

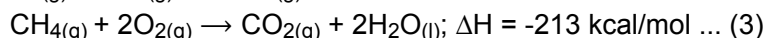
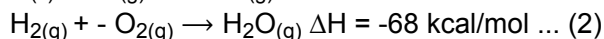
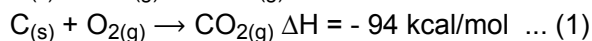
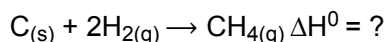
Thermodynamics Important Questions With Answers

NEET Chemistry 2023

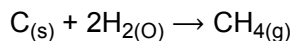
1. Heat of combustion ΔH° for $C(s)$, $H_2(g)$ and $CH_4(g)$ are -94, -68 and -213 kcal/mol respectively. Then, ΔH° for $C(s) + 2H_2(g) \rightarrow CH_4$ is :

a) -17 kcal/mol b) -111 kcal/mol c) -170 kcal/mol d) -85 kcal/mol

Solution : -



Eqn. (1) + 2 x Eqn. (2) - Eqn. (3)



$$\Delta H^\circ = [-94 - 2(68)] - (-213) \text{ kcal/mol}$$

$$\Delta H^\circ = [-94 - 136] + 213 \text{ kcal/mol}$$

$$\Delta H^\circ = -230 + 213 = -17 \text{ kcal/mol}$$

2. ΔH for the reaction, $OF_2 + H_2O \rightarrow O_2 + 2HF$ (B.E. of O-F, O-H, H-F and O=O are 44, 111, 135 and 119 kcal mol⁻¹ respectively)

a) -222 kcal b) -88 kcal c) -111 kcal d) -79 kcal

Solution : -

$$\Delta H = \sum B.E._R - \sum B.E._P$$

$$= (2 \times 44 + 2 \times 111) - (119 + 2 \times 135) = -79 \text{ kcal}$$

3. The work done during the expansion of a gas from a volume of 4 dm³ to 6 dm³ against a constant external pressure of 3 atm, is:

a) -6 J b) -608 J c) +304 J d) -304 J

Solution : -

Work done during the expansion, $W = -pdV$

$$W = -3 \text{ atm} (6 \text{ dm}^3 - 4 \text{ dm}^3)$$

$$= -3 \text{ atm} (\text{dm}^3) (1 \text{ dm}^3 = 1 \text{ L})$$

$$= -3 \text{ atm} \times 2 \text{ L}$$

$$= -6 \text{ L atm}$$

$$\text{Now, } 1 \text{ L atm} = 101.32 \text{ J}$$

$$W = -6 \times 101.32 \text{ J} = -607.92 \text{ J} \approx -608 \text{ J}$$

4. Consider entropy (S) as a thermodynamic parameter, the criterion for the spontaneity of any process is

a) $\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$ b) $\Delta S_{\text{system}} - \Delta S_{\text{surroundings}} > 0$ c) $\Delta S_{\text{system}} > 0$ only

d) $\Delta S_{\text{surroundings}} > 0$ only

Solution : -

Entropy (S) is the measure of randomness or disorder of the molecules. It is an extensive property and a state function.

A process is spontaneous if and only if the entropy of the universe increases.

Therefore, for spontaneous process,

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

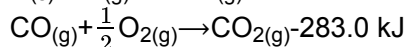
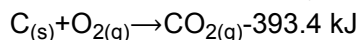
5. When the system does not exchange heat with the surroundings, the process is:

- a) isothermal **b) adiabatic** c) thermal d) isochoric.

Solution : -

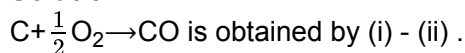
In adiabatic process, system does not exchange heat with surroundings and temperature keeps increasing.

6. What will be the enthalpy of combustion of carbon to produce carbon monoxide on the basis of data given below:



- a) + 676.4 kJ b) - 676.4 kJ **c) -110.4 kJ** d) + 110.4 kJ

Solution : -



$$-393.4 - (-283.0) = -110.4 \text{ kJ}$$

7. If the enthalpy change or the transition of liquid water to steam is 30 kJ mol^{-1} at 27°C , the entropy change for the process would be:

- a) $10 \text{ J mol}^{-1} \text{ K}^{-1}$ b) $10 \text{ J mol}^{-1} \text{ K}^{-1}$ c) $0.1 \text{ J mol}^{-1} \text{ K}^{-1}$ **d) $100 \text{ J mol}^{-1} \text{ K}^{-1}$**

Solution : -

According to question : $\Delta H = 30 \text{ kJ mol}^{-1}$

$$T = 273 + 27 = 300 \text{ K}$$

$$\text{Then, } \Delta S_T = \frac{\Delta H_T}{T} = \frac{3 \times 10^4}{300} \text{ J mol}^{-1} \\ = 100 \text{ J mol}^{-1} \text{ K}^{-1}$$

8. Work done on an ideal gas in a cylinder when it is compressed by an external pressure in a single step is shown below:



Which of the following graphs will show the work done on the gas?



