I. Multiple Choice Questions (Type-I)

1. Thermodynamics is not concerned about______.
(i) energy changes involved in a chemical reaction.
(ii) the extent to which a chemical reaction proceeds.
(iii) the rate at which a reaction proceeds.
(iv) the feasibility of a chemical reaction.
Solution:
Option (iii) is the answer.

2. Which of the following statements is correct?
(i) The presence of reacting species in a covered beaker is an example of an open system.
(ii) There is an exchange of energy as well as a matter between the system and the surroundings in a closed system.
(iii) The presence of reactants in a closed vessel made up of copper is an example of a closed system.
(iv) The presence of reactants in a thermos flask or any other closed insulated vessel is an example of a closed system.
Solution:
Option (iii) is the answer.

3. The state of a gas can be described by quoting the relationship between___.
(i) pressure, volume, temperature
(ii) temperature, amount, pressure
(iii) the amount, volume, temperature
(iv) pressure, volume, temperature, amount
Solution:
Option (iv) is the answer.

4. The volume of gas is reduced to half from its original volume. The specific heat will be _______.
(i) reduce to half
(ii) be doubled
(iii) remain constant
(iv) increase four times
Solution:
Option (iii) is the answer.

5. During complete combustion of one mole of butane, 2658 kJ of heat is released. The thermochemical reaction for above change is
(i) $2C_4H_{10}(g) + 13O_2(g)$ □→ $8CO_2(g) + 10H_2O(l)$ $\Delta_cH = -2658.0$ kJ mol^{-1}
(ii) $C_4H_{10}(g) + 13/2\ O_2(g)$ □→ $4CO_2(g) + 5H_2O(g)$ $\Delta_cH = -1329.0$ kJ mol^{-1}
(iii) $C_4H_{10}(g) + 13/2\ O_2(g)$ □→ $4CO_2(g) + 5H_2O(l)$ $\Delta_cH = -2658.0$ kJ mol^{-1}
(iv) $C_4H_{10}(g) + 13/2\ O_2(g)$ □→ $4CO_2(g) + 5H_2O(l)$ $\Delta_cH = +2658.0$ kJ mol^{-1}
Solution:

Option (iii) is the answer.

6. $\Delta_f U^o$ of formation of CH_4 (g) at certain temperature is –393 kJ mol–1. The value of $\Delta_f H^o$ is
(i) zero
(ii) < $\Delta f\ U^o$
(iii) > $\Delta f\ U^o$
(iv) equal to $\Delta f\ U^o$
Solution;
Option (ii) is the answer.

7. In an adiabatic process, no transfer of heat takes place between system and surroundings. Choose the correct option for free expansion of an ideal gas under adiabatic condition from the following.
(i) $q = 0, \Delta T \neq 0, w = 0$
(ii) $q \neq 0, \Delta T = 0, w = 0$
(iii) $q = 0, \Delta T = 0, w = 0$
(iv) $q = 0, \Delta T < 0, w \neq 0$
Solution:
Option (iii) is the answer.

8. The pressure-volume work for an ideal gas can be calculated by using the expression w= ∫Pexdv. The work can also be calculated from the pV– a plot by using the area under the curve within the specified limits. When an ideal gas is compressed (a) reversibly or (b) irreversibly from volume Vi to Vf. choose the correct option.
(i) w (reversible) = w (irreversible)
(ii) w (reversible) < w (irreversible)
(iii) w (reversible) > w (irreversible)
(iv) w (reversible) = w (irreversible) + pex.ΔV
Solution:
Option (ii) is the answer.

9. The entropy change can be calculated by using the expression ΔS = qrev/T When water freezes in a glass beaker, choose the correct statement amongst the following :
(i) ΔS (system) decreases but ΔS (surroundings) remains the same.
(ii) ΔS (system) increases but ΔS (surroundings) decreases.
(iii) ΔS (system) decreases but ΔS (surroundings) increases.
(iv) ΔS (system) decreases and ΔS (surroundings) also decreases.
Solution:
Option (iii) is the answer.

