

THERMODYNAMICS

DEFINITION:

Thermodynamics deals with energy interaction b/w two bodies & its effect on the properties of matter.

Scope of thermodynamics:

- **Feasibility of a process**
- **Extent of a process**
- **Efficiency of a process**

TERMS USED IN THERMODYNAMICS

System + Boundary + Surrounding = Universe

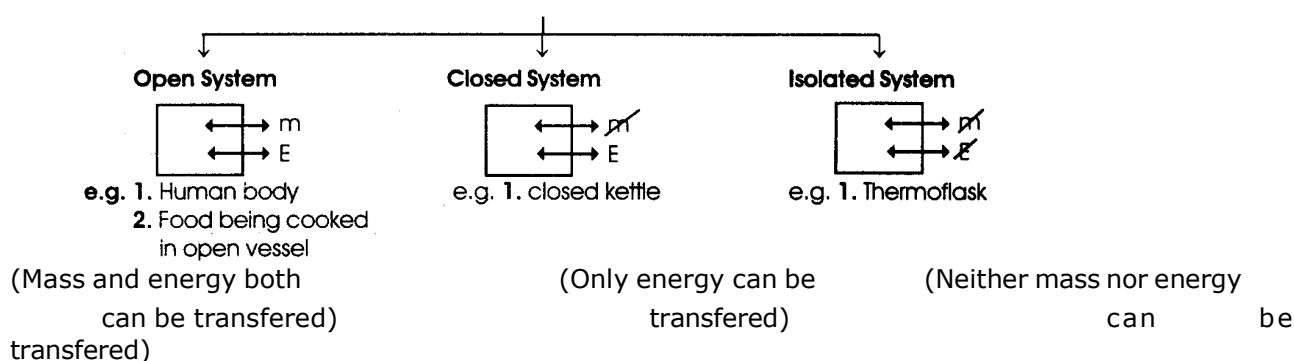
SYSTEM : The part of the universe under thermodynamical observation is called system.

SURROUNDINGS : All the part of the universe excepting system is called surroundings.

BOUNDARY : The part which separates system and surroundings is called boundary it may be rigid or flexible.

It may be diathermic (Heat can be exchanged) or adiabatic

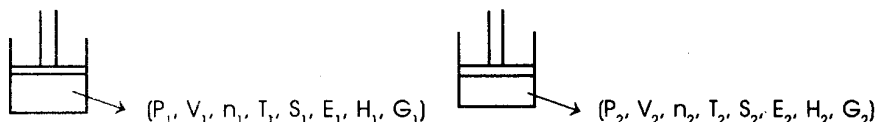
Types of Systems



STATE VARIABLES

State or condition of a system is described by certain measurable properties & these measurable properties are called state variables. e.g. mass, temperature, volume, pressure etc.

STATE FUNCTION



State function depends only on initial & final state of the system. It does not depend on the path or how process was carried out.

e.g. $\Delta U = \int_i^f du$ Where $\Delta U = u_f - u_i$

$$\int_i^f dT = \Delta T = T_f - T_i$$

Sol. The parameters which are required to completely define the state of the system are called **state functions**.

State functions are path independent function.

Process-1 $\Rightarrow \Delta P = \Delta P \Leftarrow$ **Process - II**

$$\Delta V = \Delta V$$

$$\Delta n = \Delta n$$

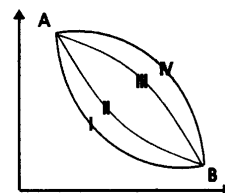
$$\Delta T = \Delta T$$

$$\Delta E = \Delta E$$

$$\Delta H = \Delta H$$

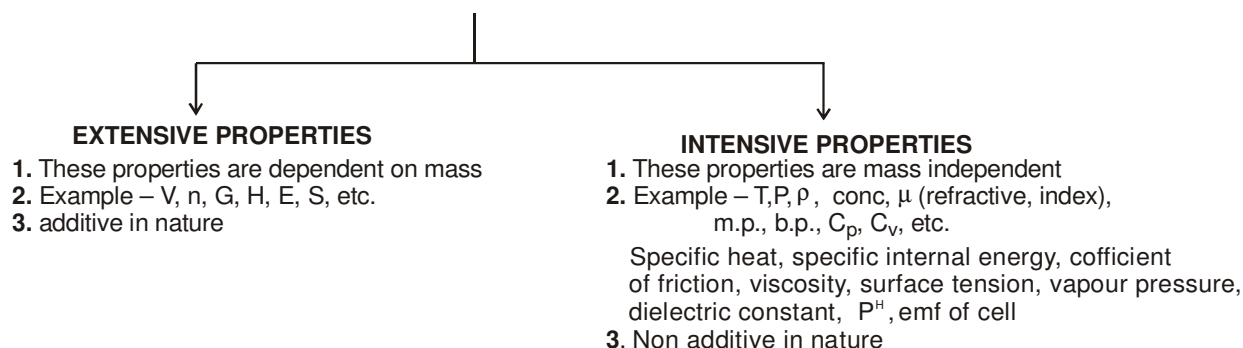
$$\Delta G = \Delta G$$

$$\Delta S = \Delta S$$



- Path independent means the difference in state functions will be same for any path followed between two states.

PHYSICAL PROPERTIES



PATH FUNCTION

Path function depends on the initial as well as final state of a system & also depends on the path of the process. e.g. heat and work.

CONDITION FOR A FUNCTION TO BE STATE FUNCTION

Euler's theorem $f = f(T, V)$. If f is a state function then

$$\frac{\partial}{\partial T} \left[\left(\frac{\partial f}{\partial V} \right)_T \right]_V = \frac{\partial}{\partial V} \left[\left(\frac{\partial f}{\partial T} \right)_V \right]_T$$

$$PV = nRT \quad \Rightarrow P = \frac{nRT}{V}$$

if pressure is a state function then

$$\frac{\partial}{\partial T} \left[\left(\frac{\partial P}{\partial V} \right)_T \right]_V = \frac{\partial}{\partial V} \left[\left(\frac{\partial P}{\partial T} \right)_V \right]_T \Rightarrow \left(\frac{\partial P}{\partial V} \right)_T = \frac{-nRT}{V^2} \Rightarrow \left(\frac{\partial P}{\partial T} \right)_V = \frac{nR}{V}$$

$$\frac{\partial}{\partial T} \left[\frac{-nRT}{V^2} \right]_V = \frac{-nR}{V^2} \Rightarrow \frac{\partial}{\partial V} \left[\left(\frac{\partial P}{\partial T} \right)_V \right]_T = \frac{-nR}{V^2}$$

Hence P is a state function.

e.g. $f(x, y) = ye^x + xy + x \ln y$

Show that $f(x, y)$ is a state function.

Sol. $\left(\frac{\partial f}{\partial x}\right)_y = ye^x + y + \ln y$ $\left(\frac{\partial f}{\partial y}\right)_x = e^x + x + x \cdot \frac{1}{y}$

$$\frac{\partial}{\partial x} \left[\left(\frac{\partial f}{\partial y} \right)_x \right]_y = \frac{\partial}{\partial x} [e^x + x + x/y]_y = e^x + 1 + \frac{1}{y}$$

$$\frac{\partial}{\partial y} \left[\left(\frac{\partial f}{\partial x} \right)_y \right]_x = \frac{\partial}{\partial y} [ye^x + y + \ln y]_x$$

$$= e^x + 1 + \frac{1}{y}$$

Hence $f(x, y)$ is a state function.

Two other important result from differential calculus will be used frequently.

Consider a function. $z = f(x, y)$. which can be rearranged $x = g(y, z)$ or $y = h(x, z)$

For example, $PV = nRT$, $P = \frac{nRT}{V}$, $T = \frac{PV}{nR}$

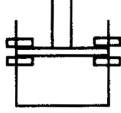
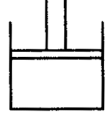
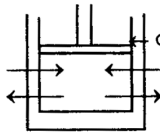
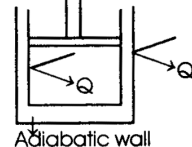
in this case

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z}$$

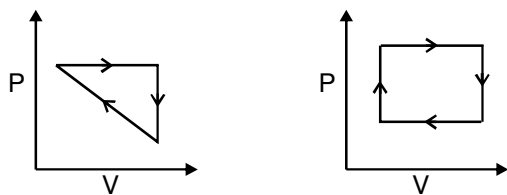
The cyclic rule will also be used.

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

THERMODYNAMIC PROCESSES

| | PROCESS | SPECIAL CONDITION | CONSTRAINTS |
|------|--------------------|---|--|
| (1). | Isochoric process | $V = \text{constant}$, $\Delta V = 0$ |  Piston is not allowed to move |
| (2). | Isobaric process | $P = \text{constant}$, $\Delta P = 0$ |  Piston is free to move |
| (3). | Isothermal process | $T = \text{constant}$, $\Delta T = 0$ |  diathermal wall |
| (4). | Adiabatic process | $Q = \text{neither enters nor leaves the system}$ |  Adiabatic wall |

(5) Cyclic Process: System undergoes series of changes & ultimately comes back to initial state.



REVERSIBLE & IRREVERSIBLE PROCESS

(1) Quasi-Static(Reversible)Process: If system & surrounding can restore their original state by reversing the direction of the process then process is called reversible process. In reversible process, there is no loss of energy.

These are slow process as it takes infinite time. System & surrounding are always in equilibrium. Reversible process is a theoretical process. Reversible process is most efficient with respect to work.

In reversible process $P_{\text{ext}} = P_{\text{int}}$

If all the above criteria are not fulfilled by any process, then it is known as irreversible process.

* irreversible process is a fast process. It takes definite time for completion

* **In irreversible process $P_{\text{ext}} \neq P_{\text{int}}$.**

*It is an actual process. It is carried out in multiple stages and it tends towards reversible process.



HEAT AND WORK

Heat & work both are forms of energy. Both are boundary phenomena and take place at the interface of the system & surroundings.

