

CHAPTER

6

Thermodynamics

Section-A

JEE Advanced/ IIT-JEE

A Fill in the Blanks

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

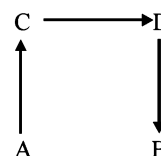
B True / False

1. First law of thermodynamics is not adequate in predicting the direction of a process. (1982 - 1 Mark)
2. Heat capacity of a diatomic gas is higher than that of a monoatomic gas. (1985 - ½ Mark)

C MCQs with One Correct Answer

1. The difference between heats of reaction at constant pressure and constant volume for the reaction :
 $2\text{C}_6\text{H}_6(l) + 15\text{O}_2(g) \rightarrow 12\text{CO}_2(g) + 6\text{H}_2\text{O}(l)$ at 25°C in kJ is (1991 - 1 Mark)
 - (a) -7.43
 - (b) +3.72
 - (c) -3.72
 - (d) +7.43
2. For which change $\Delta H \neq \Delta E$: (1995S)
 - (a) $\text{H}_{2(g)} + \text{I}_{2(g)} \rightarrow 2\text{HI}(g)$
 - (b) $\text{HCl} + \text{NaOH} \rightarrow \text{NaCl}$
 - (c) $\text{C}_{(s)} + \text{O}_{2(g)} \rightarrow \text{CO}_{2(g)}$
 - (d) $\text{N}_{2(g)} + 3\text{H}_{2(g)} \rightarrow 2\text{NH}_{3(g)}$
3. The ΔH_f° for $\text{CO}_2(g)$, $\text{CO}(g)$ and $\text{H}_2\text{O}(g)$ are -393.5, -110.5 and -241.8 kJ mol⁻¹ respectively. The standard enthalpy change (in kJ) for the reaction $\text{CO}_2(g) + \text{H}_2(g) \rightarrow \text{CO}(g) + \text{H}_2\text{O}(g)$ is (2000S)
 - (a) 524.1
 - (b) 41.2
 - (c) -262.5
 - (d) -41.2
4. In thermodynamics, a process is called reversible when (2001S)
 - (a) surroundings and system change into each other.
 - (b) there is no boundary between system and surroundings.
 - (c) the surroundings are always in equilibrium with the system.
 - (d) the system changes into the surroundings spontaneously.

5. Which one of the following statements is false? (2001S)
 - (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.
6. One mole of a non-ideal gas undergoes a change of state (2.0 atm, 3.0 L, 95(K) \rightarrow (4.0 atm, 5.0 L, 245K) with a change in internal energy, $\Delta U = 30.0 \text{ L atm}$. The change in enthalpy (ΔH) of the process in L atm is (2002S)
 - (a) 40.0
 - (b) 42.3
 - (c) 44.0
 - (d) not defined, because pressure is not constant
7. Which of the reaction defines ΔH_f° ? (2003S)
 - (a) $\text{C}_{(\text{diamond})} + \text{O}_{2(g)} \rightarrow \text{CO}_{2(g)}$
 - (b) $\frac{1}{2}\text{H}_{2(g)} + \frac{1}{2}\text{F}_{2(g)} \rightarrow \text{HF}(g)$
 - (c) $\text{N}_{2(g)} + 3\text{H}_{2(g)} \rightarrow 2\text{NH}_{3(g)}$
 - (d) $\text{CO}(g) + \frac{1}{2}\text{O}_{2(g)} \rightarrow \text{CO}_{2(g)}$
8. 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 (2004S)
 - (a) 11.4 kJ
 - (b) -11.4 kJ
 - (c) 0 kJ
 - (d) 4.8 kJ
9. The enthalpy of vapourization of 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 (2004S)
 - (a) 250 K
 - (b) 400 K
 - (c) 450 K
 - (d) 600 K
10. The direct conversion of A to B is difficult, hence it is carried out by the following shown path :



Given

$\Delta S_{(A \rightarrow C)} = 50 \text{ e.u.}$, $\Delta S_{(C \rightarrow D)} = 30 \text{ e.u.}$, $\Delta S_{(B \rightarrow D)} = 20 \text{ e.u.}$, where e.u. is the entropy unit, then $\Delta S_{(A \rightarrow B)}$ is (2006 - 3M, -1)

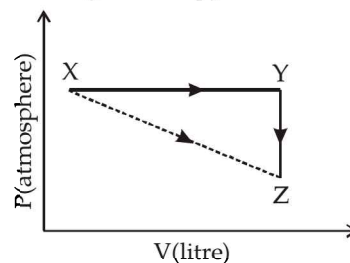
- (a) +60 e.u.
- (b) +100 e.u.
- (c) -60 e.u.
- (d) -100 e.u.