Solution : -

The pressure is constant and equal to P_{ex} .

Also, the process is a single step.

Therefore, it is a straight line parallel to volume axis and has a value of P_{ex} .

Also, work done = $P_{\text{ex}} \cdot \Delta V = \text{Area under the P-V curve}$.

9. $\Delta U = q + w$, is mathematical expression for:

- a) first law of thermodynamics** b) second law of thermodynamics c) third law of thermodynamics
d) zeroth law of thermodynamics

Solution : -

First law of thermodynamics is represented mathematically as $\Delta U = q + w$, where ΔU internal is change in internal energy, q is heat absorbed and w is work done.

10. The entropy change in the fusion of one mole of a solid melting at 27⁰C (latent heat of fusion is 2930 J mol⁻¹) is:
 a) **9.77 JK⁻¹ mol⁻¹** b) 10.73 JK⁻¹ mol⁻¹ c) 2930 JK⁻¹ mol⁻¹ d) 108.5 JK⁻¹ mol⁻¹

Solution : -

$$\Delta S = \frac{\Delta H}{T} = \frac{2930 \text{ J mol}^{-1}}{(27 + 273) \text{ K}}$$

$$= \frac{2930 \text{ J mol}^{-1}}{300 \text{ K}} = 9.77 \text{ JK}^{-1} \text{ mol}^{-1}$$

11. If ΔH is the change in enthalpy and ΔE , the change in internal energy accompanying a gaseous reaction?

- a) ΔH is always greater than ΔE
 b) $\Delta H < \Delta E$ only if the number of moles of products is greater than the number of moles of the reactants
 c) ΔH is always less than ΔE
 d) **$\Delta H < \Delta E$ only if the number of moles of products is less than the number of moles of the reactants**

Solution : -

We know that

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

$$\Delta H = \Delta E + \Delta(nRT)$$

When number of moles in product is less than number of moles in reactant.

So, $\Delta n = \text{ve}$

So, $\Delta H < \Delta E$

12. Which of the following does not represent enthalpy change during phase transformation?

- a) Standard enthalpy of fusion b) Standard enthalpy of vaporisation c) Standard enthalpy of sublimation
 d) **Standard enthalpy of formation**

Solution : -

There is no phase change in formation. A new product is formed during the reaction.

13. Which of the following reactions will have the value of enthalpy of neutralisation as -57.1 kJ mol⁻¹?

- a) $\text{CH}_3\text{COOH} + \text{NaOH} \rightarrow \text{CH}_3\text{COONa} + \text{H}_2\text{O}$ b) **$\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O}$** c) $\text{HCl} + \text{NH}_4\text{OH} \rightarrow \text{NH}_4\text{Cl} + \text{H}_2\text{O}$
 d) $\text{HCOOH} + \text{NaOH} \rightarrow \text{HCOONa} + \text{H}_2\text{O}$

Solution : -

According to experimental data, Enthalpy of neutralisation is -57.1 kJ mol⁻¹ for a strong acid and a strong base (This value to be remembered).

14. **Assertion:** The solubility of most salts in water increases with rise of temperature.

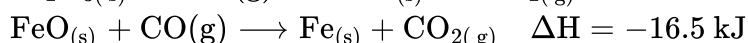
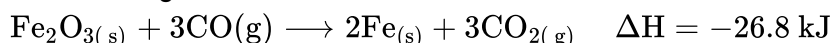
Reason: For most of the ionic compounds, $\Delta_{sol} H^\circ$ is positive and the dissociation process is endothermic.

- a) **If both assertion and reason are true and reason is the correct explanation of assertion.**
 b) If both assertion and reason are true but reason is not the correct explanation of assertion.
 c) If assertion is true but reason is false. d) If both assertion and reason are false

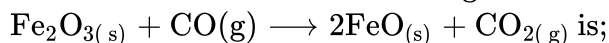
Solution : -

Solubility of the most of the salt rises with increase in temperature. This is because with increase in temperature, kinetic energy of the molecules increases and the solvent molecules break apart the solute molecules that are held together by intermolecular attractions more effectively. Also for most of the ionic compounds, change in enthalpy is positive and hence the dissolution process is endothermic. For endothermic reaction, increase in temperature leads the reaction to forward reaction.