Work ———— Mechanical work $\Rightarrow F \cdot d$
 Electrical work $\Rightarrow v \cdot i \cdot t$
 Gravitational work $\Rightarrow mgh$

SIGN CONVENTION OF HEAT & WORKDONE

Expansion $\longrightarrow W \Rightarrow -ve$

Compression $\Rightarrow W \Rightarrow +ve$

Heat given to the system $\Rightarrow +ve$

Heat loss (it released) $\Rightarrow -ve$

Types of equilibrium

- (1) Thermal equilibrium \longrightarrow Equality of temperature
- (2) Mechanical equilibrium \longrightarrow Equality of pressure
- (3) Material equilibrium \Rightarrow no. of moles constant

When all the three equilibrium are established in a system, system is in true thermodynamics equilibrium

• **For Isobaric Process :**

$$Q = nC_p\Delta T \quad \text{and} \quad Q = \Delta H$$

$$\Delta H = nC_p\Delta T = \frac{n\gamma R\Delta T}{(\gamma - 1)}$$

For isochoric process

$$Q = nC_v\Delta T \quad \text{and} \quad Q = \Delta E$$

$$\Delta E = nC_v\Delta T = \frac{nR\Delta T}{\gamma - 1}$$

For liquid and solids

$$C_p \simeq C_v$$

$$U = \frac{f}{2}nRT$$

$$\Delta U = \frac{f}{2}RT\Delta n_g$$

$$\Delta n_g C_v T = \frac{f}{2}RT\Delta n_g$$

$$C_v = \frac{f}{2}R$$

Total degree of freedom = $3n$

where n = no of atoms

for vibrational $u = f nRT$

$$C_{v \text{ vibrational}} = f_{\text{vibrational}} \cdot R$$

$$\text{Total} \quad C_v = \left(\frac{f_{\text{trans}}}{2} + \frac{f_{\text{rotate}}}{2} + f_{\text{vibrational}} \right) \cdot R$$

LAW OF THERMODYNAMICS

(1) ZEROth LAW

Based on thermal equilibrium if A & B, & B & C are in thermal equilibrium then A & C must be in thermal equilibrium.

(2) FIRST LAW OF THERMODYNAMICS

First law of thermodynamics is based on energy conservation

$$\begin{aligned} E_2 &= E_1 + q + w & (E_1 \text{ is the } E_i) \\ E_2 - E_1 &= q + w & (E_1 + q + w \text{ is } E_f) \\ & & (E_i = E_f) \end{aligned}$$

$$\Delta E = q + w$$

or

$$\Delta U = q + w$$

For an isolated system, $q = 0$, $w = 0$

$$\Delta U = 0$$

$$\text{or} \quad U = \text{constant}$$

For cyclic process.

$$\oint du = 0$$

$$\Rightarrow \oint (dq + dw) = 0$$

$$\Rightarrow \boxed{q + w = 0}$$

Work done = $-F_{\text{ext}} \cdot dx$

$$= -P \cdot A \cdot dx$$

$$\boxed{dW = -P_{\text{ext}} dV}$$

for expansion $\rightarrow dW = -ve$

compression $\rightarrow dW = +ve$

$$dq = CdT \Rightarrow dq_v = C_v dT$$

$$C_v = \frac{dq_v}{dT} = \frac{q_v}{\Delta T}$$

For an isochoric process $dv = 0$

$$dU = q_v \Rightarrow \boxed{dU = C_v dT}$$

$$dU = n C_v dT$$

$$\boxed{\Delta U = n C_v (T_2 - T_1)}$$

If C_v is a function of temperature

$$\Delta U = n \int_{T_1}^{T_2} C_v dT$$

We know that

$$U = f(T, V, P)$$

consider

$$U = f(T, V)$$

$$du = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial u}{\partial v} \right)_T dv$$

For isochoric process $dv = 0$

$$dU = \left(\frac{\partial u}{\partial T} \right)_V dT$$

for 1 mole of gas

$$C_v dT = \left(\frac{\partial U}{\partial T} \right)_V dT$$

$$C_v = \left(\frac{\partial u}{\partial T} \right)_V \Rightarrow \boxed{du = C_v dT}$$

For an ideal gas $U = f(T)$ only

$$\left(\frac{\partial U}{\partial V} \right)_T = 0$$

$$du = C_v dT$$

$$\Delta U = n C_v \Delta T = n C_v (T_2 - T_1)$$

$$\boxed{\Delta U = n C_v \Delta T = n C_v (T_2 - T_1)}$$

ENTHALPY

$$- \quad H = U + PV$$

$$dH = dU + d(PV)$$

$$\int dH = \int dU + P \int dV$$

at constant pressure

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

From, 1st law of thermodynamics at constant pressure.

$$dU = dq_p + dW$$

$$dU = dq_p - PdV$$

$$dq_p = dU + PdV$$

$$dH = dU + PdV$$

$$\Delta H = \Delta U + P\Delta V \quad \text{.....(1)}$$

at constant volume

$$\Delta H = \Delta U + V\Delta P \quad \text{.....(2)}$$

When P & V both changes

$$\Delta H = \Delta U + (P_2V_2 - P_1V_1) \quad \text{.....(3)}$$

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

$$\Delta H = \Delta U + d(nRT)$$

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

For an ideal gas expansion or compression

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

$$\begin{aligned} \Delta H &= nC_v\Delta T + nR\Delta T \\ &= n\Delta T[C_v + R] \end{aligned}$$

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

We know that,

$$H = f(T, P)$$

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

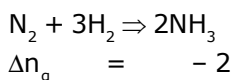
At constant pressure

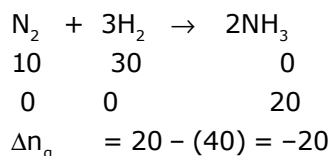
$$dP = 0$$

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT$$

$$C_p = \left(\frac{\partial H}{\partial T}\right)_P$$

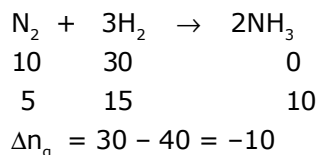
**Calculation of Δn_g for any chemical reaction:





$$\Delta n_g = n_{g(f)} - n_{g(i)}$$

If reaction is 50% completed.



WORKDONE CALCULATION

(1) Isochoric process:

$$V = \text{constant}$$

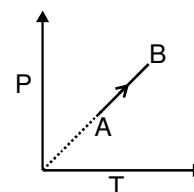
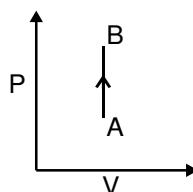
$$dV = 0$$

$$W = 0$$

$$dU = dq_v$$

$$\Delta U = q_v = nC_v\Delta T$$

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



(2) Isobaric process:

$$W = -P_{\text{ext}}(V_2 - V_1)$$

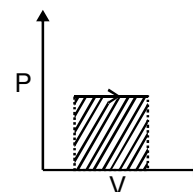
Reversible & isobaric process

$$W = -P(V_2 - V_1)$$

$$= -nR(T_2 - T_1)$$

Irreversible & isobaric process

$$P_1 = P_2 = P_{\text{ext}}$$



For reversible & irreversible isobaric or isochoric process, workdone is same.

3. Isothermal process.

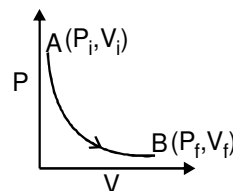
(a) Reversible Expansion or compression

$$W = -P \int dv$$

$$= -\int P_{\text{gas}} dV$$

$$= -\int \frac{nRT}{V} dV$$

$$\Rightarrow W = -nRT \ln \frac{V_f}{V_i}$$



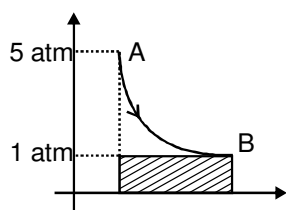
$$W = -nRT \ln \frac{P_i}{P_f}$$

In Expansion $W = -ve$

$$\Delta E = 0$$

$$q = -W$$

(b) Single stage irreversible expansion



$$W = -P_{\text{ext}}(V_2 - V_1)$$

$$|W_{\text{rev}}| > |W_{\text{irr}}| \text{ (in case of expansion)}$$

$$W = -P_{\text{ext}} \left[\frac{nRT}{P_2} - \frac{nRT}{P_1} \right]$$

$$W = -nRT P_{\text{ext}} \left[\frac{1}{P_2} - \frac{1}{P_1} \right]$$

(c) Two Stage irreversible Expansion:

Stage I.

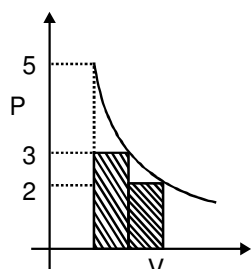
$$P'_{\text{ext}} = 3 \text{ atm}$$

$$P_i = 5 \text{ atm}$$

Stage II.

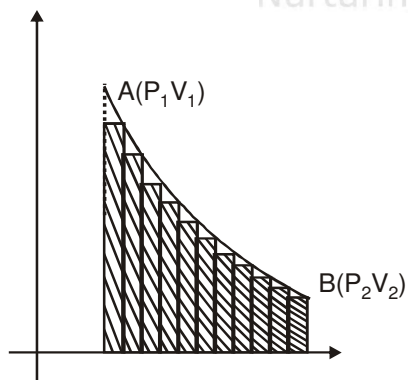
$$P''_{\text{ext}} = 2 \text{ atm}$$

$$P_f = 2 \text{ atm}$$



Workdone in 2nd stage > Workdone in 1st stage

(d) n- stage expansion

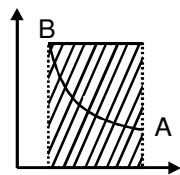


MOTION IIT-JEE|AIEEE
CBSE|SAT|NTSE
OLYMPIADS
Nurturing potential through education

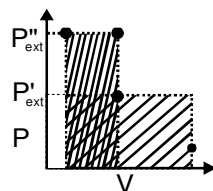
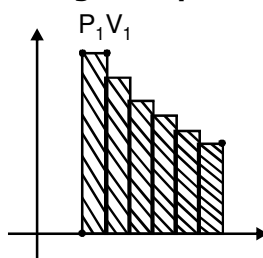
Compression - (One stage Compression)

$$|W_{\text{irr}}| = P_{\text{ext}} \Delta V$$

$$P_1 = 1 \text{ atm}, P_2 = 5 \text{ atm}, P_{\text{ext}} = 5 \text{ atm}$$



$$|W_{\text{irr}}| > |W_{\text{rev}}| \quad \text{For compression}$$

Two stage Comp.**n stage Comp**

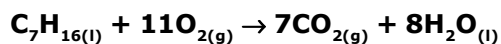
Ex.1 2 moles of an ideal gas initially present in a piston fitted cylinder at 300 K, and 10 atm are allowed to expand against 1 atm but the piston was stopped before it established the mechanical equilibrium. If temperature were maintained constant through out the change and system delivers 748.26 J of work, determine the final gas pressure and describe the process on PV diagram.

Sol. $W_{\text{irr}} = -748.26$

$$W_{\text{irr}} = -P_{\text{ext}} \left[\frac{1}{P_2} - \frac{1}{P_1} \right] nRT$$

$$P_2 = 4 \text{ atm}$$

Ex.2 1150 Kcal heat is released when following reaction is carried out at constant volume.