11. The value of $\log_{10} K$ for a reaction $A \rightleftharpoons B$ is
(Given : $\Delta_r H_{298K}^\circ = -54.07 \text{ kJ mol}^{-1}$, $\Delta_r S_{298K}^\circ = 10 \text{ JK}^{-1} \text{ mol}^{-1}$ and $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$; $2.303 \times 8.314 \times 298 = 5705$) (2007)
(a) 5 (b) 10
(c) 95 (d) 100
12. For the process $\text{H}_2\text{O}(l)$ (1 bar, 373 K) \rightarrow $\text{H}_2\text{O}(g)$ (1 bar, 373 K), the correct set of thermodynamic parameters is (2007)
(a) $\Delta G = 0$, $\Delta S = +ve$ (b) $\Delta G = 0$, $\Delta S = -ve$
(c) $\Delta G = +ve$, $\Delta S = 0$ (d) $\Delta G = -ve$, $\Delta S = +ve$
13. The species which by definition has **ZERO** standard molar enthalpy of formation at 298 K is (2010)
(a) $\text{Br}_2(g)$ (b) $\text{Cl}_2(g)$
(c) $\text{H}_2\text{O}(g)$ (d) $\text{CH}_4(g)$
14. The standard enthalpies of formation of $\text{CO}_2(g)$, $\text{H}_2\text{O}(l)$ and glucose(s) at 25°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 (JEE Advanced 2013-I)
(a) $+2900 \text{ kJ}$ (b) -2900 kJ
(c) -16.11 kJ (d) $+16.11 \text{ kJ}$
15. For the process $\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g)$ at $T = 100^\circ\text{C}$ and 1 atmosphere pressure, the correct choice is (JEE Adv. 2014)
(a) $\Delta S_{\text{system}} > 0$ and $\Delta S_{\text{surroundings}} > 0$
(b) $\Delta S_{\text{system}} > 0$ and $\Delta S_{\text{surroundings}} < 0$
(c) $\Delta S_{\text{system}} < 0$ and $\Delta S_{\text{surroundings}} > 0$
(d) $\Delta S_{\text{system}} < 0$ and $\Delta S_{\text{surroundings}} < 0$
16. One mole of an ideal gas at 300 K in thermal contact with surroundings expands isothermally from 1.0 L to 2.0 L against a constant pressure of 3.0 atm. In this process, the change in entropy of surroundings (ΔS_{surr}) in JK^{-1} is (1 L atm = 101.3 J) (JEE Adv. 2016)
(a) 5.763 (b) 1.013
(c) -1.013 (d) -5.763

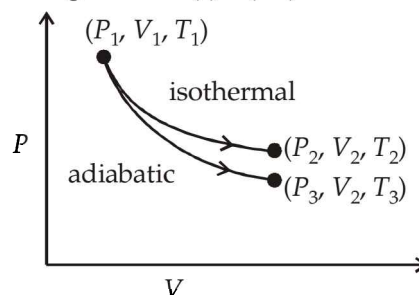
D MCQs with One or More Than One Correct

1. Identify the intensive quantities from the following: (1993 - 1 Mark)
(a) Enthalpy (b) Temperature
(c) Volume (d) Refractive Index
2. The following is (are) endothermic reaction(s): (1999 - 3 Marks)
(a) Combustion of methane
(b) Decomposition of water
(c) Dehydrogenation of ethane to ethylene
(d) Conversion of graphite to diamond
3. Among the following the state function(s) is (are) (2009)
(a) Internal energy
(b) Irreversible expansion work
(c) Reversible expansion work
(d) Molar enthalpy
4. Among the following, the intensive property is (properties are) (2010)
(a) molar conductivity (b) electromotive force
(c) resistance (d) heat capacity
5. 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?

