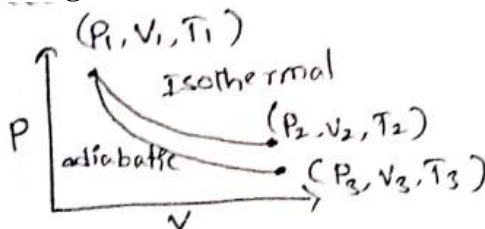


SRIGAYATRI EDUCATIONAL INSTITUTIONS

INDIA

THERMODYNAMICS UT-03

1. **What is Correct about isothermal expansion of ideal gas ?**
 1) $q_{rev} = q_{irr}$ 2) $W_{rev} > W_{irr}$ 3) $W_{rev} > W_{irr} = 0$ 4) $W_{rev} > W_{irr}$
2. **In a change from state A to State B**
 1) ΔE depends upon the path adopted by 'A' to change into "B"
 2) ΔE depends Only on the initial and final state
 3) 'w' depends only on the initial and final state
 4) 'q' depends only on the initial and final state
3. **An ideal gas expands in volume from $1 \times 10^{-3} m^3$ to $1 \times 10^{-2} m^3$ at 300 k against a constant pressure $1 \times 10^5 Nm^{-2}$. The work done is**
 1) 900 kJ 2) 270 KJ 3) -900 kJ 4) -900 J
4. **16g of oxygen of gas expands isothermally and reversibly at 300 k from $10 dm^3$ to $1000 dm^3$. The work done is (inJ)**
 1) Zero 2) -2872 J 3) +2875 J 4) Infinite
5. **based on the first law of thermodynamics which of the following is correct**
 1) For an isothermal process, $q = + w$ 2) For an isochoric process, $\Delta U = -q$
 3) For an adiabatic process, $\Delta U = -w$ 4) For a cyclic process, $q = - w$
6. **$\Delta_f U^0$ of formation of $CH_4(g)$ at certain temperature is $-393 KJmol^{-1}$. The value of $\Delta_f H$ is**
 1) Zero 2) $< \Delta_f U^0$ 3) $> \Delta_f U^0$ 4) Equal to $\Delta_f U^0$
7. **For the Gaseous reaction involving the complete combustion of isobutane :**
 1) $\Delta H = \Delta E$ 2) $\Delta H > \Delta E$ 3) $\Delta H = \Delta E = 0$ 4) $\Delta H < \Delta E$
8. **The molar enthalpy of vaporization of C_6H_6 at its boiling point (353 K) is 7.4 K cal / mol. The molar internal energy change of vaporization is :**
 1) 6.694 K Cal/ mol 2) 62.47 Kcal/mol 3) 8.106 Kcal /mol 4) 7.4 Kcal /mol
9. **The ΔH_f^0 of $CaCO_{3(s)}$, $CaO_{(s)}$ and $CO_{2(g)}$ are -1206.9 , -635.1 and $-393.5 KJ/mol$ respectively Their S^0 values are 92.9, 38.2 and 213.7 j/K respectively at 1000^0C and 1 atm. The partial pressure of CO_2 in the reaction $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$ is approximately**
 1) 1.25 atm 2) 9.75 atm 3) 0.03 atm 4) 0.98 atm
10. **An ideal gas with $C_v = 3R$ expands adiabatically into a vacuum thus doubling its volume. The final temperature is given by**
 1) $T_2 = T_1 [2^{-1/3}]$ 2) $T_2 = T_1$ 3) $T_2 = 2T_1$ 4) $T_2 = \frac{T_1}{2}$
11. **The reversible expansion of an ideal gas under adiabatic and isothermal conditions is shown in the figure which of the following statement is correct**



- 1) $T_3 > T_1$ 2) $T_1 = T_2$
- 3) $\Delta U_{isothermal} > \Delta U_{adiabatic}$ 4) $W_{isothermal} > W_{adiabatic}$