Find the heat change at constant pressure.

The pressure of liquid is a linear function of volume ($P = a + bV$) and the internal energy of the liquid is $U = 34 + 3PV$ find $a, b, w, \Delta E$ & ΔH for change in state from 100 Pa, 3m³ to 400 Pa, 6m³

Sol. $100 = a + bV$

$$\Rightarrow 100 = a + 3b$$

Also, $400 = a + 6b$

$$\Rightarrow \begin{aligned} a &= -200 \\ b &= 100 \end{aligned}$$

$$\begin{aligned} \Delta U &= 34 + 3(P_2V_2 - P_1V_1) \\ &= 6300 \text{ J} \end{aligned}$$

$$\begin{aligned} \Delta H &= \Delta U + P_2V_2 - P_1V_1 \\ &= 6300 + 2100 = 8400 \text{ J} \end{aligned}$$

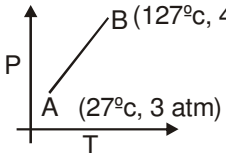
P is a linear function

$$P_{\text{ext}} = \frac{400 + 100}{2} = 250$$

$$\begin{aligned} W &= -P_{\text{ext}}(dV) \\ &= -250(6 - 3) = -750 \text{ J} \end{aligned}$$

Ex.3 4 moles of an ideal gas ($C_v = 15 \text{ J}$) is subjected to the following process represented on $P - T$ graph. From the given data find out whether the process is isochoric or not? also calculate q , w , ΔU , ΔH ,

Sol.



$PV = nRT$
 $4V = 4R \times 400$
 $V = 400 R \quad \dots\dots(1)$
 $3V = 4R \times 300$
 $V = 400 R \quad \dots\dots(2)$
 \Rightarrow i.e., V is constant
 $w = 0$
 $\Delta U = nC_v \Delta T \Rightarrow 4 \times 15 \times 100 = 6000 \text{ J}$
 $\Delta H = nC_p \Delta T \Rightarrow n(C_v + R) \Delta T$
 $\Rightarrow 4 \times (15 + 8.3) \times 100$
 $\Rightarrow 9320 \text{ J}$
 $q = \Delta U = 6 \text{ kJ}$

Ex.4 2 mole of a gas at 1 bar and 300 K are compressed at constant temperature by use of a constant pressure of 5 bar. How much work is done on the gas?

Sol. $w = -nRT \times P_{\text{ext}} \left[\frac{1}{P_2} - \frac{1}{P_1} \right]$
 $= 19953.6 \text{ J}$

Ex.5 2 moles of an ideal diatomic gas ($C_v = 5/2 R$) at 300 K, 5 atm expanded irreversibly and adiabatically to a final pressure of 2 atm against a constant pressure of 1 atm.

(1) Calculate final temperature q , w , ΔH & ΔU

(2) Calculate corresponding values if the above process is carried out reversibly.

Sol.. $w = C_v(T_2 - T_1) = -P_{\text{ext}} R \left[\frac{T_2}{P_2} - \frac{T_1}{P_1} \right]$

Given $T_2 = 270 \text{ K}$
 $P_{\text{ext}} = 1, P_2 = 2, P_1 = 5$
 $q = 0$
 $w = \Delta U = nC_v \Delta T$
 $= -1247.1 \text{ J}$
 $\Delta H = nC_p \Delta T$
 $= 1745.94 \text{ J}$

If process is reversible $PV^\gamma = \text{Constant}$
 $P^{1-\gamma} T^\gamma = \text{Constant}$
 $T = 231 \text{ K}$

ADIABATIC IDEAL GAS EXPANSION & COMPRESSION

$$dq = 0$$

$$dU = dW \Rightarrow \Delta U = W$$

$$W = nC_V \Delta T = nC_V (T_2 - T_1)$$

For an ideal gas $C_p - C_v = R$

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

REVERSIBLE ADIABATIC EXPANSION OR COMPRESSION

$$nC_V dT = -P_{\text{ext}} dV$$

$$P_{\text{int}} = dP = P_{\text{ext}}$$

$$P_{\text{int}} = P_{\text{gas}} = \frac{nRT}{V}$$

$$\int nC_V dT = - \int \frac{nRT}{V} dV$$

$$C_V \int \frac{dT}{T} = -R \int \frac{dV}{V}$$

$$C_V \ln \frac{T_2}{T_1} = -R \ln \frac{V_2}{V_1}$$

$$\frac{R}{\gamma - 1} \ln \frac{T_2}{T_1} = -R \ln \frac{V_2}{V_1} \Rightarrow \frac{1}{\gamma - 1} \ln \frac{T_2}{T_1} = -\ln \frac{V_2}{V_1}$$

$$\ln \frac{T_2}{T_1} = -(\gamma - 1) \ln \frac{V_2}{V_1} \Rightarrow \ln \frac{T_2}{T_1} = \ln \left(\frac{V_1}{V_2} \right)^{\gamma - 1}$$

$$\Rightarrow \frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{\gamma - 1}$$

$$\Rightarrow T_2 (V_2)^{\gamma - 1} = V_1^{\gamma - 1} T_1$$

$$TV^{\gamma - 1} = \text{Constant}$$

$$\frac{PV}{nR} V^{\gamma - 1} = \text{Constant}$$

$$\Rightarrow PV^\gamma = \text{Constant}$$

IRREVERSIBLE ADIABATIC COMPRESSION & EXPANSION

$$dU = dW$$

$$\Rightarrow nC_V(T_2 - T_1) = -P_{\text{ext}} dV$$

$$nC_V(T_2 - T_1) = -P_{\text{ext}} [V_2 - V_1]$$

$$nC_V(T_2 - T_1) = -P_{\text{ext}} \left[\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1} \right]$$

$$= -P_{\text{ext}} nR \left[\frac{T_2}{P_2} - \frac{T_1}{P_1} \right]$$

$$C_V(T_2 - T_1) = -P_{\text{ext}} R \left[\frac{T_2}{P_2} - \frac{T_1}{P_1} \right]$$

COMPARISON OF REVERSIBLE ISOTHERMAL & REVERSIBLE ADIABATIC IDEAL GAS EXPANSION.

- (1) If final volumes are same.

Isothermal process.

$$P_1 V_1 = P_{\text{iso}} V_2$$

$$\Rightarrow \frac{V_2}{V_1} = \frac{P_1}{P_{\text{iso}}}$$

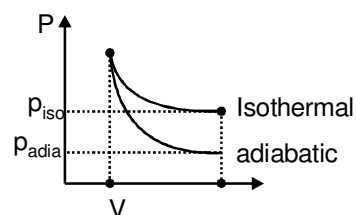
Adiabatic process.

$$P_1 V_1^\gamma = P_{\text{adia}} V_2^\gamma$$

$$\Rightarrow \left(\frac{V_2}{V_1} \right)^\gamma = \frac{P_1}{P_{\text{adia}}}$$

$$\frac{V_2}{V_1} > 1 \Rightarrow \left(\frac{V_2}{V_1} \right)^\gamma > \frac{V_2}{V_1} \Rightarrow \frac{P_1}{P_{\text{adia}}} > \frac{P_1}{P_{\text{iso}}}$$

$$\Rightarrow P_{\text{iso}} > P_{\text{adia}}$$



- (2) If final pressures are same

Isothermal process.

$$P_1 V_1 = P_2 V_{\text{iso}}$$

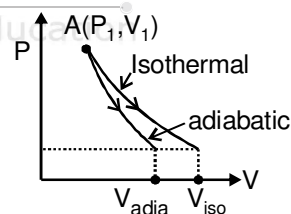
$$\frac{V_1}{V_{\text{iso}}} = \frac{P_2}{P_1} \quad \dots\dots(1)$$

$$P_1 V_1^\gamma = P_2 V_{\text{adia}}^\gamma$$

$$\frac{V_1}{V_{\text{adia}}} = \left(\frac{P_2}{P_1} \right)^{1/\gamma}$$

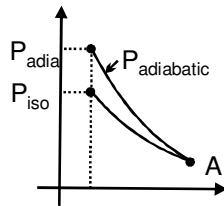
in ideal gas expansion, $|W_{\text{iso}}| > |W_{\text{adia}}|$

$$\text{Hence } \Rightarrow V_{\text{iso}} > V_{\text{adia}}$$



Compression

- (1) If final volumes are same



For isothermal process

$$P_1 V_1 = P_{iso} V_2$$

$$\frac{V_1}{V_2} = \frac{P_{iso}}{P_1} \quad \dots\dots\dots(1)$$

Adiabatic process.

$$P_1 V_1^\gamma = P_{adia} V_2^\gamma$$

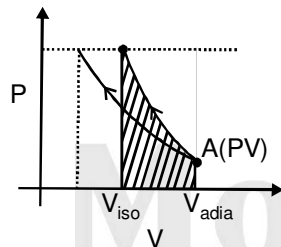
$$\left(\frac{V_1}{V_2}\right)^\gamma = \frac{P_{adia}}{P_1} \quad \dots\dots\dots(2)$$

$$\Rightarrow \left(\frac{V_1}{V_2}\right)^\gamma = \frac{V_1}{V_2}$$

$$\Rightarrow \frac{P_{adia}}{P_1} > \frac{P_{iso}}{P_1}$$

$$\boxed{P_{adia} > P_{iso}}$$

- (2) If final pressures are same



$$P_1 V_1 = P_2 V_{iso} \quad \dots\dots\dots(1)$$

$$P_1 V_1^\gamma = P_2 V_{adia}^\gamma \quad \dots\dots\dots(2)$$

$$\left(\frac{V_1}{V_{adia}}\right)^\gamma = \frac{P_2}{P_1} \Rightarrow \frac{V_{adia}}{V_1} = \left(\frac{P_1}{P_2}\right)^{1/\gamma}$$

$$\Rightarrow \frac{V_1}{V_{adia}} = \left(\frac{P_2}{P_1}\right)^{1/\gamma} < \frac{P_2}{P_1}$$

$$\frac{V_1}{V_{adia}} < \frac{V_1}{V_{iso}}$$

$$\Rightarrow \boxed{V_{adia} > V_{iso}}$$

POLYTROPIC PROCESS

$$PV^x = \text{Const}$$

$$W = - \int P_{\text{ext}} dV$$

$$= - \int P_{\text{gas}} dV$$

$$= -k \int_{V_1}^{V_2} V^{-x} dV \Rightarrow w = \frac{-k}{-x+1} [V_2^{-x+1} - V_1^{-x+1}]$$

$$= \frac{-1}{-x+1} [V_2 k V_2^{-x} - V_1 k V_1^{-x}]$$

$$W = \frac{1}{x-1} [P_2 V_2 - P_1 V_1]$$

MOLAR HEAT CAPACITY OF POLYTROPIC PROCESS

$$dU = dq + dW$$

$$nC_v dT = nC_m dT + (-PdV)$$

$$C_m = C_v + \frac{PdV}{ndT} \quad \dots\dots\dots(1)$$

$$PV = nRT$$

$$KV^{-x}V = nRT$$

$$kV^{-x+1} = nRT$$

$$k(-x+1)V^{-x} \frac{dV}{dT} = nR$$

$$\frac{dV}{dT} = \frac{nR}{k(1-x)V^{-x}} = \frac{nR}{(1-x)P}$$

$$C_m = C_v + \frac{p}{n} \frac{nR}{(1-x)P}$$

$$\Rightarrow \boxed{C_v + \frac{R}{1-x} = C} \quad x \neq 1$$

LIMITATIONS OF FIRST LAW OF THERMODYNAMICS

1. First law of thermodynamics does not give information regarding the direction of propagation of a process
2. First law of thermodynamics does not tell us why an equilibrium is attained.
3. First law of thermodynamics does not tell us when an equilibrium will be attained.
4. First law of thermodynamics does not give information about why there can not be 100 percent conversion of heat into work