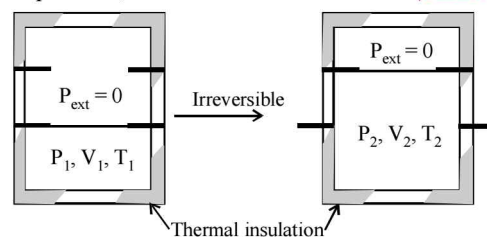
[Take ΔS as change in entropy and was work done]. (2012)



- (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) $\Delta S_{X \rightarrow Y \rightarrow Z} = \Delta S_{X \rightarrow Y}$
6. 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) $T_1 = T_2$ (2012 - II)
(b) $T_3 > T_1$
(c) $w_{\text{isothermal}} > w_{\text{adiabatic}}$
(d) $\Delta U_{\text{isothermal}} > \Delta U_{\text{adiabatic}}$
7. 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 are P_2 , V_2 and T_2 , respectively. For this expansion, (JEE Adv. 2014)



- (a) $q = 0$ (b) $T_2 = T_1$
(c) $P_2 V_2 = P_1 V_1$ (d) $P_2 V_2^\gamma = P_1 V_1^\gamma$

E Subjective Problems

1. The enthalpy for the following reaction (ΔH°) at 25°C are given below: (1981 - 2 Marks)
- (i) $\frac{1}{2} \text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{OH}(g)$ 10.06 kcal
(ii) $\text{H}_2(g) \rightarrow 2\text{H}(g)$ 104.18 kcal
(iii) $\text{O}_2(g) \rightarrow 2\text{O}(g)$ 118.32 kcal
- Calculate the O-H bond energy in the hydroxyl radical.

2. The molar heats of combustion of $C_2H_2(g)$, $C(\text{graphite})$ and $H_2(g)$ are 310.62 kcal, 94.05 kcal and 68.32 kcal, respectively. Calculate the standard heat of formation of $C_2H_2(g)$.
(1983 - 2 Marks)
3. The heat energy, q , absorbed by a gas ΔH , is true at what condition(s).
(1984 - 1 Mark)
4. 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 (25°C). (1984 - 4 Marks)
5. 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 gas. (1985 - 2 Marks)
6. 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. (1986 - 2 Marks)
7. 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 :
(1988 - 2 Marks)
 $H_f(Al_2O_3) = 399$ 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.
8. An athlete is given 100 gm 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 avoid 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.
(1989 - 2 Marks)
9. 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. (1989 - 2 Marks)
10. 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.
(1990 - 5 Marks)
- | | | |
|--|---|--------|
| $\Delta H^\circ_{\text{combustion}}(\text{ethane})$ | = | -372.0 |
| $\Delta H^\circ_{\text{combustion}}(\text{propane})$ | = | -530.0 |
| $\Delta H^\circ_{C(s) \rightarrow C(g)}$ | = | 172.0 |
| Bond energy of H-H | = | 104.0 |
| $\Delta H^\circ_f \text{ of } H_2O(l)$ | = | -68.0 |
| $\Delta H^\circ_f \text{ of } CO_2(g)$ | = | -94.0 |
11. 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.
(1991 - 5 Marks)
12. 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:
Compound $H_2(g)$ $CH_4(g)$ $C_2H_6(g)$ $C(\text{graphite})$
 ΔH° (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.
(1992 - 3 Marks)
13. 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 as 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 6x 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. (1993 - 3 Marks)
Heats of combustion :
 $CH_4 = 809$ kJ/mol; $C_4H_{10} = 2878$ kJ/mol
14. The polymerisation of ethylene to linear polyethylene is represented by the reaction
(1994 - 2 Marks)
 $nCH_2=CH_2 \longrightarrow \text{---} [CH_2-CH_2]_n \text{---}$
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 polymerisation per mole of ethylene at 298 K.
15. 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⁻¹. Use these data to estimate the magnitude of the resonance energy of benzene. (1996 - 2 Marks)
16. 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; C , 715 kJ/mol; O , 249 kJ/mol. Average bond energies :
 $C-H = 415$ kJ/mol, $C-O = 365$ kJ/mol, $O-H = 463$ kJ/mol
(1997 - 5 Marks)
17. 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.)
(1997 - 2 Marks)
18. 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.
(1998 - 5 Marks)