10. On the basis of thermochemical equations (a), (b) and (c), find out which of the algebric relationships given in options (i) to (iv) is correct.
(a) C (graphite) + O_2 (g) → CO_2 (g) ; ΔrH = x kJ mol–1

(b) C (graphite) +12 O2 (g) → CO (g) ; ΔrH = y kJ mol–1
(c) CO (g) +12 O2 (g) □→ CO2 (g) ; ΔrH = z kJ mol–1
(i) z = x + y
(ii) x = y – z
(iii) x = y + z
(iv) y = 2z – x
Solution:
Option (iii) is the answer.

11. Consider the reactions given below. On the basis of these reactions find out which of the algebric relations given in options (i) to (iv) is correct?
(a) C (g) + 4 H (g) □→ CH4 (g); ΔrH = x kJ mol–1
(b) C (graphite,s) + 2H2 (g) □→ CH4 (g); ΔrH = y kJ mol–1
(i) x = y
(ii) x = 2y
(iii) x > y
(iv) x < y
Solution:
Option (iii) is the answer.

12. The enthalpies of elements in their standard states are taken as zero. The enthalpy of formation of a compound
(i) is always negative
(ii) is always positive
(iii) maybe positive or negative
(iv) is never negative
Solution:
Option (iii) is the answer.

13. Enthalpy of sublimation of a substance is equal to
(i) enthalpy of fusion + enthalpy of vapourisation
(ii) enthalpy of fusion
(iii) enthalpy of vapourisation
(iv) twice the enthalpy of vapourisation
Solution:
Option (i) is the answer.

14. Which of the following is not correct?
(i) ΔG is zero for a reversible reaction
(ii) ΔG is positive for a spontaneous reaction
(iii) ΔG is negative for a spontaneous reaction
(iv) ΔG is positive for a non-spontaneous reaction
Solution:
Option (ii) is the answer.

II. Multiple Choice Questions (Type-II)
In the following questions, two or more options may be correct.

15. Thermodynamics mainly deals with
(i) interrelation of various forms of energy and their transformation from one form to another.
(ii) energy changes in the processes which depend only on initial and final states of the microscopic systems containing a few molecules.
(iii) how and at what rate these energy transformations are carried out.
(iv) the system in equilibrium state or moving from one equilibrium state to another equilibrium state.
Solution:
Option (i) and (iv) are the answers.

16. In an exothermic reaction, heat is evolved, and the system loses heat to the surrounding. For such a system
(i) qp will be negative
(ii) ∆rH will be negative
(iii) qp will be positive
(iv) ∆rH will be positive
Solution:
Option (i) and (ii) are the answers.

17. The spontaneity means, having the potential to proceed without the assistance of an external agency. The processes which occur spontaneously are
(i) flow of heat from colder to warmer body.
(ii) gas in a container contracting into one corner.
(iii) gas expanding to fill the available volume.
(iv) burning carbon in oxygen to give carbon dioxide.
Solution:
Option (iii) and (iv) are the answers.

18. For an ideal gas, the work of reversible expansion under isothermal condition can be calculated by using the expression w = – nRT ln Vf/Vi
A sample containing 1.0 mol of an ideal gas is expanded isothermally and reversibly to ten times of its original volume, in two separate experiments. The expansion is carried out at 300 K and 600 K respectively. Choose the correct option.
(i) Work done at 600 K is 20 times the work done at 300 K.
(ii) Work done at 300 K is twice the work done at 600 K.
(iii) Work done at 600 K is twice the work done at 300 K.
(iv) ∆U = 0 in both cases.
Solution:
Option (iii) and (iv) are the answers.

19. Consider the following reaction between zinc and oxygen and choose the correct

options out of the options given below :
2 Zn (s) + O2 (g) □→ 2 ZnO (s) ; ΔH = – 693.8 kJ mol–1
(i) The enthalpy of two moles of ZnO is less than the total enthalpy of two moles of Zn and one mole of oxygen by 693.8 kJ.
(ii) The enthalpy of two moles of ZnO is more than the total enthalpy of two moles of Zn and one mole of oxygen by 693.8 kJ.
(iii) 693.8 kJ mol–1 energy is evolved in the reaction.
(iv) 693.8 kJ mol–1 energy is absorbed in the reaction.
Solution:
Option (i) and (iii) are the answers.