SECOND LAW OF THERMODYNAMICS

Statement(I) : Second law of thermodynamics states that heat can never be converted into work with 100% efficiency

Statement(II) : No engine in this world can be constructed which operates in cycles and converts all the heat from source to work.

Statement(III) : No refrigeratator can be designed which operates in cycles and rejects heat from sink to source, perpetually (self - functioning).

Entropy : Entropy is the direct measurement of randomness or disorderness. Entropy is an extensive property & it is a state function

$ds = \frac{dq_{rev}}{T}$ for reversible process. entropy is related with complexity of the molecule within the system.

$EtOH > MeOH$

$C_2H_6(g) > C_2H_5(g)$

$N_2O_4 > NO_2$

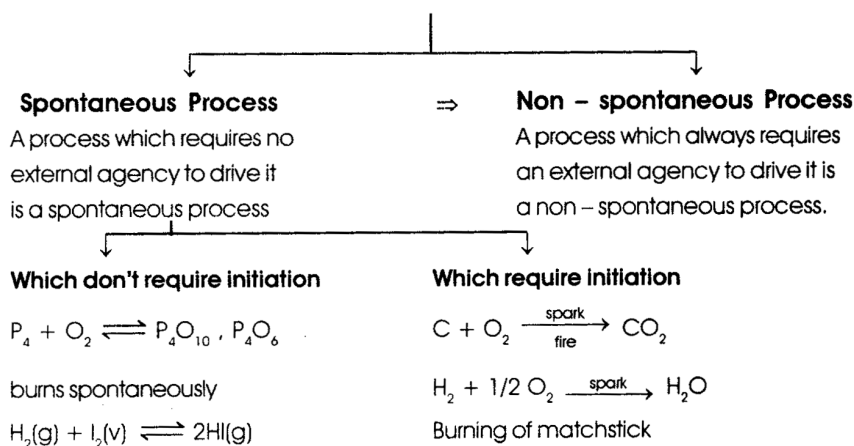
$O_2 > N_2$ (molecular wt.)

Gas > Liq > Amorphous solid > crystalline solid

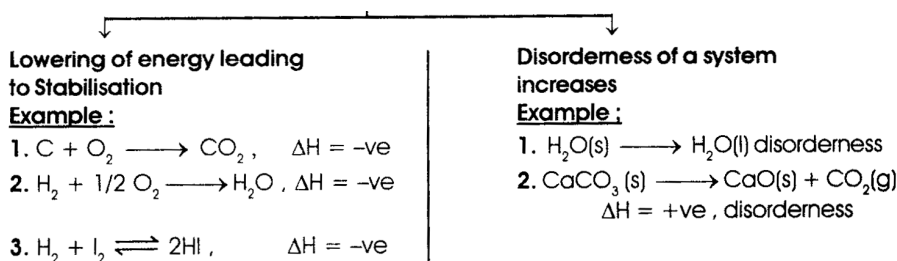
Entropy always increases in the following process

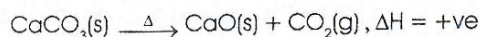
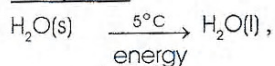
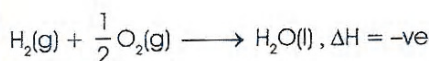
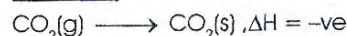
- (1) $s \rightarrow l, l \rightarrow g, s \rightarrow g,$
- (2) Isothermal expansion of ideal gas.
- (3) Mixing of two non reacting gases.
- (4) In chemical reaction in which
 $\Delta n_g > 0$
- (5) Heating of any substance

CLASSIFICATION OF PROCESS BASED ON SPONTANEITY



Why Spontaneity



Exception :**Exception**

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

Points to ponder :

Why a system always moves towards disorderness ?

Answer : A system moves towards disorderness because the probability of moving towards disorderness is very high.

DISORDERNESS**For Reversible process :**

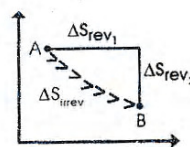
$$\Delta S = \frac{Q_{\text{reversible}}}{T} \quad Q_{\text{reversible}} = \text{constant}$$

$$\Delta S = \int \frac{dQ_{\text{reversible}}}{T} \quad Q_{\text{reversible}} = \text{Variable}$$

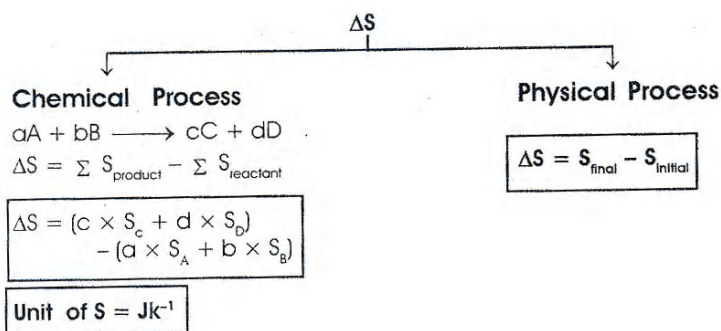
Note : Irreversible process

$$\Delta S_{\text{irreversible}} = \Delta S_{\text{rev1}} + \Delta S_{\text{rev2}}$$

$$\Delta S_{\text{irreversible}} = \frac{Q_{\text{rev1}}}{T_1} + \frac{Q_{\text{rev2}}}{T_2}$$



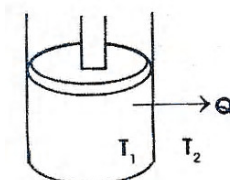
The entropy change for an irreversible process can be calculated by substituting it with equivalent reversible process. Both will have same entropy change.

**ENTROPY CHANGE OF UNIVERSE**

$$\Delta S_{\text{system}} = \frac{-Q}{T_1}$$

$$\Delta S_{\text{surrounding}} = \frac{+Q}{T_1}$$

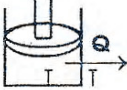
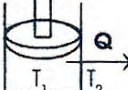
$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$$



SPONTANEITY

1. $\Delta S_{\text{universe}} > 0 \Rightarrow$ Spontaneous
2. $\Delta S_{\text{universe}} = 0 \Rightarrow$ Equilibrium
3. $\Delta S_{\text{universe}} < 0 \Rightarrow$ Non-spontaneous.

ENTROPY CHANGE (ΔS)

| In a reversible process | In an irreversible process |
|---|--|
|  $\Delta S_{\text{system}} = -Q/T$ $\Delta S_{\text{surrounding}} = +Q/T$ $\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$ $= -Q/T + Q/T$ <div style="border: 1px solid black; padding: 2px; display: inline-block;">$\Delta S_{\text{universe}} = 0$</div> <p>In a reversible process $\Delta S_{\text{universe}}$ is zero. Hence system is always in equilibrium.</p> |  $T_1 > T_2$ $1/T_1 < 1/T_2 \text{ or } 1/T_2 - 1/T_1 > 0.$ <p>Now, $\Delta S_{\text{system}} = -Q/T_1$</p> $\Delta S_{\text{surrounding}} = +Q/T_2$ $\Delta S_{\text{universe}} = Q/T_2 - Q/T_1$ $\Delta S_{\text{universe}} = Q(1/T_2 - 1/T_1)$ <div style="border: 1px solid black; padding: 2px; display: inline-block;">$\Delta S_{\text{universe}} > 0$</div> <p>In an irreversible process $\Delta S_{\text{universe}} > 0$ hence the process is always spontaneous</p> |

CALCULATION OF ENTROPY CHANGE

(A) General heating or cooling

$$ds = \frac{dq_{\text{rev}}}{T}$$

$$\Delta S = \int ds = \int \frac{dq_{\text{rev}}}{T} = \int_{T_1}^{T_2} nC_V dT$$

If C is temperature independent

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

If C is a function of Temperature

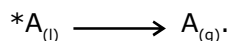
$$C = a + bT$$

$$\Delta S = n \int_{T_1}^{T_2} \left(\frac{a+bT}{T} \right) dT$$

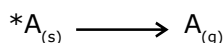
$$\Delta S = n \left[a \ln \frac{T_2}{T_1} + b(T_2 - T_1) \right]$$

(B) In phase transformation

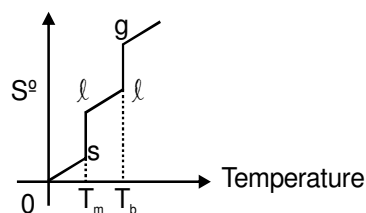
$$\Delta S_{\text{fus}} = \frac{q_{\text{rev}}}{T_m} = \frac{n \Delta H_{\text{fusion}}}{T_m}$$



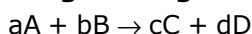
$$\Delta S_{\text{vap}} = \frac{n\Delta H_{\text{vap}}^{\circ}}{T_B}$$



$$\Delta S_{\text{sub}} = \frac{n\Delta H_{\text{sub}}^{\circ}}{T}$$



(C) Entropy change during chemical reaction.



$$\Delta S^{\circ} = \text{entropy of product} - \text{entropy of reactant}$$

For any chemical reaction

$$\int_{\Delta S_1}^{\Delta S_2} ds = \int_{T_1}^{T_2} \frac{C_d T}{T}$$

$$\Delta S_2 - \Delta S_1 = C_V \ln \frac{T_2}{T_1}$$

(D) Calculation of entropy change during expansion/compression of ideal gas from $P_1 V_1 T_1$ to $P_2 V_2 T_2$

