

Today's GOAL



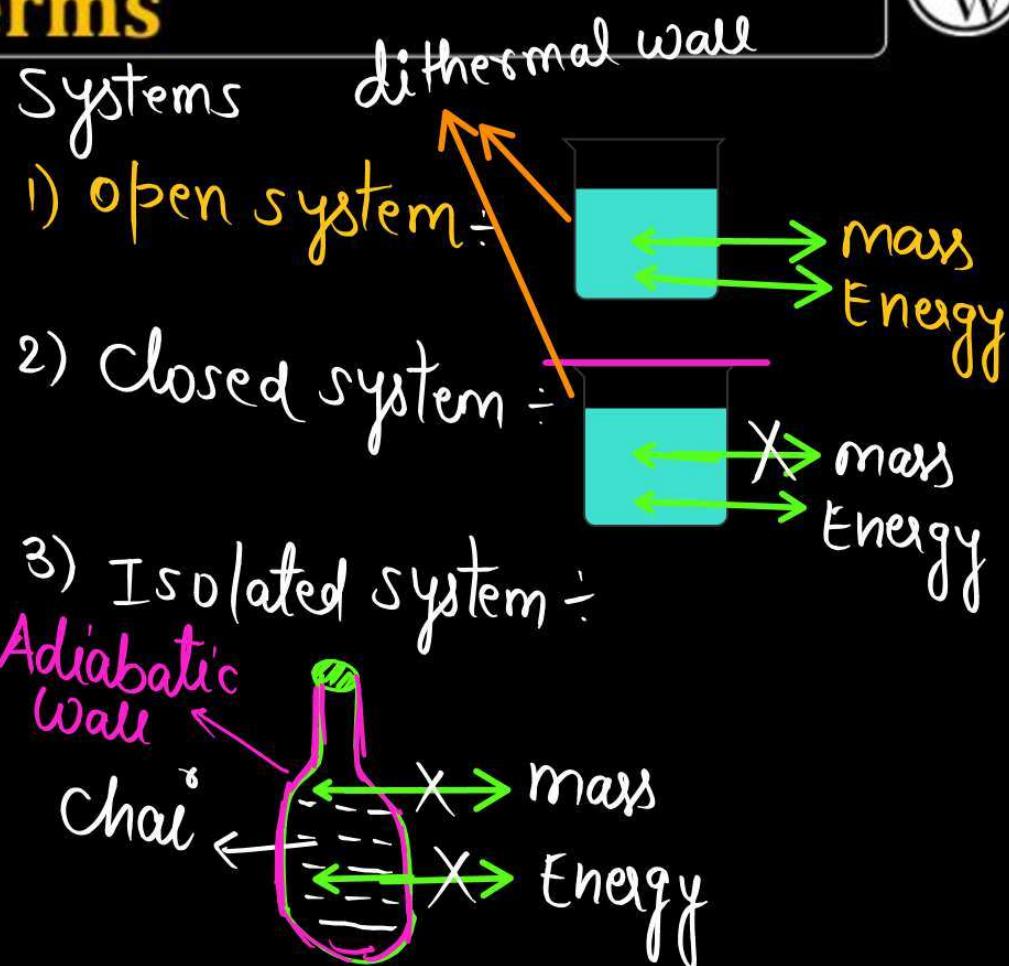
Thermodynamics

Basic Terms

System : The part of universe which is under observation.

Surroundings : The rest of the part of the universe (other than sys)

The Universe = sys + surr



Prop of system

1. Intensive

mass or size independent

$$\frac{E}{E} = I$$

molar $\rightarrow I$
specific $\rightarrow I$

Examples

T, P, C_m, C_s, d, M, V.P, R.I, M.P,
B.P, Surface tension, Viscosity

2. Extensive

mass or size dependent

Examples

w, V, C, E, H, G, S,

State and Path Functions

1. State function

Depends on initial and final state

$$(P_1, V_1, T_1) \longrightarrow (P_2, V_2, T_2)$$

ΔU , ΔH , ΔG , ΔS , etc

$$U_2 - U_1$$

2. Path Function

Path dependent

w , q , C or C_T
Work Heat Total heat capacity

Internal Energy

- ① The sum of all energies like K.E, P.E, B.E etc
- ② The absolute value of internal energy can not be determine but we can calculate the change in Internal energy
- ③ ΔU or $\Delta E = (U_2 - U_1)$ or $(E_2 - E_1)$
- ④ State funcⁿ
- ⑤ ΔU is depends on temp

1st Law of thermodynamics

Energy conservation

$$\Delta U = q + w$$

ΔU = change in internal energy

q = Heat

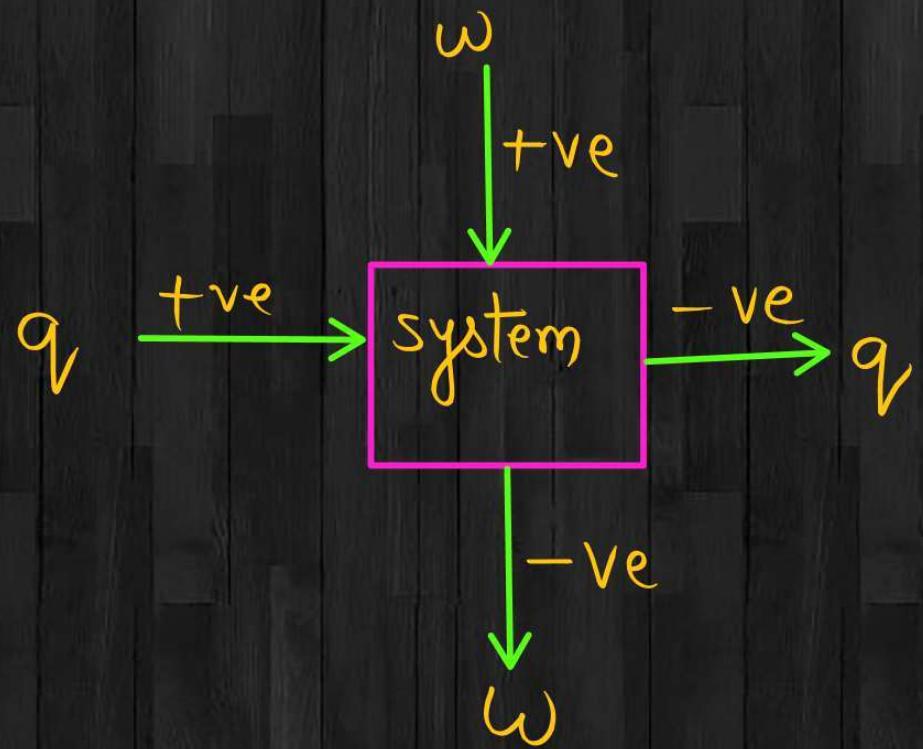
w = work

Q. Find ΔU if a system absorbs 15 kJ of heat and does 5kJ of work?

$$q = +15 \text{ kJ} \quad w = -5 \text{ kJ}$$

$$\Delta U = 15 - 5 = 10 \text{ kJ}$$

- ① work done by the system = -ve
- ② work done on the system = +ve
- ③ Heat absorbed by the system = +ve
- ④ Heat released by the system = -ve