III. Short Answer Type

20. 18.0 g of water completely vapourises at 100°C and 1 bar pressure and the enthalpy change in the process is 40.79 kJ mol–1. What will be the enthalpy change for vapourising two moles of water under the same conditions? What is the standard enthalpy of vapourisation for water?
Solution:
Enthalpy change of vapourisation for 1 mole = 40.79 kJ mol–1 enthalpy change of vapourisation for 2 moles of water = (40.79 × 2) = 81.58kJ mol–1
for water ΔHvapourisation, ^{0} will be equal to =40.79 kJ mol–1

21. One mole of acetone requires less heat to vaporise than 1 mol of water. Which of the two liquids has a higher enthalpy of vapourisation?
Solution:
Among the two liquids, water has a higher enthalpy of vapourisation (consuming higher heat energy).
Therefore, ΔHvapourisation (water) > ΔHvapourisation (acetone).

22. Standard molar enthalpy of formation, Δf HΘis just a special case of enthalpy of reaction, Δr HΘ. Is the Δr HΘfor the following reaction same as Δf HΘ? Give the reason for your answer.
CaO(s) + CO2(g) → CaCO3(s) ; ΔfHΘ = –178.3 kJ mol–1
Solution:
The given reaction CaO(s) + CO2(g) →CaCO3(s) is indicating that it is occurring in the standard form of 1 mole of each substance. And the molar enthalpy of formation ΔfHΘ = –178.3 kJ mol–1 Given for CaCO3 is also showing the standard conditions.
So,ΔfHΘ = –178.3 kJ mol–1 = Δr HΘ .

23. The value of ΔfHΘfor NH3 is – 91.8 kJ mol–1. Calculate the enthalpy change for the following reaction :
2NH3(g) → N2(g) + 3H2(g)
Solution:
Enthalpy change of a reaction is calculated as
: Σbond enthalpy of reactants- Σbond enthalpy of products
for the decomposition 2NH3(g) →N2(g) + 3H2(g) ΔrHΘ will be =
- (– 91.8 kJ mol–1) = + 91.8 kJ mol–1
for 2 moles of NH3 enthalpy change of the reaction will be ΔrH = (2 X 91.8) = 183.6 kJ mol–1 .

24. Enthalpy is an extensive property. In general, if the enthalpy of an overall reaction A→B along one route is Δr H and Δr H1, ΔrH2, ΔrH3 ..... represent enthalpies of intermediate reactions leading to product B. What will be the relation between ΔrH for overall reaction and ΔrH1, ΔrH2..... etc. for intermediate reactions.
Solution:
For the reaction, A→B the formation of B goes through several intermediate reactions with different enthalpy values Δr H1, ΔrH2, ΔrH3....., and the overall enthalpy change is Δr H.

25. The enthalpy of atomisation for the reaction CH4(g)→ C(g) + 4H (g) is 1665 kJ mol–1. What is the bond energy of the C–H bond?
Solution:
For 1 C-H bond, the bond energy will be equal to 1/4 that of the enthalpy of atomisation
= (1665/4) = 416.25 kJ mol–1.

26. Use the following data to calculate Δlattice HΘfor NaBr.

Δsub HΘfor sodium metal = 108.4 kJ mol–1
Ionization enthalpy of sodium = 496 kJ mol–1
Electron gain enthalpy of bromine = – 325 kJ mol–1
Bond dissociation enthalpy of bromine = 192 kJ mol–1
Δf HΘfor NaBr (s) = – 360.1 kJ mol–1
Solution:
Sublimation of the metal(ΔsubHΘ) →Ionization of the metal (ΔiHΘ) →Dissociation of the non-metal (ΔdissHΘ) →Gain of electrons by the non-metal(ΔegHΘ)
Δf HΘ =Δsub HΘ+Δi HΘ+1/2 dissHΘ + ΔegHΘ+ ΔlattticeHΘ
To calculate the lattice enthalpy of NaBr,
Na(s) → Na(g) ; ΔsubHΘ =108.4 kJ mol–1 (i)
Na→ Na+ + e- ; ΔiHΘ = 496 kJ mol–1 (ii)
1/2 Br2→ Br ; 1/2 ΔdissHΘ = ( ) = 96 kJ mol–1 (iii)
Br + e-→ Br- ;ΔegHΘ= – 325 kJ mol–1 (iv)
enthalpy of formation Δf HΘ = processes (i) + (ii) + (ii) + (iv)
Δlattice HΘ = Δf HΘ - ΔsubHΘ - ΔiHΘ - 1/2 ΔdissHΘ –ΔegHΘ
= -735.5kjmol-1.