15. The following two reactions are known:



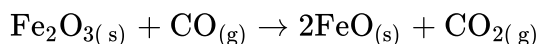
The value of ΔH for the following reaction



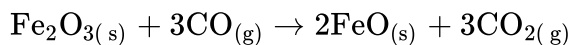
- a) +6.2 kJ b) +10.3 kJ c) -43.3 kJ d) -10.3 kJ

Solution : -

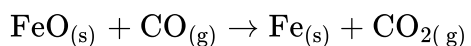
We know the reaction:



Given

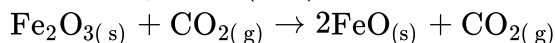


$$\Delta H = -26.8 \text{ kJ} \quad \dots\dots\dots(i)$$



$$\Delta H = -16.5 \text{ kJ} \quad \dots\dots\dots(ii)$$

Then change heat (ΔH) for reaction



From equation (i), (ii) :

$$\text{equation (i)} - 2 \times \text{equation (ii)}$$

$$\therefore \Delta H = -26.8 + 33.0 = +6.2 \text{ kJ}$$

16. For the gas phase reaction,

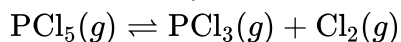


which of the following conditions are correct?

- 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 : -

Given reaction,



The reaction given is an example of decomposition reaction and know that decomposition reactions are endothermic in nature, i.e., $H > 0$.

$$\text{Further } \Delta n = (1 + 1) - 1 = +1$$

Thus, more number of molecules are present in products which shows more randomness i.e., $\Delta S > 0$ (ΔS is positive)

17. During an isothermally expansion of an ideal gas, its

- a) internal energy increases b) enthalpy decreases c) enthalpy remains unaffected
d) enthalpy reduces to zero

Solution : -

An isothermal process is a change of a system, in which the temperature remains constant. For an ideal gas during an isothermal expansion the enthalpy, as well as internal energy, remains constant.

During isothermal expansion of an ideal gas, $\Delta E = 0$, $\Delta T = 0$

From the definition of enthalpy,

$$H = E + PV$$

$$\text{or } \Delta H = \Delta E + \Delta(PV)$$

$$\text{or } \Delta H = \Delta E + \Delta(nRT) \{ \text{Since, } PV = nRT \text{ for an ideal gas} \}$$

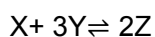
$$\text{or } \Delta H = \Delta E + nR\Delta T$$

$$\text{or } \Delta H = 0$$

18. For reversible reaction: $X(\text{g}) + 3Y(\text{g}) \rightleftharpoons 2Z(\text{g})$; $\Delta H = -40 \text{ kJ}$

Standard entropies of X, Y and Z are 60, 40 and 50 $\text{J K}^{-1}\text{mol}^{-1}$ respectively. The temperature at which the above reaction is in equilibrium is

- a) 273 K b) 600 K c) 500 K d) 400 K

Solution : -

$$\Delta S = 2 \times 50 - (60 + 3 \times 40) = -80 \text{ kJ}$$

$$\Delta G = \Delta H - T\Delta S \text{ when } \Delta G = 0$$

$$T = \frac{\Delta H}{\Delta S} = -40 \times \frac{1000}{-80} = 500 \text{ K}$$

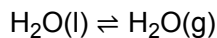
19. At what temperature liquid water will be in equilibrium with water vapour?

$$\Delta H_{\text{vap}} = 40.73 \text{ kJ mol}^{-1}; \Delta S_{\text{vap}} = 0.109 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

- a) 282.4 K b) **373.6 K** c) 100 K d) 400 K

Solution : -

The given reaction is:-



Now, at equilibrium, $\Delta G = 0$

Now, from Gibb's free energy change equation

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

$$\Rightarrow \Delta H = T \Delta S$$

$$\Rightarrow T = \frac{\Delta H}{\Delta S} = \frac{40.73}{0.1079} = 373.6 \text{ K}$$

($\because \Delta H_{\text{vap}} = 40.73 \text{ kJ/mol}$, $\Delta S_{\text{vap}} = 0.109 \text{ kJ K}^{-1} \text{ mol}^{-1}$)

20. **Assertion:** If both ΔH° and ΔS° are positive then reaction will be spontaneous at high temperature.

Reason: All processes with positive entropy change are spontaneous.

- a) If both assertion and reason are true and reason is the correct explanation of assertion.
 b) If both assertion and reason are true but reason is not the correct explanation of assertion.
c) If assertion is true but reason is false. d) If both assertion and reason are false.

Solution : -

Spontaneity of a process depends upon ΔG° which combines both factors ΔH° and ΔS° . For the spontaneity, ΔG° should be negative. If ΔH° is +ve, ΔS° is +ve then ΔG° to be -ve only when $T \Delta S > \Delta H$ which is possible at high temperature.

21. Which is the correct order of bond energy of single, double and triple bonds between carbon atoms?

- a) $\text{C} - \text{C} > \text{C} = \text{C} > \text{C} \equiv \text{C}$ b) $\text{C} = \text{C} > \text{C} \equiv \text{C} > \text{C} - \text{C}$ c) $\text{C} \equiv \text{C} > \text{C} - \text{C} > \text{C} = \text{C}$ **d) $\text{C} \equiv \text{C} > \text{C} = \text{C} > \text{C} - \text{C}$**

Solution : -

Carbon has all 4 valence electrons. So it easily bonds with other carbon atoms to form long chains Carbon atoms. Apart from single bond carbon also forms double bonds in compounds like alkenes or triple bonds in compounds like alkynes.

