Speed Test-34

- (b) In insulated system no heat or matter is exchanged. q = 0 : $\Delta E = W$. The work done on the system increases internal energy.
- (c) $\Delta H = H_2 H_1 = (E_2 + P_2V_2) (E_1 + P_1V_1)$ $= (E_2 - E_1) + (P_2V_2 - P_1V_1)$ $=30+4\times5-2\times3=441$. atm
- (d) Given $\Delta H = 41 \text{ kJ mol}^{-1} = 41000 \text{ J mol}^{-1}$ 3. T = 100°C = 273 + 100 = 373 K $\Delta U = \Delta H - \Delta nRT = 41000 - (1 \times 8.314 \times 373)$ = 37898.88 J mol⁻¹ ~ 37.9 kJ mol⁻¹
- (a) Process is isothermal reversible expansion, hence $\Delta U = 0$, therefore q = -W. Since q = +208 J, W = -208 J
- (b) An intensive property is a physical quantity whose value does not depend on the amount of the substance for which it is measured.
- Kirchoff's equation, $\frac{\Delta H_2 \Delta H_1}{T_2 T_2} = \Delta C_P$
- (a) Heat capacity at constant volume $(q_v) = \Delta E$ Heat capacity of constant pressure $(q_n) = \Delta H$ $\Delta H = \Delta E + \Delta nRT$ or $\Delta H - \Delta E = \Delta nRT$ $\Delta n = \text{no. of moles of gaseous products}$ - no. of moles of gaseous reactants

= 12 - 15 = -3

 $\Delta H - \Delta E = -3 \times 8.314 \times 298 J = -7.43 kJ$

- (b) Desired equation is $H_2O(1) \rightarrow H_2O(g)$, $\Delta H = ?$ (Equation II - Equation I) $\Delta H = -245.5 \text{ kJ} - (-286 \text{ kJ}) = 40.5 \text{ kJ}$
- (a) $C_2H_5OH(\ell) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(\ell)$ Bomb calorimeter gives ΔU of the reaction Given, $\Delta U = -1364.47 \text{ kJ mol}^{-1}$

$$\Delta H = \Delta U + \Delta n_g RT = -1364.47 - \frac{1 \times 8.314 \times 298}{1000}$$

=-1366.93 kJ mol⁻¹

- 10. (a) $\Delta S_{(A \to B)} = \Delta S_{(A \to C)} + \Delta S_{(C \to D)} \Delta S_{(B \to D)}$ =50+30-20=60 e.u.
- 11. (a) $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O_2 \rightarrow CO_3 + 2H_2O_3 \rightarrow CO_4 + 2H_2O_5 \rightarrow CO_4 + 2H_2O_5 \rightarrow CO_5 \rightarrow CO_5 + 2H_2O_5 \rightarrow CO_5 \rightarrow CO_5 \rightarrow CO_5 + 2H_2O_5 \rightarrow CO_5 \rightarrow CO_$ $C + O_2 \rightarrow CO_2$; $\Delta H = -40 \text{ kcal....}(2)$

$$2H_2 + O_2 \rightarrow 2H_2O$$
; $\Delta H = -20 \text{ kcal......}(3)$
(2) + (3) - (1) we have, $C + 2H_2 \rightarrow CH_4$
or $\Delta H = -20 + (-40) - (-20) = -40 \text{ kcal}$

- 12. (b) Enthalpy of reaction $= B.E_{(Reactant)} - B.E_{(Product)}$ $= \left[B.E_{(C=C)} + 4B.E_{(C-H)} + B.E_{(H-H)} \right]$ $- \left[B.E_{(C-C)} + 6B.E_{(C-H)} \right]$ $= [606.1 + (4 \times 410.5) + 431.37)] - [336.49 + (6 \times 410.5)]$
- 13. (a) $\Delta G = \Delta H T\Delta S$, $\Delta H + ve$, ΔS is + ve; $T\Delta S > \Delta H$ for spontaneous process. It will make ΔG, -ve
- $\Delta H = \Delta E + \Delta nRT$ For $\Delta H \neq \Delta E$, $\Delta n \neq 0$ 14. (d) Where $\Delta n = \text{no.}$ of moles of gaseous products – no. of moles of gaseous reactants

(a) $\Delta n = 2 - 2 = 0$

 $=-120.0 \text{ kJ mol}^{-1}$

- (b) $\Delta n = 0$ (: they are either in solid or liquid state)
- (c) $\Delta n = 1 1 = 0$ (... C is in solid state) (d) $\Delta n = 2 - 4 = -2$

· (d) is correct answer

- 15. (b) The species in its elemental form has zero standard molar enthalpy of formation at 298 K. At 298K, Cl2 is gas while Br, is liquid.
- (b) High pressure reduces volume, decreases entropy, 16. hence ΔS negative.