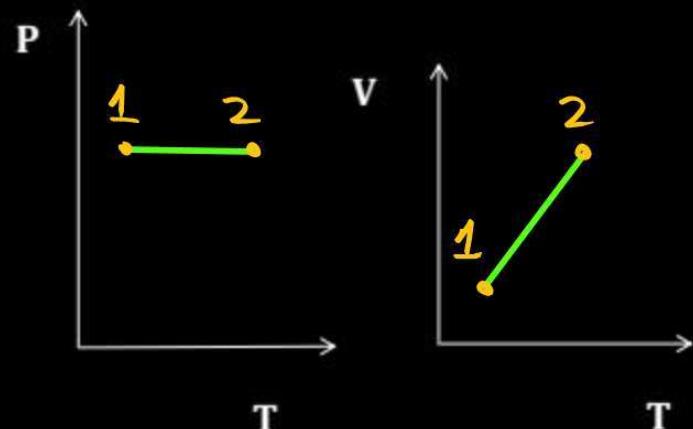
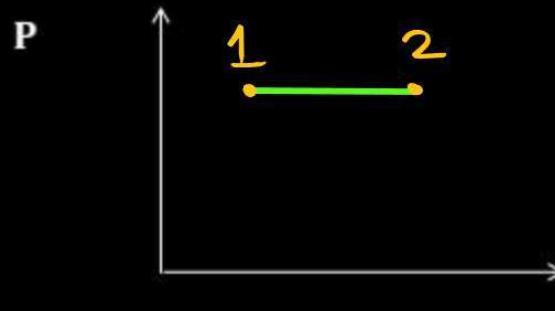


$$(Pv = nRT)$$

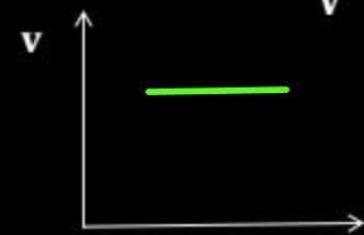
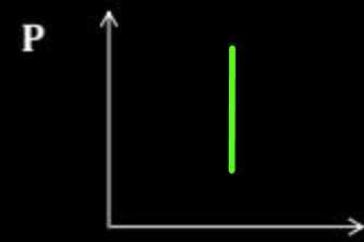
Processes



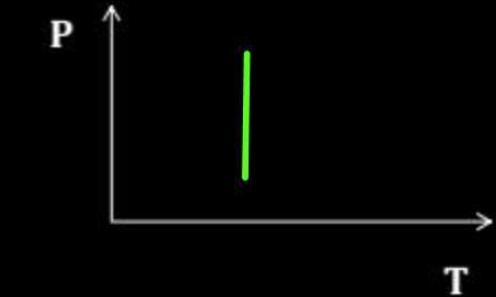
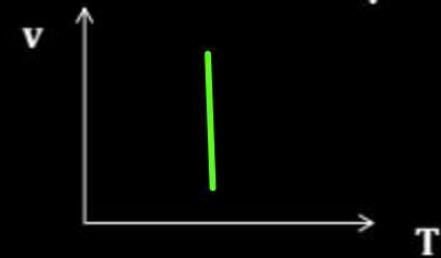
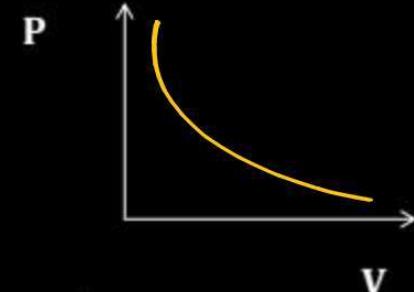
Isobaric ($\Delta P = 0$)



Isochoric ($\Delta V = 0$)



Isothermal ($\Delta T = 0$)



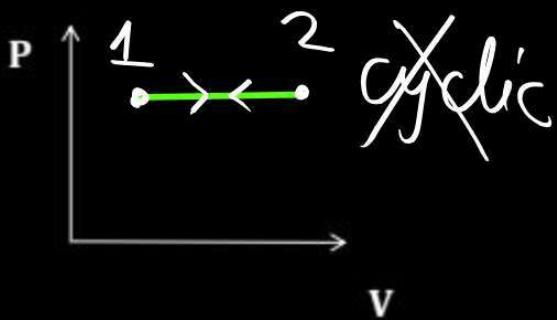
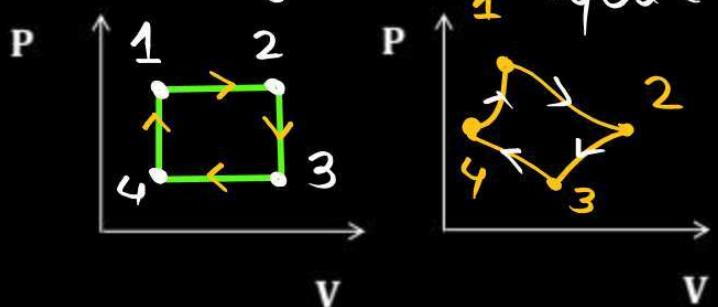
Processes

at const
External
pressure

Rev

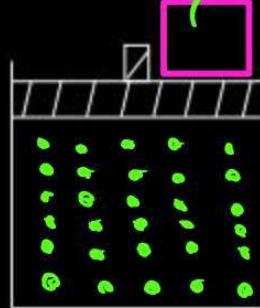
P
W

Cyclic The process in which initial and final states are same with the formation of loop.



Irreversible

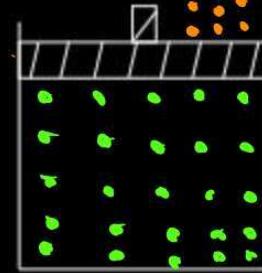
fixed
mass



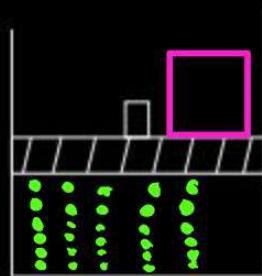
Fast
at const
Ext
pressure
one step

Reversible

variable
pressure



slow
Infinite
steps
Variable
pressure



Heat Capacity (C)