A carbon-carbon bond is very strong. The carbon to carbon triple bond has dissociation energy of $348 \frac{\text{kJ}}{\text{mol}}$, followed by a double bond with $614 \frac{\text{kJ}}{\text{mol}}$ and single bond having $839 \frac{\text{kJ}}{\text{mol}}$.

22. **Assertion:** The difference between ΔH and ΔU is not Significant for systems consisting of only solids and/or liquids.

Reason: Solids and liquids do not suffer any significant volume changes upon heating.

- a) If both assertion and reason are true and reason is the correct explanation of assertion.**
 b) If both assertion and reason are true but reason is not the correct explanation of assertion.
 c) If assertion is true but reason is false. d) If both assertion and reason are false

Solution : -

For solids and liquids, volume changes are insignificant.

$$\therefore \Delta V = 0$$

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

Therefore, the difference between ΔH and ΔU is almost negligible for solids and liquids.

23. The statement "The change of enthalpy of a chemical reaction is same whether the reaction takes place in one or several steps" is

- a) Le Chatelier's law b) van't Hoff's law c) first law of thermodynamics **d) Hess's law.**

Solution : -

The statement "The change of enthalpy of a chemical reaction is same whether the reaction takes place in one or several steps" is Hess's law of constant heat summation.

24. What will be the work done when one mole of a gas expands isothermally from 15 L to 50 L against a constant pressure of 1 atm at 25°C?
 a) - 3542 cal b) - 843.3 cal **c) - 718 cal** d) - 60.23 cal

Solution : -

As we know that, work done in isothermal expansion is given as-

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

Given:-

n = No. of moles = 1 mole

R = Gas constant = 2 cal

T = constant temperature associated with the process = 25°C = (25 + 273) K = 298K

V₁ = Initial volume = 15 L

V₂ = Final volume = 50 L

$$\therefore W = -2.303 \times 1 \times 2 \times 298 \times \log \left(\frac{50}{15} \right)$$

$$\Rightarrow W = -1372.588 \times (\log 10 - \log 3)$$

$$\Rightarrow W = -1372.588 \times 0.523 = -717.86 \approx -718 \text{ cal}$$

Hence the work done will be -718 cal.

25. For which one of the following equation is $\Delta H^\circ_{\text{react}}$ equal to ΔH°_f for the product?
a) $\text{Xe(g)} + 2\text{F}_2(\text{g}) \rightarrow \text{XeF}_4(\text{g})$ b) $2\text{CO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g})$ c) $\text{N}_2(\text{g}) + 3\text{O}(\text{g}) \rightarrow \text{N}_2\text{O}_3(\text{g})$
 d) $\text{CH}_4(\text{g}) + 2\text{Cl}_2(\text{g}) \rightarrow \text{CH}_2\text{Cl}_2(\text{l}) + 2\text{HCl}(\text{g})$

Solution : -

Heat of formation, ΔH°_f of a substance is the amount of heat absorbed or released when one mole of this substance is formed directly from its constituent elements.

In option (a), one mole of XeF₄ is formed from its constituent elements i.e., Xe and F₂ thus, the equation has equal value of ΔH°_r and ΔH°_f . In option (b), the constituent atoms should be carbon and oxygen only but the reactant used is CO thus,

$$\Delta H^\circ_r \neq \Delta H^\circ_f$$

In option (c), the reactant used is O₃ which is again not in its element form thus,

$$\Delta H^\circ_r \neq \Delta H^\circ_f$$

In option (d), two products are formed thus

$$\Delta H^\circ_r \neq \Delta H^\circ_f$$

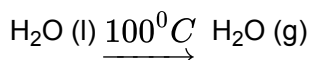
26. The correct relationship between free energy change in a reaction and the corresponding equilibrium constant K is:
 a) $\Delta G^\circ = -RT \ln K$ b) $\Delta G = RT \ln K$ **c) $\Delta G = -RT \ln K$** d) $-\Delta G^\circ = RT \ln K_C$

Solution : -

The correct relationship between free energy change in a reaction and the corresponding equilibrium constant K is $-\Delta G = RT \ln K$ or $\Delta G = -RT \ln K$

27. Standard enthalpy of vaporisation $\Delta_{\text{vap}} H^\circ$ for water at 100°C is 40.66 kJ mol⁻¹. The internal energy of vaporization of water at 100°C (in kJ mol⁻¹) is: (assume water vapour to behave like an ideal gas).
a) +37.56 b) -43.76 c) +43.76 d) +40.66

Solution : -



$$\Delta H^\circ = 40.66 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ = \Delta u^\circ + \Delta n_g RT$$

$$\Delta n_g = 1, R = 8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}$$

$$T = 100 + 273 = 373 \text{ K}$$

$$\Rightarrow 40.66 = \Delta u^0 + (1) (8.314 \times 10^{-3}) \times 373$$

$$\Delta u^0 = 37.56 \text{ kJ mol}^{-1}$$

28. The enthalpy of solution of sodium chloride is 4 kJ mol^{-1} and its enthalpy of hydration of ions is -784 kJ mol^{-1} . What will be the lattice enthalpy of sodium chloride?