12. When the following reaction was carried out in a bomb calorimeter, ΔU is found to be -740.0 kJ/mol of $NH_2CN_{(s)}$ at 300 k $NH_2CN_{(s)} + \frac{3}{2}O_{2(g)} \rightarrow N_{2(g)} + CO_{2(g)} + H_2O(l)$ Calculate ΔH_{300k} for the reaction
- 1) -919.57 KJ 2) $+738.75$ KJ 3) -824.75 KJ 4) -738.75 kJ
13. For the reaction $2CO_{(g)} + O_{2(g)} \rightarrow 2CO_2; \Delta H = -500$ kJ Two moles of CO and one mole of O_2 are taken in a container of volume 2L. They completely form two, moles of CO_2 , the gas deviate appreciably from ideal behavior. If pressure in vessel change from 35 to 20 atm find the magnitude of ΔU at 500 k
- 1) 503 kJ 2) 400 KJ 3) 480 KJ 4) 320 KJ
14. If heat of dissociation of $CHCl_2COOH + H_2O$ is $CHCl_2COOH + KOH \rightarrow CHCl_2COOK + H_2O$ is
- 1) -13.8 kcal 2) $+13$ Kcal 3) -14.4 Kcal 4) -13 kcal
15. For the reaction : $X_2O_{4(l)} \rightarrow 2XO_{2(g)}$
 $\Delta U = 2.1$ Kcal $\Delta S = 20$ Cal k^{-1} at 300 k Hence ΔG is
- 1) 9.3 Kcal 2) 2.7 Kcal 3) -2.7 Kcal 4) -9.3 Kcal
16. Standard entropies of X_2, Y_2 and XY_3 are 60, 30 and $50 JK^{-1} mol^{-1}$ respectively For the reaction $\frac{1}{2}X_2 + \frac{3}{2}Y_2 \rightleftharpoons XY_3$, $\Delta H = -30$ KJ to be at equilibrium, the temperature should be,
- 1) 1200 k 2) 1000 k 3) 750 k 4) 500 k
17. Calculate ΔH_f^0 for chloride ion from the following data
- $\frac{1}{2}H_{2(g)} + \frac{1}{2}Cl_{2(g)} \rightarrow HCl_{(g)}; \Delta H_f^0 = -92.4$ kJ
 $HCl_{(g)} + nH_2O \rightarrow H_{aq}^+ + Cl_{(aq)}^-; \Delta H_f^0 = -74.8$ kJ
 ΔH_f^0 of $H_{(aq)}^+ = 0.0$ KJ
- 1) -167.2 KJ 2) -165.2 KJ 3) -157.2 KJ 4) -147.2 KJ
18. The incorrect expression among the following is :
- 1) ΔG system = $-T$ 2) In isothermal process, $W_{rev} = -nRT \ln \frac{V_f}{V_i}$
3) $\ln k = \frac{\Delta H^0 - T\Delta S^0}{RT}$ 4) $K = e^{-\Delta G^0 / RT}$
19. 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 $37.0^\circ C$ As it does so, it absorbs 208 J of heat. The value of q and w for the process will be : ($R = 8.314$ J/mol k) ($\ln 7.5 = 2.01$)
- 1) q = $+208$ J, w = -208 J 2) q = -208 J, w = -208 J
3) q = -208 J, w = $+208$ J 4) q = $+208$ J, w = $+208$ J
20. 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 $27^\circ C$ is
- 1) $42.3 J mol^{-1} K^{-1}$ 2) $35.8 J mol^{-1} K^{-1}$ 3) $32.3 J mol^{-1} K^{-1}$ 4) $38.3 J mol^{-1} K^{-1}$
21. A reaction is spontaneous at low temperature but non – spontaneous at high temperature Which of the following is true for the reaction
- 1) $\Delta H > 0, \Delta S > 0$ 2) $\Delta H < 0, \Delta S > 0$ 3) $\Delta H > 0, \Delta S = 0$ 4) $\Delta H < 0, \Delta S < 0$
22. The entropy values (in $jk^{-1} mol^{-1}$) of $H_{2(g)} = 130.6$ $Cl_{2(g)} = 223.0$ and $HCl_{(g)} = 186.7$ at 298 k and 1 atm pressure then entropy change for the reaction $H_{2(g)} + Cl_{2(g)} \rightarrow 2HCl_{(g)}$ is
- 1) $+540.3$ 2) $+727.3$ 3) -166.9 4) $+19.8$