19. Estimate the average S-F bond energy in SF_6 . The values of standard enthalpy of formation of $\text{SF}_6(\text{g})$, $\text{S}(\text{g})$ and $\text{F}(\text{g})$ are : -1100, 275 and 80 kJ mol^{-1} respectively. (1999 - 3 Marks)
20. 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. $C_{V,m}$ for argon is $12.48 \text{ JK}^{-1} \text{ mol}^{-1}$. (2000 - 4 Marks)
21. Show that the reaction $\text{CO}(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g})$ at 300 K, is spontaneous and exothermic, when the standard entropy change is $-0.094 \text{ kJ mol}^{-1} \text{ K}^{-1}$. The standard Gibbs free energies of formation for CO_2 and CO are -394.4 and $-137.2 \text{ kJ mol}^{-1}$, respectively. (2000 - 3 Marks)
22. Diborane is a potential rocket fuel which undergoes combustion according to the reaction. (2000 - 2 Marks)
 $\text{B}_2\text{H}_6(\text{g}) + 3 \text{O}_2(\text{g}) \rightarrow \text{B}_2\text{O}_3(\text{s}) + 3\text{H}_2\text{O}(\text{g})$
 From the following data, calculate the enthalpy change for the combustion of diborane.
- $$2\text{B}(\text{s}) + \frac{3}{2} \text{O}_2(\text{g}) \longrightarrow \text{B}_2\text{O}_3(\text{s}) \quad \Delta H = -1273 \text{ kJ mol}^{-1}$$
- $$\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \longrightarrow \text{H}_2\text{O}(\ell) \quad \Delta H = -286 \text{ kJ mol}^{-1}$$
- $$\text{H}_2\text{O}(\ell) \longrightarrow \text{H}_2\text{O}(\text{g}) \quad \Delta H = 44 \text{ kJ mol}^{-1}$$
- $$2\text{B}(\text{s}) + 3\text{H}_2(\text{g}) \longrightarrow \text{B}_2\text{H}_6(\text{g}) \quad \Delta H = 36 \text{ kJ mol}^{-1}$$
23. When 1-pentyne (A) is treated with 4 N alcoholic KOH at 175°C , it is converted slowly 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 :
- $$\text{B} \rightleftharpoons \text{A} \quad \Delta G_1^\circ = ? \quad \text{B} \rightleftharpoons \text{C} \quad \Delta G_2^\circ = ?$$
- 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). (2001 - 10 Marks)
24. Two moles of a perfect gas undergo the following processes: (2002 - 5 Marks)
- a reversible isobaric expansion from (1.0 atm, 20.0 L) to (1.0 atm, 40.0 L);
 - a reversible isochoric change of state from (1.0 atm, 40.0 L) to (0.5 atm, 40.0 L);
 - a reversible isothermal compression from (0.5 atm, 40.0 L) to (1.0 atm, 20.0 L).
- Sketch with labels each of the processes on the same P-V diagram.
 - Calculate the total work (w) and the total heat change (q) involved in the above processes.
 - What will be the values of ΔU , ΔH and ΔS for the overall process?
25. 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. (2003 - 2 Marks)
26. An insulated container contains 1 mol 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. (2004 - 2 Marks)
27. In the following equilibrium $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$ (2004 - 2 Marks)
- 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 : $\Delta G_f^\circ(\text{N}_2\text{O}_4) = 100 \text{ kJ}$; $\Delta G_f^\circ(\text{NO}_2) = 50 \text{ kJ}$
- Find ΔG of the reaction at 298 K.
 - Find the direction of the reaction
28. For the reaction, $2\text{CO} + \text{O}_2 \longrightarrow 2\text{CO}_2$; $\Delta H = -560 \text{ kJ}$. Two moles of CO and one mole of O_2 are taken in a container of volume 1 L. 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. (1 L atm = 0.1 kJ) (2006 - 6M)

F Match The Following

DIRECTION (Q. 1 & 2): Each question contains statements given in two columns, which have to be matched. The statements in Column-I are labelled A, B, C and D, while the statements in Column-II are labelled p, q, r, s and t. Any given statement in Column-I can have correct matching with ONE OR MORE statement(s) in Column-II. The appropriate bubbles corresponding to the answers to these questions have to be darkened as illustrated in the following example :

If the correct matches are A-p, s and t; B-q and r; C-p and q; and D-s then the correct darkening of bubbles will look like the given.

	p	q	r	s	t
A	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>
B	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
C	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
D	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>

1. Match the transformations in column I with appropriate options in column II (2011)

Column-I

- $\text{CO}_2(\text{s}) \rightarrow \text{CO}_2(\text{g})$
- $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
- $2\text{H}^\bullet \rightarrow \text{H}_2(\text{g})$
- $\text{P}_{(\text{white, solid})} \rightarrow \text{P}_{(\text{red, solid})}$