- a) $+780 \text{ kJ mol}^{-1}$ b) $+394 \text{ kJ mol}^{-1}$ c) **$+788 \text{ kJ mol}^{-1}$** d) $+398 \text{ kJ mol}^{-1}$

Solution : -

$$\Delta H_{sol} = \Delta H_{lattice} + \Delta H_{hyd} = \Delta H_{lattice} + (-784) \Delta H_{lattice} = 4 - (-784) = +788 \text{ kJ mol}^{-1}$$

29. A gaseous system is initially characterised by 500 mL volume and 1 atm pressure at 298 K. This system is allowed to do work as

(i) In isobaric conditions it expands to 800 mL resulting a decrease in pressure and temperature to 0.6 atm and 273 K respectively.

(ii) In adiabatic conditions it is allowed to expand upto 800 mL and results a decrease in pressure and temperature to 0.6 atm and 273 K respectively.

If Gibbs energy change in (i) is ΔG_a and in (ii) is ΔG_b then what will be the ratio of $\frac{\Delta G_a}{\Delta G_b}$?

- a) 0 b) **1** c) between 0-1 d) >1

Solution : -

$\frac{\Delta G_a}{\Delta G_b} = 1$ as Gibbs energy is a state function and initial and final states are same in (i) and (ii).

30. The volume of gas is reduced to half from its original volume. The specific heat will _____.

- a) be reduced to half b) be doubled c) **remain constant** d) be increased four times

Solution : -

The specific heat is an intensive property which does not depend on the quantity or size of matter.

31. **Assertion:** ΔH for an exothermic reaction is negative and for an endothermic reaction is positive.

Reason: Enthalpy is an extensive property.

a) If both assertion and reason are true and reason is the correct explanation of assertion.

b) **If both assertion and reason are true but reason is not the correct explanation of assertion.**

c) If assertion is true but reason is false. d) If both assertion and reason are false

Solution : -

In an exothermic reaction, heat is evolved and the system loses heat to the surrounding. Therefore, q_p will be negative and hence ΔH will be negative.

$$[\because q_p = H - H_1 = \Delta H].$$

Similarly in an endothermic reaction heat is absorbed, q_p is positive hence ΔH will be positive.

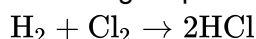
Enthalpy is an extensive property as it depends on the quantity of matter.

32. Bond dissociation enthalpy of H_2Cl_2 and HCl are 434, 242 and 431 kJ mol^{-1} respectively.

- a) 93 kJ mol^{-1} b) -245 kJ mol^{-1} c) **-93 kJ mol^{-1}** d) 245 kJ mol^{-1}

Solution : -

According to question HCl reaction



Putting the given values, we get enthalpy of formation of

$$\Delta H_{f(\text{HCl})} = [(B \cdot E)_{\text{K-H}} + (B \cdot E)_{\text{Cl-Cl}}] - [2 \times B \cdot E \cdot (\text{H} - \text{Cl})]$$

Hence, enthalpy of formation for

$$1 \text{ mol HCl} = \frac{-186}{2} \text{ kJ} = -93 \text{ kJ}$$

33. A chemical reaction will be spontaneous if it is accompanied by a decrease in

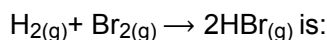
a) entropy of the system b) enthalpy of the system c) internal energy of the system

d) free energy of the system

Solution : -

Gibbs free energy of a system will decide the Spontaneity of a process. If ΔG is negative, then the process is spontaneous.

34. If the bond energies of H-H, Br-Br and H-Br are 433, 192 and 364 kJ mol⁻¹ respectively, then ΔH^0 for the reaction



is:
a) -261 kJ b) +103 kJ c) +261 kJ **d) -103 kJ**

Solution : -

$$\Delta H^0 = \Sigma \text{ bond energy (reactants)} - \Sigma \text{ bond energy (products)}$$

$$= 433 + 192 - 2 \times 364 = -103 \text{ KJ}$$

35. An ideal gas does work on its surroundings when it expands by 2.5 L against external pressure 2 atm. This work done is used to heat up 1 mole of water at 293 K. What would be the final temperature of water in kelvin if specific heat for water is 4.184 Jg⁻¹K⁻¹?