From Ist law of thermodynamics

$$dE = dq + dW$$

$$dq = -dW + dE$$

$$TdS = PdV + nC_V dT$$

$$dS = \frac{P}{T} dV + nC_V \frac{dT}{T}$$

$$dS = \frac{nR}{V} dV + \frac{nC_V dT}{T}$$

$$\Delta S = \int dS = nR \ln \frac{V_2}{V_1} + nC_V \ln \frac{T_2}{T_1}$$

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

For ideal gas

$$\Delta S = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2} \cdot \frac{T_2}{T_1}$$

$$= nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2} + nR \ln \frac{T_2}{T_1}$$

$$= nR \ln \frac{P_1}{P_2} + (C_V + R)n \ln \frac{T_2}{T_1}$$

$$\Delta S = nR \ln \frac{P_1}{P_2} + nC_P \ln \frac{T_2}{T_1}$$

Conclusion ΔS increasesWhen $T \uparrow$ $V \uparrow$ & $P \downarrow$ If C_v is temperature dependent

$$\Delta S = n \int C_v \frac{dT}{T} + nR \ln \frac{V_2}{V_1}$$

$$\Delta S = n \int \frac{(a+bT)}{T} dT + nR \ln \frac{V_2}{V_1}$$

$$\Delta S = n \left[a \ln \frac{T_2}{T_1} + b(T_2 - T_1) \right] + nR \ln \frac{V_2}{V_1}$$

Calculation of entropy change during isothermal Expansion;

| Process | ΔS_{system} | ΔS_{surr} | ΔS_{Total} |
|---|--|--|---------------------------|
| 1. Reversible $\Delta E = q_{\text{rev}} + w_{\text{rev}}$ $\Delta E = 0$ | $\Delta S_{\text{system}} = \frac{q_{\text{rev}}}{T} = -\frac{w_{\text{rev}}}{T} = nR \ln \frac{V_2}{V_1} = +ve$ | $\Delta S_{\text{surr}} = -\frac{q_{\text{process}}}{T} = -nR \ln \frac{V_2}{V_1} = -ve$ | 0 |
| 2. Irreversible Free expansion $\Delta E = 0, w = 0$ | $nR \ln \frac{V_2}{V_1}$ | 0 | > 0 |
| 3. Irreversible expansion $\Delta E = q_{\text{irr}} + w_{\text{irr}}$ | $nR \ln \frac{V_2}{V_1}$ | $\Delta S = -\frac{q_{\text{irr}}}{T} = \frac{w_{\text{irr}}}{T} = -ve$ | > 0 |

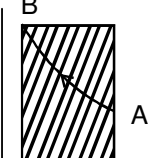
because $\frac{w_{\text{rev}}}{T} = \frac{-nRT}{T} \ln \frac{V_2}{V_1} = -nR \ln \frac{V_2}{V_1}$

$$nR \ln \frac{V_2}{V_1} = \frac{-w_{\text{rev}}}{T}$$

$$w_{\text{rev}} > w_{\text{irr}}$$

$$\Delta S_{\text{total}} = +ve$$

Calculation of entropy change during isothermal compression.

| Process | ΔS_{syst} | ΔS_{surr} | ΔS_{Total} |
|---|--|---|---------------------------|
| 1. Reversible Process | $\Delta S_{\text{syst}} = \frac{q_{\text{rev}}}{T} = -\frac{w_{\text{rev}}}{T} = nR \ln \frac{V_2}{V_1} = -ve$ | $\Delta S_{\text{surr}} = -\frac{q_{\text{process}}}{T} = \frac{w_{\text{rev}}}{T} = -nR \ln \frac{V_2}{V_1} = +ve$ | 0 |
| 2. Irreversible compression  | $\Delta S_{\text{sys}} = nR \ln \frac{V_2}{V_1} = -ve$ | $\Delta S_{\text{surr}} = \frac{-q_{\text{irr}}}{T} = \frac{w_{\text{irr}}}{T} = +ve$ | > 0 |

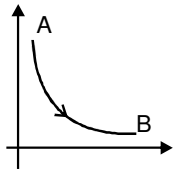
$$q_{\text{irr}} + w_{\text{irr}} = 0$$

$$|w_{\text{irr}}| > |w_{\text{rev}}|$$

$$< 0 \quad > 0$$

$$\Rightarrow |q_{\text{irr}}| > |q_{\text{rev}}|$$

Calculation of entropy change during for adiabatic expansion of ideal gas.

| | | | |
|---|--|--|------|
| 1. Process  | $\Delta S_{\text{sys}} = \frac{q_{\text{rev}}}{T}$ $= nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$ <p style="text-align: center;"> \downarrow -ve \downarrow +ve $= 0$ </p> | $\Delta S_{\text{surr}} = \frac{-q_{\text{process}}}{T} = 0$ | 0 |
| 2. Irreversible Process free expansion | $nR \ln \frac{V_2}{V_1}$ | 0 | + ve |

For reversible process

$$\Delta E = q_{\text{rev}} + w_{\text{rev}}$$

$$\quad \quad \quad \parallel$$

$$\quad \quad \quad 0$$

$$nC_V dT = -100 \text{ (let)}$$

$$(T_2 - T_1) = K (-100)$$

Where K is constant

$$T_2 = T_1 - 100K$$

For irreversible process

$$\Delta E = q_{\text{irr}} + w_{\text{irr}}$$

$$\quad \quad \quad \parallel$$

$$\quad \quad \quad 0$$

$$T_2' - T_1 = -90K$$

$$T_2' = T_1 - 90K$$

This means that the final temperature of irreversible process is greater than reversible process.

$$\Delta S = nC_V \ln \frac{T_2'}{T_1} + nR \ln \frac{V_2}{V_1}$$

\downarrow -ve \downarrow +ve

$$= nC_V \ln \frac{T_2'}{T_1} - nC_V \ln \frac{T_2}{T_1}$$

$$= nC_V \ln \frac{T_2'}{T_2}$$

$$\Rightarrow T_2' > T_2$$

$$\Rightarrow \Delta S = +ve$$

$$\Delta S_{\text{surr}} = \frac{-q_{\text{process}}}{T} = 0$$

$$\Rightarrow \Delta S_{\text{total}} = +ve$$

Calculation of entropy change in adiabatic compression.

| | | | |
|---------------------------------------|--|---|---|
| 1. Reversible | $\Delta S = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$ <p style="text-align: center;"> \downarrow +ve \downarrow -ve $= 0$ </p> | 0 | 0 |
| 2. Irreversible adiabatic compression | <p>For reversible process</p> $\Delta E = q_{\text{rev}} + w_{\text{rev}}$ $\Delta E = 100$ $dT = 100\text{K}$ <p>For irreversible process</p> $i_{\text{irr}} \quad \Delta E = q_{\text{irr}} + w_{\text{irr}}$ $= 110$ | 0 | 0 |

$$dT = 110$$

For reversible

$$(T_2 - T_1) = 100\text{K}$$

$$T_2 = T_1 + 100\text{K}$$

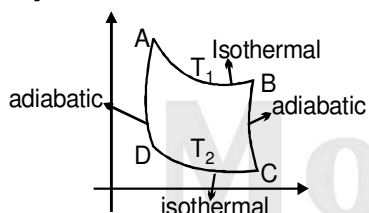
for irreversible $T'_2 = T_1 + 110\text{K}$

$$T'_2 > T_2$$

$$\begin{aligned} \Delta S_{\text{irr}} &= nC_V \ln \frac{T'_2}{T_1} + nR \ln \frac{V_2}{V_1} \\ &= nC_V \ln \frac{T'_2}{T_1} - nC_V \ln \frac{T_2}{T_1} \\ &= nC_V \ln \frac{T'_2}{T_2} > 0 \end{aligned}$$

CARNOT CYCLE

Carnot cycle is based on 4 reversible process.



- (1) Reversible isothermal expansion from A to B.**

$$\Delta E_{AB} = 0,$$

$$W_{AB} = -nRT_1 \ln \frac{V_2}{V_1}$$

- (2) Reversible adiabatic expansion from B to C**

$$\Delta E_{BC} = nC_V(T_2 - T_1)$$

$$W_{BC} = \Delta E_{BC}$$

- (3) Isothermal compression from C to D**

$$\Delta E_{CD} = 0,$$

$$W_{CD} = -nRT_2 \ln \frac{V_4}{V_3}$$

$$q_{CD} = -W_{CD}$$

(4) Adiabatic compression from D to A.

$$\Delta E_{DA} = nC_V(T_1 - T_2)$$

$$W_{DA} = \Delta E_{DA}$$

$$\Delta E_{\text{Cycle}} = 0$$

$$W_{\text{cycle}} = -nRT_1 \ln \frac{V_2}{V_1} + nC_V(T_2 - T_1) - nRT_2 \ln \frac{V_4}{V_3} + nC_V(T_1 - T_2)$$

$$= -nR \left[T_1 \ln \frac{V_2}{V_1} + T_2 \ln \frac{V_4}{V_3} \right]$$

$$\text{For BC, } T_1 V_2^{\gamma-1} = T_2 V_3^{\gamma-1}$$

$$\text{For DA, } T_1 V_1^{\gamma-1} = T_2 V_4^{\gamma-1}$$

$$\left(\frac{V_2}{V_1} \right)^{\gamma-1} = \left(\frac{V_3}{V_4} \right)^{\gamma-1} \Rightarrow \boxed{\frac{V_2}{V_1} = \frac{V_3}{V_4}}$$

$$W_{\text{cycle}} = -nR(T_1 - T_2) \ln V_2/V_1$$

Efficiency of any engine may be given as

$$\eta = \frac{|W_{\text{net}}|}{q_1 \text{ (Heat given)}}$$

$$\eta = \frac{nR(T_1 - T_2) \ln \frac{V_2}{V_1}}{nRT_1 \ln \frac{V_2}{V_1}} = \frac{(T_1 - T_2)}{T_1}$$

$$\boxed{\eta = 1 - \frac{T_2}{T_1}}$$

$$\Delta E_{\text{cycle}} = q_{\text{cyc}} + w_{\text{cycle}}$$

$$w_{\text{cycle}} = -q_{\text{cycle}} = \frac{(q_1 + q_2)}{q_1}$$

$$\frac{q_1 + q_2}{q_1} = 1 - \frac{T_2}{T_1}$$

$$1 + \frac{q_2}{q_1} = 1 - \frac{T_2}{T_1}$$

$$\Rightarrow \frac{q_2}{T_2} + \frac{q_1}{T_1} = \sum \frac{q_{\text{rev}}}{T} = 0$$

$$\Rightarrow \oint ds = 0$$

This means ΔS is a state function

Gibb's Free Energy (G)