17. (d)
$$\Delta S^{\circ} = 2S^{\circ}_{HCl} - (S^{\circ}_{H2} + S^{\circ}_{Cl_{2}})$$

 $= 2 \times 186.7 - (130.6 + 223.0)$
 $= 19.8 \text{ JK}^{-1} \text{mol}^{-1}$
18. (a) $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$

For a spontaneous reaction ΔG° < 0

or
$$\Delta H^{\circ} - T\Delta S^{\circ} \le 0 \Rightarrow T > \frac{\Delta H^{\circ}}{\Delta S^{\circ}}$$

$$\Rightarrow T > \frac{179.1 \times 10^3}{160.2} > 1117.9K \approx 1118 K$$

19. (d) For the reaction, $C_{(s)} + \frac{1}{2}O_{2(g)} \longrightarrow CO$ $\Delta H = \Delta U + \Delta nRT$ or $\Delta H - \Delta U = \Delta nRT$

$$\Delta n = 1 - \frac{1}{2} = \frac{1}{2} \; ; \; \Delta H - \Delta U = \frac{1}{2} \times 8.314 \times 298$$

= 1238.78 J mol⁻¹ 20. (c) $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$; $-RT \ln K = \Delta H^{\circ} - T\Delta S^{\circ}$

S-C-18 SOLUTIONS

$$\ell nK = -\frac{\Delta H^o - T\Delta S^o}{RT}$$

21. (a) $\operatorname{Fe}_2 \operatorname{O}_2(s) + 3\operatorname{CO}(g) \longrightarrow 2\operatorname{Fe}(s) + 3\operatorname{CO}_2(g)$; $\Delta H = -26.8 \text{ kJ}$

FeO(s)+CO(g)
$$\longrightarrow$$
 Fe(s)+CO₂(g);
 Δ H=-16.5 kJ ...(ii)
eq. (i) -2 × eq. (ii), we get

 $Fe_2O_2(s) + CO(g) \longrightarrow 2FeO(s) + CO_2(g)$ $\Delta H = -26.8 + 33.0 = +6.2 \text{ kJ}$

22. **(b)** At equilibrium $\Delta G = 0$ Hence, $\Delta G = \Delta H - T_e \Delta S = 0$

$$\therefore \Delta H = T_e \Delta S$$
 or $T_e = \frac{\Delta H}{\Delta S}$

For a spontaneous reaction

ΔG must be negative which is possible only if $\Delta H - T\Delta S < 0$

$$\therefore \Delta H\!<\!T\Delta S \ \ \text{or} \ \ T>\frac{\Delta H}{\Delta S}; \ T_e < T$$

23. **(b)** $N_2 + 3H_2 \longrightarrow 2NH_3 \Delta H = 2 \times -46.0 \text{ kJ mol}^{-1}$ Let x be the bond enthalpy of N - H bond then [Note: Enthalpy of formation or bond formation enthalpy is given which is negative but the given reaction involves bond breaking hence values should

> $\Delta H = \Sigma$ Bond energies of reactants – Σ Bond energies of products

$$2 \times -46 = 712 + 3 \times (436) - 6x$$

 $-92 = 2020 - 6x$
 $6x = 2020 + 92$

be taken as positive.1

6x = 2112

x = +352 kJ/mol

24. (c) For a reaction to be at equilibrium $\Delta G = 0$. Since $\Delta G = \Delta H - T\Delta S$ so at equilibrium $\Delta H - T\Delta S = 0$ or $\Delta H = T\Delta S$ For the reaction

$$\frac{1}{2}X_2 + \frac{3}{2}Y_2 \longrightarrow XY_3; \quad \Delta H = -30kJ \text{ (given)}$$

Calculating ΔS for the above reaction, we get

$$\Delta S = 50 - \left[\frac{1}{2} \times 60 + \frac{3}{2} \times 40 \right] J K^{-1}$$

=50 - (30 + 60) J K⁻¹ = -40 J K⁻¹

At equilibrium, $T\Delta S = \Delta H$ [∵ ΔG = 0]

$$T \times (-40) = -30 \times 1000 \ [\because 1kJ = 1000J]$$

or
$$T = \frac{-30 \times 1000}{-40}$$
 or 750 K

25. (a) According to first law of thermodynamics energy can neither be created nor destroyed although it can be converted from one form to another.