a) **300** b) 600 c) 200 d) 1000

Solution : -

Work done, $W = -P_{\text{ext}} \cdot dV$

$$W = -2 \times 2.5 = -5 \text{ L atm} = -506.3 \text{ J}$$

Because this work is used in raising the temperature of water, so work done is equal to the heat supplied i.e.,

$$W = q = m \cdot c_s \Delta T$$

Given that, $m = 18 \text{ g}$ (= 1 mole), $C_s = 4.184 \text{ J g}^{-1}\text{K}^{-1}$,

$q = +506.3 \text{ J}$, $\Delta T = ?$ (Heat is given to water)

$$\Delta T = \frac{q}{c_s \cdot m} = \frac{506.3}{4.184 \times 18} = 6.72$$

$$\therefore \text{Final temperature, } T_f = T_1 + \Delta T = 293 + 6.72$$

$$= 299.72 \text{ K} \approx 300 \text{ K}$$

36. According to the first law of thermodynamics, $\Delta U = q + w$. In special cases the statement can be expressed in different ways. Which of the following is not a correct expression?

a) At constant temperature: $q = -w$ b) When no work is done: $\Delta U = q$

c) In gaseous system: $\Delta U = q + P\Delta V$ **d) When work is done by the system: $\Delta U = q + w$**

Solution : -

At constant temperature, $\Delta T = 0$

$$\therefore \Delta U = nC_v \Delta T$$

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

$$q = -w$$

When work done is zero, $w = 0$

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

$$\therefore \Delta U = q$$

In gaseous system, $w = P\Delta V$

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

$$\therefore \Delta U = q + P\Delta V$$

When work is done by the system, w is negative.

$$\therefore \Delta U = q - w$$

37. For an ideal gas, consider only P- V work in going from an 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. Which of the following choice(s) is (are) correct? [Take ΔA_0 as change in entropy and W as work done]

a) $\Delta S_{X \rightarrow Z} = \Delta S_{X \rightarrow Y} + \Delta S_{Y \rightarrow Z}$ b) $w_{X \rightarrow Z} = w_{X \rightarrow Y} + w_{Y \rightarrow Z}$ c) $w_{X \rightarrow Y \rightarrow Z} \neq w_{X \rightarrow Y}$ d) $\Delta S_{X \rightarrow Y \rightarrow Z} = \Delta S_{X \rightarrow Y}$

Solution : -

As ΔS does not depend on path and only depends on initial and final stages i.e., it is a state function thus $\Delta S_{X \rightarrow Z} = \Delta S_{X \rightarrow Y} + \Delta S_{Y \rightarrow Z}$ and $\Delta S_{Y \rightarrow Z}$ is not zero thus

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

As we know that work is not a state function and depends on path,

$$\text{Thus, } w_{X \rightarrow Z} \neq w_{X \rightarrow Y} + w_{Y \rightarrow Z}$$

$$w_{X \rightarrow Y} = PdV \text{ (P is constant)}$$

$$w_{Y \rightarrow Z} = 0 \text{ (V is constant)}$$

$$w_{X \rightarrow Z} = 2.303nRT \log \frac{V_2}{V_1}$$

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

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

38. The pressure-volume work for an ideal gas can be calculated by using the expression $W = - \int_{v_1}^{v_2} P_{ex} dV$ The

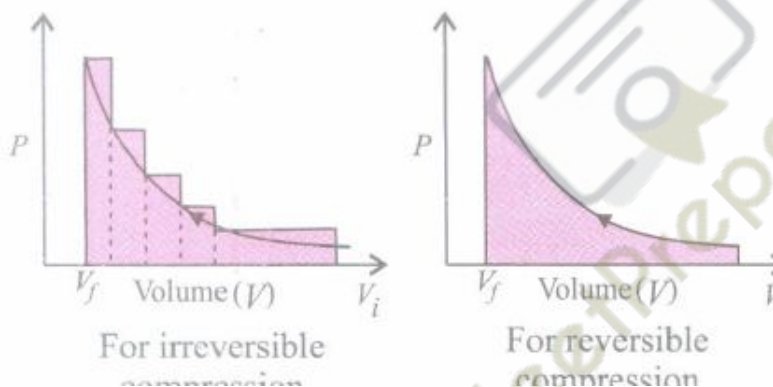
work can also be calculated from the

PV - plot by using the area under the curve within the specified limits. When an ideal gas is compressed (i) reversibly or (ii) irreversibly from volume V_i to V_f . Choose the correct option.

a) $W_{\text{reversible}} = W_{\text{irreversible}}$ b) $W_{\text{reversible}} < W_{\text{irreversible}}$ c) $W_{\text{reversible}} > W_{\text{irreversible}}$

d) $W_{\text{reversible}} = W_{\text{irreversible}} + P_{\text{ex}} \Delta V$

Solution : -



In both the curves, work done on the gas is represented by the shaded area and the area under the curve is always more in irreversible compression.