or C_T

1. C The amount of Heat absorbed by a system to increase its temp by 1°C

$$C \text{ or } C_T = \frac{+q}{\Delta T}$$

2. C_m

$$C_m = \frac{+q}{n\Delta T}$$

3. C_s or S

$$C_s \text{ or } S = \frac{+q}{\omega\Delta T}$$

4. C_p

$$C_p = \frac{+q_p}{\Delta T}$$

$$[\Delta H = nC_{p,m}\Delta T]$$

5. $C_{p,m}$

$$C_{p,m} = \frac{+q_p}{n\Delta T}$$

6. $C_{p,s}$

$$C_{p,s} = \frac{+q_p}{\omega\Delta T}$$

7. C_v

$$C_v = \frac{+q_v}{\Delta T}$$

$$[\Delta U = nC_{v,m}\Delta T]$$

8. $C_{v,m}$

$$C_{v,m} = \frac{+q_v}{n\Delta T}$$

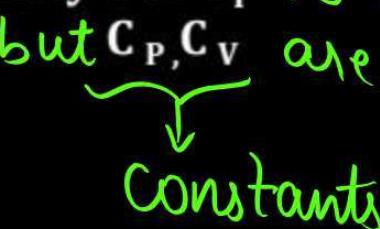
9. $C_{v,s}$

$$C_{v,s} = \frac{+q_v}{\omega\Delta T}$$

Important points related to heat capacity

1. Mayer's relation

$$C_{P,m} - C_{V,m} = R$$

2. Heat capacity C or C_T is a path funcⁿ
but C_P, C_V are not pathfuncⁿ

Constants

3. Heat Capacity may vary from $-\infty$ to ∞ depending upon the process

$$4. C_T = n C_m = w C_s$$

$$C_m = M.W C_s$$

5. Isothermal $C = \infty$
Isobaric $C = C_P$
Isochoric $C = C_V$
Adiabatic ($q=0$) $C = 0$

Adiabatic process

$$q_v = 0$$

$$C_V = \frac{fR}{2}$$

$$C_P - C_V = R$$

P
W

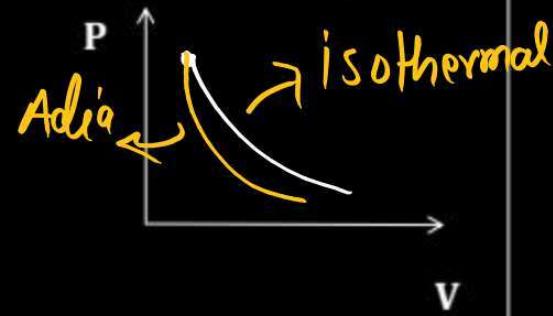
$$q_v = 0$$

for Rev adia process
 $PV^{\gamma} = \text{const}$

$$\gamma = \frac{C_P}{C_V} (\gamma > 1)$$

$$\gamma = 1 + \frac{2}{f}$$

$f = \text{degree of freedom}$



Gas
 Mono atomic
 He, Ne, etc

$$f = \frac{3+0}{T} = 3$$

$$C_V = \frac{3R}{2}$$

$$C_P = \frac{5R}{2}$$

$$\gamma = \frac{5}{3}$$

Diatomeric
 $\text{H}_2, \text{O}_2, \text{N}_2$ etc

$$f = \frac{3+2}{T} = 5$$

$$C_V = \frac{5R}{2}$$

$$C_P = \frac{7R}{2}$$

$$\gamma = \frac{7}{5}$$

Triatomic
 Linear
 CO_2

$$f = \frac{3+3}{T} = 6$$

$$C_V = \frac{6R}{2} = 3R$$

$$C_P = 4R$$

$$\gamma = \frac{4}{3}$$

Triatomic
 non Linear
 SO_2

W, q, ΔU and ΔH Calculation

$$\Delta U = q + w$$



Process	Work done <u>by</u> the sys	q	ΔU (q_v)	ΔH (q_p)
1. Reversible Isothermal	$w = -nRT \ln\left(\frac{V_2}{V_1}\right)$ $w = -nRT \ln\left(\frac{P_1}{P_2}\right)$	$q = -w$	0	0
2. Irreversible Isothermal ($P_{ext} = P_2$)	$w = -P_{ext}(V_2 - V_1)$ $= -P_{ext}\left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1}\right)$	$q = -w$	0	0
3. Isobaric	$w = -P_{ext}(V_2 - V_1)$ $= -P_{ext}\left(\frac{nRT_2}{P} - \frac{nRT_1}{P}\right)$	$q = q_p$	$q_v = nC_{V,m}\Delta T$	$q_p = nC_{P,m}\Delta T$

Work done by the system = $-P_{\text{ext}} \Delta V$

Rev isothermal

$$P_{\text{ext}} = P_{\text{in}} \pm dP$$

$$P_{\text{ext}} \approx P_{\text{in}}$$

$$\omega = -P_{\text{ext}} \Delta V$$

$$\omega = -P_{\text{in}} \Delta V$$

$$\omega = -P_{\text{in}} \int_{V_1}^{V_2} dV$$

$$\omega = -nRT \left(\ln V \right)_{V_1}^{V_2}$$

$$\omega = -nRT \ln \left(\frac{V_2}{V_1} \right)$$

W, q, ΔU and ΔH Calculation

$$\Delta V = \vec{q} + \vec{\omega}$$

$\Delta V = \vec{q}$ ($\vec{\omega} = \vec{0}$)



Process	work done by the sys	q	ΔU (q _v)	ΔH (q _p)
4. Isochoric	0	q _v = 0	ΔU = N C _{V,m} ΔT	ΔH = N C _{P,m} ΔT
5. Rev. Adiabatic	$\omega = \frac{nR\Delta T}{\gamma - 1}$	q _v = 0	"	"
6. Irr. Adiabatic	$\omega = \frac{nR\Delta T}{\gamma - 1}$	q _v = 0	"	"

How to find final Temp in Adiabatic process

Rev

$$Pv^{\gamma} = \text{const}, \quad T v^{\gamma-1} = \text{const}$$

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

Irr

$$\Delta U = W_{ad}$$

$$n c_{v,m} \Delta T = - P_{ext} (V_2 - V_1)$$

$$n c_{v,m} \Delta T = - P_{ext} \left(\frac{n R T_2}{P_2} - \frac{n R T_1}{P_1} \right)$$

W, q, ΔU and ΔH Calculation

P
W

Process	work done by the sys	q	ΔU (q _v)	ΔH (q _p)
<u>7. Cyclic process</u> All state func ⁿ = 0	$W = \text{Area enclosed}$ C.W loop $\omega = -ve$ A.C.W loop $\omega = +ve$	$q = -\omega$	0	0
<u>8. Polytropic process</u> $PV^{\gamma} = \text{const}$	$\omega = \frac{nR\Delta T}{\gamma-1}$ 1,2 Isobaric 1,3 Isothermal 1,4 Adia 1,5 Isochoric	$q = nC_m \Delta T$ $(C_m = C_v + \frac{R}{1-\gamma})$	$nC_v m \Delta T$	$nC_p m \Delta T$

Relation b/w ΔH and ΔU

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

Heat of Rxn (Enthalpy of Rxn)

Internal energy change

$R = \text{gas const}$

$$R = \frac{25}{3} \text{ J/mol-K}$$

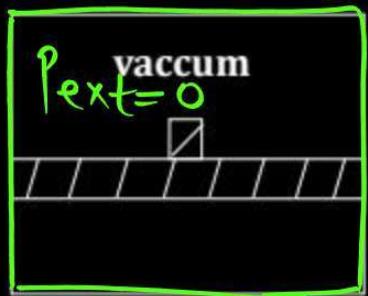
$$R = 2 \frac{\text{cal}}{\text{mol-K}}$$

$$\Delta U_p = q_v + \Delta n_g RT$$

$\Delta n_g = \frac{\text{no. of moles of gas products}}{\text{no. of moles of gas reactant}}$

Free Expansion

Expansion against vacuum



$$\omega = 0, q = 0, \Delta U = 0$$

Practice upto 1st Law of Thermodynamics

1. The work done during the expansion of gas from a volume of 14 dm^3 to 16 dm^3 against a constant external pressure of 2 atm at const pressure is?

$$\begin{aligned}\omega &= -P_{\text{ext}}(\Delta V) \quad 1 \text{ Latm} = 100 \text{ J} \\ &= -2(16-14) \\ &= -2 \times 2 \\ &= -4 \text{ Latm} \\ &= 24 \text{ Cal} \\ &= 100 \times 10^7 \text{ erg}\end{aligned}$$

2. If ΔH for Rxn $N_2 + 3H_2 \rightarrow 2NH_3$ is -92 kJ at 300 K find ΔU (in kJ) at 300 K ?

$$\begin{aligned}\Delta H &= \Delta U + \Delta n g R T \\ -92 \times 10^3 &= \Delta U + (-2) \times \frac{25}{3} \times 300 \\ -92000 &= \Delta U - 5000 \\ \Delta U &= -92000 + 5000 \\ \Delta U &= -87000 \text{ J} \\ \Delta U &= -87 \text{ kJ}\end{aligned}$$

Practice upto 1st Law of Thermodynamics

3. 3 moles of an ideal gas expanded spon into vacuum. The work done will be?

$$\omega = 0$$

4. Which is not state funcⁿ.
- (A) $q_p = \Delta H$ (B) $q_v = \Delta U$
(C) $W_{ad} = \Delta U$ (D) $W_{isother}$

Practice upto 1st Law of Thermodynamics

5. Which is intensive prop
- (A) ΔH
 - (B) ΔU
 - (C) Volume
 - (D) Specific heat

6. 1 mole of an ideal gas at 300k is expanded isothermally from initial volume of 1L to 10L .find W, q and ΔU (in cal)? $\Delta V = 0$