Column-II

- phase transition
- allotropic change
- ΔH is positive
- ΔS is positive
- ΔS is negative

2. Match the thermodynamic processes given under Column-I with the expressions given under Column-II. (JEE Adv. 2015)

Column-I

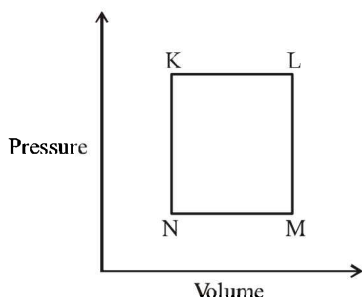
- (A) Freezing of water at 273 K and 1 atm
 (B) Expansion of 1 mol of an ideal gas into a vacuum under isolated conditions
 (C) Mixing of equal volumes of two ideal gases at constant temperature and pressure in an isolated container
 (D) Reversible heating of $\text{H}_2(\text{g})$ at 1 atm from 300 K to 600 K, followed by reversible cooling to 300 K at 1 atm

Column-II

- (p) $q=0$
 (q) $w=0$
 (r) $\Delta S_{\text{sys}} < 0$
 (s) $\Delta U=0$
 (t) $\Delta G=0$

G Comprehension Based Questions

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



(JEE Adv. 2013)

- The succeeding operations that enable this transformation of states are
 - Heating, cooling, heating, cooling
 - Cooling, heating, cooling, heating
 - Heating, cooling, cooling, heating
 - Cooling, heating, heating, cooling
- The pair of isochoric processes among the transformation of states is
 - K to L and L to M
 - L to M and N to K
 - L to M and M to N
 - M to N and N to K

H Assertion & Reason Type Questions

1. Read the following statement and explanation and answer as per the options given below :

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. (2000S)

- If both assertion and reason are CORRECT, and reason is the CORRECT explanation of the assertion.
- If both assertion and reason are CORRECT, but reason is NOT the CORRECT explanation of the assertion.

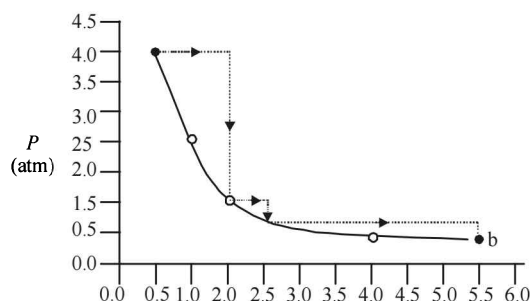
- If assertion is CORRECT, but reason is INCORRECT.
- If assertion is INCORRECT, but reason is CORRECT.

Statement - 1 : There is a natural asymmetry between converting work to heat and converting heat to work. and
Statement - 2 : No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work. (2008S)

- Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
- Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1
- Statement-1 is True, Statement-2 is False
- Statement-1 is False, Statement-2 is True

I Integer Value Correct Type

- 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^{-1} , the numerical value for the enthalpy of combustion of the gas in kJ mol^{-1} is (2009 - 6M)
- 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 graphs 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 : (2010)