Hence,

$$W_{\text{irreversible}} > W_{\text{reversible}}$$

39. ΔG is the net energy available to do useful work and is a measure of free energy. If a reaction has positive enthalpy change and positive entropy change, under what conditions will the reaction be spontaneous?

a) ΔG will be positive at low temperature hence reaction is spontaneous at low temperature.

b) ΔG is negative at high temperature hence reaction is spontaneous at high temperature.

c) ΔG is negative at low temperature hence reaction is spontaneous at low temperature.

d) ΔG is negative at all temperatures hence reaction is spontaneous at all temperatures.

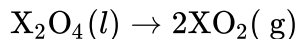
Solution : -

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

For a spontaneous reaction if ΔH is +ve and $\Delta S = +ve$, ΔG will be negative when $T\Delta S > \Delta H$ i.e., $\Delta G = \Delta H - T\Delta S$

For a spontaneous reaction if ΔH is +ve and $\Delta S = +ve$, ΔG will be negative when $T\Delta S > \Delta H$.

40. For the reaction :



$$\Delta U = 2.1 \text{ k cal}, \Delta S = 20 \text{ cal K}^{-1} \text{ at } 300 \text{ K}$$

Hence ΔG is :

- a) 2.7 cal **b) -2.7 cal** c) 9.3 cal d) -9.3 cal

Solution : -

The change in Gibbs Free energy is given by

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

where

ΔH is the enthalpy of the reaction

ΔS is the entropy of the reaction

and ΔU is the change in internal energy

Δn_g is the (number of gaseous moles in product) - (number of gaseous moles in reactant) = 2 - 0 = 2

R is the gas constant = 2 cal

But,

$$\Delta H = (2.1 \times 10^3) + (2 \times 2 \times 300) = 3300 \text{ cal}$$

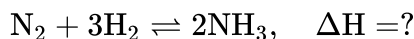
Hence,

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

$$\Delta G = 3300 - (300 \times 20)$$

$$\Delta G = -2700 \text{ cal} = -2.7 \text{ cal}$$

41. For the reaction,



- a) $\Delta E + 2RT$ **b) $\Delta E - 2RT$** c) $\Delta H = RT$ d) $\Delta E - RT$

Solution : -

According to enthalpy equation

$$\underset{\substack{\text{Enthalpy} \\ \text{change}}}{\Delta H} = \underset{\substack{\text{Internal} \\ \text{energy}}}{\Delta E} + \Delta n_g RT$$

$$\Delta n = 2 - (1 + 3)$$

$$[\Delta n = n_P - n_R]$$

Product Reactant

mole mole

$$= 2 - 4 = -2$$

$$\Delta H = \Delta E + (-2)RT$$

$$\Delta H = \Delta E - 2RT$$

42. 2 mole of an ideal gas at 27°C temperature is expanded reversibly from 2 lit to 20 lit. Find the entropy change (R = 2 cal/mol K).

- a) 92.1 b) 0 c) 4 **d) 9.2**

Solution : -

For isothermal reversible expansion

$$w = q = nRT \times 2.303 \log \frac{v_2}{v_1}$$

where, given $n = 2$, $R = 2$, $V_2 = 20$, $V_1 = 2$,

$$q = 2RT \times 2.303 \log \frac{20}{2}$$

$$q = 2 \times 2 \times T \times 2.303 \times 1 = 9.2 T$$

Hence, entropy change,

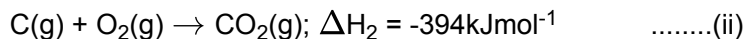
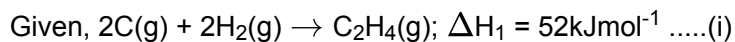
$$\Delta S = \frac{q}{T} = \frac{9.2T}{T} = 9.2 \text{ cal.}$$

43. In endothermic reactions, the reactants

- a) have more energy than products b) have as much energy as the products
 c) are at low temperature than products **d) have less energy than the products**

44. If enthalpies of formation of $C_2H_4(g)$, $CO_2(g)$ and $H_2O(l)$ at $25^\circ C$ and 1 atm pressure are 52, - 394 and - 286 kJ/mol^{-1} respectively, then the enthalpy of combustion of $C_2H_4(g)$ will be:
 a) -141.2 kJ/mol **b) -1412 kJ/mol^{-1}** c) + 14.2 kJ/mol d) + 1412 kJ/mol

Solution : -



Reaction involved for combustion of $C_2H_4(g)$ is,



$2 \times [Eq.(ii) + Eq.(iii)] - Eq.(i)$, we get Eq.(iv)

$$\therefore \Delta = 2[\Delta H_2 + \Delta H_3] - \Delta H_1$$

$$= 2[-394 - 286] - 52$$

$$= -1360 - 52 = -1412 \text{ kJ mol}^{-1}.$$

45. Dissolution of ammonium chloride in water is an endothermic reaction, yet it is a spontaneous process. This is due to the fact that:

- a) ΔH is +ve, ΔS is -ve b) ΔH is -ve, ΔS is +ve **c) ΔH is +ve, ΔS is +ve and $\Delta H < T\Delta S$**
 d) ΔH is +ve and $\Delta H > T\Delta S$

Solution : -

$$\Delta H > 0 \text{ (endothermic reaction)}$$

$$\text{Now, } \Delta G = \Delta H - T\Delta S$$

For spontaneous process, $\Delta G < 0$

$$\text{Therefore, } \Delta G = \Delta H - T\Delta S < 0$$

$$\text{But } \Delta H > 0$$

Therefore for ΔG to be negative, $\Delta S > 0$ and $\Delta H < T\Delta S$.

46. The correct thermodynamic conditions for the spontaneous reaction at all temperatures is
 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 : -

The correct thermodynamic conditions for the spontaneous reaction at all temperatures is

$$\Delta H < 0 \text{ and } \Delta S > 0$$

$$\text{Under these conditions, } \Delta G = \Delta H - T\Delta S < 0$$

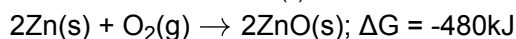
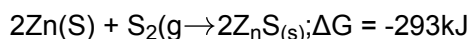
The correct thermodynamic conditions for the spontaneous reaction at all temperatures is

$$\Delta H < 0 \text{ and } \Delta S > 0$$

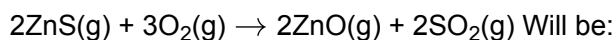
$$\text{Under these conditions, } \Delta G = \Delta H - T\Delta S < 0$$

Note: for spontaneous reactions, $\Delta G < 0$, for non spontaneous reactions, $\Delta G > 0$, for reactions at equilibrium, $\Delta G = 0$

47. The factor of ΔG values is important in metallurgy. The ΔG values for the following reactions at $800^\circ C$ are given as

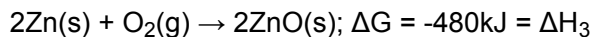
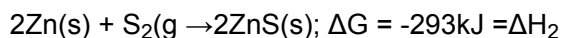
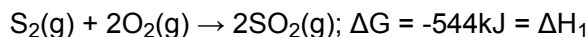


The ΔG for the reaction,



- a) -357 kJ **b) -731 kJ** c) -773 kJ d) - 229 kJ

Solution : -



$$\Delta H = \Delta H_1 + \Delta H_3 - \Delta H_2 = -731\text{kJ}$$

48. Which of the following statements is not correct?

- a) For a spontaneous process, ΔG must be negative.
- b) Enthalpy, entropy, free energy etc. are state variables.
- c) A spontaneous process is reversible in nature.**
- d) Total of all possible kinds of energy of a system is called its internal energy.

Solution : -

For a spontaneous process, $\Delta G < 0$

The variables which depend only on the initial and final states of the system are state variables.

Therefore, enthalpy, entropy and free energy are state variables.

A spontaneous process is not reversible in nature as for opposite reaction to occur, a force has to be applied.

The internal energy is the total of all possible kinds of energy in the system.

49. Assume each reaction is carried out in an open container. For which reaction will $\Delta H = \Delta E$?

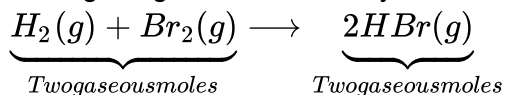
- a) $\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \rightarrow 2\text{HBr}(\text{g})$**
- b) $\text{C}(\text{s}) + 2\text{H}_2\text{O}(\text{g}) \rightarrow 2\text{H}_2(\text{g}) + \text{CO}_2(\text{g})$
- c) $\text{PCl}_5(\text{g}) \rightarrow \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$
- d) $2\text{CO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g})$

Solution : -

As we know, $\Delta H = \Delta E + \Delta n_g RT$

So, the reaction for which Δn_g is zero, i.e., number of gaseous moles are same on reactant and product side then $\Delta H = \Delta E$.

Among the given reaction, only formation of HBr has $\Delta n_g = 0$



$$\Delta n_g = 2 - 2 = 0$$

Hence, $\Delta H = \Delta E + \Delta n_g RT$

$$\Delta H = \Delta E + 0 \Rightarrow \Delta H = \Delta E$$

50. Which of the following relationships is not correct?

- a) $\Delta H = \Delta U + \Delta n_g RT$
- b) $\Delta H_{\text{sub}} = \Delta H_{\text{fusion}} + \Delta H_{\text{vap}}$
- c) $\Delta H_r^\circ = \sum H_{f(\text{reactants})}^\circ - \sum H_{f(\text{products})}^\circ$**
- d) $\Delta H_r^\circ = \sum B.E. \text{ of reactants} - \sum B.E. \text{ of products}$