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

$$= -2.3 \times 1 \times 2 \times 300 \log\left(\frac{10}{1}\right)$$

$$= -4.6 \times 300 \text{ Cal}$$

$$q = -w = +4.6 \times 300 \text{ Cal}$$

Practice upto 1st Law of Thermodynamics

7. 5 mol of O₂ gas is heated at const volume from 10°C to 20°C find ΔU
 (given C_{p,m} = 7 cal/mol-k R = 2 cal/mol-k)

$$\Delta U = n C_{p,m} \Delta T$$

$$= 5 (C_{p,m} - R) (T_2 - T_1)$$

$$= 5 (7 - 2) \times (20 - 10)$$

$$= 5 \times 5 \times 10$$

$$= 250$$

8. If a gas absorbs 100 J of Heat and expands by 500 cm³ against a const pressure of 2 × 10⁵ N/m² find ΔU?

$$q = +100 \text{ J}, \omega = -P_{\text{ext}} \Delta V$$

$$\omega = -2 \times 10^5 \times 500 \times 10^{-6}$$

$$\omega = -1000 \times 10^{-1}$$

$$\omega = -100 \text{ J}$$

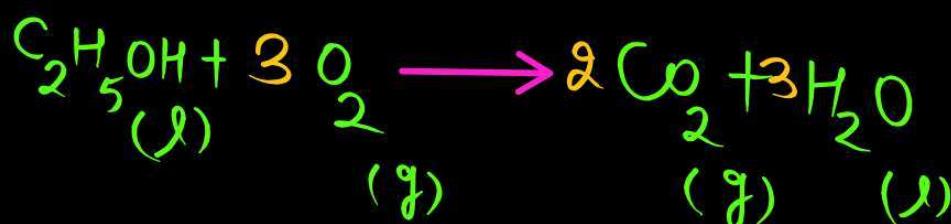
$$\Delta U = q + \omega$$

$$= 100 - 100 = 0$$

Practice upto 1st Law of Thermodynamics



9. Find Δn_g if we consider the combustion of 1 mol liq ethanol if reactants and products are at 298 K?



$$\Delta n_g = 2 - 3 = -1$$

10. A gas expands adiabatically at const pressure such that $T \propto V^{-1/2}$ find γ ?

$$T = k V^{-\frac{1}{2}}$$

$$T V^{\frac{1}{2}} = k$$

$$T V^{\gamma-1} = k$$

$$\gamma - 1 = \frac{1}{2}$$

$$\gamma = 3/2$$

Practice upto 1st Law of Thermodynamics

$$(\bar{T}_1 > \bar{T}_2)$$

11. 1 mol of an ideal gas ($C_{vm} = \frac{5R}{2}$) at 300k and 5 atm is expanded adiabatically to a final pressure of P_2 2 atm against a constant pressure of P_{ext} 2 atm. find final temp of gas?

Irr Adia

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

$$1 \times \frac{5R}{2} (\bar{T}_2 - 300) = -2 \left(\frac{1 \times R \times \bar{T}_2}{2} - \frac{1 \times R \times 300}{5} \right)$$

$$\frac{5\bar{T}_2}{2} - \frac{5 \times 300}{2} = \left(-2\bar{T}_2 + 2 \times 300 \right)$$

$$\frac{5\bar{T}_2}{2} - 750 = -\bar{T}_2 + 120$$

$$\frac{5\bar{T}_2}{2} + \bar{T}_2 = 750 + 120$$

$$\frac{7\bar{T}_2}{2} = 870 \quad \begin{aligned} \bar{T}_2 &= 2 \times 870 \\ &= 248.5 K \end{aligned}$$

Practice upto 1st Law of Thermodynamics

P
W

$$T_1 = 300 \text{ K}, V_1 = 2 \text{ L}, V_2 = 16 \text{ L}$$

$$T V^{\gamma-1} = \text{const}$$

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

$$T_1 V_1^{2/3} = T_2 V_2^{2/3}$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{2/3}$$

- $\gamma = 5/3$
12. Calculate the final temp of a monoatomic ideal gas that is expanded Rev and adia from 2L to 16L at 300 K?

$$\begin{aligned} \frac{T_2}{300} &= \left(\frac{2}{16} \right)^{2/3} \\ &= \left(\frac{1}{8} \right)^{2/3} \\ &= \left(\frac{1}{2} \right)^{3 \times 2/3} \\ &= \frac{1}{4} \end{aligned}$$

$$\begin{aligned} \frac{T_2}{300} &= \frac{1}{4} \\ T_2 &= \frac{300}{4} \\ T_2 &= 75 \text{ K} \end{aligned}$$

Entropy

① The degree of randomness or disorder ness

$$S < L < G$$

② Math. entropy can be defined as the heat absorbed by the system in rev process at a particular temp.

③

$$\Delta S = + \frac{q_{rev}}{T}$$

④ State funcⁿ

(in cyclic process) $\Delta S = 0$

⑤ Extensive prop

⑥ Unit $\rightarrow \frac{J}{K}$

Calculation of Entropy in diff process

General formula :-

$$\Delta S = nC_{V,m} \ln\left(\frac{T_2}{T_1}\right) + nR \ln\left(\frac{V_2}{V_1}\right)$$

$$\Delta S = nC_{P,m} \ln\left(\frac{T_2}{T_1}\right) + nR \ln\left(\frac{P_1}{P_2}\right)$$

Case① In Isobaric process

$$\Delta S = nC_{P,m} \ln\left(\frac{T_2}{T_1}\right)$$

Case② Isochoric process

$$\Delta S = nC_{V,m} \ln\left(\frac{T_2}{T_1}\right)$$

Case③ Isothermal

$$\Delta S = nR \ln\left(\frac{V_2}{V_1}\right) = nR \ln\left(\frac{P_1}{P_2}\right)$$

Rev Adia

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

$$\Delta S = 0$$

Rev Adia processes are also known as isoentropic processes

Irr Adia

General formulae

Entropy during phase transition

$S \rightleftharpoons L$

$$\Delta S_{\text{fus}} = \frac{\Delta H_{\text{fus}}}{T}$$

$L \rightleftharpoons G$

$$\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T}$$

$S \rightleftharpoons G$

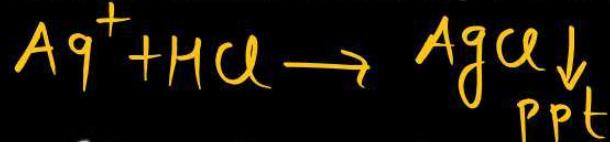
$$\Delta S_{\text{sub}} = \frac{\Delta H_{\text{sub}}}{T}$$

Some famous points related to entropy

1. Entropy Graphite > Diamond ✓
2. On rusting of Fe , Entropy increases ✓
3. On dissolution , Entropy increases ✓



4. Silver ion on reaction with HCl, Entropy decreases ✓



5. On boiling of Egg , Entropy increases ✓

Denaturation of protein

6. On stretching of rubber band , Entropy decreases due to Alignment of molecules
7. On mixing , Entropy increases ✓

⑧ T ↑ avg KE ↑ , Entropy ↑

⑨ P ↓ Entropy ↑

Entropy Practice

1. The enthalpy change for transition of liq to steam is 40 kJ/mol at 400 k
find ΔS for the process?

$$\begin{aligned}\Delta S &= \frac{\Delta H}{T} \\ &= \frac{40 \times 1000}{400} \\ &= 100 \frac{\text{J}}{\text{mol-K}}\end{aligned}$$

2. 3 mol of an ideal gas expand rev from a volume of 8 dm³ to 80 dm³ at 300 K find ΔS (J/k)?