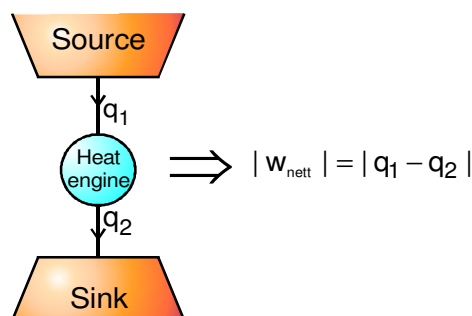
$$G_{\text{system}} = H_{\text{system}} - TS_{\text{system}}$$

$$W = W_{\text{expansion}} + W_{\text{non-expansion}}$$

$$W_{\text{non-expansion}} = w_{\text{useful}} \text{ (useful work)}$$

$$\Delta G = W_{\text{non expansion}} = W_{\text{useful}}$$

All those energy which is available with the system which is utilized in doing useful work is called Gibb's free energy :



• R_x :

1. $\Delta G_{\text{system}} = \Delta H_{\text{system}} - T\Delta S_{\text{system}} = -T\Delta S_{\text{universe}} = W_{\text{non expansion}} = W_{\text{useful}}$

2. $\Delta G_{\text{system}} = -T\Delta S_{\text{universe}}$

3. (a) $\Delta S_{\text{universe}} > 0$ or $\Delta G_{\text{system}} < 0 \Rightarrow$ Spontaneous

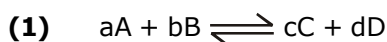
(b) $\Delta S_{\text{universe}} = 0$ or $\Delta G_{\text{system}} = 0 \Rightarrow$ Equilibrium

(c) $\Delta S_{\text{universe}} < 0$ or $\Delta G_{\text{system}} > 0 \Rightarrow$ Non-Spontaneous

| ΔH | ΔS | ΔG | Result (T) . |
|------------|------------|------------|------------------------------------|
| +ve | +ve | -ve | T should be high for spontaneity |
| +ve | -ve | +ve | Non-spontaneous at all temperature |
| -ve | +ve | -ve | Spontaneous at all temperature |
| -ve | -ve | -ve | T should be low for spontaneity |

APPLICATION OF (ΔG)

• R_x :



ΔG° = Standard Gibbs free energy change ($P = 1 \text{ atm}$, 298 K)

ΔG = Gibbs free energy change at any condition.

NERST EQUATION

$\Delta G = \Delta G^\circ + 2.303 RT \log Q$; Q = Reaction Quotient

$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$

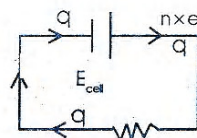
At equilibrium, $\Delta G = 0$ and $Q = K_{\text{eq}}$.

$0 = \Delta G^\circ + 2.303 RT \log k_{\text{eq}}$

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

$\sum G^\circ(\text{product}) - \sum G^\circ(\text{Reactant}) = -2.303 RT \log k_{\text{eq}}$

$\Delta H^\circ - T\Delta S^\circ = -2.303 RT \log k_{\text{eq}}$



(2) $W_{\text{cell}} = q \times E$

$\Delta G = -W_{\text{cell}}$

$\Delta G = -q \times E_{\text{cell}}$

Now, one mole e^- have charge 96500 coulomb = 1 Faraday (F)

n mole of e^- will have charge = $n \times F$ or $q = n \times F$

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

$\Delta G^\circ = -nFE_{\text{cell}}^\circ$

THIRD LAW OF THERMODYNAMICS

$$\lim_{T \rightarrow 0} S = 0$$

Third law of thermodynamics states that as the temperature approaches absolute zero, the entropy of perfectly crystalline substance also approaches zero.

APPLICATION OF THIRD LAW OF THERMODYNAMICS

$$\Delta S = \int_{T_1}^{T_2} \frac{dQ_{\text{reversible}}}{T}$$

$$S_{T_2} - S_{T_1} = \int_{T_1}^{T_2} \frac{dQ_{\text{reversible}}}{T}$$

Taking $T_2 = T$ and $T_1 = 0^\circ\text{K}$.

$$S_T - 0 = \int_{T_0}^T \frac{dQ_{\text{reversible}}}{T} \Rightarrow S_T = \int_{T_0}^T \frac{dQ_{\text{reversible}}}{T} \quad \text{For perfectly crystalline substance}$$

- The entropy of perfectly crystalline substance can be determined using third law of thermodynamics.

or

- With the help of third law of thermodynamics we can calculate the exact value of entropy.

 ΔG AND NON PV WORK (NON EXPANSION/COMPRESSION)

$(\Delta G)_{T,P}$ is a measure of useful work a non PV work (non expansion work) that can be produced by a chemical transformation.e.g.electrical work .

For reversible reaction at constant T & P

$$dU = dq + dW_{\text{total}}$$

$$dU = dq + dW_{P,V} + dW_{\text{non } P,V}$$

$$dU = T.dS - P.dV + dW_{\text{non } P,V}$$

$$dU + P.dV = T.dS + dW_{\text{non } P,V}$$

$$dH = T.dS + dW_{\text{non } P,V}$$

$$(dG_{\text{sys}})_{T,P} = dW_{\text{non } P,V}$$

$$(\Delta G_{\text{sys}})_{T,P} = W_{\text{nonpv}}$$

Useful work done on the system = increase in Gibb's energy of system at constant T & P.

$$-(\Delta G_{\text{sys}})_{T,P} = -W_{\text{non } P,V}$$

$$-(\Delta G_{\text{sys}})_{T,P} = -W_{\text{by, non } P,V}$$

Useful work done by the system = decrease in Gibb's energy of system at constant T & P .

If $(\Delta G_{\text{sys}})_{T,P} = 0$, then system is unable to deliver useful work.

THERMODYNAMIC RELATION

For reversible process in which non expansion work is not possible

$$dU = dq + dw$$

$$dU = T.dS - P.dV$$

$$H = U + PV$$

$$dH = dU + P.dV + V.dP$$

$$dH = T.dS - PdV + PdV + V.dP$$

$$dH = T.dS + V.dP$$

$$G = H - TS$$

$$dG = dH - T.dS - S.dT$$

$$dG = T.dS + V.dP - T.dS - S.dT$$

$$dG = V.dP - S.dT \quad \text{For a particular system (s/ } \ell \text{ /g)}$$

- (1) At constant temperature $dG = V.dP$ or $\left(\frac{\partial G}{\partial P}\right)_T = V$

(A) For a system is s/ ℓ phase

$$\int dG = \int V.dP$$

$$\Delta G = V\Delta P$$

(B) For an ideal gas, expansion/compression :-

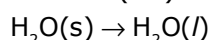
$$\int dG = \int V.dP = \int \frac{nRT}{P} dP$$

$$\Delta G = nRT \ln \frac{P_2}{P_1} = nRT \ln \frac{V_1}{V_2}$$

- (2) At constant pressure : $dG = -S.dT$ or $\left(\frac{\partial G}{\partial T}\right)_P = -S$

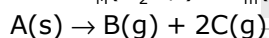
* For phase transformation/chemical reaction

$$d(\Delta G) = \Delta V.dP - \Delta S dT$$

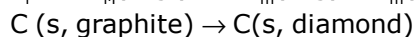


$$\Delta V = V_m(H_2O, l) - V_m(H_2O, s)$$

$$\Delta S = S_m(H_2O, l) - S_m(H_2O, s)$$



$$\Delta_r S = S_m(B, g) + 2S_m(C, g) - S_m(A, s)$$



$$\Delta V = V_m(C, \text{diamond}) - V_m(C, \text{graphite})$$

At constant temperature:-

$$d(\Delta G) = \Delta V. dP$$

$$\Delta G_{P_2} - \Delta G_{P_1} = \Delta V[P_2 - P_1]$$

At constant pressure

$$\int d(\Delta_r G) = -\int (\Delta_r S).dT$$

$$\Delta_r G_{T_2} - \Delta_r G_{T_1} = -\Delta_r S(T_2 - T_1)$$

Solved Problems

Ex.1 Show that pressure of a fixed amount of an ideal gas is a state function $V = \frac{nRT}{p}$

Sol. $\left(\frac{\partial V}{\partial T}\right)_p = \frac{nR}{p} \quad \Rightarrow \quad \frac{\partial}{\partial p} \left[\left(\frac{\partial V}{\partial T}\right)_p \right]_T = \frac{-nR}{p^2}$

$$\left(\frac{\partial V}{\partial T}\right)_T = -\frac{nRT}{p^2} \quad \frac{\partial}{\partial T} \left[\left(\frac{\partial V}{\partial p}\right)_T \right]_p = \frac{-nR}{p^2}$$

Ex.2 Calculate work done for the expansion of a substance 3m^3 to 5m^3 against.

- (a) Constant pressure = 10^5 Pa
 (b) A variable pressure = $(10 + 5V)$ Pa

Sol. (a) $W = -PdV = -10^5(5-3) = -2 \times 10^5 \text{ J}$

(B) $W = - \int (10 + 5V) dV$

$$= - \left(10V + \frac{5V^2}{2} \right)_3^5 = - \left[(10 \times 2) + \frac{5}{2} \times 16 \right]$$

$$= - (20 + 40) = -60$$

Ex.3 Calculate change in internal energy for a gas under going from state-I (300 K , $2 \times 10^{-2} \text{ m}^3$) to state -II (400 K , $4 \times 10^{-2} \text{ m}^3$) for one mol. of vanderwaal gas.

- (a) If gas is ideal [$C_v = 12 \text{ J/K/mol}$]
 (b) If gas is real

$\left\{ \text{Given : } \left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P \right.$

$C_v = 12 \text{ J/k/mol}$

$a = 2 \text{ J.m. / mol}^2 \}$ (Not in JEE)

Sol. (a) $\Delta U = nC_v(T_2 - T_1) = 1 \times 12 \times 100 = 1200 \text{ J}$

(b) $du = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$

$$\left[\begin{aligned} &\left(P + \frac{a}{V^2} \right) (V - b) = RT \\ &P = \frac{RT}{V - b} - \frac{a}{V^2} \\ &\Rightarrow \frac{\partial P}{\partial T} = \frac{R}{V - b} \end{aligned} \right]$$

$$= \left(\frac{\partial U}{\partial T}\right)_V dT + \left[T \left(\frac{\partial P}{\partial T}\right)_V - P \right] dV$$

$$= C_v dT + \frac{a}{V^2} dV$$

$$dU = C_v(T_2 - T_1) + a \left(\frac{1}{V_1} - \frac{1}{V_2} \right)$$

$$= C_v(100) + a \left(\frac{1}{4} \right) \times 10^2$$

$$= 12 \times 100 + 2 \left(\frac{1}{4} \right) \times 100 = 1250$$

Ex. 4 One mole of an ideal gas is expanded isothermally at 300 K from 10 atm to 1 atm. Calculate q , w , ΔU & ΔH under the following conditions.