Section-B

JEE Main / AIEEE

- If an endothermic reaction is non-spontaneous at freezing point of water and becomes feasible at its boiling point, then
 (a) ΔH is -ve, ΔS is +ve [2002]
 (b) ΔH and ΔS both are +ve
 (c) ΔH and ΔS both are -ve
 (d) ΔH is +ve, ΔS is -ve
- A heat engine absorbs heat Q_1 at temperature T_1 and heat Q_2 at temperature T_2 . Work done by the engine is $J(Q_1 + Q_2)$. This data [2002]
 (a) violates 1st law of thermodynamics
 (b) violates 1st law of thermodynamics if Q_1 is -ve
 (c) violates 1st law of thermodynamics if Q_2 is -ve
 (d) does not violate 1st law of thermodynamics.
- For the reactions, [2002]
 $2C + O_2 \rightarrow 2CO_2$; $\Delta H = -393 \text{ J}$
 $2Zn + O_2 \rightarrow 2ZnO$; $\Delta H = -412 \text{ J}$
 (a) carbon can oxidise Zn
 (b) oxidation of carbon is not feasible
 (c) oxidation of Zn is not feasible
 (d) Zn can oxidise carbon.
- The heat required to raise the temperature of body by 1 K is called [2002]
 (a) specific heat (b) thermal capacity
 (c) water equivalent (d) none of these.
- The internal energy change when a system goes from state A to B is 40 kJ/mole. If the system goes from A to B by a reversible path and returns to state A by an irreversible path what would be the net change in internal energy? [2003]
 (a) > 40 kJ (b) < 40 kJ
 (c) Zero (d) 40 kJ
- If at 298 K the bond energies of C—H, C—C, C=C and H—H bonds are respectively 414, 347, 615 and 435 kJ mol⁻¹, the value of enthalpy change for the reaction
 $H_2C = CH_2(g) + H_2(g) \rightarrow H_3C - CH_3(g)$ at 298 K will be [2003]
 (a) -250 kJ (b) +125 kJ
 (c) -125 kJ (d) +250 kJ
- In an irreversible process taking place at constant T and P and in which only pressure-volume work is being done, the change in Gibbs free energy (dG) and change in entropy (dS), satisfy the criteria [2003]
 (a) $(dS)_{V,E} > 0, (dG)_{T,P} < 0$ (b) $(dS)_{V,E} = 0, (dG)_{T,P} = 0$
 (c) $(dS)_{V,E} = 0, (dG)_{T,P} > 0$ (d) $(dS)_{V,E} < 0, (dG)_{T,P} < 0$
- The correct relationship between free energy change in a reaction and the corresponding equilibrium constant K_c is [2003]
 (a) $-\Delta G = RT \ln K_c$ (b) $\Delta G^\circ = RT \ln K_c$
 (c) $-\Delta G^\circ = RT \ln K_c$ (d) $\Delta G = RT \ln K_c$
- The enthalpy change for a reaction does **not** depend upon [2003]
 (a) use of different reactants for the same product
 (b) the nature of intermediate reaction steps
 (c) the differences in initial or final temperatures of involved substances
 (d) the physical states of reactants and products
- An ideal gas expands in volume from 1×10^{-3} to $1 \times 10^{-2} \text{ m}^3$ at 300 K against a constant pressure of $1 \times 10^5 \text{ Nm}^{-2}$. The work done is [2004]
 (a) 270 kJ (b) -900 kJ
 (c) -900 (d) 900 kJ
- The enthalpies of combustion of carbon and carbon monoxide are -393.5 and -283 kJ mol⁻¹ respectively. The enthalpy of formation of carbon monoxide per mole is [2004]
 (a) -676.5 kJ (b) 676.5 kJ
 (c) 110.5 kJ (d) -110.5 kJ
- Consider an endothermic reaction $X \rightarrow Y$ with the activation energies E_b and E_f for the backward and forward reactions, respectively. In general [2005]
 (a) there is no definite relation between E_b and E_f
 (b) $E_b = E_f$
 (c) $E_b > E_f$
 (d) $E_b < E_f$
- Consider the reaction: $N_2 + 3H_2 \rightarrow 2NH_3$ carried out at constant temperature and pressure. If ΔH and ΔU are the enthalpy and internal energy changes for the reaction, which of the following expressions is true? [2005]
 (a) $\Delta H > \Delta U$ (b) $\Delta H < \Delta U$
 (c) $\Delta H = \Delta U$ (d) $\Delta H = 0$
- If the bond dissociation energies of XY, X_2 and Y_2 (all diatomic molecules) are in the ratio of 1 : 1 : 0.5 and ΔH_f for the formation of XY is -200 kJ mole⁻¹. The bond dissociation energy of X_2 will be [2005]
 (a) 400 kJ mol⁻¹ (b) 300 kJ mol⁻¹
 (c) 200 kJ mol⁻¹ (d) 100 kJ mol⁻¹