27. Given that ΔH = 0 for mixing of two gases. Explain whether the diffusion of these gases into each other in a closed container is a spontaneous process or not?
Solution:
A negative ΔG means the reaction will be the spontaneous included contribution of the other factors like enthalpy(H) and entropy(S).
ΔG= ΔH - TΔS
ΔH being 0,
ΔG will be negative (as the positive value of ΔS will give a more negative TΔS)
ΔH=0 ; ΔG= -TΔS= negative.

28. The heat has a randomising influence on a system and temperature is the measure of average chaotic motion of particles in the system. Write the mathematical relation which relates these

three parameters.

Solution:

The mathematical relation which relates these three parameters is ΔS = qrev/T
where ΔS is the change in entropy and T stands for temperature.

29. Increase in enthalpy of the surroundings is equal to the decrease in enthalpy of the system. Will the temperature of the system and surroundings be the same when they are in thermal equilibrium?

Solution:

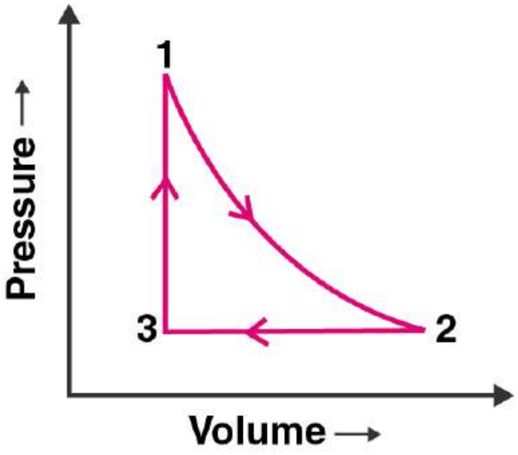
As thermal equilibrium obeys the zeroth law of thermodynamics, temperature of system and surroundings will be the same when they are in thermal equilibrium.

30. As thermal equilibrium obeys the zeroth law of thermodynamics, temperature of system and surroundings will be the same when they are in thermal equilibrium.

Solution:

For the given reaction N2O4 (g) ⇋2NO2 (g) the value of Kp = 0.98.
Hence, ΔrG⁰ = - RT ln(0.98)
Since ln(0.98) has a negative value, the value of ΔrG⁰ becomes positive. Therefore, the reaction is non-spontaneous.

31. A sample of 1.0 mol of a monoatomic ideal gas is taken through a cyclic process of expansion and compression as shown in Fig. 6.1. What will be the value of ΔH for the cycle as a whole?



Solution:

In the following cyclic (1 → 2 →3 →1) process the initial and final point is the same (i.e. 1). Hence the enthalpy change or ΔH= 0, in other words, there will be no change in enthalpy.

32. The standard molar entropy of H2O (l) is 70 J K–1 mol–1. Will the standard molar entropy of H2O(s) be more, or less than 70 J K–1 mol–1?

Solution:

The entropy of H2O(s) <entropy of H2O (l). The standard molar entropy of H2O(s) will also be less

than 70 J K–1 mol–1.

33. Identify the state functions and path functions out of the following :
enthalpy, entropy, heat, temperature, work, free energy.
Solution:
State functions: enthalpy, entropy, temperature and free energy.
Path functions: Heat and work

34. The molar enthalpy of vapourisation of acetone is less than that of water. Why?
Solution:
Water has strong hydrogen bonds and the high polarity also adds up in resulting it to boil at higher temperatures. Hence water has a higher molar enthalpy than acetone.

35. Which quantity out of ΔrG and $\Delta rG\Theta$will be zero at equilibrium?
Solution:
At equilibrium $\Delta rG\Theta = - RT \ln K$.
$\Delta rG\Theta$ can only be 0 when the value of K is =1. So, for all the other K values $\Delta rG\Theta$ cannot be zero.

36. Predict the change in internal energy for an isolated system at constant volume.
Solution:
For an isolated system q=0 and w=0
And according to 1st law of thermodynamics: $\Delta U= q + w$ (U=internal energy)
Therefore, change in internal energy for an isolated system $\Delta U = 0$.