(i) Expansion is carried out reversibly.

(ii) Expansion is carried out irreversibly

Sol. Isothermal process

(i) For ideal gas $\Delta U = 0$ $\Delta H = 0$

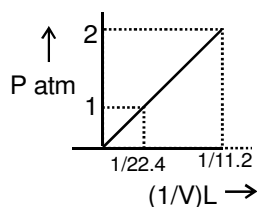
$$q = -w$$

$$w_{\text{rev}} = -nRT \ln \frac{P_1}{P_2} = -1 \times R \times 300 \ln \frac{10}{1} = -690.9R$$

$$(ii) W_{\text{irrev}} = -P_{\text{ext}}(V_2 - V_1) = -P_{\text{ext}} \left(\frac{nRT}{P_2} - \frac{nRT}{P_1} \right)$$

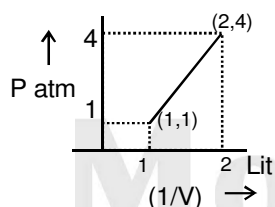
$$= -1 \times 1 \times R \times 300 \left[\frac{1}{1} - \frac{1}{10} \right] = -270R$$

Ex. 5 Calculate work done for an ideal gas ($\ln 2 = 0.7$)



$$w = -nRT \ln \frac{P_1}{P_2} = -22.4 \times \ln \frac{1}{2} = 22.4 \times 0.7 = 15.68$$

Ex. 6 Calculate $w = ?$ ($\ln 2 = 0.7$)



Sol. P - V Relation from plot

$$y = mx + C$$

$$1 = m + C \quad \dots\dots\dots(1)$$

$$4 = 2m + C \quad \dots\dots\dots(2)$$

$$\Rightarrow m = 3, C = -2$$

$$\text{Hence, } P = \frac{3}{V} - 2$$

$$w_{\text{rev}} = -\int P dv = -\int_1^{1/2} \left(\frac{3}{V} - 2 \right) dv = -\int_1^{1/2} (3 \ln v - 2v) dv$$

$$= -\left[3 \ln \frac{1}{2} - 2 \left(\frac{1}{2} - 1 \right) \right] = 3 \times 0.7 - 1 = 1.1 \text{ lit atm}$$

Ex. 7 One mole of an ideal gas is expanded from (10 atm, 10 lit) to (2 atm, 50 litre) isothermally. First against 5 atm then against 2 atm. Calculate work done in each step and compare it with single step work done with 2 atm.

Sol.

(i) $P_1 V_1 = P_2 V_2$

Vol. of system at 5 atm = $\frac{10 \times 10}{5} = 20$ lit.

$w_{\text{irrev}} = -P_{\text{ext}}(V_2 - V_1) = -5(20 - 10) = -50$ atm lit.

(ii) Work done against 2 atm

$$\begin{array}{ccc} P_1 & V_1 & \longrightarrow P_2 & V_2 \\ 5 \text{ atm} & 20 \text{ lit} & & 2 \text{ atm} & 50 \text{ lit} \end{array}$$

$w_{\text{irrev}} = -P_{\text{ext}}(V_2 - V_1) = -2(50 - 20) = -60$ atm lit.

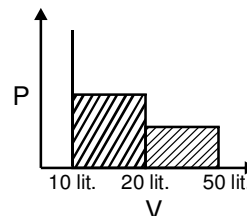
$w_{\text{total}} = -50 - 60 = -110$ atm lit.

Total work done in single step.

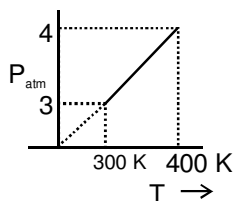
$$\begin{array}{ccc} P_1 & V_1 & \longrightarrow P_2 & V_2 \\ 10 \text{ atm} & 10 \text{ lit} & & 2 \text{ atm} & 50 \text{ lit} \end{array}$$

$w = -2(50 - 10) = -80$ lit

magnitude of work done in more than one step is more than single step work done.



Ex 8. For 1 mole of monoatomic gas. Calculate w , ΔU , ΔH , q



Sol. Isochoric process

$w = 0$

$q = dU = C_v (T_2 - T_1) = \frac{3}{2} \times (400 - 300) = 150 R$

$\Delta H = C_p \Delta T = \frac{5}{2} R (400 - 300) = 250 R$

Ex 9 One mole of a non linear triatomic ideal gas is expanded adiabatically at 300 K from 16 atm to 1 atm.

Calculate Work done under the following conditions.

(i) Expansion is carried out reversibly.

(ii) Expansion is carried out irreversibly

Sol. $q = 0$

$$w = \Delta U = C_v(T_2 - T_1)$$

C_v for triatomic non linear gas = $3R$

(i) For rev. process.

$$P_1^{1-\gamma} T_1^\gamma = P_2^{1-\gamma} T_2^\gamma \quad r = \frac{4}{3} \quad T_2 = T_1 \left(\frac{P_1}{P_2} \right)^{\frac{1-\gamma}{\gamma}} = 300(16)^{\frac{1-\frac{4}{3}}{\frac{4}{3}}} = 300(2^4)^{-1/4} = 150 \text{ K}$$

$$\Delta U = w = 3R(150 - 300) = -450 \text{ R}$$

(ii) $n = 1$

$$-P_{\text{ext}}(V_2 - V_1) = C_v(T_2 - T_1)$$

$$-P_{\text{ext}} \left(\frac{RT_2}{P_2} - \frac{RT_1}{P_1} \right) = 3R(T_2 - T_1)$$

$$-1 \left(\frac{RT_2}{1} - \frac{RT_1}{16} \right) = 3R(T_2 - T_1)$$

$$-\frac{R}{16}(16T_2 - T_1) = 3R(T_2 - T_1)$$

$$-16T_2 + T_1 = 48T_2 - 48T_1$$

$$49T_1 = 64T_2$$

$$T_2 = \frac{49}{64} \times 300$$

$$T_2 = 229.69$$

$$w_{\text{irr}} = C_v(T_2 - T_1) + 3R(229.69 - 300) = -210.93 \text{ R}$$

Ex 10 One mole of an non linear triatomic ideal gas is compressed adiabatically at 300 K from 1 atm to 16 atm.

Calculate Work done under the following conditions.

(i) Expansion is carried out reversibly.

(ii) Expansion is carried out irreversibly.

Sol. $q = 0$ Adiabatic process

(i) $w_{\text{rev}} = \Delta U = C_v(T_2 - T_1)$

$$P^{1-\gamma} T^\gamma = K$$

$$T_2 = 300 \left(\frac{1}{16} \right)^{\frac{1-4/3}{4/3}} = 600 \text{ K}$$

$$w = 3R(600 - 300) = 900 \text{ R}$$

$$(ii) \quad w_{irr} = -P_{ext}(V_2 - V_1) = -P_{ext} \left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1} \right)$$

$$-P_{ext} \left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1} \right) = C_v(T_2 - T_1)$$

$$-16 \left(\frac{RT_2}{16} - \frac{RT_1}{1} \right) = 3R(T_2 - T_1)$$

$$-(T_2 - 16 T_1) = 3(T_2 - T_1)$$

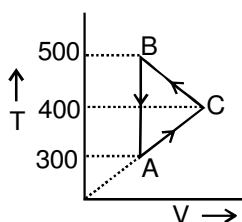
$$-T_2 + 16 T_1 = 3T_2 - 3T_1$$

$$4T_2 = 19 T_1$$

$$T_2 = \frac{19}{4} \times 300 = 1425 \text{ K}$$

$$w = \Delta U = 3R(1425 - 300) = 3375 R$$

Ex 11. Calculate work done is process BC for 1 mol of an ideal gas if total 600 cal heat is released by the gas in whole process



Sol. For cyclic process

$$dU = 0$$

$$q = -w$$

$$PV_1 = 1 \times R \times 300$$

$$PV_2 = 1 \times R \times 400$$

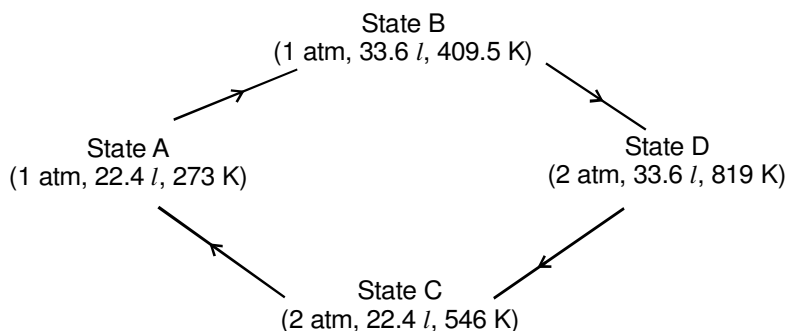
$$\Rightarrow P(V_2 - V_1) = R(400 - 300)$$

$$q = -(w_{BA} + w_{AC} + w_{CB})$$

$$-600 = -(0 + (-) 2) \times (400 - 300) + w_{CB}$$

$$w_{CB} = 800 \text{ cal}$$

Ex 12 Calculate entropy change in each step for an ideal gas (monoatomic)



Sol. $\Delta S_{A-B} = nC_p \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2} = nC_p \ln \frac{409.5}{273} = C_p \ln \frac{3}{2}$

$$\Delta S_{AC} = nC_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} = C_v \ln \frac{546}{273} = C_v \ln 2$$

$$\Delta S_{C-D} = nC_p \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2} = nC_p \ln \frac{819}{546} = C_p \ln \frac{3}{2}$$

$$\Delta S_{AC} = nC_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

$$= nC_v \ln \frac{819}{409.5} = C_v \ln \frac{3}{2}$$

Ex 13 One mole of an ideal gas is expanded isothermally at 300 K from 10 atm to 1 atm. Find the values of

ΔS_{sys} , ΔS_{surr} & ΔS_{total} under the following conditions.

(i) Expansion is carried out reversibly.

(ii) Expansion is carried out irreversibly

(iii) Expansion is free.

