \dfrac{P_2V_2 - P_1V_1}{\gamma-1}$	q = 0 PV^γ =constant $TV^{\gamma-1}$ =constant $TP^{1-\gamma/\gamma}$ = constant	$\Delta U = nC_V\Delta T$	$\Delta H = nC_p\Delta T$	
Irreversible adiabatic process	$w = \dfrac{nC_v(T_2 - T_1)}{P_2V_2 - P_1V_1}$ $\dfrac{}{\gamma-1}$				
Polytropic process	$w = \dfrac{P_2V_2 - P_1V_1}{n-1}$ $w = \dfrac{R(T_2 - T_1)}{n-1}$	$q = \displaystyle\int_{T_1}^{T_2} C_V dT$ $+ \displaystyle\int_{T_1}^{T_2} \dfrac{R}{1-n} dT$	$\Delta U = nC_V\Delta T$	$\Delta H = nC_p\Delta T$	

Handwritten annotations:

only for Ideal gas

$PV^{\gamma} = Constant$

$TV^{\gamma-1} = Const \, t$

$\boxed{T_2}$ find Karo

$C_p - C_v = nR$

$C_{p,m} - C_{v,m} = R$ } only for Ideal gas

$T_2 = \curvearrowright$

$\overbrace{PV^{\gamma} = Const}$

Free expansion (Always Irreversible) $\equiv$ $P_{ext} \equiv 0$

Entropy

Measure of the randomness (disorder) of a system.

Isothermal

$$\Delta T = 0$$
$$\Delta U = 0$$
$$\Delta H = 0$$
$$W = 0$$
$$\Delta U = Q + W$$
$$0 = Q + 0$$
$$Q = 0$$

Adiabatic
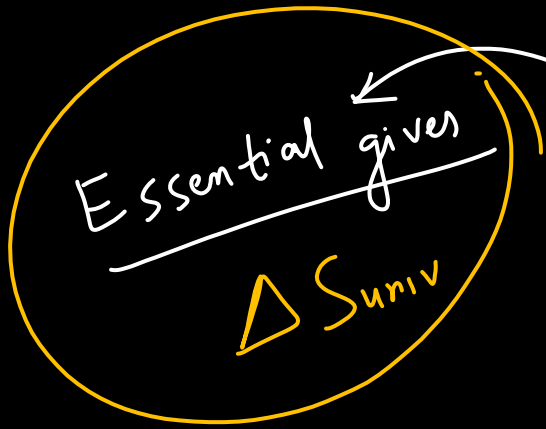
$$Q = 0$$
$$P_{ext} = 0$$
$$W = 0$$
$$\Delta U = 0$$
$$\Delta T = 0$$
$$\Delta H = 0$$