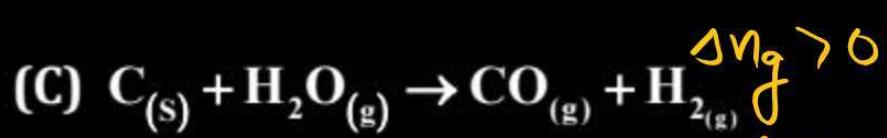
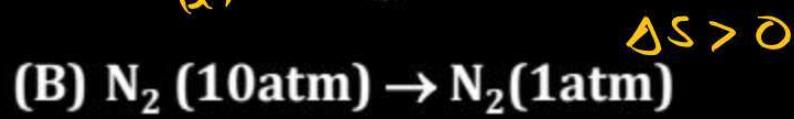
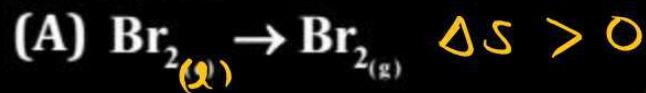
$$\begin{aligned}\Delta S &= nR \ln \frac{V_2}{V_1} \\ &= 3 \times \frac{25}{3} \times 2.3 \log\left(\frac{80}{8}\right) \\ &= 25 \times 2.3\end{aligned}$$

(S < L < G)

Entropy Practice



3. $\Delta S < 0$ for

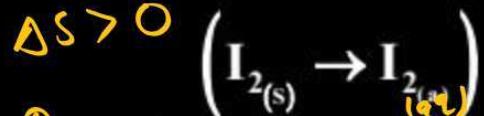


$T \downarrow$ Entropy \downarrow

$$\Delta S < 0$$

4. $\Delta S < 0$ for

(A) Dissolution of I_2 in a solvent



$\Delta S < 0$ (B) HCl is added to $\underline{\text{AgNO}_3}$ and $\underline{\text{AgCl}}$ ppt is formed

$\Delta S > 0$ (C) A partition is removed to allow gases to mix

$\Delta S > 0$ (D) On boiling of egg

2nd Law of thermo-D (SLOT)

The Entropy of Univ is always increasing
or

for all natural process $\Delta S_{\text{Univ}} > 0$
(Irr process)

for Rev process $\Delta S_{\text{Univ}} = 0$

$$\Delta S_{\text{Univ}} \geq 0$$

for Irr process

q amount of heat is released by the system ($T_1 > T_2$)

$$\Delta S_{sys} = -\frac{q}{T_1} ; \Delta S_{surr} = +\frac{q}{T_2}$$

$$\begin{aligned}\Delta S_{univ} &= \Delta S_{sys} + \Delta S_{surr} \\ &= -\frac{q}{T_1} + \frac{q}{T_2} \\ &> 0\end{aligned}$$

for rev process

q amount of heat is released by the sys. ($T_1 = T_2$)

$$\Delta S_{sys} = -\frac{q}{T_1} \quad \Delta S_{surr} = +\frac{q}{T_2}$$

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

$$\begin{aligned}&= -\frac{q}{T_1} + \frac{q}{T_2} \quad T_1 = T_2 \\ &= 0\end{aligned}$$

Gibb's free energy

① The part of energy which is used to do max useful work

OR

The decrease in gibb's free energy is equal to max useful work (non-exp work)

$$-\Delta G = \omega_{\text{useful}}$$

② Gibbs Helmholtz eqⁿ

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

③ State funcⁿ

④ Extensive

⑤ ΔG is used to predict
the spont of the Rxn.

⑥

$$\Delta G_{sys} = -T \Delta S_{univ}$$

- 1) $\Delta S_{univ} > 0 ; \Delta G_{sys} < 0$ Spont
- 2) $\Delta S_{univ} < 0 ; \Delta G_{sys} > 0$ nonspont
- 3) $\Delta S_{univ} = 0 ; \Delta G_{sys} = 0$ Eq^m

Criteria for spontaneity

$$[\Delta G_{\text{sys}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}}]$$



ΔH	ΔS	Condition
+ ve	+ ve	$ \Delta H < T\Delta S $
+ ve	- ve	Always non spont.
- ve	+ ve	Always spont.
- ve	- ve	$ \Delta H > T\Delta S $

Gibb's free energy Practice

1. For a rxn $\Delta H = \cancel{40.63} \text{ kJ/mol}$ and $\cancel{\Delta S} = 100 \text{ J/k}$ find ΔG at 27°C ?

$$\begin{aligned}\Delta G &= \Delta H - T\Delta S \\ &= 40.63 \times 10^3 - 300 \times 100 \\ &= 40630 - 30000 \\ &= 10630 \\ &= 10.63 \text{ kJ/mol}\end{aligned}$$

2. Fav. condⁿ for for spont rxn when $\underline{\Delta H}$ and $\underline{\Delta S}$ both are +ve?

$$\Delta H = +ve, \Delta S = +ve$$

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

+ve +ve

$$|\Delta H| < |T\Delta S|$$

Gibb's free energy Practice



3. For Rxn $N_2 + 3H_2 \rightarrow 2NH_3$ $\Delta H = -100$ kJ and $\Delta S = -200 \text{ J/k}$ Calculate temp at which rxn will proceed in forward dirⁿ?

$$\Delta H = -100 \text{ kJ} = -100000 \text{ J}$$

$$\Delta S = -200 \text{ J/K}$$

At eq^m $\Delta G = 0$

$$\Delta H - T\Delta S = 0$$

$$T = \frac{\Delta H}{\Delta S}$$

$$T = \frac{-100000}{-200}$$

$$T = 500 \text{ K} \checkmark$$

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

-ve -ve

$|\Delta H| > |T\Delta S|$ for spont

$$T \leq 500$$

$$\underline{\Delta G < 0}$$



PYQs



Single answer correct



Q.

An ideal gas is allowed to expand from 1 L to 10 L against a constant external pressure of 1 bar. The work done in kJ is (2019 Main, 12 April I)

a. - 9.0

b. + 10.0

c. - 0.9

d. - 2.0

Solution: $W = -P_{\text{ext}} \Delta V$

$$= -1 \times (9)$$

$$= -9 \text{ L bar}$$

$$= -900 \text{ J}$$

$$= -0.9 \text{ kJ}$$



Q.

The difference between ΔH and ΔU ($\Delta H - \Delta U$), when the combustion of one mole of heptane (*l*) is carried out at a temperature T , is equal to

(2019 Main, 10 April II)

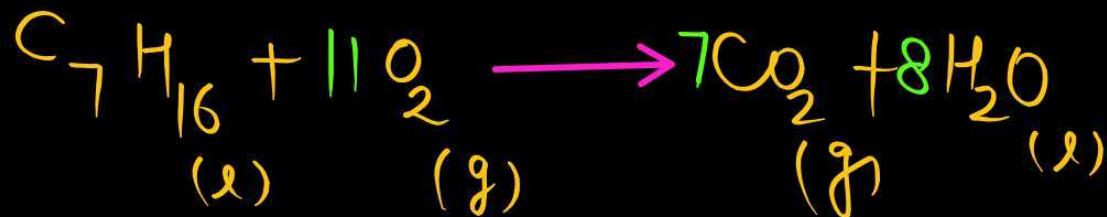
- a. $-4 RT$
 c. $4 RT$

- b. $3 RT$
 d. $-3 RT$

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

$$(\Delta H - \Delta U) = -4 RT$$

Solution:



$$\Delta n_g = 7 - 11 = -4$$



Q.

A process will be spontaneous at all temperature if

(2019 Main, 10 April I)

a.

$\Delta H > 0$ and $\Delta S < 0$

b.

$\Delta H < 0$ and $\Delta S > 0$

c.

$\Delta H < 0$ and $\Delta S < 0$

d.

$\Delta H > 0$ and $\Delta S > 0$

Solution:

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

$$\Delta H = -ve, \Delta S = +ve$$



Q.

During compression of a spring the work done is 10 kJ and 2 kJ escaped to the surroundings as heat. The change in internal energy (in kJ) is
(2019 Main, 9 April II)

a. 8

$$\omega = +10 \text{ kJ}$$

b. -12

c. 12

$$q_v = -2 \text{ kJ}$$

d. -8

Solution:

$$\Delta U = 10 - 2$$

$$= 8 \text{ kJ}$$



Q.

Among the following the set of parameters that represents path functions, is ΔV (A) $q + W$ (B) q (C) W (D) $H - TS$

(2019 Main, 9 April I)

a.

(A) and (D)

b.

(A), (B) and (C)

c.

(B), (C) and (D)

d.