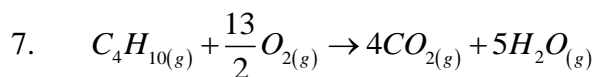
36. If butane on combustion gives carbon monoxide. Find the number of O_2 molecule required
37. The value of $\log_{10} K$ for a reaction $A \rightarrow B$ is
 (Given $\Delta H_{r298k}^0 = -54.07 \text{ Jk mol}^{-1}$
 $\Delta S_{r298k}^0 = -10 \text{ Jk}^{-1} \text{ mol}^{-1}$ and
 $R = 8.314 \text{ Jk}^{-1} \text{ mol}^{-1}$, $2.303 \times 8.314 \times 298 = 5705$
38. For the reaction, $2CO + O_2 \rightarrow 2CO_2$; $\Delta H = 560 \text{ KJ}$. 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 of ΔU in kJ 500 k (1 L.atm = 0.1 kJ)
39. The Work done by a system is 8 joule, when 40 joule heat is supplied to it, what is the increase in internal energy of system in Joules
40. What is Δn for combustion of 1 mole of benzene, when both the reactants and the products are gases at 298K.

KEYSHEET

1	2	2	2	3	4	4	2	5	2	6	2	7	2	8	1	9	2	10	2
11	1	12	4	13	1	14	4	15	3	16	1	17	1	18	3	19	1	20	4
21	4	22	4	23	4	24	2	25	4	26	2	27	3	28	2	29	1	30	3
31	4	32	3	33	1	34	5	35	8	36	3	37	10	38	563	39	32	40	0.5

SOLUTIONS

- $W_{rev} > W_{irr}$
- ΔE is a state function
- $W = -P(V_2 - V_1)$
- $W = -2.303 nRT \log \frac{V_2}{V_1}$
- $\Delta U = q + w$
 for an isothermal process, $\Delta U = 0$ $q = -w$
 For an isochoric process, $w = 0$, $\Delta U = q$
 For an adiabatic process $q = 0$, $\Delta U = w$
 For a cyclic process, $\Delta U = 0$ $q = -w$,
- The reaction is
 $CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}$
 $\Delta n_g = (n_p - n_r) = 1 - 3 = -2$
 As $\Delta_f H^0 = \Delta_f U^0 + \Delta n_g RT$
 $\Delta n_g = -2$
 $\Delta H^0 < \Delta U^0$

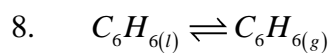


$$\Delta n_{(g)} = 9 - \left(\frac{13}{2} + 1 \right) = \frac{3}{2}$$

$$\Delta n_{(g)} = +ve$$

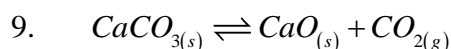
$$\Delta_f H = \Delta_f E + \Delta n_g RT$$