$$\int dS = \frac{1}{T} \int \delta q_{rev}$$

$$\Delta S_r = \frac{q_{rev}}{T}$$

$$C = \frac{\Delta q}{\Delta T}$$

Essential gives ΔS_{univ}

Second law of thermodynamics

➢ **The entropy of an isolated system / Universe always tends to increase in a spontaneous process the entropy of the Universe increases.**
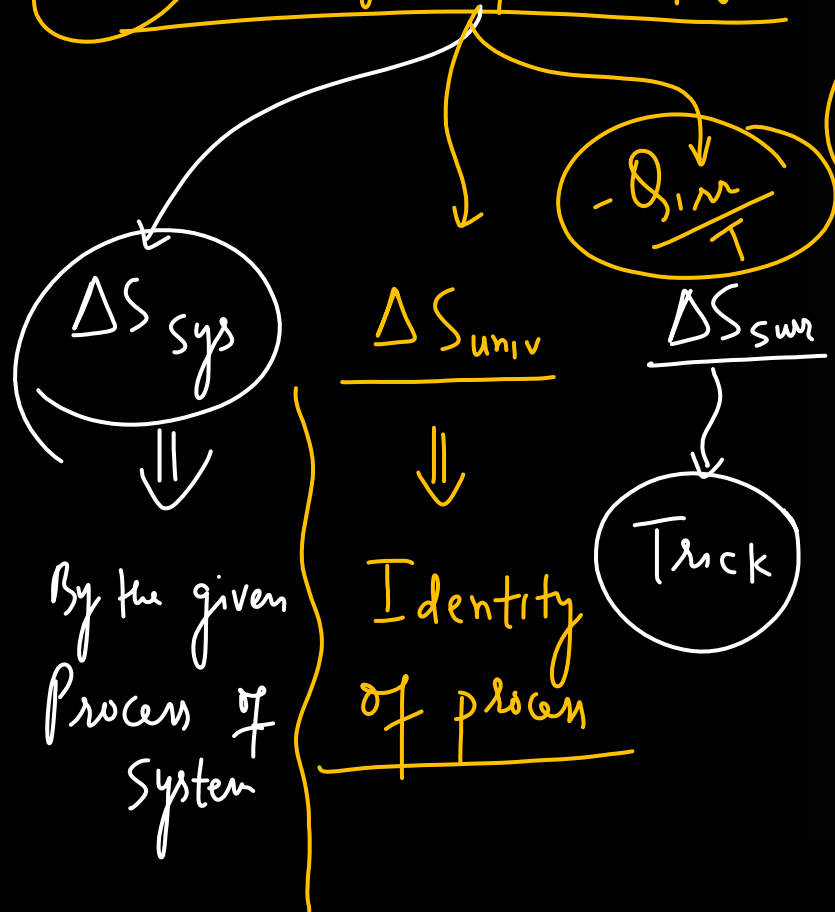
For a spontaneous/irreversible process:

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} > 0$$

For a reversible process:

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} = 0$$

(KFC) 3 Types of Entropy

Entropy calculation for different processes

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

ΔS_{sys}

$-\frac{Q_{svr}}{T}$

ΔS_{sys}

ΔS_{univ}

ΔS_{svr}

$\Downarrow$

By the given Process of System

$\Downarrow$

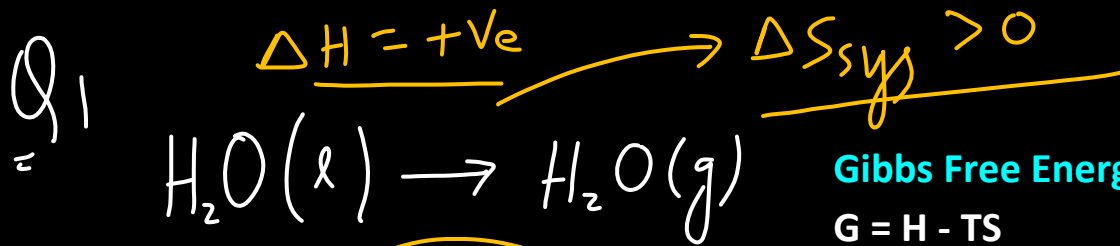Identity of process

$\Downarrow$

Trick

For isothermal process ($T_2 = T_1$)

$$\Delta S_{sys} = nR \ln \frac{V_2}{V_1}$$

For isochoric process ($V_2 = V_1$)

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

For isobaric process ($q = nC_p dT$)

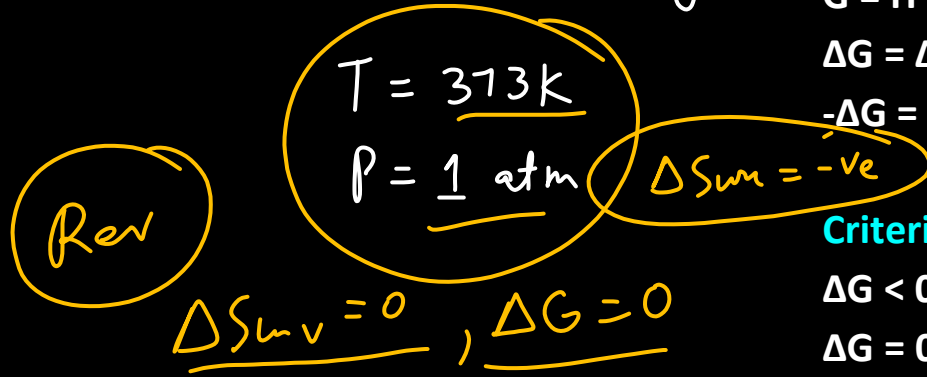$$\Delta S_{sys} = nC_p \ln \left(\frac{T_2}{T_1}\right)$$