(B) and (C)

Solution:



Q. 5 moles of an ideal gas at 100 K are allowed to undergo reversible compression till its temperature becomes 200 K. If $C_{V,m} = 28 \text{ JK}^{-1} \text{ mol}^{-1}$, calculate ΔU and ΔpV for this process. ($R = 8.0 \text{ JK}^{-1} \text{ mol}^{-1}$)

(2019 Main, 8 April II)

- a. $\Delta U = 2.8 \text{ kJ}; \Delta(pV) = 0.8 \text{ kJ}$
- b. $\Delta U = 14 \text{ J}; \Delta(pV) = 0.8 \text{ J}$
- c. $\Delta U = 14 \text{ kJ}; \Delta(pV) = 4 \text{ kJ}$
- d. $\Delta U = 14 \text{ kJ}; \Delta(pV) = 18 \text{ kJ}$

Solution: $\Delta U = n C_{V,m} \Delta T$

$$= 5 \times 28 \times 100$$

$$= 140 \times 100$$

$$= 14000 = 14 \text{ kJ}$$

$$\Delta(pV) = n R \Delta T$$

$$= 5 \times 8 \times 100$$

$$= 4000 = 4 \text{ kJ}$$



Q.

Which one of the following equations does not correctly represent the first law of thermodynamics for the given processes involving an ideal gas ? (Assume non-expansion work is zero)

(2019 Main, 8 April I)

$$\Delta U = q + \omega, \Delta V = 0$$

$$\Delta U = q + \omega, q = 0$$

- a. Cyclic process : $q = -W$
- b. Adiabatic process : $\Delta U = -W$
- c. Isochoric process : $\Delta U = q$
- d. Isothermal process : $q = -W$

Solution:

$$\Delta U = q + \omega$$

$$\Delta U = q + \omega$$

$$\omega = 0$$

$$\Delta V = 0$$



Q.

The reaction, $\text{MgO}(s) + \text{C}(s) \rightarrow \text{Mg}(s) + \text{CO}(g)$, for which $\Delta_r H^\circ = +491.1 \text{ kJ mol}^{-1}$ and $\Delta_r S^\circ = 198.0 \text{ JK}^{-1} \text{ mol}^{-1}$, is not feasible at 298 K. Temperature above which reaction will be feasible is

a. 2040.5 K

$$\Delta Q = 0$$

c. 2380.5 K

$$\Delta H - T\Delta S = 0$$

b. 1890.0 K

d. 2480.3 K

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

($\Delta G < 0$) +ve +ve

$$|\Delta H| < |T\Delta S|$$

Solution:

$$T = \frac{\Delta H}{\Delta S}$$

$$T = \frac{+491.1 \times 10^3}{198} =$$

Q.

The process with negative entropy change is

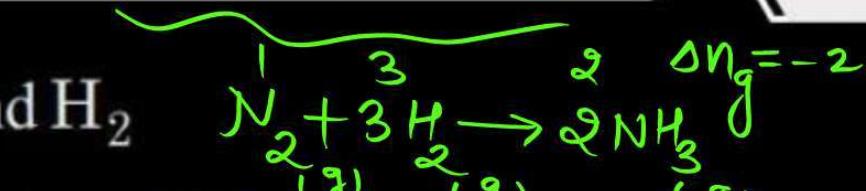
$$\Delta S < 0$$

(2019 Main, 10 Jan II)



a.

synthesis of ammonia from N₂ and H₂



b.

dissociation of CaSO₄(s) to CaO(s) and SO₃(g)



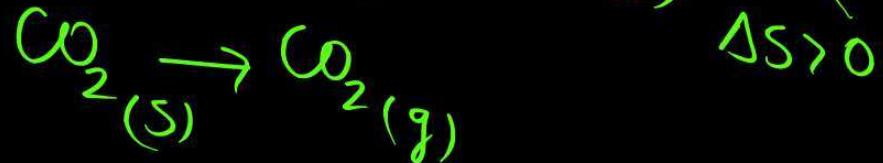
c.

dissolution of iodine in water



d.

sublimation of dry ice



$$\Delta S > 0$$

$$\Delta n_g > 0$$

$$\Delta S < 0$$

Solution:

$$\Delta S > 0$$



Q.

A process has $\Delta H = 200 \text{ J mol}^{-1}$ and $\Delta S = 40 \text{ JK}^{-1} \text{ mol}^{-1}$.

Out of the values given below, choose the minimum temperature above which the process will be spontaneous

(2019 Main, 10 Jan I)

a. 20 K

$$T = \frac{\Delta H}{\Delta S}$$

c. 5 K

$$= \frac{200}{40}$$

b. 4 K

d. 12 K

Solution:

$$T = 5 \text{ K}$$



Q.

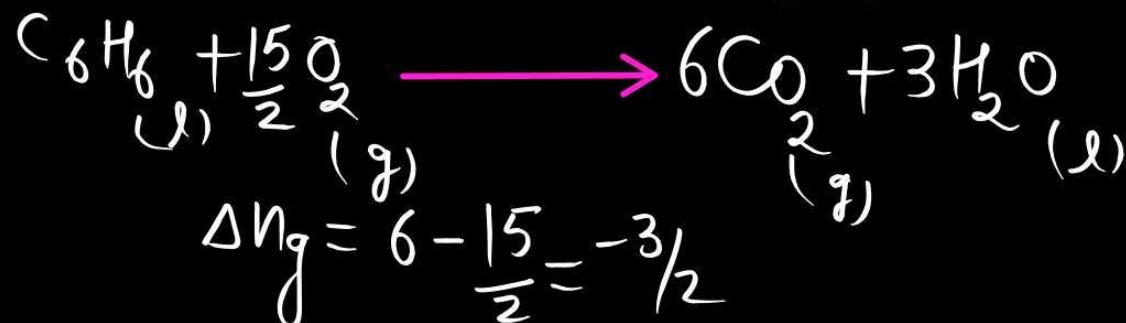
The combustion of benzene (*l*) gives $\text{CO}_2(g)$ and $\text{H}_2\text{O}(l)$. Given that heat of combustion of benzene at constant volume q_v is $-3263.9 \text{ kJ mol}^{-1}$ at 25° C ; heat of combustion (in kJ mol^{-1}) of benzene at constant pressure will be ($R = 8.314 \text{ JK}^{-1}\text{mol}^{-1}$) $q_p = ?$.

(2018 Main)

- a. 4152.6
- c. 3260

- b. -452.46
- d. -3267.6

$$\begin{aligned} q_p &= q_v + \Delta n_g R T \\ q_p &= -3263.9 - 3 \times 10^3 \times \frac{25}{2} \times \frac{298}{3} \\ q_p &= ? \end{aligned}$$

Solution:

Q.

ΔU is equal to

$$\Delta U = \cancel{q} + \cancel{w}$$

(2017 Main)



a.

isochoric work

c.

adiabatic work

b.

isobaric work

d.

isothermal work

Solution:

Q.

A piston filled with 0.04 mole of an ideal gas expands reversibly from 50.0 mL to 375 mL at a constant temperature of 37.0°C. As it does so, it absorbs 208 J of heat. The values of q and W for the process will be $\Delta V = 6 \text{ L}$ $q = +208 \text{ J}$ $W = -208 \text{ J}$ $(R = 8.314 \text{ J/mol K}, \ln 7.5 = 2.01)$

(2013 Main)



- a. $q = + 208 \text{ J}, W = - 208 \text{ J}$
- b. $q = - 208 \text{ J}, W = - 208 \text{ J}$
- c. $q = - 208 \text{ J}, W = + 208 \text{ J}$
- d. $q = + 208 \text{ J}, W = + 208 \text{ J}$

Solution:



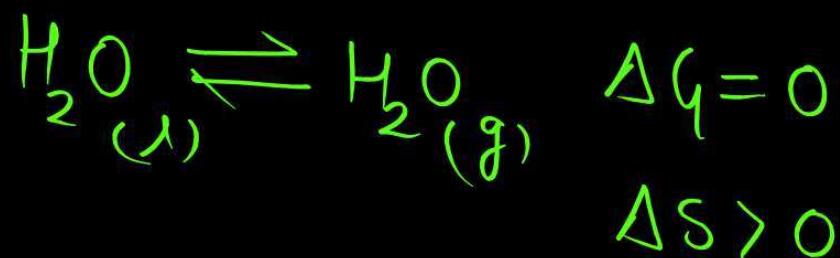
Q.