15. An ideal gas is allowed to expand both reversibly and irreversibly in an isolated system. If T_i is the initial temperature and T_f is the final temperature, which of the following statements is correct? [2006]
- $(T_f)_{\text{rev}} = (T_f)_{\text{irrev}}$
 - $T_f = T_i$ for both reversible and irreversible processes
 - $(T_f)_{\text{irrev}} > (T_f)_{\text{rev}}$
 - $T_f > T_i$ for reversible process but $T_f = T_i$ for irreversible process
16. The standard enthalpy of formation ($\Delta_f H^\circ$) at 298 K for methane, $\text{CH}_4(\text{g})$ is $-74.8 \text{ kJ mol}^{-1}$. The additional information required to determine the average energy for C–H bond formation would be [2006]
- the first four ionization energies of carbon and electron gain enthalpy of hydrogen
 - the dissociation energy of hydrogen molecule, H_2
 - the dissociation energy of H_2 and enthalpy of sublimation of carbon
 - latent heat of vapourization of methane
17. The enthalpy changes for the following processes are listed below: [2006]
- | | |
|---|-----------------------------|
| $\text{Cl}_2(\text{g}) \rightarrow 2\text{Cl}(\text{g})$, | $242.3 \text{ kJ mol}^{-1}$ |
| $\text{I}_2(\text{g}) \rightarrow 2\text{I}(\text{g})$, | $151.0 \text{ kJ mol}^{-1}$ |
| $\text{ICl}(\text{g}) \rightarrow \text{I}(\text{g}) + \text{Cl}(\text{g})$, | $211.3 \text{ kJ mol}^{-1}$ |
| $\text{I}_2(\text{s}) \rightarrow \text{I}_2(\text{g})$, | $62.76 \text{ kJ mol}^{-1}$ |
- Given that the standard states for iodine and chlorine are $\text{I}_2(\text{s})$ and $\text{Cl}_2(\text{g})$, the standard enthalpy of formation for $\text{ICl}(\text{g})$ is: [2006]
- $+16.8 \text{ kJ mol}^{-1}$
 - $+244.8 \text{ kJ mol}^{-1}$
 - $-14.6 \text{ kJ mol}^{-1}$
 - $-16.8 \text{ kJ mol}^{-1}$
18. $(\Delta H - \Delta U)$ for the formation of carbon monoxide (CO) from its elements at 298 K is [2006]
- $(R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1})$
- $-2477.57 \text{ J mol}^{-1}$
 - $2477.57 \text{ J mol}^{-1}$
 - $-1238.78 \text{ J mol}^{-1}$
 - $1238.78 \text{ J mol}^{-1}$
19. In conversion of lime-stone to lime,
- $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ the values of ΔH° and ΔS° are $+179.1 \text{ kJ mol}^{-1}$ and 160.2 J/K respectively at 298 K and 1 bar. Assuming that ΔH° and ΔS° do not change with temperature, temperature above which conversion of limestone to lime will be spontaneous is [2007]
- 1118 K
 - 1008 K
 - 1200 K
 - 845 K
20. Assuming that water vapour is an ideal gas, the internal energy change (ΔU) when 1 mol of water is vapourised at 1 bar pressure and 100°C , (given : molar enthalpy of vapourisation of water at 1 bar and $373 \text{ K} = 41 \text{ kJ mol}^{-1}$ and $R = 8.3 \text{ J mol}^{-1} \text{ K}^{-1}$) will be [2007]
- $41.00 \text{ kJ mol}^{-1}$
 - $4.100 \text{ kJ mol}^{-1}$
 - $3.7904 \text{ kJ mol}^{-1}$
 - $37.904 \text{ kJ mol}^{-1}$
21. Identify the correct statement regarding a spontaneous process: [2007]
- Lowering of energy in the process is the only criterion for spontaneity.
 - For a spontaneous process in an isolated system, the change in entropy is positive.
 - Endothermic processes are never spontaneous.
 - Exothermic processes are always spontaneous.
22. Oxidising power of chlorine in aqueous solution can be determined by the parameters indicated below:
- $$\frac{1}{2}\text{Cl}_2(\text{g}) \xrightarrow{\frac{1}{2}\Delta_{\text{diss}}H^\circ} \text{Cl}(\text{g}) \xrightarrow{\Delta_{\text{eg}}H^\circ} \text{Cl}^-(\text{g})$$
- $$\xrightarrow{\Delta_{\text{hyd}}H^\circ} \text{Cl}^-(\text{aq})$$
- (using the data,
- $\Delta_{\text{diss}}H_{\text{Cl}_2}^\circ = 240 \text{ kJ mol}^{-1}$, $\Delta_{\text{eg}}H_{\text{Cl}}^\circ = -349 \text{ kJ mol}^{-1}$,
- $\Delta_{\text{hyd}}H_{\text{Cl}^-}^\circ = -381 \text{ kJ mol}^{-1}$), will be [2008]
- $+152 \text{ kJ mol}^{-1}$
 - -610 kJ mol^{-1}
 - -850 kJ mol^{-1}
 - $+120 \text{ kJ mol}^{-1}$
23. Standard entropy of X_2 , Y_2 and XY_3 are 60, 40 and $50 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively. For the reaction,
- $$\frac{1}{2}\text{X}_2 + \frac{3}{2}\text{Y}_2 \rightarrow \text{XY}_3, \Delta H = -30 \text{ kJ}$$
- to be at equilibrium, the temperature will be [2008]
- 1250 K
 - 500 K
 - 750 K
 - 1000 K
24. On the basis of the following thermochemical data : [2009]
- $(\Delta_f G^\circ H_{(\text{aq})}^+ = 0)$
- $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}); \Delta H = 57.32 \text{ kJ}$
- $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \longrightarrow \text{H}_2\text{O}(\text{l}); \Delta H = -286.20 \text{ kJ}$
- The value of enthalpy of formation of OH^- ion at 25°C is:
- -228.88 kJ
 - $+228.88 \text{ kJ}$
 - -343.52 kJ
 - -22.88 kJ
25. The standard enthalpy of formation of NH_3 is $-46.0 \text{ kJ mol}^{-1}$. If the enthalpy of formation of H_2 from its atoms is -436 kJ mol^{-1} and that of N_2 is -712 kJ mol^{-1} , the average bond enthalpy of N–H bond in NH_3 is [2010]
- -964 kJ mol^{-1}
 - $+352 \text{ kJ mol}^{-1}$
 - $+1056 \text{ kJ mol}^{-1}$
 - $-1102 \text{ kJ mol}^{-1}$
26. For a particular reversible reaction at temperature T , ΔH and ΔS were found to be both +ve. If T_e is the temperature at equilibrium, the reaction would be spontaneous when [2010]
- $T_e > T$
 - $T > T_e$
 - T_e is 5 times T
 - $T = T_e$