37. Although heat is a path function but heats absorbed by the system under certain specific conditions is independent of path. What are those conditions? Explain.
Solution;
Heat is independent of the path under 2 conditions:
1. When the volume of the system is kept constant-
By 1st law of thermodynamics:
$q = \Delta U + (-w)$
and $-w = p\Delta V$
Therefore , $q = \Delta U + p\Delta V$
$\Delta V = 0$ (at constant volume)
Hence, $q_v = \Delta U + 0 = \Delta U$= change in internal energy
2. When the pressure of the system is kept constant –
At constant pressure, $q_p= \Delta U + p\Delta V$
But , $\Delta U + p\Delta V = \Delta H$
Therefore , $q_p = \Delta H$ = change in enthalpy.

38. Expansion of gas in a vacuum is called free expansion. Calculate the work is done and the change in internal energy when 1 litre of an ideal gas expands isothermally into a vacuum until its total volume is 5 litre?
Solution:
Work done in vacuum is calculated by :

-w = Text (Vinitial - Vfinal)
Pext= 0
–w = 0x(5-1) = 0.
For isothermal expansion q=o
q= ΔU + (-w)
Hence ΔU will be 0.

39. Heat capacity (Cp) is an extensive property but specific heat (c) is an intensive property. What will be the relation between Cpand c for 1 mol of water?

Solution;

1 mole of water = 18 g.
Hence, for water Heat capacity = 18 × specific heat.
i.e. Cp = 18 × C .

40. The difference between CP and CV can be derived using the empirical relation H = U + PV. Calculate the difference between CP and CV for 10 moles of an ideal gas.

Solution:

For an ideal gas, the difference between these two is CP - CV = nR, the universal gas constant and where n= no. of moles

Hence for 10 moles of an ideal gas CP - CV = 10 R
CP - CV = 10 × 8.314 J
= 83.14 J

41. If the combustion of 1g of graphite produces 20.7 kJ of heat, what will be molar enthalpy change? Give the significance of the sign also.

Solution:

The heat of combustion ΔHc of graphite (i.e. carbon) is given as = 20.7 kJ for 1g of graphite (C).
1 mole of Carbon = 12 g
Hence the molar enthalpy change (enthalpy for 1 mole)
= (20.7 × 12)= 248.4 KJ mol-1
Since the heat is evolved, the actual molar enthalpy change
= -248.4 KJ mol-1

In combustion reactions, heat is always evolved i.e. it is an exothermic reaction. Hence the sign of ΔH for the reaction will always be negative (for the process to occur).

42. The net enthalpy change of a reaction is the amount of energy required to break all the bonds in reactant molecules minus the amount of energy required to form all the bonds in the product molecules. What will be the enthalpy change for the following reaction?

$H_2(g) + Br_2(g) \rightarrow 2HBr(g)$

Given that Bond energy of H_2, Br_2 and HBr is 435 kJ mol–1, 192 kJ mol–1 and 368 kJ mol–1 respectively.

Solution:

For the reaction
$H_2(g) + Br_2(g) \rightarrow 2HBr(g)$
Enthalpy change
= (Bond energy of H-H bond + Br-Br bond) – (2 × bond energy of H-Br)

= (435 + 192) kJ mol–1 – (2 × 368) kJ mol–1
= -109 kJ mol–1

43. The enthalpy of vapourisation of CCl_4 is 30.5 kJ mol–1. Calculate the heat required for the vapourisation of 284 g of CCl_4 at constant pressure. (Molar mass of CCl_4 = 154 g mol–1).

Solution:

The enthalpy of vapourisation is given for 1 mole of CCl_4 = 30.5 kJ mol–1
Hence, for 284 g, it will be = (mole no. × 30.5) kJ
Molar mass of CCl_4 = 154 g mol–1 that means 154 g = 1 mole.
Therefore , 284 g = (284g/154gmol-1)= 1.84 mole.
Hence the heat required for the vapourisation of 284 g of CCl_4 at constant pressure = (1.84 mol ×30.5 KJ mol-1) kJ
=56.12 KJ