For the process $\text{H}_2\text{O}(l)(1 \text{ bar}, 373 \text{ K}) \rightarrow \text{H}_2\text{O}(g)$
 $(1 \text{ bar}, 373 \text{ K})$, the correct set of thermodynamic parameters is

(2007, 3M)

- a. $\Delta G = 0, \Delta S = + \text{ ve}$ b. $\Delta G = 0, \Delta S = - \text{ ve}$
 c. $\Delta G = + \text{ ve}, \Delta S = 0$ d. $\Delta G = - \text{ ve}, \Delta S = + \text{ ve}$

Solution:



Q.

The direct conversion of A to B is difficult, hence it is carried out by the following shown path



$$\begin{aligned}\Delta S_{A \rightarrow B} &= \Delta S_{A \rightarrow C} + \Delta S_{C \rightarrow D} + \Delta S_{D \rightarrow B} \\ &= 50 + 30 - 20 \\ &= 60 \text{ eu}\end{aligned}$$

Given that $\Delta S_{(A \rightarrow C)} = 50 \text{ eu}$
 $\Delta S_{(C \rightarrow D)} = 30 \text{ eu}$ **eu (entropy unit)**

$\Delta S_{(D \rightarrow B)} = -20 \text{ eu}$ where, eu is entropy unit

Then, $\Delta S_{(A \rightarrow B)}$ is

(2006, 3M)

a. + 100 eu

b. +60 eu

c. -100 eu

d. -60 eu

Solution:



Q.

A monoatomic ideal gas undergoes a process in which the ratio of p to V at any instant is constant and equals to 1. What is the molar heat capacity of the gas?

(2006, 3M)

a. $\frac{4R}{2}$ $\frac{P}{V} = 1$

c. $\frac{5R}{2}$ $P V^{-1} = 1$

b. $\frac{3R}{2}$

d. 0

Solution:

$$x = -1$$

$$C_m = C_{V,m} + \frac{R}{1-x}$$

$$\begin{aligned} C_m &= \frac{3R}{2} + \frac{R}{1-(-1)} \\ &= \frac{3R}{2} + \frac{R}{2} = \frac{4R}{2} \end{aligned}$$



Q.

One mole of monoatomic ideal gas expands adiabatically at initial temperature T against a constant external pressure of 1 atm from 1 L to 2 L. Find out the final temperature ($R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$) (IRR Adia)

(2005, 1M)

a. T

b. $\frac{T}{(2)^{5/3 - 1}}$

c. $T - \frac{2}{3 \times 0.082}$

d. $T + \frac{2}{3 \times 0.082}$

Solution:

$$nC_{v,m}(T_2 - T_1) = -P_{ext} \left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1} \right)$$

$$1 \times \frac{3R}{2}(T_2 - T) = -1(v_2 - v_1)$$

$$\frac{3R}{2}(T_2 - T) = -1(v_2 - v_1)$$

$$\frac{3R}{2}(T_2 - T) = -1$$

$$T_2 - T = -\frac{2}{3R}$$

$$T_2 = T - \frac{2}{3R}$$



Q.

2 moles of an ideal gas expanded isothermally and reversibly from 1 L to 10 L at 300 K. What is the enthalpy change?

(2004, 1M)

- a. 4.98 kJ
- c. -11.47 kJ

- b. 11.47 kJ
- d. 0 kJ

Solution:



Q.

One mole of a non-ideal gas undergoes a change of state (2.0 atm, 3.0 L, 95 K) \longrightarrow (4.0 atm, 5.0 L, 245 K) with a change in internal energy, $\Delta E = 30.0 \text{ L-atm}$. The change in enthalpy (ΔH) of the process in L-atm is (2002, 3M)

a. 40.0

b. 42.0

c. 44.0 $\left[\Delta H = \Delta U + \Delta(PV) \right]$

d. not defined, because pressure is not constant

Solution:

$$\Delta H = \Delta U + (P_2 V_2 - P_1 V_1)$$

$$= 30 + (4 \times 5 - 2 \times 3)$$

$$= 30 + 14$$

$$= 44 \text{ L atm}$$

Q.

Which of the following statements is false?

(2001, 1M)



- a. Work is a state function
- b. Temperature is a state function
- c. Change in the state is completely defined when the initial and final states are specified
- d. Work appears at the boundary of the system

Solution:



Q.

In thermodynamics, a process is called reversible when _____ (2001, 1M)

- a. surroundings and system change into each other
 - b. there is no boundary between system and surroundings
 - c. the surroundings are always in equilibrium with the system
 - d. the system changes into the surroundings spontaneously

Solution:



Q.

The difference between heats of reaction at constant pressure and constant volume for the reaction



(1991, 1M)

a. - 7.43

b. + 3.72

c. - 3.72

d. + 7.43

Solution:

$$\Delta q_p - \Delta q_v = \Delta n g RT$$

$$= -3 \times \frac{25}{3} \times 298 \text{ J}$$



More than one correct

Q.

An ideal gas in thermally insulated vessel at internal pressure = p_1 , volume = V_1 and absolute temperature = T_1 expands irreversibly against zero external pressure, as shown in the diagram. The final internal pressure, volume and absolute temperature of the gas are p_2 , V_2 and T_2 , respectively. For this expansion



Advanced

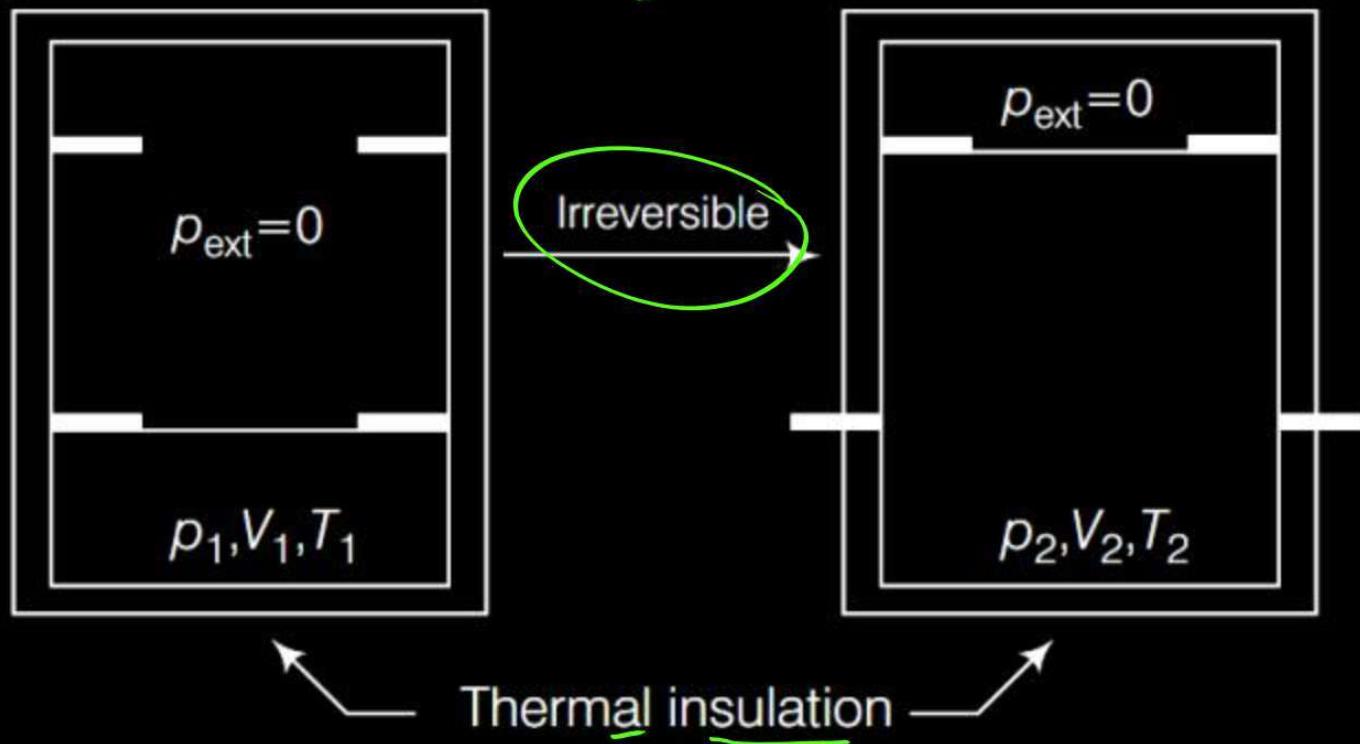
(2014 Adv)