27. The entropy change involved in the isothermal reversible expansion of 2 mole of an ideal gas from a volume of 10 dm^3 to a volume of 100 dm^3 at 27°C is: [2011]
 (a) $38.3 \text{ J mol}^{-1} \text{ K}^{-1}$ (b) $35.8 \text{ J mol}^{-1} \text{ K}^{-1}$
 (b) $32.3 \text{ J mol}^{-1} \text{ K}^{-1}$ (d) $42.3 \text{ J mol}^{-1} \text{ K}^{-1}$
28. The incorrect expression among the following is: [2012]
 (a) $\frac{\Delta G_{\text{system}}}{\Delta S_{\text{total}}} = -T$
 (b) In isothermal process, $w_{\text{reversible}} = -nRT \ln \frac{V_f}{V_i}$
 (c) $\ln K = \frac{\Delta H^\circ - T\Delta S^\circ}{RT}$ (d) $K = e^{-\Delta G^\circ/RT}$
29. A piston filled with 0.04 mol of an ideal gas expands reversibly from 50.0 mL to 375 mL at a constant temperature of 37.0°C . As it does so, it absorbs 208 J of heat. The values of q and w for the process will be: [JEE M 2013]
 ($R = 8.314 \text{ J/mol K}$) ($\ln 7.5 = 2.01$)
- (a) $q = +208 \text{ J}$, $w = -208 \text{ J}$ (b) $q = -208 \text{ J}$, $w = -208 \text{ J}$
 (c) $q = -208 \text{ J}$, $w = +208 \text{ J}$ (d) $q = +208 \text{ J}$, $w = +208 \text{ J}$
30. For complete combustion of ethanol,
 $\text{C}_2\text{H}_5\text{OH}(l) + 3\text{O}_2(g) \longrightarrow 2\text{CO}_2(g) + 3\text{H}_2\text{O}(l)$,
 the amount of heat produced as measured in bomb calorimeter, is $1364.47 \text{ kJ mol}^{-1}$ at 25°C . Assuming ideality the enthalpy of combustion, $\Delta_c H$, for the reaction will be:
 ($R = 8.314 \text{ kJ mol}^{-1}$) [JEE M 2014]
 (a) $-1366.95 \text{ kJ mol}^{-1}$ (b) $-1361.95 \text{ kJ mol}^{-1}$
 (c) $-1460.95 \text{ kJ mol}^{-1}$ (d) $-1350.50 \text{ kJ mol}^{-1}$
31. The heats of combustion of carbon and carbon monoxide are -393.5 and $-283.5 \text{ kJ mol}^{-1}$, respectively. The heat of formation (in kJ) of carbon monoxide per mole is: [JEE M 2016]
 (a) -676.5 (b) -110.5
 (c) 110.5 (d) 676.5