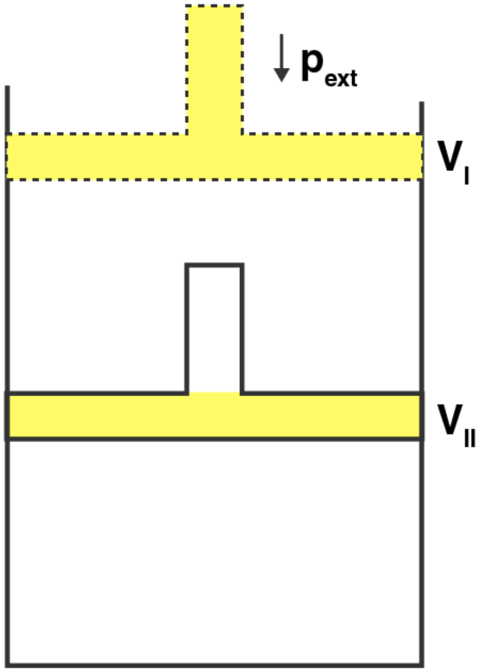
44. The enthalpy of reaction for the reaction :

$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$ is $\Delta_r H^\ominus = -572$ kJ mol–1
What will be standard enthalpy of formation of H_2O (l)?

Solution:

For the given reaction : $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$
the standard enthalpy of reaction is $\Delta_r H^\ominus = -572$ kJ mol–1 , so the half of $\Delta_r H^\ominus$ will be the standard molar enthalpy of formation ;
$\Delta_f H^\ominus = 1/2 \times \Delta_r H^\ominus = (-572/2) = -286$ kJ mol–1 .

45. What will be the work done on an ideal gas enclosed in a cylinder, when it is compressed by constant external pressure, pext in a single step as shown in Fig? 6.2. Explain graphically.



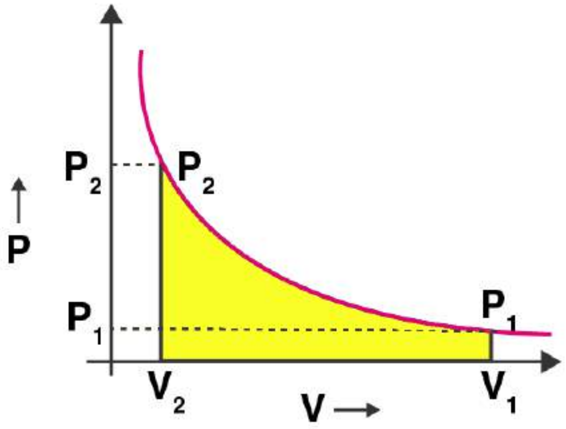
Solution:

From this graph we can obtain the be the work done on the ideal gas enclosed in the cylinder in 1 step: the area covered by P-V graph (shaded region) is the actual value of the work done is:
= length × breadth = pext ΔV = AVI (or BVII) × (VI - VII)

46. How will you calculate work done on an ideal gas in a compression, when a change in pressure is carried out in infinite steps?

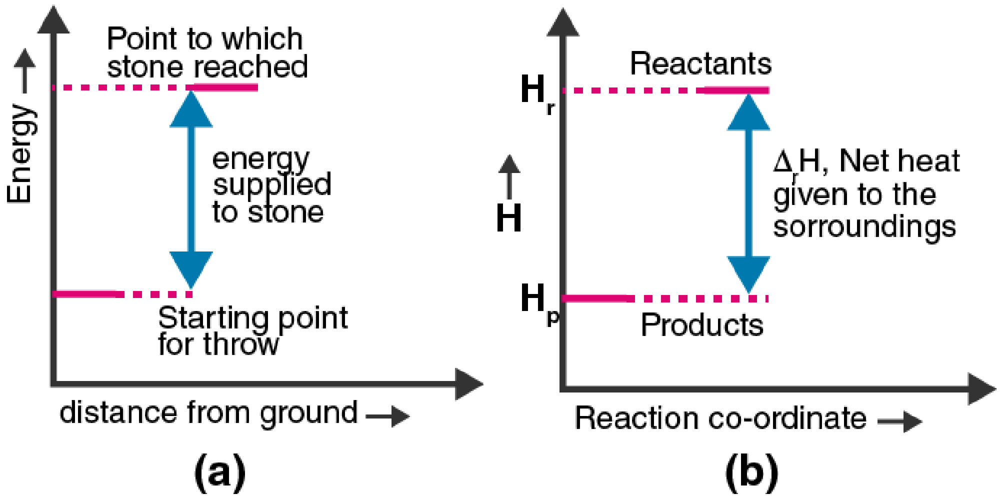
Solution:

When an ideal gas in a compression, where the change in pressure is carried out in infinite steps i.e. through a reversible process, the work done can be calculated only through the observation of pressure vs volume plot of the process.