$$\therefore \Delta H > \Delta E$$



$$\Delta H = \Delta E + \Delta n_{(g)} RT$$

$$7.4 = \Delta E + 1 \times 2 \times 10^{-3} \times 353$$



$$K_p = P_{CO_2}^1$$

$$\Delta_f^0 H = \sum \Delta_f^0 H_p - \sum \Delta_f^0 H_R$$

$$= [(-635.1) + (-393.5)] - (-1206.9)$$

$$= 178.3 \text{ KJ / mol}$$

$$\Delta_f^0 S = \sum S_p^0 - \sum S_R^0$$

$$= (38.2 + 2.3.7) - (92.9)$$

$$\Delta_f^0 S = 159 \text{ j / mol} = 0.159 \text{ kJ / mol}$$

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

$$= 178.3 - 1273 \times 0.159$$

$$= -24.107 \text{ KJ / Mol}$$

$$\text{Also } \Delta_f^0 G = -2.303RT \log K$$

$$-24.107 = -2.303 \times 8.314 \times 10^{-3} \times 1273 \log K_p$$

$$\log k_p = \frac{24.107}{24.374} = 0.98$$

$$K_p = 9.75 \text{ atm}$$

10. It is free expansion where $\Delta T = 0$

11. $T_3 > T_1$ is incorrect

In an isothermal process, T constant

$$T_2 = T_1$$

Area under P-V graph

$$W_{\text{Isothermal}} > W_{\text{adiabatic}}$$

$$\text{Now } \Delta U_{\text{Isothermal}} = 0$$

$$\text{In adiabatic } T_1 V_1^{r-1} = T_3 V_3^{r-1}$$

$$\frac{T_3}{T_1} = \left(\frac{V_1}{V_3} \right)^{r-1}$$

$T_3 < T_1$ Hence internal energy decreases

$$\Delta U_{\text{Isothermal}} > \Delta U_{\text{adiabatic}}$$

$$12. \quad \Delta H = \Delta U + \Delta n_g RT$$

$$\Delta H = -74000 + 0.5 \times 8.314 \times 300$$

$$= -738755 \text{ J}$$

$$= -738.75 \text{ KJ}$$

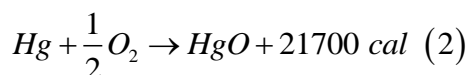
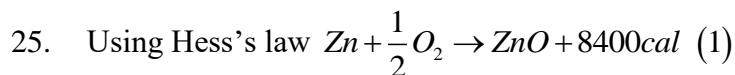
13. $\Delta U = \Delta H - V\Delta P$
 $= -500 - (2 \times (35 - 20)) \times 0.1$
 $= -503 \text{ KJ}$
14. Enthalpy of neutralization of strong acid and strong base is
 -13.7 Kcal/mol
 $\Delta H = -13.7 + 0.7$
 $= -13.0 \text{ KCal}$
15. $X_2O_{4(l)} \rightarrow 2XO_{2(g)}$
 $\Delta n_g = 2 - 0 = 2$
 $\Delta H = \Delta U + \Delta n_g RT$
 $= 2.1 + 2 \times \frac{2}{1000} \times 300$
 $\Delta H = 3.3 \text{ KCal}$
 $\Delta G = \Delta H - T\Delta S$
 $= 3.3 - 300 \times \frac{20}{1000}$
 $\Delta G = -2.7 \text{ KCal}$
16. ΔS for the reaction $\frac{1}{2}X_2 + \frac{3}{2}Y_2 \rightleftharpoons XY_3$
 $\Delta S = 50 - \left(\frac{1}{2} \times 60 + \frac{3}{2} \times 30 \right) = -255$
For equilibrium $\Delta G = 0 = \Delta H - T\Delta S$
 $T = \frac{\Delta H}{\Delta S} = \frac{-30000}{-25} = 1200 \text{ K}$
17. Given
 $\frac{1}{2}H_{2(g)} + (aq) \rightarrow H_{aq}^+ + e^- \Delta H^0 = 0 \text{ (i)}$
 $\frac{1}{2}H_{2(g)} + \frac{1}{2}Cl_{2(g)} \rightarrow HCl_{(g)}; \Delta H^0 = -92.4 \text{ KJ (ii)}$
 $HCl_{(g)} + nH_2O_{(l)} \rightarrow H_{(aq)}^+ + Cl_{(aq)}^-; \Delta H^0 = -74.8 \text{ KJ (iii)}$
(ii) + (iii) - (i)
 $\therefore \frac{1}{2}Cl_{2(g)} + (aq) + e^- \rightarrow Cl_{(aq)}^-; \Delta H = (-92.4 - 74.8) \text{ KJ} - 167.2 \text{ KJ}$
Heat of formation for $Cl_{(aq)}^- = -167.2 \text{ KJ}$
18. $\Delta G^0 = \Delta H^0 - T\Delta S^0$
 $-RT \ln K = \Delta H^0 - T\Delta S^0$
 $\ln K = -\frac{\Delta H^0 - T\Delta S^0}{RT}$
19. The process is isothermal expansion
Hence, $q = -w$ ($U = 0$)
 $\therefore q = +208 \text{ J} \quad \therefore w = -208 \text{ J}$
20. Entropy change for an isothermal reversible process is given by
 $\Delta S = nR \ln \frac{V_2}{V_1} = 2 \times 8.314 \times 2.303 \log \frac{100}{10} = 38.3 \text{ J.Mol}^{-1} \text{ K}^{-1}$
21. $\Delta G = \Delta H - T\Delta S$ when $\Delta H < 0$ and $\Delta S < 0$ then ΔG will be negative at low temperature and the reaction will be spontaneous