Vedantu

Q_1

$\Delta H = +ve \longrightarrow \Delta S_{sys} > 0$

$H_2O\,(\ell) \longrightarrow H_2O\,(g)$

Gibbs Free Energy (G)

G = H - TS

ΔG = ΔH - TΔS (at constant temperature)

-ΔG = useful work done by the system

$T = 373K$

$P = \underline{1}\ atm$
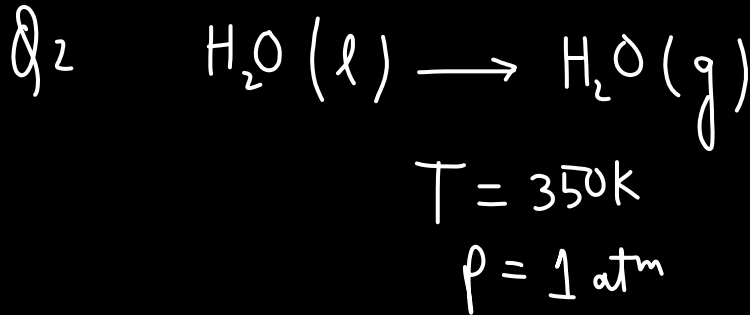
$\Delta S_{um} = -ve$

Rev

$\Delta S_{unv} = 0$, $\Delta G = 0$

Criteria for spontaneity

ΔG < 0: Process is spontaneous

ΔG = 0: Process is at equilibrium

ΔG > 0: Process is non spontaneous

$Q_2 \qquad H_2O\,(\ell) \longrightarrow H_2O\,(g)$

$T = 350K$

$P = 1\ atm$

Role of temperature on spontaneity

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

$$G = H - TS$$

$$\Delta G = \Delta H - \Delta(TS)$$

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

Sign of ΔH, ΔG and ΔS and prediction of spontaneity

ΔH	ΔS	ΔG	Remarks
-ve	+ve	-ve	Spontaneous at all temperatures
-ve	-ve	-ve (at low temperature) +ve (at high temperature)	Spontaneous Non-spontaneous
+ve	+ve	+ve (at low temperature) -ve (at high temperature)	Non-spontaneous Spontaneous
+ve	-ve	+ve	Non-spontaneous at all temperatures

Standard Free Energy Change (ΔG°)

1. $\Delta G° = -2.303\ RT\ \log_{10}K$

2.   At equilibrium $\Delta G = 0$.

3. $\Delta G_f°$ for elemental state = 0

4. $\Delta G_f° = G°_{products} - G°_{Reactants}$

Reaction enthalpy

$\Delta_r H$ = (sum of enthalpies of products) − (sum of enthalpies of reactants)

If all substances are in their standard state, the enthalpy change is called standard enthalpy of reaction. $\Delta_r H°$

Enthalpy of phase change

The amount of heat absorbed/released when one mole of a substance changes its state under standard conditions.

$\Delta_{vap} H$ = when one mole liquid converts to vapour.

$\Delta_{fus} H$ = when one mole solid converts to liquid.

$\Delta_{sub} H$ = when one mole solid converts to vapour.

Different types of enthalpies of reaction /process

Enthalpy of atomisation	When 1 mole of the substance is converted into its atoms in gaseous state.
Lattice Enthalpy	When one mole of ionic substance is converted into ions in gaseous state.
Enthalpy of hydration	When one mole of an ion is hydrated.
Enthalpy of solution	When one mole of a substance dissolves in a specific amount of solvent.
Enthalpy of Transition	When one mole of an allotropic forms convert into another allotropic form.

Hess's law $\boxed{\Delta H_{rk^n}} = \Delta H_1 + \Delta H_2 + \Delta H_3 + \ldots$

Different types of enthalpies of reaction /process

Bond dissociation enthalpy	When 1 mole of the bonds are broken from substance in gaseous state.
Resonance Energy	Extra energy released due to the resonance stabilisation per mole

$$\Delta H_{reaction} = \sum B.E (Reactts) + \sum B.E (Prdcts)$$

$$= \sum \Delta H_f (Prdc) - \sum \Delta H_f (React)$$

$$= \sum \Delta H_c (R) - \sum \Delta H_c (P)$$