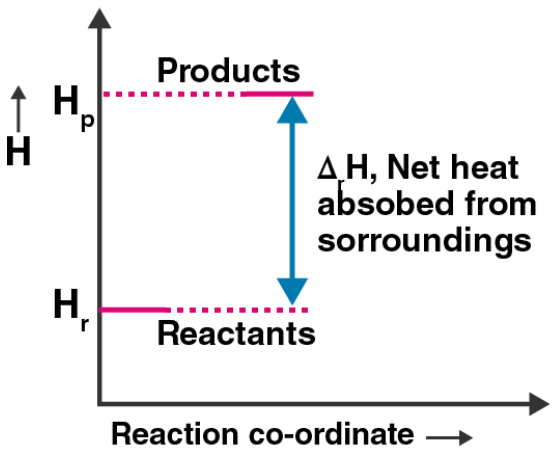
The shaded area in the above graph represents the work done in the process, by calculating the area covered we can calculate the work done.

47. Represent the potential energy/enthalpy change in
the following processes graphically.
(a) Throwing a stone from the ground to roof.
(b) 1/2 H2(g) + 1/2 Cl2(g) ⇋ HCl(g) ΔrHΘ = –92.32 kJ mol–1
In which of the processes potential energy/enthalpy change is contributing factor to the spontaneity?
Solution:



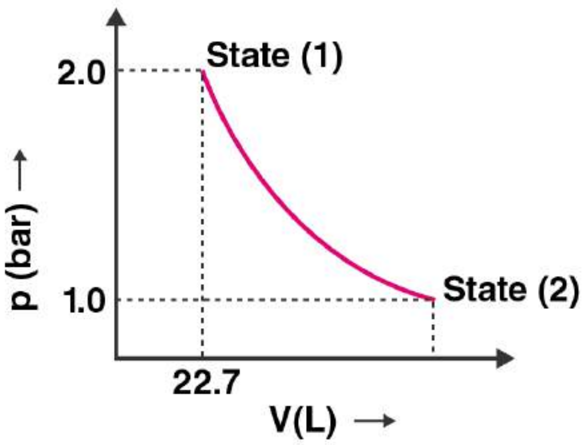
Amongst these two processes, in the process or reaction (b) the potential energy/enthalpy change is contributing factor to the spontaneity.

48. Enthalpy diagram for a particular reaction is given in Fig. 6.3. Is it possible to decide the spontaneity of a reaction from the given diagram? Explain.



Solution:
From the given enthalpy diagram it can be said the change in enthalpy ΔH is positive for the reaction, i.e. it will be endothermic. But when comes to the spontaneity of a reaction, enthalpy is just a factor and there are other important factors like entropy, Gibb's free energy also taken into consideration. Hence enthalpy alone cannot determine the spontaneity of a reaction; one must have a loo to the other contributing factors also.

49. 1.0 mol of a monoatomic ideal gas is expanded from the state (1) to state (2) as shown in Fig. 6.4. Calculate the work done for the expansion of gas from the state (1) to state (2) at 298 K.
Solution:



$W = -2.303 nRT \log (p_1/p_2)$
$= -2.303 \times 1\ \text{mol} \times 8.314\ \text{J mol}^{-1}\ \text{K}^{-1} \times 298\ \text{K} \times \log 2$
$= -2.303 \times 8.314 \times 298 \times 0.3010\ \text{J}$
$= -1717.46\ \text{J}$

50. An ideal gas is allowed to expand against a constant pressure of 2 bar from 10 L to 50 L in one step. Calculate the amount of work done by the gas. If the same expansion were carried out reversibly, will the work is done be higher or lower than the earlier case? (Given that 1 L bar =

100J)

Solution:

Amount of work done = -pext ΔV
= - 2 bar × (50 – 10) L = - 80 L bar.
Now, it is given that 1 L bar = 100 J
So , -80 L bar = (-80 × 100) = -8000 J
= -8 KJ is the amount of work done in the above process.
If it is reversible then the internal pressure will be larger than the external pressure. So the work done will own a higher value.