Sol. (i) $\Delta S_{sys} = nC_p \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2} = 0 + R \ln 10 = R \ln 10$

$$\Delta S_{surr.} = -\Delta S_{sys} = -R \ln 10$$

$$\Delta S_{total} = 0$$

(ii) $\Delta S_{sys} = R \ln 10$

$$\Delta S_{surr.} = \frac{-q_{irr}}{T}$$

$$\Delta U = 0 = q + w$$

$$q_{irr} = p_{ext}(v_2 - v_1)$$

$$q_{irr} = p_{ext} \left[\frac{RT}{p_2} - \frac{RT}{p_1} \right] = RT \left[\frac{1}{1} - \frac{1}{10} \right]$$

$$= RT \times \frac{9}{10} = \frac{9}{10} \times R \times 300 = 270R$$

$$\Delta S_{surr} = \frac{-q_{irr}}{T} = \frac{-9R}{10}$$

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} = R \ln 10 - \frac{9R}{10}$$

(iii) Free expansion $\Delta T = 0$

$$w = 0$$

$$q = 0$$

$$\Delta S_{\text{sys}} = R \ln 10$$

$$\Delta S_{\text{surr}} = \frac{-q_{\text{irr}}}{T} = 0$$

$$\Delta S_{\text{total}} = R \ln 10$$

Ex 14 One mole of a non linear triatomic ideal gas is expanded adiabatically at 300 K from 16 atm to 1 atm. Find the values of ΔS_{sys} , ΔS_{surr} & ΔS_{total} under the following conditions.

(i) Expansion is carried out reversibly.

(ii) Expansion is carried out irreversibly

(iii) Expansion is free.

Sol. For non-linear tri-atomic ideal gas

$$C_v = 3R, C_p = 4R$$

$$(i) \quad \Delta S_{\text{sys}} = nC_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} = 0$$

$$q = 0$$

$$\Delta S_{\text{surr}} = -\Delta S_{\text{sys}} = 0$$

$$\Delta S_{\text{total}} = 0$$

(ii) First of all we will have to calculate the temperature of the gas after it has undergone the said adiabatic

reversible expansion we have $q = 0$

$$\Delta U = q + w$$

$$nC_v (T_2 - T_1) = -p_{\text{ext}} (V_2 - V_1)$$

$$3R(T_2 - 300) = -1 \left[\frac{RT_2}{p_2} - \frac{RT_1}{2} \right] = -R \left[\frac{T_2}{1} - \frac{300}{16} \right]$$

$$T_2 = 229.68 \text{ K}$$

$$\Delta S_{\text{sys}} = nC_p \ln \frac{T_2}{T_1} + nR \ln \frac{p_1}{p_2}$$

$$= 4R \ln \frac{229.68}{300} + R \ln \frac{16}{1} = -1.068 R + 2.77 R = 1.702 R$$

$$\Delta S_{\text{surr}} = \frac{-q_{\text{irr}}}{T} = 0$$

$$\Delta S_{\text{total}} = \Delta S_{\text{sys}} = 1.702 R$$

(iii) In free adiabatic expansion we have

$$w = 0$$

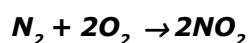
$$q = 0 \quad \Delta T = 0$$

$$\Delta S_{\text{sys}} = nR \ln \frac{p_1}{p_2} = R \ln 16 = 2.77R$$

$$\Delta S_{\text{surr}} = \frac{-q_{\text{irr}}}{T} = 0$$

$$\Delta S_{\text{total}} = \Delta S_{\text{sys}} = 2.77R$$

Ex 15 For the reaction



Given : at 1 atm, 300 K

$$S_{\text{N}_2} = 180 \text{ J/mol/K}$$

$$S_{\text{O}_2} = 220 \text{ J/mol/K}$$

$$S_{\text{NO}_2} = 240 \text{ J/mol/K}$$

$$C_p(\text{N}_2) = 30 \text{ J/mol/K}$$

$$C_p(\text{O}_2) = 30 \text{ J/mol/K}$$

$$C_p(\text{NO}_2) = 40 \text{ J/mol/K}$$

Calculate

(i) $\Delta S_{300 \text{ K}, 1 \text{ atm}}$

(ii) $\Delta S_{400 \text{ K}, 1 \text{ atm}}$

(iii) $\Delta S_{300 \text{ K}, 5 \text{ atm}}$

(iv) $\Delta S_{400 \text{ K}, 5 \text{ atm}}$

Sol. (i) $(\Delta S_r)_{300} = 2S_{\text{NO}_2} - 2S_{\text{O}_2} - S_{\text{N}_2} = 2 \times 240 - 2 \times 220 - 180 = -140 \text{ J mol}^{-1}\text{K}^{-1}$
 $(\Delta C_p)_r = 2C_p(\text{NO}_2) - 2C_p(\text{O}_2) - C_p(\text{N}_2) = 2 \times 40 - 2 \times 30 - 30 = -10 \text{ J mol}^{-1}\text{K}^{-1}$

(ii) $(\Delta S_r)_{400} = (\Delta S_r)_{300} + (\Delta C_p)_r \ln \frac{T_2}{T_1} = -140 - 10 \ln \frac{4}{3} = -142.88 \text{ J mol}^{-1}\text{K}^{-1}$

(iii) $(\Delta S_r)_{300\text{K}, 5 \text{ atm}} = (\Delta S_r)_{300\text{K}, 1 \text{ atm}} + \Delta n_g R \ln \frac{p_1}{p_2} = -140 + (-1)R \ln \frac{1}{5} = -140 + R \ln 5$
 $= -140 + 8.314 \ln 5 = -126.62 \text{ J mol}^{-1}\text{K}^{-1}$

(iv) $(\Delta S_r)_{400\text{K}, 5 \text{ atm}} = (\Delta S_r)_{400\text{K}, 1 \text{ atm}} - R \ln \frac{1}{5} = -142.88 + R \ln 5 = -129.5 \text{ J mol}^{-1}\text{K}^{-1}$

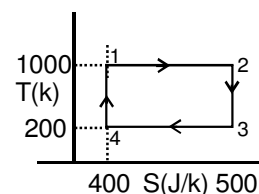
Ex 16 From the T-S diagram of a reversible carnot engine calculate :

(i) **efficiency**

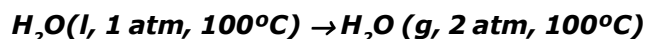
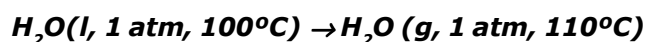
(ii) **workdone per cycle**

(iii) **Heat taken from the source and rejected to sink**

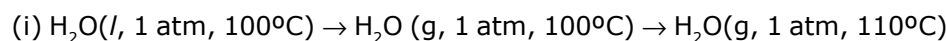
(iv) **In order to illuminate 10000 bulbs of 40 watt power each calculate the no. of cycle per second the above must go through.**



- Sol.** (i) $\eta = \frac{1000 - 200}{1000} = 80\%$
- (ii) $q_{\text{rev1-2}} = \int T ds = 1000 \times 100 \text{ J}$
 $q_{3-4} = \int T ds = -200 \times 100 \text{ J}$
 $q_{\text{net}} = 800 \times 100 = 80 \text{ kJ}$
 $W = -80 \text{ kJ}$
- (iii) $10^5 \text{ J},$
 $2 \times 10^4 \text{ J}$
- (iv) 5

Ex 17 Calculate entropy change

$$\Delta H_{\text{vap}} = 40 \text{ kJ/mol} \quad C_p(l) = 75 \text{ J/mol/K} \quad C_p(g) = 35 \text{ J/mol/K}$$

Sol. For 1 mol

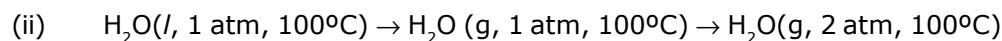
(A)

(B)

(C)

$$\Delta S_{A \rightarrow B} = \frac{\Delta H_{\text{vap}}}{T} = \frac{40 \times 1000}{373}$$

$$\Delta S_{S \rightarrow C} = n C_p(g) \ln \frac{T_2}{T_1} = 1 \times 35 \ln \frac{383}{373}$$



(A)

(B)

(C)

$$\Delta S_{A \rightarrow B} = \frac{\Delta H_{\text{vap}}}{T} = \frac{40.000}{373}$$

$$\Delta S_{S \rightarrow C} = nR \ln \frac{P_2}{P_1} = 1 \times R \ln \frac{1}{2}$$

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Ex 18 Calculate ΔG for**Given :**

$$\Delta H_{373} = 40 \text{ kJ}$$

$$C_p(\text{H}_2\text{O}, l) = 75 \text{ J/mol/K}$$

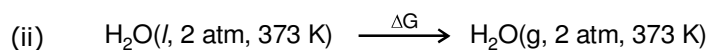
$$C_p(\text{H}_2\text{O}, g) = 35 \text{ J/mol/K}$$

Sol. (i) $\Delta H_{300} - \Delta H_{373} = (-40)(-73)$

$$\Delta H_{300} = 42920$$

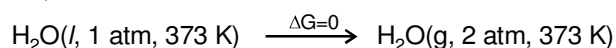
$$\Delta S = \frac{\Delta H_{300}}{300}$$

$$\Delta G_{300} = \Delta H_{300} - 300 \Delta S_{300}$$

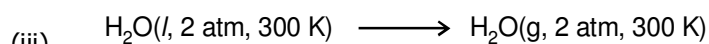


$$\downarrow \Delta G_1 = [V(1-2)]$$

$$\uparrow \Delta G_3 = nRT \ln \frac{2}{1}$$

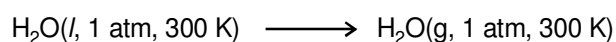


$$\Delta G = V(1-2) + \Delta G_2 + nRT \ln \frac{2}{1}$$

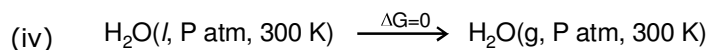


$$\downarrow \Delta G_1 = [V(P_2 - P_1)]$$

$$\uparrow \Delta G_3 = nRT \ln \frac{P_2}{P_1}$$



$$\Delta G = V(P_2 - P_1) + [\Delta H_{300} - 300\Delta S_{300}] + nRT \ln \frac{P_2}{P_1}$$



$$\downarrow \Delta G_1 = [V(1-P)]$$

$$\uparrow \Delta G_3 = nRT \ln \frac{P_2}{P_1}$$



$$V(1-P) + [\Delta H_{300} - 300\Delta S_{300}] + nRT \ln P = 0$$

$$P = 26.28 \text{ torr}$$