$$22. \quad \Delta S^0 = 2S_{HCl}^0 - (S_{H_2}^0 + S_{Cl_2}^0) = 2 \times 186.7 - (130.6 + 223.0) \\ = 19.8 JK^{-1} mol^{-1}$$

23. For spontaneous reaction, $\Delta H = \pm ve$; $\Delta S = +ve$ but in that reaction ΔS is negative, so reaction is not possible

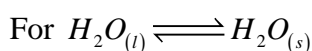
$$24. \quad \Delta S = 16 J mol^{-1} K^{-1}$$

$$T_{b.p} = \frac{\Delta H_{vapour}}{\Delta S_{vapour}} = \frac{6 \times 1000}{16} = 375 K$$



\therefore Heat of reaction = +62300 cal

$$26. \quad C_{p,m} = \frac{dq_p}{dT}$$



Temperature does not change if some heat is given to the system hence

$$C_{p,m} = \frac{+Ve}{zero} = \infty$$

27. Conceptual

28. Conceptual

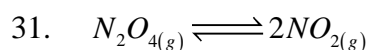
$$29. \quad \Delta G^0 = -2.303 RT \log K_p \text{ and } R = 8.313 JK^{-1} mol^{-1}$$

$$\Delta_r G^0 = -2.303 (8.314 JK^{-1} mol^{-1}) \times (298 K) (\log 2.47 \times 10^{-29})$$

$$= 163000 J mol^{-1}$$

$$= 163 K J mol^{-1}$$

30. We have $q = -w = P_{ex}(8) = 8 \text{ liter.atm}$



If N_2O_4 is 50% dissociated, the mole fraction of both the substances is given by

$$x_{N_2O_4} = \frac{1-0.5}{1+0.5}$$

$$x_{NO_2} = \frac{2 \times 0.5}{1+0.5}$$

$$P_{N_2O_4} = \frac{0.5}{1.5} \times 1 atm$$

$$P_{NO_2} = \frac{1}{1.5} \times 1 atm$$

$$K_p = \frac{(P_{NO_2})^2}{P_{N_2O_4}} = \frac{1.5}{(1.5)^2 (0.5)} = 1.33 atm$$

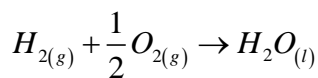
Since

$$\Delta_r G^0 = -RT \ln K_p$$

$$\Delta_r G^0 = (-8.314 JK^{-1} mol^{-1}) \times (333 K) \times (2.303) \times (0.1239)$$

$$= -763.8 K J mol^{-1}$$

$$32. \quad \Delta H = (BE)_{\text{reactant}} - (BE)_{\text{products}}$$



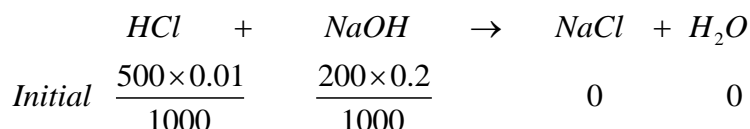
$$\Delta H = \left[(BE)_{H-H} + \frac{1}{2}(BE)_{O=O} \right]$$

$$= \left[(\Delta H)_{\text{vap}} + 2(BE)_{O-H} \right]$$

$$= x_1 + \frac{x_2}{2} - [x_4 - 2x_3]$$

$$= x_1 + \frac{x_2}{2} - x_4 + 2x_3$$

33.