a. $q = 0$

b. $T_2 = T_1$

c. $p_2V_2 = p_1V_1$

d. $p_2V_2^\gamma = p_1V_1^\gamma$



Q.

The reversible expansion of an ideal gas under adiabatic and isothermal conditions is shown in the figure. Which of the following statement(s) is (are) correct? (2012)

a. $T_1 = T_2$

b. $T_3 > T_1$

c. $W_{\text{isothermal}} > W_{\text{adiabatic}}$

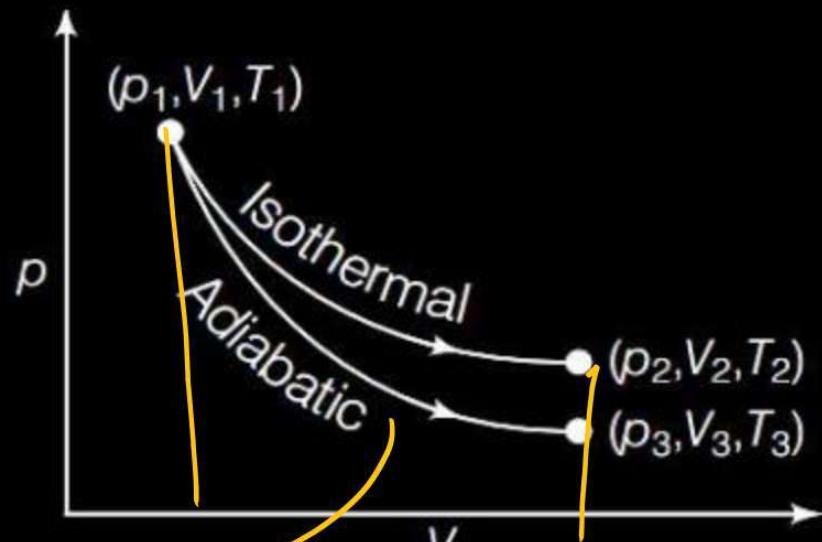
d. $\Delta U_{\text{isothermal}} > \Delta U_{\text{adiabatic}}$

Solution:

O

$$\Delta U = N R \Delta T$$

$$\Delta T = -V \frac{T_1 - T_3}{\gamma - 1}$$

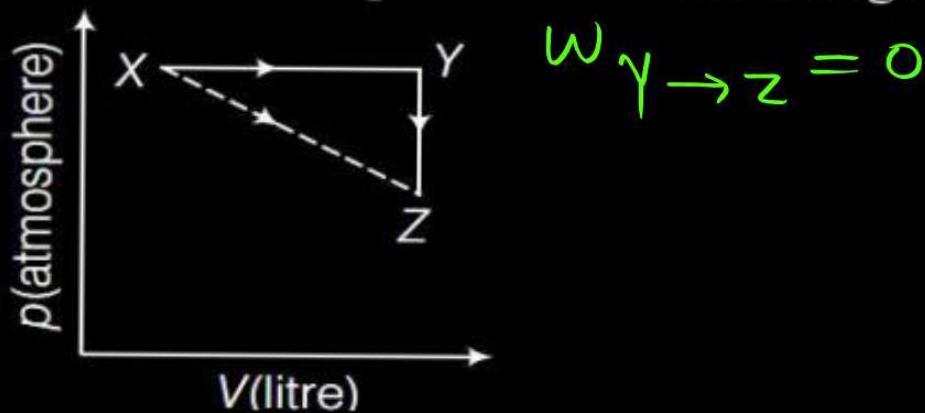


Exp $(T_1 > T_3)$

Q.*

For an ideal gas, consider only P - V work in going from initial state X to the final state Z . The final state Z can be reached by either of the two paths shown in the figure.

ΔS state
 w path



[Take ΔS as change in entropy and W as work done].

Which of the following choice(s) is (are) correct? (2012)

a.

$$\underline{\Delta S_{X \rightarrow Z}} = \underline{\Delta S_{X \rightarrow Y}} + \underline{\Delta S_{Y \rightarrow Z}}$$

b.

$$W_{X \rightarrow Z} = W_{X \rightarrow Y} + W_{Y \rightarrow Z}$$

c.

$$W_{X \rightarrow Y \rightarrow Z} = W_{X \rightarrow Y}$$

d.

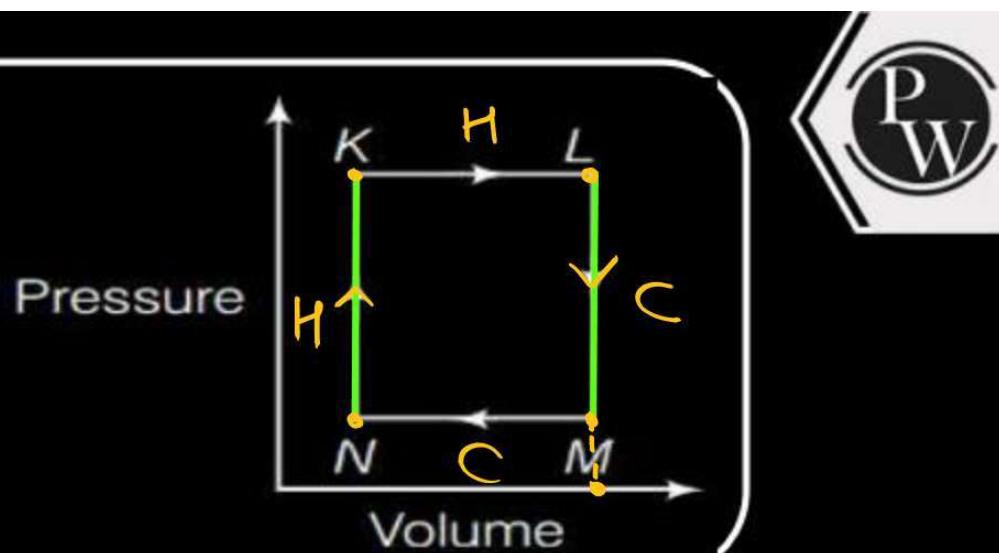
$$\Delta S_{X \rightarrow Y \rightarrow Z} = \Delta S_{X \rightarrow Y}$$



Passage Based Questions

A fixed mass m of a gas is subjected to transformation of states from K to L to M to N and back to K as shown in the figure.

(2013 Adv.)





Q.

The pair of isochoric processes among the transformation of states is

- a. K to L and L to M
- c. L to M and M to N

- b. L to M and N to K
- d. M to N and N to K

Solution:



Q.

The succeeding operations that enable this transformation of states are

- a. heating, cooling, heating, cooling
- b. cooling, heating, cooling, heating
- c. heating, cooling, cooling, heating
- d. cooling, heating, heating, cooling

Solution: