CHEMICAL THERMODYNAMICS [JEE ADVANCE PREVIOUS YEAR SOLVED PAPER]

JEE Advanced

Single Correct Answer Type

1. The difference between heats of reaction at constant pressure and constant volume for the reaction:
$2C_6H_6(l) + 15O_2(g) \rightarrow 12CO_2(g) + 6H_2O(l)$ at 25°C in kJ is

a. –7.43 **b.** + 3.72 **c.** –3.72 **d.** + 7.43

(IIT-JEE 1991)

2. For an endothermic reaction where ΔH represents the enthalpy of the reaction in kJ mol^{-1}, the minimum value for the energy of activation will be

a. less than ΔH **b.** zero
c. more than ΔH **d.** equal to ΔH

(IIT-JEE 1992)

3. For which change $\Delta H \neq \Delta E$:

a. $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
b. $HCl + NaOH \rightarrow NaCl + H_2O$
c. $C(s) + O_2(g) \rightleftharpoons CO_2(g)$
d. $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ **(IIT-JEE 1995)**

4. Molar heat capacity of water in equilibrium with ice at constant pressure is

a. zero **b.** inifinity (∞)
c. 40.45 kJ K^{-1} mol^{-1} **d.** 75.48 kJ K^{-1} mol^{-1}

(IIT-JEE 1997)

5. Standard molar enthalpy of formation of CO_2 is equal to

a. zero
b. the standard molar enthalpy of combustion of gaseous carbon
c. the sum of standard molar enthalpies of formation of CO and O_2
d. the standard molar enthalpy of combustion of carbon (graphite). **(IIT-JEE 1997)**

6. The ΔH°_f for $CO_2(g)$, $CO(g)$ and $H_2O(g)$ are –393.5, –110.5 and –241.8 kJ mol^{-1} respectively. The standard enthalpy change (in kJ) for the reaction : $CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g)$ is

a. + 524.1 **b.** + 41.2 **c.** –262.5 **d.** –41.2

(IIT-JEE 2000)

7. In thermodynamics, a process is called reversible when

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

(IIT-JEE 2001)

8. Which one of the following statement is false?

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.

(IIT-JEE 2001)

9. One mole of a non-ideal gas undergoes a change of state (2.0 atm, 3.0 L, 95(K) → (4.0 atm 5.0 L, 245 K) with a change in internal energy, $\Delta U = 30.0$ L atm. The change in enthalpy (ΔH) of the process in L atm is

a. 40.0
b. 42.3
c. 44.0
d. not defined, because pressure is not constant

(IIT-JEE 2002)

10. Which of the reaction defines ΔH°_f?

a. $C_{(diamond)} + O_2(g) \rightarrow CO_2(g)$
b. $\frac{1}{2}H_2(g) + \frac{1}{2}F_2(g) \rightarrow HF(g)$
c. $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$
d. $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$

(IIT-JEE 2003)

11. Two moles of an ideal gas is expanded isothermally and reversibly from 1 litre to 10 litre at 300 K. The enthalpy change (in kJ) for the process is

a. 11.4 kJ **b.** –11.4 kJ **c.** 0 kJ **d.** 4.8 kJ

(IIT-JEE 2004)

12. Spontaneous adsorption of a gas on solid surface is an exothermic process because

a. ΔH increases for system
b. ΔS increases for gas
c. ΔS decreases for gas
d. ΔG increases for gas

(IIT-JEE 2004)

13. The enthalpy of vapourization of a liquid is 30 kJ mol^{-1} and entropy of vapourization is 75 J mol^{-1} K. The boiling point of the liquid at 1 atm is

a. 250 K **b.** 400 K **c.** 450 K **d.** 600 K

(IIT-JEE 2004)

14. When 1 mole of a monatomic ideal gas at T K undergoes adiabatic change under a constant external pressure of 1 atm, changes volume from 1 L to 2 L. The final temperature (in K) would be

a. $\frac{T}{2^{2/3}}$ **b.** $T + \frac{2}{3 \times 0.0821}$

c. T **d.** $T - \frac{2}{3 \times 0.0821}$

(IIT-JEE 2005)

15. A monatomic 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?

a. $\frac{4R}{2}$ **b.** $\frac{3R}{2}$ **c.** $\frac{5R}{2}$ **d.** 0

(IIT-JEE 2006)

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

$$\begin{tikzcd} C \arrow[r] & D \arrow[d] \\ A \arrow[u] & B \end{tikzcd}$$

Given

$\Delta S_{(A \rightarrow C)} = 50$ e.u., $\Delta S_{(C \rightarrow D)} = 30$ e.u., $\Delta S_{(B \rightarrow D)} = 20$ e.u., where e.u. is the entropy unit, then $\Delta S_{(A \rightarrow B)}$ is

a. + 60 e.u. **b.** + 100 e.u.
c. –60 e.u. **d.** –100 e.u.

(IIT-JEE 2006)

17. $N_2 + 3H_2 \rightleftharpoons 2NH_3$

Which is correct statement if N_2 is added at equilibrium condition?

a. The equilibrium will shift to forward direction because according to IInd law of thermodynamics the entropy must increase in the direction of spontaneous reaction.
b. The condition for equilibrium is $G_{N_2} + 3G_{H_2} = 2G_{NH}$, where G is Gibbs free energy per mole of the gaseous species measured at that partial pressure. The condition of equilibrium is unaffected by the use of catalyst, which increases the rate of both the forward and backward reactions to the same extent.
c. The catalyst will increase the rate of forward reaction by α and that of backward reaction by β.
d. Catalyst will not alter the rate of either of the reaction.

(IIT-JEE 2006)

18. The value of $\log_{10} K$ for a reaction $A \rightleftharpoons B$ is (Given: $\Delta_f H^\circ_{298\,K} = -54.07$ kJ mol^{-1}, $\Delta_r S^\circ_{298\,K} = 10$ JK^{-1} mol^{-1} and $R = 8.314$ JK^{-1} mol^{-1}; $2.303 \times 8.314 \times 298 = 5705$)

a. 5 **b.** 10
c. 95 **d.** 100

(IIT-JEE 2007)

19. For the process:

$H_2O\,(l)$ (1 bar, 373 K) → $H_2O(g)$ (1 bar, 373 K), the correct set of thermodynamic parameters is

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

(IIT-JEE 2007)

20. The species which by definition has ZERO standard molar enthalpy of formation at 298 K is

a. $Br_2(g)$ **b.** $Cl_2(g)$
c. $H_2O(g)$ **d.** $CH_4(g)$

(IIT-JEE 2010)

21. Using the data provided, calculate the multiple bond energy (kJ mol^{-1}) of a $C \equiv C$ bond in C_2H_2. That energy is (take the bond energy of a C – H bond as 350 kJ mol^{-1})

$2C(s) \rightarrow 2C(g)$ $\Delta H = 1410$ kJ mol^{-1}
$2C(s) \rightarrow 2C(g)$ $\Delta H = 1410$ kJ mol^{-1}
$H_2(s) \rightarrow 2H(g)$ $\Delta H = 330$ kJ mol^{-1}

a. 1165 **b.** 837
c. 865 **d.** 815

(IIT-JEE 2012)

22. The standard enthalpies of formation of $CO_2(g)$, $H_2O(l)$ and glucose(s) at 205°C are –400 kJ/mol, –300 kJ/mol and –1300 kJ/mol, respectively. The standard enthalpy of combustion per gram of glucose at 25°C is

a. + 2900 kJ **b.** –2900 kJ

c. –16.11 kJ **d.** +16.11 kJ

(IIT-JEE 2013)

23. For the process

$$H_2O(l) \rightarrow H_2O(g)$$

At T = 100°C and 1 atmosphere pressure, the correct choice is

a. $\Delta S_{system} > 0$ and $\Delta S_{surroundings} > 0$

b. $\Delta S_{system} > 0$ and $\Delta S_{surroundings} < 0$

c. $\Delta S_{system} < 0$ and $\Delta S_{surroundings} > 0$

d. $\Delta S_{system} < 0$ and $\Delta S_{surroundings} < 0$

(JEE Advanced 2014)

Multiple Correct Answers Type

1. Identify the intensive quantities from the following:

a. Enthalpy **b.** Temperature

c. Volume **d.** Refractive Index

(IIT-JEE 1993)

2. The following is (are) endothermic reaction(s):

a. Combustion of methane

b. Decomposition of water

c. Dehydrogenation of ethane to ethylene

d. Conversion of graphite to diamond

(IIT-JEE 1999)

3. Which of the following statements is/are false?

a. Work is 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.

(IIT-JEE 2001)

4. Among the following the state function(s) is (are)

a. internal energy

b. irreversible expansion work

c. reversible expansion work

d. molar enthalpy **(IIT-JEE 2009)**

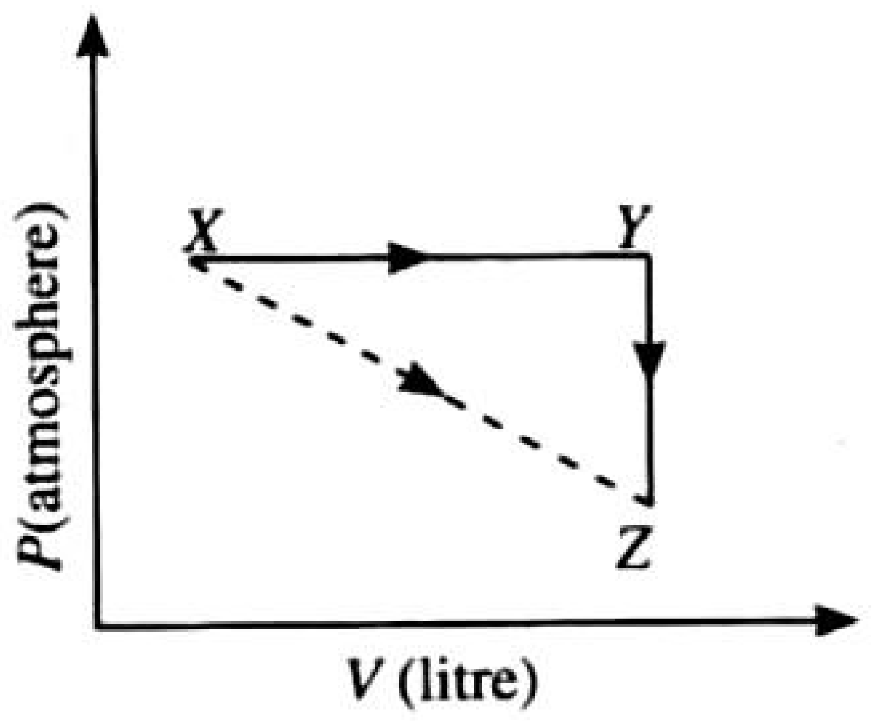
5. Among the following the intensive property is (properties are)

a. molar conductivity **b.** electromotive force

c. resistance **d.** heat capacity

(IIT-JEE 2010)

6. 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 ΔS 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. $W_{x\rightarrow y\rightarrow z} = W_{x\rightarrow y}$

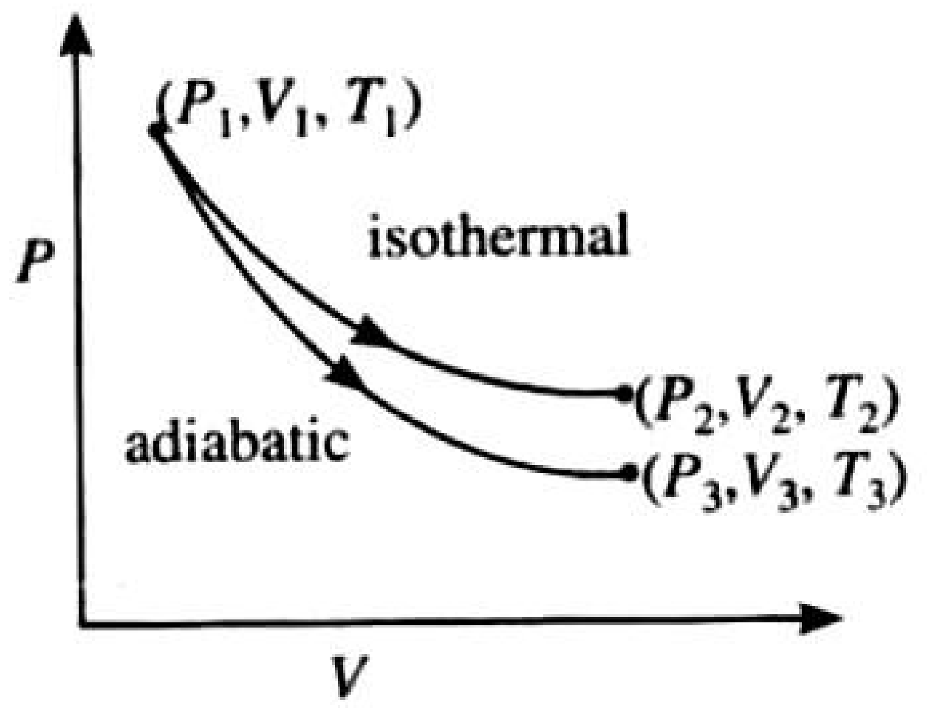
d. $\Delta S_{x\rightarrow y\rightarrow z} = \Delta S_{x\rightarrow y}$ **(IIT-JEE 2012)**

7. 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?

a. $T_1 = T_2$ **b.** $T_3 > T_1$

c. $w_{isothermal} > w_{adiabatic}$ **d.** $\Delta U_{isothermal} > \Delta U_{adiabatic}$

(IIT-JEE 2012)



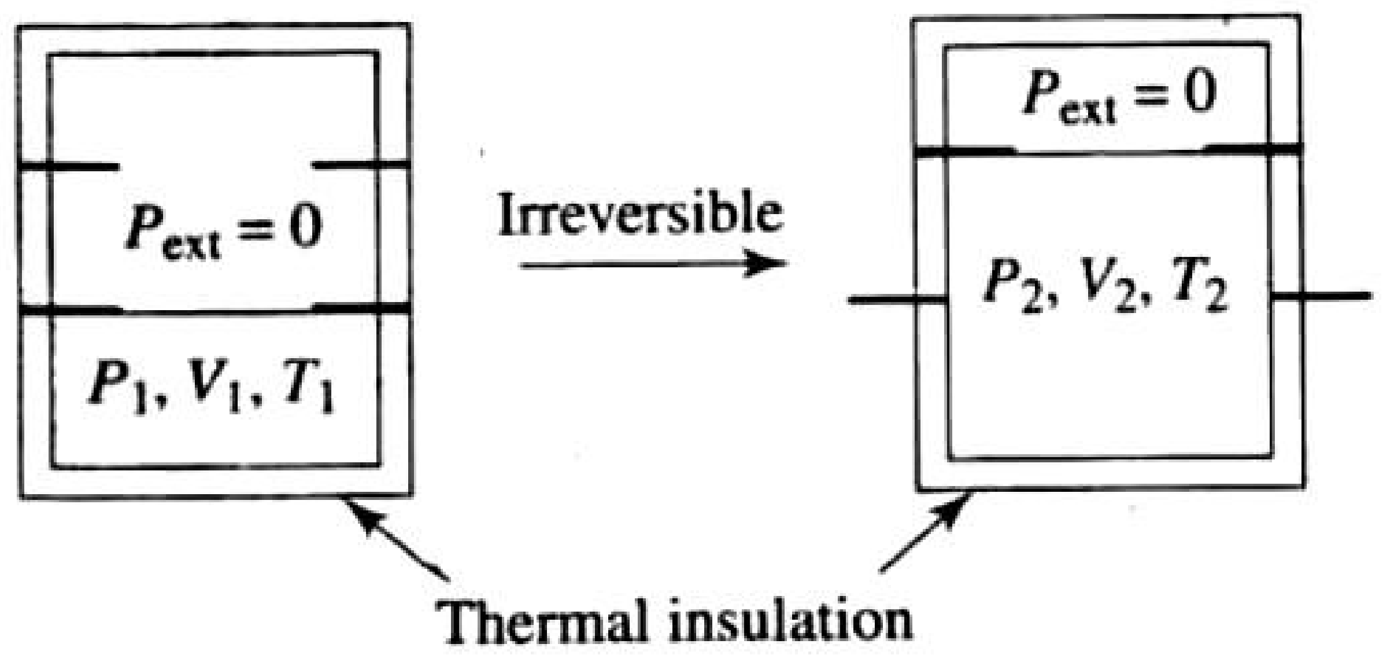
8. Benzene and naphthalene form an ideal solution at room temperature. For this process, the true statement(s) is(are)

a. ΔG is positive **b.** ΔS_{system} is positive

c. $\Delta S_{surrounding} = 0$ **d.** ΔH = 0

(JEE Advanced 2013)

9. An ideal gas in a 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 P_2, V_2 and T_2, respectively. For this expansion,



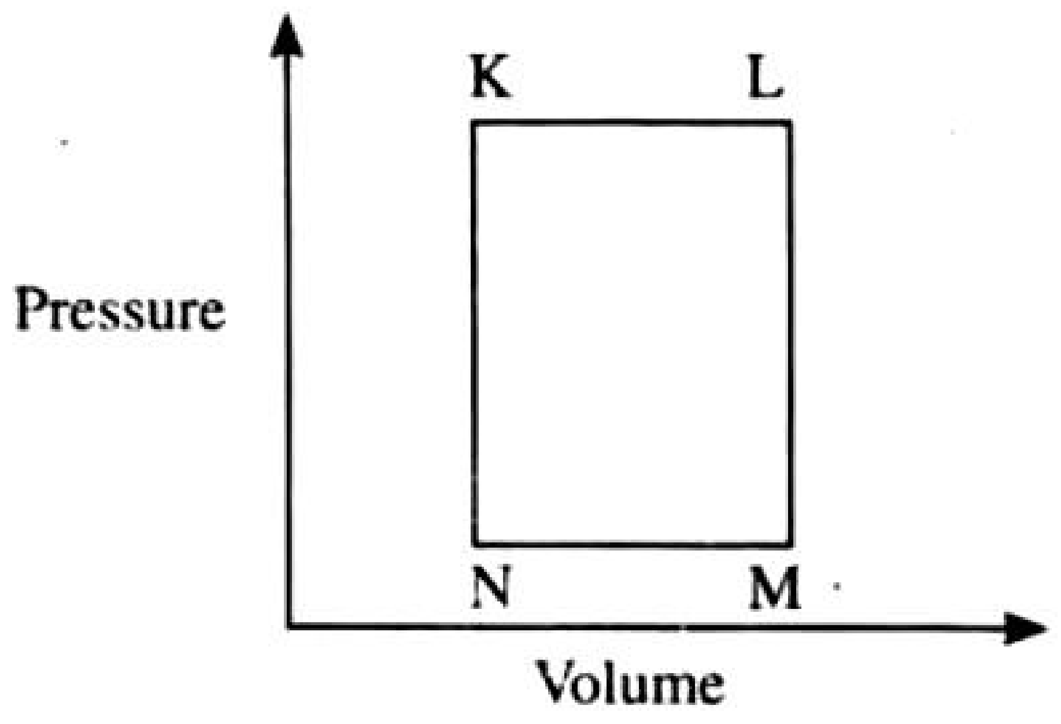
a. $q = 0$ **b.** $T_2 = T_1$

c. $P_2V_2 = P_1V_1$ **d.** $P_2V_2^{\gamma} = P_1V_1^{\gamma}$

(JEE Advanced 2014)

Linked Comprehension Type

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.



(JEE Advanced 2013)

1. 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
2. The pair of isochoric processes among the transformation of states is
   - **a.** K to L and L to M
   - **b.** L to M and N to K
   - **c.** L to M and M to N
   - **d.** M to N and N to K

Matching Column Type

1. Match the transformations in **Column I** with appropriate options in **Column II**

Column I	**Column II**
a. $CO_2(s) \rightarrow CO_2(g)$	p. phase transition
b. $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$	q. allotropic change
c. $2H \rightarrow H_2(g)$	r. ΔH is positive
d. $P_{(white,\ solid)} \rightarrow P_{(red,\ solid)}$	s. ΔS is positive
	t. ΔS is negative

(IIT-JEE 2011)

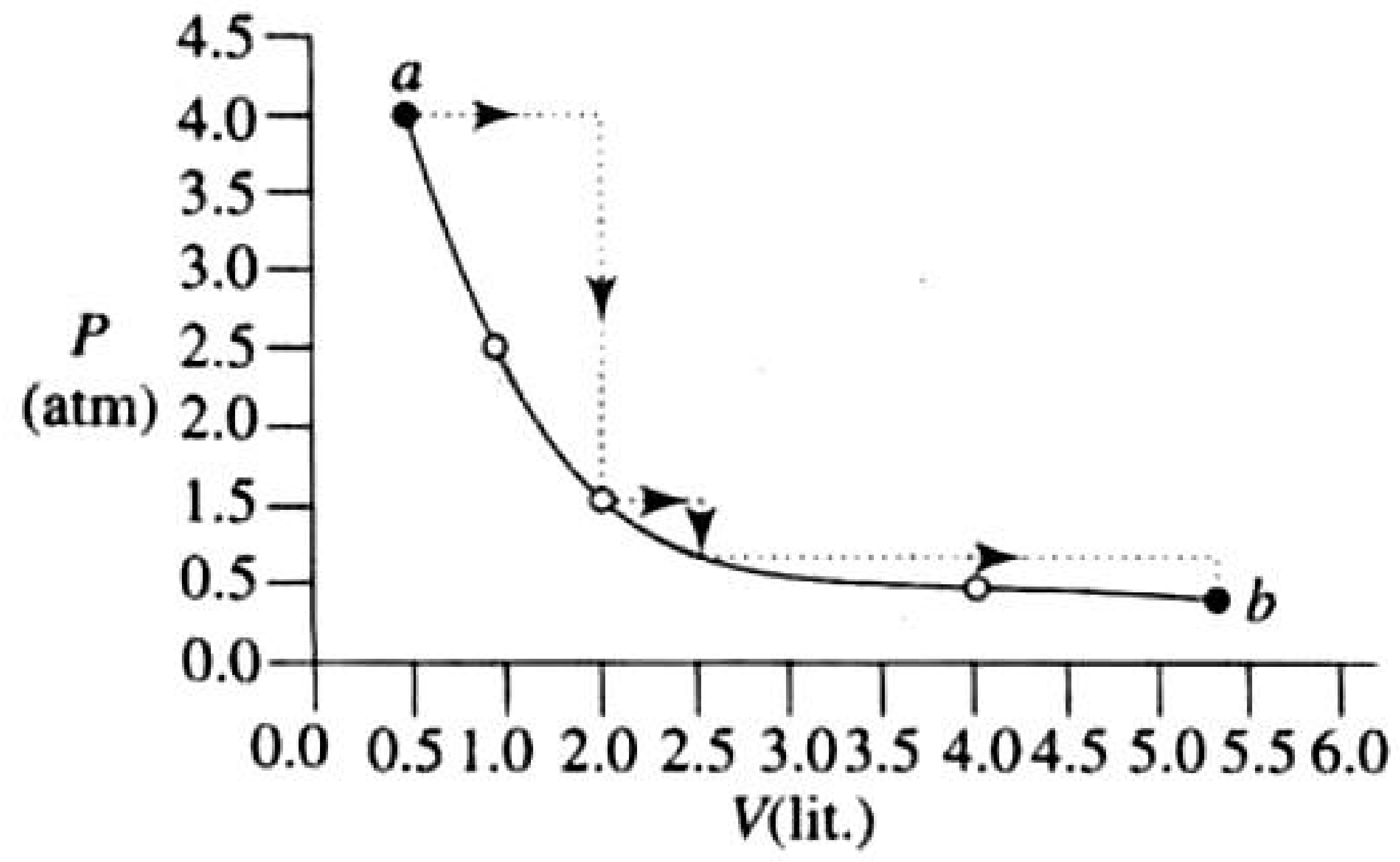
1. Match the thermodynamic processes given under Column I with the expressions given under Column II

Column I	**Column II**
a. Freezing of water at 273 K and 1 atm	p. $q = 0$
b. Expansion of 1 mol of an ideal gas into a vacuum under isolated conditions	q. $w = 0$
c. Mixing of equal volumes of two ideal gases at constant temperature and pressure in an isolated container	r. $\Delta S_{sys} < 0$
d. Reversible heating of $H_2(g)$ at 1 atm from 300 K, followed by reversible cooling to 300 K at 1 atm	s. $\Delta U = 0$
	t. $\Delta G = 0$

(JEE Advanced 2015)

Integer Answer Type

1. In a constant volume calorimeter, 3.5 g of a gas with molecular weight 28 was burnt in excess oxygen at 298.0 K. The temperature of the calorimeter was found to increase from 298.0 K to 298.45 K due to the combustion process. Given that the heat capacity of the calorimeter is 2.5 kJ K^{-}, the numerical value for the enthalpy of combustion of the gas in kJ mol^{-1} is **(IIT-JEE 2009)**
2. One mole of an ideal gas is taken from *a* to *b* along two paths denoted by the solid and the dashed lines as shown in the graph below. If the work done along the solid line path w_s and that along the dotted line path is w_d, then the integer closest to the ratio w_d/w_s is:



(IIT-JEE 2010)

3. To an evacuated vessel with movable piston under external pressure of 1 atm, 0.1 mol of He and 1.0 mol of an unknown compound (vapour pressure 0.68 atm. at 0°C) are introduced. Considering the ideal gas behaviour, the total volume (in litre) of the gases at 0°C is close to **(IIT-JEE 2011)**

Assertin-Reasoning Type

Read the following statements and explanation and answer as per the options given below:

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

1. **Assertion:** The heat absorbed during the isothermal expansion of an ideal gas against vacuum is zero.
   Reason: The volume occupied by the molecules of an ideal gas is zero.
   (IIT-JEE 2000)
2. **Assertion:** There is a natural asymmetry between converting work to heat and converting heat to work.
   Reason: No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work.
   (IIT-JEE 2008)

Fill in the Blanks Type

1. A system is said to be ______ if it can neither exchange matter nor energy with the surroundings. **(IIT-JEE 1993)**
2. The heat content of the products is more than that of the reactants in an ______ reaction. **(IIT-JEE 1993)**
3. Enthalpy is an ______ property. **(IIT-JEE 1997)**

True / False Type

1. First law of thermodynamics is not adequate in predicting the direction of a process. **(IIT-JEE 1982)**
2. Heat capacity of a diatomic gas is higher than that of a monoatomic gas. **(IIT-JEE 1985)**

Subjective Type

1. The enthalpies for the following reactions ($\Delta H°$) at 25°C are given below:

   i. $\frac{1}{2}H_2(g) + \frac{1}{2}O_2(g) \rightarrow OH(g)$ $\Delta H = 10.06$ kcal

   ii. $H_2(g) \rightarrow 2H(g)$ $\Delta H = 104.18$ kcal

   iii. $O_2(g) \rightarrow 2O(g)$ $\Delta H = 118.32$ kcal

   Calculate the O–H bond energy in the OH group. **(IIT-JEE 1981)**

2. The standard heats of formation at 298 K for $CCl_4(g)$, $H_2O(g)$, $CO_2(g)$ and $HCl(g)$ are –25.5, –57.8, –94.1 and –22.1 kcal/mol respectively. Calculate $\Delta H°_{298 K}$ for the reaction

   $$CCl_4(g) + 2H_2O(g) \rightarrow CO_2(g) + 4HCl(g)$$

   (IIT-JEE 1982)

3. The molar heats of combustion of $C_2H_2(g)$, C(graphite) and $H_2(g)$ are 310.62 kcal, 94.05 kcal and 68.32 kcal, respectively. Calculate the standard heat of formation of $C_2H_2(g)$. **(IIT-JEE 1983)**
4. The heat energy, *q*, absorbed by a gas ΔH, is true at what condition(s). **(IIT-JEE 1984)**
5. Given the following standard heats of reactions:

   i. heat of formation of water = –68.3 kcal;

   ii. heat of combustion of acetylene = –310.6 kcal;

   iii. heat of combustion of ethylene = –337.2 kcal;

   Calculate the heat of reaction for the hydrogenation of acetylene at constant volume and at (25°C). **(IIT-JEE 1984)**

6. The bond dissociation energies of gaseous H_2, Cl_2 and HCl are 104, 58 and 103 kcal/mole respectively. Calculate the enthalpy of formation of HCl (g). **(IIT-JEE 1985)**
7. The standard molar heats of formation of ethane, carbon dioxide and liquid water are –21.1, –94.1 and –68.3 kcal respectively. Calculate the standard molar heat of combustion of ethane. **(IIT-JEE 1986)**
8. An intimate mixture of ferric oxide, Fe_2O_3, and aluminium, Al, is used in solid fuel rockets. Calculate the fuel value per gram and fuel value per cc of the mixture. Heats of formation and densities are as follows:

   $H_f\ (Al_2O_3) = 399$ kcal/mole;
   $H_f\ (Fe_2O_3) = 199$ kcal/mole;
   Density of $Fe_2O_3 = 5.2$ g/cc.;
   Density of Al = 2.7 g/cc. **(IIT-JEE 1988)**

9. An athlete is given 100 g of glucose ($C_6H_{12}O_6$) of energy equivalent to 1560 kJ. He utilizes 50 percent of this gained energy in the event. In order to avoids storage of energy in the body, calculate the weight of water he would need to perspire. The enthalpy of evaporation of water is 44 kJ/mole. **(IIT-JEE 1989)**
10. The standard enthalpy of combustion at 25°C of hydrogen, cyclohexene (C_6H_{10}) and cyclohexane (C_6H_{12}) are –241, –3800 and –3920 kJ/mole respectively. Calculate the heat of hydrogenation of cyclohexene. **(IIT-JEE 1989)**
11. Using the data (all values are in kcal mol^{-1} at 25°C) given below, calculate the bond energy of C – C and C – H bonds.

    $\Delta H°_{combustion}$ (ethane) = –372.0
    $\Delta H°_{combustion}$ (propane) = –530.0
    $\Delta H° C(s) \rightarrow C(g)$ = 172.0
    Bond energy of H – H = 104.0
    $\Delta H°_f$ of H_2O (l) = –68.0
    $\Delta H°_f$ of $CO_2(g)$ = –94.0 **(IIT-JEE 1990)**

12. A gas mixture of 3.67 litres of ethylene and methane on complete combustion at 25°C produces 6.11 litres of CO_2. Find out the amount of heat evolved on burning one litre of the gas mixture. The heats of combustion of ethylene and methane are –1423 and –891 kJ mol^{-1} at 25°C. **(IIT-JEE 1991)**
13. Determine the enthalpy change of the reaction. $C_3H_8(g) + H_2(g) \rightarrow C_2H_6(g) + CH_4(g)$, at 25°, using the given heat of combustion values under standard conditions: **(IIT-JEE 1992)**

Compound	$H_2(g)$	$CH_4(g)$	$C_2H_6(g)$	C(graphite)
$\Delta H°$ (kJ/mol)	–285.8	–890.0	–1560.0	–393.5

    The standard heat of formation of $C_3H_8(g)$ is –103.8 kJ/mol. **(IIT-JEE 1992)**

14. In order to get maximum calorific output, a burner should have an optimum fuel to oxygen ratio which corresponds to 3 times as much oxygen is required theoretically for complete combustion of the fuel. A burner which has been adjusted for methane as fuel (with *x* litre/hour of CH_4 and 6*x* litre/hour of O_2) is to be readjusted for butane, C_4H_{10}. In order to get the same calorific output, what should be the rate of supply of butane and oxygen? Assume that losses due to incomplete combustion, etc., are the same for both the fuels and the gases behave ideally.
    Heats of combustion:

    $CH_4 = 809$ kJ/mol; $C_4H_{10} = 2878$ kJ/mol

    (IIT-JEE 1994)

15. The polymerization of ethylene to linear polyethylene is represented by the reaction

$$nCH_2 = CH_2 \rightarrow (CH_2 - CH_2)_n$$

where n has a large integral value. Given that the average enthalpies of bond dissociation for C = C and C − C at 298 K are + 590 and + 331 kJ mol^{-1}, respectively, calculate the enthalpy of polymerization per mole of ethylene at 298 K. **(IIT-JEE 1994)**

16. The standard molar enthalpies of formation of cyclohexane (l) and benzene (l) at 25°C are −156 and +49 kJ mol^{-1} respectively. The standard enthalpy of hydrogenation of cyclohexene (l) at 25°C is −119 kJ mol^{-}. Use these data to estimate the magnitude of the resonance energy of benzene. **(IIT-JEE 1996)**

17. The enthalpy change involved in the oxidation of glucose is −2880kJ mol^{-1}. Twenty-five percent of this energy is available for muscular work. If 100 kJ of muscular work is needed to walk one kilometer, what is the maximum distance that a person will be able to walk after eating 120 g of glucose. **(IIT-JEE 1997)**

18. Compute the heat of formation of liquid methyl alcohol in kilojoules per mole, using the following data. Heat of vaporization of liquid methyl alcohol = 38 kJ/mol. Heat of formation of gaseous atoms from the elements in their standard states; H, 218 kJ/mol; O, 249 kJ/mol; C = 715 kJ/mol. Average bond energies:

C–H = 415 kJ/mol, C–O = 356 kJ/mol,

O–H = 463 kJ/mol **(IIT-JEE 1997)**

19. Anhydrous $AlCl_3$ is covalent. From the data given below, predict whether it would remain covalent or become ionic in aqueous solution. (Ionisation energy for Al = 5137 kJ/mol^{-1}; $\Delta H_{\text{hydration}}$ for Al^{3+} = −4665 kJ/mol^{-1}; $\Delta H_{\text{hydration}}$ for Cl^- = −381 kJ/mol^{-1}.) **(IIT-JEE 1997)**

20. From the following data, calculate the enthalpy change for the combustion of cyclopropane at 298 K. The enthalpy of formation of $CO_2(g)$, $H_2O(l)$ and propene(g) are −393.5, −285.8 and 20.42 kJ mol^{-1} respectively. The enthalpy of isomerisation of cyclopropane to propene is −33.0 kJ mol^{-1}. **(IIT-JEE 1998)**

21. Estimate the average S – F bond energy in SF_6. The values of standard enthalpy of formation of $SF_6(g)$, S(g) and F(g) are: 1100, 275 and 80 kJ mol^{-1} respectively. **(IIT-JEE 1999)**

22. A sample of argon gas at 1 atm pressure and 27°C expands reversibly and adiabatically from 1.25 dm^3 to 2.50 dm^3. Calculate the enthalpy change in this process. $C_{\text{v.m.}}$ for argon is 12.48 JK^{-1} mol^{-1}. **(IIT-JEE 2000)**

23. Show that the reaction $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$ at 300 K, is spontaneous and exothermic, when the standard entropy change is −0.094 kJ mol^{-1} K^{-1}. The standard Gibbs free energies of formation for CO_2 and CO are −394.4 and −137.2 kJ mol^{-1}, respectively. **(IIT-JEE 2000)**

24. Diborane is a potential rocket fuel which undergoes combustion according to the reaction.

$$B_2H_6(g) + 3O_2(g) \rightarrow B_2O_3(s) + 3H_2O(g)$$

From the following data, calculate the enthalpy change for the combustion of diborane.

$$2B(s) + \left(\frac{3}{2}\right)O_2(g) \rightarrow B_2O_3(s);\quad \Delta H = -1273 \text{ kJ mol}^{-1} \quad \text{(i)}$$

$$H_2(g) + \left(\frac{1}{2}\right)O_2(g) \rightarrow H_2O\,(l);\quad \Delta H = -286 \text{ kJ mol}^{-1} \quad \text{(ii)}$$

$$H_2O\,(l) \rightarrow H_2O(g);\quad \Delta H = 44 \text{ kJ mol}^{-1} \quad \text{(iii)}$$

$$2B(s) + 3H_2(g) \rightarrow B_2H_6(g);\quad \Delta H = 36 \text{ kJ mol}^{-1} \quad \text{(iv)}$$

(IIT-JEE 2000)

25. When 1-pentyne (A) is treated with 4 N alcoholic KOH at 175°C, it is converted slowly converted into an equilibrium mixture of 1.3% 1-pentyne (A), 95.2% 2-pentyne (B) and 3.5% of 1, 2-pentadiene (C). The equilibrium was maintained at 175°C. Calculate ΔG° for the following equilibria:

$$B \rightleftharpoons A \quad \Delta G^\circ_1 = ?$$

$$B \rightleftharpoons C \quad \Delta G^\circ_2 = ?$$

From the calculated value of ΔG°_1 and ΔG°_2 indicate the order of stability of (A), (B) and (C). Write a reasonable reaction mechanism showing all intermediates leading to (A), (B) and (C). **(IIT-JEE 2001)**

26. Two moles of a perfect gas undergo the following processes:

a. a reversible isobaric expansion from (1.0 atm, 20.0 L) to (1.0 atm, 40.0 L);

b. a reversible isochoric change of state from (1.0 atm, 40.0 L) to (0.5 atm, 40.0 L);

c. a reversible isothermal compression from (0.5 atm, 40.0 L) to (1.0 atm, 20.0 L).

- **i.** Sketch with labels each of the processes on the same *P*–*V* diagram.
- **ii.** Calculate the total work (w) and the total heat change (q) involved in the above processes.
- **iii.** What will be the values of ΔU, ΔH and ΔS for the overall process? **(IIT-JEE 2002)**

27. C_v value of He is always 3R/2 but C_v value of H_2 is 3R/2 at low temperature and 5R/2 at moderate temperature and more than 5R/2 at higher temperature explain in two to three lines. **(IIT-JEE 2003)**

28. An insulated container contains 1 mole of a liquid, molar volume 100 ml, at 1 bar. When liquid is steeply pressed to 100 bar, volume decreases to 99 ml. Find ΔH and ΔU for the process. **(IIT-JEE 2004)**

29. In the following equilibrium:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

When 5 moles of each is taken and the temperature is kept at 298 K, the total pressure was found to be 20 bar.

Given: $\Delta G^\circ_f(N_2O_4) = 100$ kJ; $\Delta G^\circ_f(NO_2) = 50$ kJ

i. Find ΔG of the reaction at 298 K.

ii. Find the direction of the reaction

(IIT-JEE 2004)

30. For the reaction, $2CO + O_2 \rightarrow 2CO_2$; $\Delta H = -560$ kJ. Two moles of CO and one mole of O_2 are taken in a container of volume 1L. They completely form two moles of CO_2, the gases deviate appreciably from ideal behaviour. If the pressure in the vessel changes from 70 to 40 atm, find the magnitude (absolute value) of ΔU at 500 K. (1L atm = 0.1 kJ) **(IIT-JEE 2006)**

Answer Key

JEE Advanced

Single Correct Answer Type

1. a. **2.** c. **3.** d. **4.** b. **5.** d.
6. b. **7.** c. **8.** a. **9.** c. **10.** b.
11. c. **12.** c. **13.** b. **14.** d. **15.** a.
16. a. **17.** b. **18.** b. **19.** a. **20.** b.
21. d. **22.** c. **23.** b.

Multiple Correct Answers Type

1. b., d. **2.** b., c., d. **3.** a. **4.** a., d. **5.** a., b.
6. a., c. **7.** a., c., d. **8.** b., c., d. **9.** a., b., c.

Linked Comprehension Type

1. c. **2.** b.

Matching Column Type

1. (a) → (p, r, s); (b) → (r, s); (c) → (t); (d) → (p, q, t)
2. (a) → (r, t); (b) → (p, q, s); (c) → (p, q, s); (d) → (p, q, s, t)

Integer Answer Type

1. (9) **2.** (2) **3.** (7)

Assertion–Reasoning Type

1. c. **2.** a.

Fill in the Blanks Type

1. Isolated **2.** Endothermic **3.** Extensive

True/False Type

1. True **2.** False

Hints and Solutions

JEE Advanced

Single Correct Answer Type

1. a. $\Delta H - \Delta U = \Delta nRT$

$$= 3 \times 8.314 \times 298 = -7432 \text{ J} = -7.43 \text{ kJ}$$

2. c. Activation energy: E_a is the energy that must be possessed by the molecules in excess to the average energy at a given temperature to enter a chemical reaction.

Relation between activation energy and enthalpy of a reversible reaction:

If the reaction is endothermic in forward direction, then

$$E_{a(\text{backward})} = E_{a(\text{forward})} + \Delta H$$

If the reaction is exothermic in forward direction

$$E_{a(\text{backward})} = E_{a(\text{forward})} + \Delta H$$

For an endothermic reaction, where ΔH represents the enthalpy of the reaction in kJ mol^{-1}, the minimum value for the energy of activation will be slightly more than ΔH.

3. d. $\Delta H = \Delta E + \Delta nRT$

For $\Delta H \neq \Delta E$, $\Delta n \neq 0$

where Δn = No. of moles of gaseous products – No. of moles of gaseous reactants

a. $\Delta n = 2 - 2 = 0$

b. $\Delta n = 0$ (∵ they are either in solid or liquid state)

c. $\Delta n = 1 - 1 = 0$ (∵ C is in solid state)

d. $\Delta n = 2 - 4 = -2$

Therefore, (d) is correct answer.

4. b. $C_p = \left(\dfrac{\delta H}{\delta T}\right)_p$; At equilibrium T is constant that is

$\delta T = 0$; Thus $C_p = \infty$

5. d. Standard molar heat enthalpy (H°) of a compounds is equal to its standard heat of formation from most stable states of initial components.

6. b. $C + O_2 \rightarrow CO_2$; $\Delta H^\circ = -393.5$ kJ/mol (i)

$C + \frac{1}{2}O_2 \rightarrow CO$; $\Delta H^\circ = -110.5$ kJ/mol (ii)

$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$; $\Delta H^\circ = -241.8$ kJ/mol (iii)

By Eqs. (ii) + (iii) – (i)

$$CO_2 + H_2 \rightarrow CO + H_2O; \Delta H^\circ = +41.2 \text{ kJ/mol}$$

7. c. In a reversible process, the driving and the opposite forces are nearly equal, hence the system and the surroundings always remain in equilibrium with each other.

8. a. Work is not a state function because it depends upon the path followed.

9. c. $H = U + PV$

$\therefore \quad H_2 - H_1 = U_2 - U_1 + (P_2V_2 - P_1V_1)$

$\therefore \quad \Delta H = 30 + (4 \times 5 - 2 \times 3) = 44$ L atm

10. b. No doubt (a) and (b) both represent heat of formations but standard heat of formation (ΔH°_f) for CO_2 will be from:

$$C_{(graphite)} + O_2 \rightarrow CO_2$$

as $C_{(graphite)}$ is most stable form of carbon.

11. c. $\Delta H = nC_p \Delta T$ solution; since $\Delta T = 0$ so, $\Delta H = 0$

12. c. $\Delta G = \Delta H - T\Delta S$

Entropy decreases during adsorption. Entropy factor is disfavouring, therefore the enthalpy factor must favour spontaneity, so it must be exothermic and ΔH must be negative.

13. b. $T_b = \frac{\Delta H}{\Delta S} = \frac{30 \times 10^3}{75} = 400$ K

14. d. Process $\Delta H = 0$

$$\Delta E = \Delta V$$

$$\Delta W = -P\Delta V = -1$$

$$\Delta E = nC_V\Delta T$$

$$C_V = \frac{R}{\gamma - 1}, \gamma = \frac{5}{3} \text{ for monatomic gas}$$

$$\left(\gamma = \frac{C_P}{C_V}\right)$$

$$C_V = \frac{R}{\frac{5}{3} - 1} = \frac{3R}{2}$$

$$n = 1$$

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

$$T_2 = T - \frac{2}{3 \times 0.0821}$$

15. a. A monatomic ideal gas undergoes a process in which the ratio of P to V at any instant is constant and equals 1.

$$\frac{P}{V} = \text{constant}$$

$$PC^{-1} = \text{constant}$$

$$PV^{\gamma} = \text{constant}$$

$$\gamma = -1$$

Monatomic gas:

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

$$\text{Molar heat capacity } = C_V + \frac{R}{1 - \gamma}$$

$$= \frac{3}{2}R + \frac{R}{1 - (-1)} = \frac{3}{2}R + \frac{R}{2} = \frac{4R}{2}$$

16. a. $\Delta S_{(A \rightarrow B)} = \Delta S_{(A \rightarrow C)} + \Delta S_{(C \rightarrow D)} - \Delta S_{(B \rightarrow D)}$

$= 50 + 30 - 20 = 60$ e.u.

17. b. $N_2 + 3H_2 \rightleftharpoons 2NH_3$

$\Delta G = \Sigma G(\text{products}) - \Sigma G(\text{reactants})$

$\Delta G = 2 \times G(NH_3) - [G(N_2)] + [3 \times G(H_2)]$

At equilibrium, $\Delta G = 0$

$0 = 2 \times G(NH_3) - [G(N_2) + \{3 \times G(H_2)\}]$

$[G(N_2) + \{3 \times G(H_2)\}] = 2 \times G(NH_3)$

The condition of equilibrium is unaffected by the use of catalyst which increases the rate of both the forward and backward reactions to the same extent.

18. b. $A \rightleftharpoons B$

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

$\Delta G^\circ = -2.303 \text{ RT} \log_{10} K$

$-2.303 \text{ RT} \log_{10} K = \Delta H^\circ - T\Delta S^\circ$

$2.303 \text{ RT} \log_{10} K = T\Delta S^\circ - \Delta H^\circ$

$$\log_{10} K = \frac{T\Delta S^\circ - \Delta H^\circ}{2.303RT} = \frac{298 \times 10 + 54.07 \times 1000}{2.303 \times 8.314 \times 298} = 10$$

19. a. $\underset{(1 \text{ bar}, 373 \text{ K})}{H_2O(l)} \rightleftharpoons \underset{(1 \text{ bar}, 373 \text{ K})}{H_2O(g)}$

At 100°C $H_2O(l)$ has equilibrium with $H_2O(g)$, therefore $\Delta G = 0$.

Because liquid molecules are converting into gas molecules, therefore $\Delta S = +\text{ve}$.

20. b. The species in its elemental form has zero standard molar enthalpy of formation at 298 K. At 298 K, Cl_2 is gas while Br_2 is liquid.

21. d.

i. $2C(s) + H_2(g) \rightarrow H - C \equiv C - H(g)$ $\Delta H = 225 \text{ kJ mol}^{-1}$

ii. $2C(s) \rightarrow 2C(g)$ $\Delta H = 1410 \text{ kJ mol}^{-1}$

iii. $H_2(s) \rightarrow 2H(g)$ $\Delta H = 330 \text{ kJ mol}^{-1}$

From equation (i):

$225 = [2 \times \Delta H_{C(s) \rightarrow C(g)} + 1 \times BE_{H-H}] - [2 \times BE_{C-H} + 1 \times BE_{C \equiv C}]$

$225 = [1410 + 1 \times 330] - [2 \times 350 + 1 \times BE_{C=C}]$

$225 = [1410 + 330] - [700 + BE_{C \equiv C}]$

$225 = 1740 - 700 - BE_{C=C}$

$225 = 1040 - BE_{C \equiv C}$

$BE_{C \equiv C} - 1040 - 225 = 815 \text{ kJ mol}^{-1}$

22. c. $C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$

$$\Delta_{f \text{ comb.} C_6H_{12}O_6} H^\circ = 6\Delta_f H^\circ_{CO_2} + 6\Delta_f H^\circ_{H_2O(l)} - \Delta_f H^\circ_{C_6H_{12}O_6(s)}$$

$$= 6 \times (-400) + 6 \times (-300) - (-1300)$$

$$= -2900 \text{ kJ/mol}$$

$\therefore$ Standard enthalpy of combustion per gram of glucose

$$= \frac{-2900}{180} = -16.11 \text{ kJ}$$

23. b. Given conditions are boiling conditions for water due to which

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

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

$$\Delta S_{system} = -\Delta S_{surroundings}$$

For process, $\Delta S_{system} > 0$

$$\Delta S_{surroundings} < 0$$

Multiple Correct Answers Type

1. b., d.
Properties independent of mass are intensive properties. Hence (b) and (d) which are independent of mass are the obvious choices.

2. b., c., d.
All combustion reactions are exothermic in nature.

3. a.
Work is not a state function, but it is a path function.

4. a., d.
Internal energy and molar enthalpy are state functions. Work (reversible or irreversible) is a path function.

5. a., b.
Mass independent properties (molar conductivity and electromotive force) are intensive properties. Resistance and heat capacity are mass dependent, hence extensive properties.

6. a., c.
$\Delta S_{x\to z} = \Delta S_{x\to y} + \Delta S_{y\to z}$ [Entropy is a state function, hence additive]
$W_{x\to y\to z} = W_{x\to y}$ [Work done in y→z, zero because it is an isochoric process].

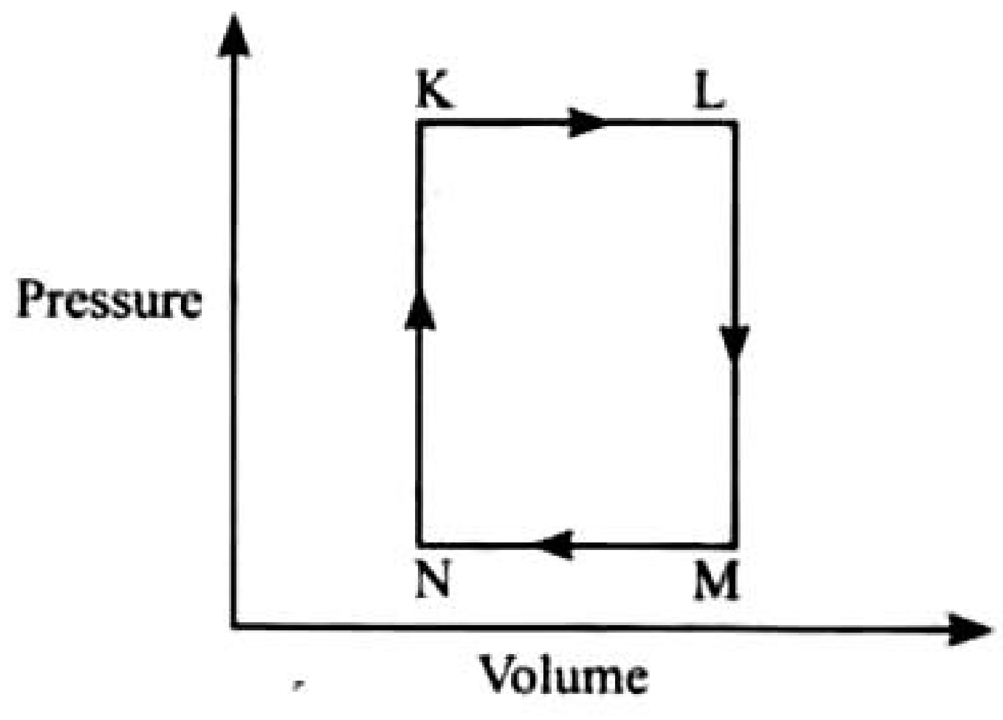
7. a., c., d.
a. $T_1 = T_2$ because process is isothermal.
c. Work done in adiabatic process is less than in isothermal process because area covered by isothermal curve is more than the area covered by the adiabatic curve.
d. In adiabatic process expansion occurs by using internal energy, hence, it decreases while in isothermal process temperature remains constant that's why no change in internal energy.

8. b., c., d.
For ideal solution, $\Delta S_{\text{system}} > 0 \quad \Delta S_{\text{surrounding}} = 0 \quad \Delta H_{\text{mixing}} = 0$

9. a., b., c.
Work against zero external pressure is zero $q = 0$ as it is free expansion so $w = 0$
$\Rightarrow \quad \Delta U = 0 \quad \text{so } \Delta T = 0$
$\Rightarrow \quad T_2 = T_1 \quad \text{so } P_1V_1 = P_2V_2$

Linked Comprehension Type

1. c.



$K \to L \Rightarrow V$ increases at constant P
Hence T increases (Heating) i.e., isobaric process
$L \to M \Rightarrow P$ decreases at constant V
Hence T decreases (Cooling) i.e., isochoric process
$M \to N \Rightarrow V$ decreases at constant P
Hence T decreases (Cooling) i.e., isobaric process
$N \to K \Rightarrow P$ increases at constant V
Hence T increases (Heating) i.e., isochoric process

2. b. L to M and N to K, both are having constant volume therefore these processes are isochoric.

Matching Columns Type

1. (a) → p, r, s; (b) → r, s; (c) → t; (d) → p, q, t

a. $CO_2(s) \to CO_2(g)$
It is phase transition. The process is endothermic (sublimation). Gas is produced, so entropy increases.

b. On heating $CaCO_3$ decomposes. So, process is endothermic. The entropy increases as gaseous product is formed.

c. $2H \to H_2(g)$
Entropy decreases as number of gaseous particles decreases.

d. It is phase transition.
White and red P are allotropes.
Red P is more stable than white.
So ΔS is –ve. So red P has less randomness.

2. (a) → r, t; (b) → p, q, s; (c) → p, q, s; (d) → p, q, s, t

(a) → r, t

$$H_2O(l) \rightleftharpoons H_2O(s)$$

It is at equilibrium at 273 K and 1 atm
So ΔS_{sys} is negative
As it is an equilibrium process, so $\Delta G = 0$.

(b) → p, q, s
Expansion of 1 mole of an ideal gas in vacuum under isolated condition:
Hence, $w = 0$
and $\quad q_p = C_p dT \qquad (\because dT = 0)$
$\Rightarrow \quad q = 0$
$\quad \Delta U = C_v dT \qquad (\because dT = 0)$
$\quad \Delta U = 0$

(c → p, q, s)
Mixing of two ideal gases at constant temperature:
Hence, $\Delta T = 0$
$\therefore \quad q = 0$
$\quad \Delta U = 0$
also $\quad w = 0 \qquad (\Delta U = q + w)$

(d → p, q, s, t)
Reversible heating and cooling of gas follows same path also the initial and final position is same.

$$\text{Hence} \quad \left.\begin{matrix} q = 0 \\ w = 0 \end{matrix}\right\} \text{Path same}$$

$$\left.\begin{matrix} \Delta U = 0 \\ \Delta G = 0 \end{matrix}\right\} \text{State function}$$

Integer Answers Type

1. (9) Energy released by combustion of 3.5 g gas = 2.5 × (298:45 – 298) kJ
$= 2.5 \times 0.45$ kJ

$$\text{Energy released by 1 mole of gas} = \frac{2.5 \times 0.45}{3.5/28} = 9 \text{ kJ/mol}^{-1}$$

2. (2)

w_d = work done along dotted line $\Sigma P\Delta V$

$$= 4 \times 1.5 + 1 \times 1 + 2.5 \times \frac{2}{3} = 8.65 \text{ L atm}$$

w_s = It is reversible isothermal process

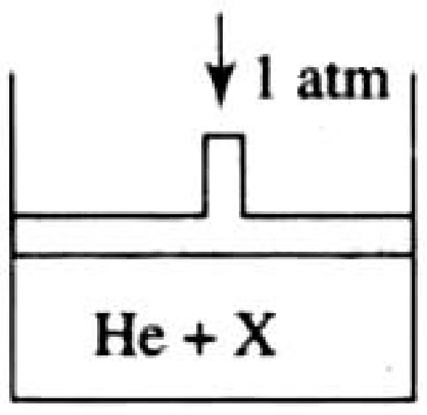
$$= 2.303\, nRT \log\left(\frac{V_2}{V_1}\right)$$

$$= 2.303 \times (PV)\log\left(\frac{V_2}{V_1}\right)$$

$$= 2.303 \times 2 \log\frac{5.5}{0.5} = 4.79 \text{ L atm}$$

$$\frac{w_d}{w_s} = \frac{8.65}{4.79} \approx 2$$

3. (7)



For He, $n = 0.1$, $P = 0.32$ atm., $V = ?$, $T = 273$

For any ideal gas, $PV = nRT$

$$0.32 \times V = 0.1 \times 0.0821 \times 273$$

$V = 7$ litre

(unknown compound X will not follow ideal gas equation)

Assertion-Reasoning Type

1. c. $q = \Delta U - W$. For isothermal expansion $\Delta U = 0$. Also $W = 0$, because $W = P \times \Delta V$ and $P = 0$. Also volume occupied by molecules is not zero for ideal gas as it does not exist in gaseous state at 0 k.

2. a. Assertion is true because it is not possible to convert whole of heat to work. For such a conversion we need an efficiency of 100% but so far we have not been able to get such a machine (Carnot engine).

Reason is true because it is not possible to convert the whole of heat absorbed from a reservoir into work. Some of the heat is always given to the sink.

Also reason is correct explanation for assertion. Thus the correct choice is option (a).

Fill in the Blanks Type

1. isolated
2. endothermic
3. extensive (because its value does not depend on quantity of substance)

True / False Type

1. **True:**

   It only tells that if a process occurs the heat gained by one end would be exactly equal to heat lost by the other. It does not predict the direction.

2. **False:**

   $\frac{C_p}{C_v}$ for monoatomic gas = 1.66

   $\frac{C_p}{C_v}$ for diatomic gas = 1.40

Subjective Type

1. Required equation is

$H(g) + O(g) \rightarrow O-H(g)$; $\Delta H = ?$

Given: $\frac{1}{2}H_2(g) + \frac{1}{2}O_2(g) \rightarrow OH(g)$; $\Delta H = +10.06$ kcal

$H(g) \rightarrow \frac{1}{2}H_2(g)$; $\Delta H = -52.09$ kcal

$O(g) \rightarrow \frac{1}{2}O_2(g)$; $\Delta H = -59.16$ kcal

Adding, $H(g) + O(g) \rightarrow OH(g)$; $\Delta H = -101.19$ kcal

2. Writing the given chemical reaction,

$CCl_4(g) + 2H_2O(g) \rightarrow CO_2(g) + 4HCl(g)$; $\Delta H^\circ_{298\,K} = ?$

$\Delta H^\circ_{298\,K} = \Sigma$ Heat of formation of products $-\Sigma$ Heat of formation of reactants

$$= [\Delta H_{f(CO_2)} + 4\Delta H_{f(HCl)}] - [\Delta H_{f(CCl_4)} + 2\Delta H_{f(H_2O)}]$$

$$= [-94.1 + 4 \times (-22.1)] - [-25.5 + 2 \times (-57.8)] = -41.4 \text{ kcal}$$

3. The required equation is:

$2C(s) + H_2(g) \rightarrow C_2H_2$; $\Delta H = ?$

Writing the thermochemical equations for the given data

i. $C_2H_2(g) + \frac{5}{2}O_2(g) \rightarrow 2CO_2(g) + H_2O(l)$; $\Delta H = -310.62$ kcal

ii. $C(s) + O_2(g) \rightarrow CO_2(g)$; $\Delta H = -94.05$ kcal

iii. $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$; $\Delta H = -68.32$ kcal

For getting the above required reaction, we will have to

a. Bring C_2H_2 in the product that can be done by reversing the equation (i) to give equation (iv).

b. Multiply equation (ii) by 2 to get 2C atoms in the reactants and thus equation (v) is obtained.

c. Keep equation (iii) as such.

d. Add equations (iv), (v) and (iii).

iv. $2CO_2 + H_2O \rightarrow C_2H_2 + \frac{5}{2}O_2$; $\Delta H = 310.62$ kcal

v. $2C + 2O_2 \rightarrow 2CO_2$; $\Delta H = -188.10$ kcal

vi. $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$; $\Delta H = -68.32$ kcal

On adding, $2C + H_2 \rightarrow C_2H_2$; $\Delta H = 54.20$ kcal

Hence the standard heat of formation of $C_2H_2(g) = 54.20$ kcal

4. If heat is absorbed at constant pressure, then

$q_p = \Delta E - (-P\Delta V)$

or $q_p = E_2 - E_1 - [-P(V_2 - V_1)]$

or $q_p = (E_2 + PV_2) - (E_1 + PV_1) = H_2 - H_1 = \Delta H$

5. The required equation is

$C_2H_2(g) + H_2(g) \rightarrow C_2H_4(g)$; $\Delta H = ?$

Given,

a. $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$; $\Delta H = -68.3$ kcal (i)

b. $C_2H_2(g) + \frac{5}{2}O_2(g) \rightarrow H_2O(l) + 2CO_2(g)$; $\Delta H = -310.6$ kcal (ii)

c. $C_2H_4(g) + 3O_2 \rightarrow 2H_2O(l) + 2CO_2(g)$; $\Delta H = -337.2$ kcal (iii)

The required equation can be achieved by adding Eqs. (i) and (ii) and subtracting (iii)

$$C_2H_2(g) + H_2(g) + 3O_2(g) - C_2H_4(g) - 3O_2(g)$$
$$\rightarrow 2CO_2 + 2H_2O(l) - 2CO_2(g) - 2H_2O(l)$$

or $$C_2H_2(g) + H_2(g) \rightarrow C_2H_4(g)$$
$$\Delta H = -68.3 - 310.6 - (-337.2)$$
$$= -378.9 + 337.2 = -41.7 \text{ kcal}$$

We know that,
$$\Delta H = \Delta U + \Delta nR$$
or $$\Delta U = \Delta H - \Delta nRT$$
$$\Delta n = (1-2) = -1,\ R = 2 \times 10^{-3} \text{ kcal mol}^{-1}\text{ K}^{-1}$$
and $$T = (25 + 273) = 298 \text{ K}$$

Substituting the values in above equation,
$$\Delta U = -41.7 - (-1)(2 \times 10^{-3})(298)$$
$$= -41.7 + 0.596 = -41.104 \text{ kcal}$$

6. The required equation is

$$\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \rightarrow HCl(g);\quad \Delta H = ?$$
$$\Delta H = \left[\frac{1}{2}\Delta H_{H-H} + \frac{1}{2}\Delta H_{Cl-Cl}\right] - [\Delta H_{H-Cl}]$$
$$= \frac{1}{2} \times 104 + \frac{1}{2} \times 58 - 103 = -22 \text{ kcal mol}^{-1}$$

7. The required chemical equation for combustion of ethane is

$$2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(l);\ \Delta H^\circ = ?$$

The equation involves 2 moles of C_2H_6; heat of combustion of ethane will be $= \frac{\Delta H^\circ}{2}$

The thermochemical equations for the given data are written as below.

i. $C(s) + O_2(g) \rightarrow CO_2(g);\quad \Delta H^\circ_f = -94.1$ kcal

ii. $H_2(g) + ½\, O_2(g) \rightarrow H_2O(g);\quad \Delta H^\circ_f = -68.3$ kcal

iii. $2C(s) + 3H_2(g) \rightarrow C_2H_6(g);\quad \Delta H^\circ_f = -21.1$ kcal

We know that

$$\Delta H^\circ = \Delta H^\circ_{f\,(\text{products})} - \Delta H^\circ_{f\,(\text{reactants})}$$
$$= [4 \times \Delta H^\circ_{f\,(CO_2)} + 6\Delta H^\circ_{f\,(H_2O)}]$$
$$- [2\Delta H^\circ_{f\,(C_2H_6)} + 7\Delta H^\circ_{f\,(O_2)}]$$
$$= [4 \times (-94.1) + 6 \times (-68.3)]$$
$$- [2 \times (-21.1) + 7 \times 0]$$
$$= -376.4 - 409.8 + 42.2 = -744.0 \text{ kcal}$$

$$\frac{\Delta H^\circ}{2} = \text{Heat of combustion of ethane} = -\frac{744.0}{2} = -372.0 \text{ kcal}$$

8.
$$\underset{2\times 56+48=160}{Fe_2O_3} + \underset{2\times 27=54}{2Al} \rightarrow 2Fe + Al_2O_3$$

Heat of reaction = 399 – 199 = 200 kcal [Al and Fe are in their standard states]

Total weight of reactants = 160 + 54 = 214 g

$$\therefore \text{ Fuel value/gram} = \frac{200}{214} = 0.9346 \text{ kcal/g}$$

$$\text{Volume of Al} = \frac{54}{2.7} = 20 \text{ cc}$$

$$\text{Volume of } Fe_2O_3 = \frac{160}{5.2} = 30.77 \text{ cc}$$

Total volume = 20 + 30.77 = 50.77 cc

$$\therefore \text{ Fuel value per cc} = \frac{200}{50.77} = 3.94 \text{ kcal/cc}$$

9. 100 g of glucose = 1560 kJ

$$\text{Energy utilized in body} = \frac{50}{100} \times 1560 = 780 \text{ kJ}$$

Energy left unutilized in body = 1560 – 780 = 780 kJ

Energy to be given out = 1560 – 780 = 780 kJ

Enthalpy of evaporation of water = 44 kJ/mole = 44 kJ/18g of water [1 mole H_2O = 18 g water]

Hence amount water to be perspired to avoid storage of energy

$$= \frac{18}{44} \times 780 = 319.1 \text{ g}$$

10. The required reaction is

$$\underset{\text{Cyclohexene}}{C_6H_{10}(g)} + H_2(g) \rightarrow \underset{\text{Cyclohexane}}{C_6H_{12},(g)},\ \Delta H_1 = ? \qquad (1)$$

The given facts can be written as:

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O,\ \Delta H_2 = -241 \text{ kJ/mol} \qquad (2)$$

$$C_6H_{10}(g) + \frac{17}{2}O_2 \rightarrow 6CO_2,(g) + 5H_2O;\ \Delta H_3 = -3800 \text{ kJ/mol} \qquad (3)$$

$$C_6H_{12}(g) + 9O_2(g) \rightarrow 6CO_2(g) + 6H_2O,\ \Delta H_4 = -3920 \text{ kJ/mol} \qquad (4)$$

The required reaction (1) can be obtained by adding equations (2) and (3) and subtracting (4) from the sum of (2) and (3).

$$C_6H_{10}(g) + H_2(g) \rightarrow C_6H_{12}(g)$$
$$\Delta H_1 = [\Delta H_2 + \Delta H_3] - (\Delta H_4)$$
$$= [-241 + (-3800)] - (-3920)$$
$$= (-241 - 3800) - (-3920)$$
$$= -4041 + 3920 = -121 \text{ kJ/mole}$$

11. $C_2H_6(g) + \frac{7}{2}O_2 \rightarrow 2CO_2(g) + 3H_2O(l);\quad \Delta H = -372.0$

$$\Delta H^\circ_{f(C_2H_6)} = 2 \times (-94.0) + 3 \times (-68.0) + 372.0 = -20 \text{ kcal}$$

$C_3H_8(g) + 5O_2 \rightarrow 3CO_2(g) + 4H_2O(l);\quad \Delta H = -530.0$

$$\Delta H^\circ_{f\,(C_3H_8)} = 2 \times (-94.0) + 4 \times (-68.0) + 530.0 = -24 \text{ kcal}$$

$$2C(s) + 3H_2(g) \rightarrow C_2H_6(g);\qquad \Delta H = -20.0$$
$$2C(g) \rightarrow 2C(s);\qquad \Delta H = -344.0$$
$$6H(g) \rightarrow 3H_2(s);\qquad \Delta H = -312.0$$

Adding $2C(g) + 6H(g) \rightarrow C_2H_6(g);\qquad \Delta H = -676.0$ kcal

So, enthalpy of formation of 6C – H bonds and one C – C bond is – 676.0 kcal.

$$3C(s) + 4H_2(g) \rightarrow C_3H_8(g);\qquad \Delta H = -24.0$$
$$3C(g) \rightarrow 3C(s);\qquad \Delta H = -516.0$$
$$8H(g) \rightarrow 4H_2(g);\qquad \Delta H = -416.0$$

Adding $3C(g) + 8H(g) \rightarrow C_3H_8(g);\qquad \Delta H = -956.0$ kcal

So, enthalpy of formation of 8C – H and 2C – C bonds is –956 kcal.

Let the bond energy of C – C be x and of C – H be y kcal.

In ethane $x + 6y = 676$

In propane $2x + 8y = 956$

On solving, $x = 82$ and $y = 99$

Thus, bond energy of C – C = 82 kcal and

bond energy of C – H = 99 kcal.

12. $\underset{\text{a litre}}{C_2H_4} + 3O_2 \rightarrow \underset{\text{2a litre}}{2CO_2} + 2H_2O$

$\underset{\text{(3.67-a) litre}}{CH_4} + 2O_2 \rightarrow \underset{\text{(3.67-a) litre}}{CO_2} + 2H_2O$

Given, $2a + 3.67 - a = 6.11$

$a = 2.44$ litre

Volume of ethylene in mixture = 2.44 litre

Volume of methane in mixture = 1.23 litre

Volume of ethylene in 1 litre mixture $= \dfrac{2.44}{3.67} = 0.6649$ litre

Volume of methane in 1 litre mixture $= \dfrac{1.23}{3.67} = 0.3351$ litre

Now we know that volume of 1 mol. of any gas at 25°C (298 K)

$= \dfrac{22.4 \times 298}{273} = 24.45\ l$

[∵ Volume at NTP = 22.4 L]

Thus, heat evolved by burning 0.6649 litre of ethylene $= -\dfrac{1423}{24.5} \times 0.6649 = -38.69$ kJ

and heat evolved by burning 0.3351 litre of methane $= -\dfrac{891}{24.45} \times 0.3351 = -12.21$ kJ

So, total heat evolved by burning 1 litre of mixture = –38.69 – 12.21 = –50.90 kJ.

13. From the given data, we can write:

i. $H_2 + \frac{1}{2}O_2 \rightarrow H_2O;$ $\Delta H_1 = -285.8$ kJ/mol

ii. $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O;$ $\Delta H_2 = -890$ kJ/mol

iii. $C_2H_6 + \frac{7}{2}O_2 \rightarrow 2CO_2 + 3H_2O;$ $\Delta H_3 = -1560$ kJ/mol

iv. $C(s) + O_2 \rightarrow CO_2;$ $\Delta H_4 = -393.5$ kJ/mol

v. $3C(s) + 4H_2 \rightarrow C_3H_8(g);$ $\Delta H_5 = -103.8$ kJ/mol

The required reaction is $C_3H_8(g) + H_2(g) \rightarrow C_2H_6(g) + CH_4(g)$, $\Delta H = ?$

It can be obtained by the following calculations.

$3 \times (iv) - (v) + 5(i) - (iii) - (ii)$

In other words, $\Delta H = 3\Delta H_4 - \Delta H_5 + 5\Delta H_1 - \Delta H_2 - \Delta H_3$

$\therefore \Delta H = 3(-393.5) - (-103.8) + 5(-285.8) + 890 + 1560$

$= -2609.5 + 2553.8 = -55.7$ kJ/mol

14. Suppose x litre of CH_4 contains n-moles of CH_4 so heat liberated from n-moles of CH_4 = 809 n-kJ.

Number of moles of C_4H_{10} required for liberation of the same amount of heat $= \dfrac{809\,n}{2878}$

Hence, the volume of n-moles of C_4H_{10} will be the same as that of CH_4 i.e., x litre

Therefore, volume of $\dfrac{809\,n}{2878}$ moles of $C_4H_{10} = \dfrac{x}{n} \times \dfrac{809\,n}{2878}$

$= 0.281\ (x)$ L

Thus, butane should be supplied at the rate of $0.281 \times L/h$.

Combustion of C_4H_{10} is represented as follows:

$$C_4H_{10}(g) + \frac{13}{2}O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l)$$

$\therefore$ Rate of supply of oxygen $= 3 \times \dfrac{13}{2} \times 0.281\ (x)\ L/h$

$= 5.48\ L/h$ per 0.2811 (×) L of C_4H_{10} per hour.

15. $nCH_2 = CH_2 \rightarrow \left(CH_2 - CH_2 \right)_n$

There are equal number of C – H bonds on both sides but on reactant side there are nC = C bonds and on product side $(2n + 1)$ C – C bonds.

Enthalpy of polymerisation

$= n\Delta H_{(C=C)} - (2n + 1)\Delta H_{(C-C)}$

$= 590n - (2n + 1)(331)$

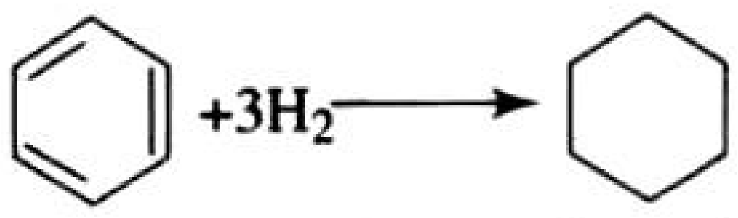
$= 590n - 662n$ [$2n + 1 \rightarrow 2n$ as n is very large]

$= -72\ n$ kJ mol^{-1}

Enthalpy of polymerisation per mole

$= \dfrac{\Delta H}{n} = \dfrac{72n}{n} = -72$ kJ mol^{-1}

16. Standard enthalpy of hydrogenation of cyclohexene (–119 kJ/mol^{-1}) means the enthalpy of hydrogenation of one C = C double bond. Now benzene has three C = C double bonds, the enthalpy of the reaction would be $= 3 \times -119 = -357$ kJ/mol^{-1}



Actual enthalpy of the reaction can be evaluated as follows.

$\Delta H_{(\text{Reaction})} = \Delta H^\circ_f\,(\text{Product}) - \Delta H^\circ_f\,(\text{Reactants})$

$= -156 - (49 + 0)$

$= -205$ kJ mol^{-1}

$\therefore$ Resonance energy $= \Delta H_{\text{Exp}} - \Delta_{\text{cal}}$

$= -357 - (-205) = -152$ kJ mol^{-1}

17. Energy available for muscular work by 1 mole of glucose $= \dfrac{2880 \times 25}{100} = 720$ kJ mol^{-1}

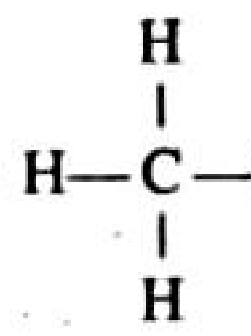
Thus 180 g of glucose (mol. wt. of glucose) supplies 720 kJ

120 g of glucose will supply $= \dfrac{720}{180} \times 120 = 480$ kJ

100 kJ is needed to walk 1 km

Hence, 480 kJ is needed to walk $\dfrac{1}{100} \times 480 = 4.8$ km

18. The required thermochemical equation is



$C(g) + 4H(g) + O(g) \rightarrow H\!-\!\underset{H}{\overset{H}{C}}\!-\!O\!-\!H;\ \Delta H_f = ?$

The given data is as follows:

i. $CH_3OH\ (l) \rightarrow CH_3OH(g),$ $\Delta H = 38$ kJ mol^{-1}

ii. $\frac{1}{2}H_2(g) \rightarrow H(g),$ $\Delta H = 218$ kJ mol^{-1}

iii. C (graphite) $\rightarrow C(g),$ $\Delta H = 715$ kJ mol^{-1}

iv. $\frac{1}{2}O_2(g) \rightarrow O(g),$ $\Delta H = 249$ kJ mol^{-1}

v. $C - H(g) \rightarrow C(g) + H(g),$ $\Delta H = 415$ kJ mol^{-1}

vi. $C - O(g) \rightarrow C(g) + O(g),$ $\Delta H = 356$ kJ mol^{-1}

vii. $O - H(g) \rightarrow O(g) + H(g),$ $\Delta H = 463$ kJ mol^{-1}.

$$\Delta H_f = \left[\Delta H_{C(s)\rightarrow C(g)} + 2\Delta H_{H-H} + \frac{1}{2}\Delta H_{O=O}\right]$$
$$-[3\Delta H_{C-H} + \Delta H_{C-O} + \Delta H_{O-H} + \Delta H_{vap.CH_3OH}]$$
$$= [715 + 2 \times 436 + 249] - [3 \times 415 + 356 + 463 + 38]$$
$$= -266 \text{ kJ mol}^{-1}$$

19. For ionization $\Delta H_{ionisation} > \Delta H_{Hydration}$

Total hydration energy of Al^{3+} and $3Cl^-$ ions of $AlCl_3$ $(\Delta H_{hydration})$

$= (\text{Hydration energy of } Al^{3+} + 3 \times \text{Hydration energy of } Cl^-)$

$= [-4665 + 3(-381)]\ kJ\ mole^{-1} = -5808\ kJ\ mole^{-1}$

This amount of energy is more than that required for the ionization of Al into Al^{3+} (Ionisation energy of Al to $Al^{3+} = 5137\ kJ\ mol^{-1}$). Due to this reason, $AlCl_3$ becomes ionic in aqueous solution. In aqueous solution it exists in ionic form as below.

$$AlCl_3 + 6H_2O \rightarrow [Al(H_2O)_6]^{3+} + 3Cl^-$$

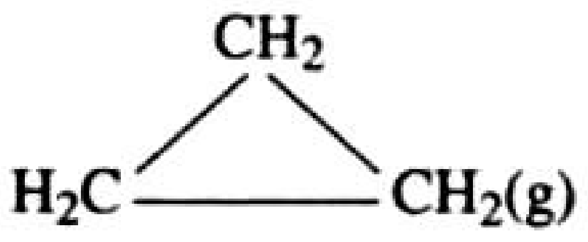
$$AlCl_3 + aq. \rightarrow AlCl_{3(aq)};\quad \Delta H = ?$$

ΔH = [Energy released during hydration –Energy used during ionization]

$$= [-4665 - 3 \times 381 + 5137] = -671\ kJ/mol$$

Thus formation of ions will take place.

20.



$\rightarrow CH_3CH = CH_2(g); \Delta H = -33.0\ kJ/mol$ (i)

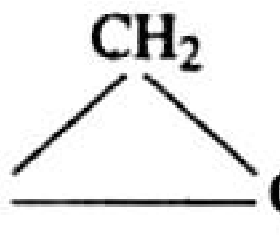
$C(s) + O_2 \rightarrow CO_2(g); \Delta H = -393.5\ kJ/mol$ (ii)

$H_2(g) + 1/2O_2(g) \rightarrow H_2O(l); \Delta H = -285.8\ kJ/mol$ (iii)

$3C(s) + 3H_2(g) \rightarrow CH_3{-}CH = CH_2(g); \Delta H = 20.42\ kJ/mol$ (iv)

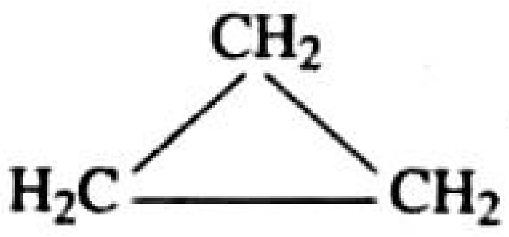
To calculate the value of ΔH follow the following steps. (iv) – (i) yields

$3C(s) + 3H_2(g) \rightarrow$



$; \Delta H = 53.42\ kJ/mol$

The required reaction is



$+ \frac{9}{2} O_2(g) \rightarrow 3CO_2(g) + 3H_2O(l); \Delta H = ?$

Hence, ΔH is calculated as follows:

On the basis of concept of standard heat of formation

$$\Delta H = [(3 \times \Delta H_f \text{ of } CO_2(g) + 3 \times \Delta H_f \text{ of } H_2O(l)] - \left(\Delta H_f \text{ of formation of cyclopropane} + \frac{9}{2} \times \Delta H_f \text{ of } O_2\right)]$$

$$= [(3 \times -393.5 + 3 \times -285.8)] - \left(53.42 + \frac{9}{2} \times 0\right)$$

(because ΔH_f of $O_2 = 0$)

$$= -2091.32\ kJ\ mol^{-1}$$

21. Given $S(s) + 3F_2(g) \rightarrow SF_6(g)\ ; \Delta H = -1100\ kJ$ (i)

$S(s) \rightarrow S(g); \Delta H = 275\ kJ$ (ii)

$1/2F_2(g) \rightarrow F(g); \Delta H = 80\ kJ$ (iii)

To get $SF_6(g) \rightarrow S(g) + 6F(g)$

We can proceed as [(ii) + 6 × (iii) – (i)]

$$= [275 + 6 \times 80 - (-1100)] = 275 + 480 + 1100 = 1855\ kJ$$

$\therefore SF_6(g) \rightarrow S(g) + 6F(g); \Delta H = 1855\ kJ/mol$

Thus average bond energy for S – F bond $= \frac{1855}{6} = 309.16\ kJ$

22. For adiabatic expansion, we have

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

and $\Delta H = nC_p\,\Delta T.$

$$\ln\frac{300}{T_2} = \frac{8.31}{12.48}\ln\frac{2.50}{1.25}$$

Solving, we get $T_2 = 188.5\ K$

No. of moles of argon gas, $n = \frac{PV}{RT} = \frac{1 \times 1.25}{0.082 \times 300} = 0.05$

Now we know that

$\Delta H = nC_p\Delta T = 0.05 \times 20.8\ (188.5 - 300) = -115.41$ Joules

$[\because C_P = C_v + R = 12.48 + 8.314 = 20.8]$

23. For the following reaction

$$CO(g) + \left(\frac{1}{2}\right)O_2(g) \rightarrow CO_2(g)$$

$\Delta G°$ can be calculated as follows:

$$\Delta G° \text{ (for reaction)} = G°_{CO_2} - G°_{CO} - \left(\frac{1}{2}\right)G°_{O_2}$$

$$= -394.4 - (-137.2) - 0$$

$$= 257.2\ kJ\ mol^{-1}$$

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

$$-257.2 = \Delta H° - 298 \times (-0.094)$$

or $\Delta H° = -285.2\ kJ/mol$

$\Delta G°$ is –ve, hence the process is spontaneous, and $\Delta H°$ is also –ve, hence the process is also exothermic.

24. The required equation

$$B_2H_6(g) + 3O_2(g) \rightarrow B_2O_3(s) + 3H_2O(g)$$

can be obtained from

Eq. (i) + 3 Eq. (ii) + 3 Eq. (iii) – Eq. (iv)

$= -1273 - 858 + 132 - 36$

$= -2035\ kJ\ mol^{-1}$

i.e., Enthalpy of combustion of diborane is $-2035\ kJ\ mol^{-1}$.

25.

$$\underset{\substack{(A)\\1.3}}{\text{Pentyne-1}} \rightleftharpoons \underset{\substack{(B)\\95.2}}{\text{Pentyne-2}} + \underset{\substack{(C)\\3.5}}{\text{1, 2-pentadiene}}$$

$$K_{eq} = \frac{[B][C]}{[A]} = \frac{95.2 \times 3.5}{1.3} = 256.31$$

$$B \rightleftharpoons A$$

$$K_1 = \frac{[A]}{[B]} = \frac{[C]}{K_{eq}} = \frac{3.5}{256.31} = 0.013$$

$$\Delta G°_1 = -2.303\,RT\log K_1$$

$$= -2.303 \times 8.314 \times 448 \log 0.013$$

$$= 16178\ J = 16.178\ kJ$$

For $B \rightleftharpoons C$

$$K_2 = \frac{[C]}{[B]} = \frac{K_{eq}[A]}{[B]^2} = \frac{256.31 \times 1.3}{(95.2)^2} = 0.037$$

$$\Delta G°_2 = -2.303\,RT\log K_2$$

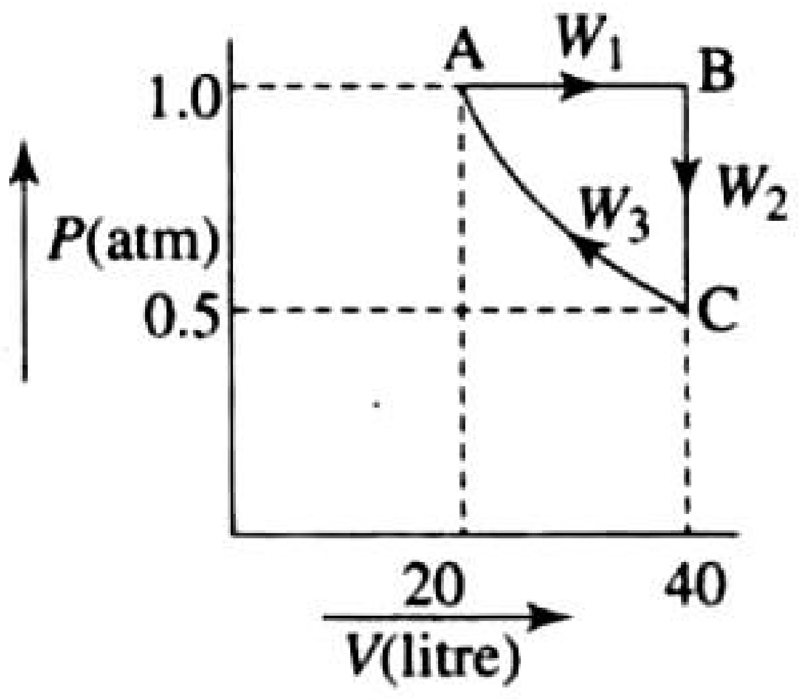
$$= -2.303 \times 8.314 \times 448 \log 0.037$$

$$= 12282\ J = 12.282\ kJ$$

Stability will lie in the order

B > C > A.

26. **i.**



AB → Isobaric process

BC → Isochoric process

CA → Isothermal compression

ii. Total work = $w_{AB} + w_{BC} + w_{CA}$

$$= -P \times \Delta V + 0 + 2.303\, nRT \log\left(\frac{V_2}{V_1}\right)$$

$$= -1 \times 20 \times 101.3 + 0 + 2.303 \times 2 \times 8.314 \times T \log\left(\frac{40}{20}\right) \quad \text{(i)}$$

$PV = nRT$ (at A)

$$1 \times 20 = 2 \times 0.0821 \times T$$

$$T = \frac{20}{2 \times 0.0821} = 121.8 \text{ K}$$

From (i),

Total work = $-2026 + 2.303 \times 2 \times 8.314 \times 121.8 \log 2$ $= -622.06$ J

$$w = q = -622.06 \text{ J}$$

iii. In cyclic process:

$$\Delta U = 0,\ \Delta H = 0 \text{ and } \Delta S = 0$$

27. Helium molecule is monoatomic so it has just three degrees of freedom corresponding to the three translational motion at all temperature and hence C_v value is always 3/2 R. Hydrogen molecules are diatomic which are not rigidly held so they vibrate about a well defined average separation. For hydrogen molecule we have rotational and vibrational motion both besides translational motion. These two additional contributions increase its total heat capacity. Contribution from vibrational motion is not appreciable at low temperature but increases from 0 to R on raising temperature.

28. For adiabatic process, $W = P(V_2 - V_1)$

Here $P_1 = 1$ bar, $P_2 = 100$ bar, $V_1 = 100$ mL, $V_2 = 99$ mL; for adiabatic process, $q = 0 \setminus \Delta U = w$

$$\Delta U = q + W$$

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

$= 0 - \{100\,(99 - 100)\} = 100$ bar mL

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + (P_2V_2 - P_1V_1)$$

$$= 100 + [100 \times 99) - (1 \times 100)]$$

$$= 100 + (9900 - 100) = 9900 \text{ bar mL}$$

29. i. The reaction is:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

Since number of moles of both N_2O_4 and NO_2 are same hence their partial pressure will also be same.

Initially $p_{N_2O_4} = p_{NO_2} = 10$

Reaction quotient $= \dfrac{[p_{NO_2}]^2}{[p_{N^2O_4}]} = \dfrac{100}{10} = 10$

$$\Delta G^\circ = 2\Delta G^\circ_{f(NO_2)} - 2\Delta G^\circ_{f(N_2O_4)} = 100 - 100 = 0$$

We know that $\Delta G = \Delta G^\circ - 2.303\, RT \log Kp$

$= 0 - 2.303 \times 8.314 \times 298 \log 10$

$= -5705$ J

ii. Since ΔG is negative hence reaction will be spontaneous in forward direction.

30. $\Delta H = \Delta U + \Delta(PV) = \Delta U + V\Delta P \qquad (\because \Delta V = 0)$

or $\quad \Delta U = \Delta H - V\Delta P = -560 - [1(40 - 70) \times 0.1]$

$= -560 + 3 = -557$ kJ mol^{-1}

So the magnitude is **557** kJ mol^{-1}

$\because \Delta G^\circ = -2.303\, RT \log K_p$ at equilibrium $\Delta G^\circ = 0$

$\therefore \quad -2.303\, RT \log K_p = 0$

$\log K_p = 0$ or $K_p = 1$