moles

$$= 0.05 \qquad \qquad \qquad = 0.04$$

$$\text{Final moles } 0.05 - 0.04 = 0.01 \qquad \qquad \qquad 0.04 \qquad \qquad 0.04$$

In neutralization of 1 mole of NaOH by 1 mole of HCl heat evolved = 57.3 KJ

To neutralize 0.04 mole of NaOH by 0.04 mole of HCl heat evolved = $57.3 \times 0.04 \text{KJ} = 2.292 \text{KJ}$

$$34. \quad \Delta_{\text{sys}}S = \frac{q_{\text{sys}}}{T_{\text{sys}}} = \frac{-300}{273 + 127}$$

$$= \frac{-300}{400} = \frac{-3}{5} \text{JK}^{-1}$$

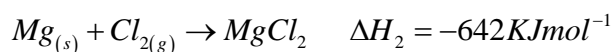
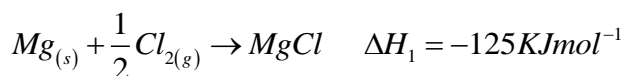
$$\Delta_{\text{surr}}S = \frac{-q_{\text{sys}}}{T_{\text{surr}}} = \frac{-300}{273 + 27}$$

$$= \frac{300}{300} = +1 \text{JK}^{-1}$$

$$\Delta_{\text{total}}S \text{ or } \Delta_{\text{universe}}S = \Delta_{\text{sys}}S + \Delta_{\text{surr}}S$$

$$= \frac{-3}{4} + 1 = \frac{1}{4} = 0.25 \text{JK}^{-1}$$

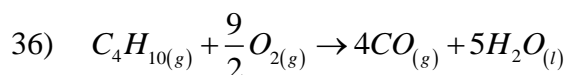
$$35. \quad 2MgCl \rightarrow Mg + MgCl_2 \quad \Delta H = ?$$



$$\Delta H = \Delta H_2 - 2\Delta H_1 = -642 - (2 \times -125) = -392 \text{KJmol}^{-1}$$

$$\therefore -49x - 392$$

$$x = 8$$



NUMERILCAL QUESTIONS

37. For the equilibrium $A \rightarrow B$

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

$$\Delta G^0 = -2.303RT \log_{10} K$$

$$-2.303RT \log_{10} K = \Delta H^0 - T\Delta S^0$$

$$2.303RT \log_{10} K = T\Delta S^0 - \Delta H^0$$

$$\log_{10} K = \frac{T\Delta S^0 - \Delta H^0}{2.303RT} = \frac{298 \times 10 - 54.08 \times 1000}{2.303 \times 8.314 \times 298} = 10$$

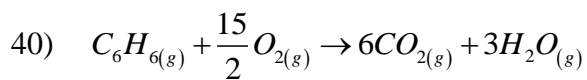
38) $\Delta H = \Delta U + \Delta(PV) = \Delta U + V\Delta P$

$$\Delta U = \Delta H - V\Delta P = -560 - 1 \times 30 \times 0.1$$

$$\text{Absolute value} = 563 \text{KJ}$$

39) $q = 40 \text{ J}$; $w = -8 \text{ J}$ (work done by the system)

$$\Delta E = q + w = 40 - 8 = 32 \text{ J}$$



$$\Delta n = 6 + 3 - 1 - \frac{15}{2} = \frac{+1}{2} = 0.5$$