> NOTE: Carnot cycle is based upon this principle but during the conversion of heat into work some mechanical energy is always converted to other form of energy hence this data violates 1st law of thermodynamics.

The standard enthalpy of the combustion of glucose can be calculated by the eqn.

> $C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$ $\Delta H_c = 6 \times \Delta H_f(CO_2) + 6 \times \Delta H_f(H_2O) - \Delta H_f[C_6H_{12}O_6]$ $\Delta H^{\circ} = 6(-400) + 6(-300) - (-1300)$ $\Delta H^{\circ} = -2900 \text{ kJ/mol}$

For one gram of glucose, enthalpy of combustion

$$\Delta H^{\circ} = -\frac{2900}{180} = -16.11 \text{kJ/g}$$

27. (d) (i) $2C(s) + H_2(g) \longrightarrow H - C \equiv C - H(g)$

 $\Delta H = 225 \text{ kJmol}^{-1}$

(ii)
$$2C(s) \longrightarrow 2C(g)$$
 $\Delta H = 1410 \text{ kJ mol}^{-1}$
 $C(s) \longrightarrow C(g) \Delta H = \frac{1410}{2} = 705 \text{kJmol}^{-1}$

 $\Delta H = 330 \text{ kJmol}^{-1}$ (iii) $H_2(g) \longrightarrow 2H(g)$ From equation (i):

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

$$\begin{array}{l} -[2\times BE_{C-H} + 1\times BE_{C=C}] \\ 225 = [1410 + 1\times 330] - [2\times 350 + 1\times BE_{C=C}] \\ 225 = [1410 + 330] - [700 + BE_{C=C}] \\ 225 = 1740 - 700 - BE_{C=C} \\ BE_{C=C} = 815 \text{ kJ mol}^{-C} \end{array}$$

28. (b) ΔH_N for strong base and strong acid

=
$$-13.7 \text{ kcal eq}^{-1}$$

 $\Delta H_{\text{ion}}(CH_3COOH)$
= $-12.5 - (-13.7) = 1.2 \text{ kcal mol}^{-1}$
 $\Delta H_{\text{ion}}(NH_4OH)$
= $-10.5 - (-13.7) - \Delta H_{\text{ion}}(CH_3COOH)$
= $13.7 - 10.5 - 1.2$
= 2 kcal mol^{-1}

29. (b) Write the proper chemical equations.

C(graphite)+
$$O_2(g) \rightarrow CO_2(g)$$

 $\Delta H = -393kJ$ (i)

$$\mathrm{H}_2(\mathrm{g}) + \frac{1}{2}\mathrm{O}_2(\mathrm{g}) \to \mathrm{H}_2\mathrm{O}(\mathrm{l})$$

$$\Delta H = -286kJ$$
(ii)
 $C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$
 $\Delta H = -1360kJ$ (iii)

From $(2 \times I + 3 \times II) - (III)$ we get

$$2C + 3H_2 + \frac{1}{2}O_2 \rightarrow C_2H_5OH$$

$$\therefore 2(-393kJ) + 3(-286kJ) - (-1360kJ) = -284kJ$$

30. (a)
$$\Delta H_{hyd.} = \Delta H_{sol.} - \Delta H_{lattice}$$

= 1-180 = -179 kcalmol⁻¹

Then
$$\Delta H_{hyd.}(Na^+) + \Delta H_{hyd.}(Cl^-) = -179$$

or
$$\Delta H_{hyd.}(Na^+) + \frac{2}{3} \Delta H_{hyd}(Na^+) = -179$$

or
$$\Delta H_{hyd} (Na^+) = -107.4 \, kcal \, mol^{-1}$$

31. (a) For non spontaneous reaction

$$\Delta G = + ve$$

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

$$\Delta S = 121 \text{ JK}^{-1}$$

For $\Delta G = +ve$

ΔH has to be positive. Hence the reaction is endothermic.

The minimum value of ΔH can be obtained by putting

$$\Delta H = T\Delta S = 298 \times 121 J$$

= 36.06 kJ

32. (c) The standard enthalpy of reaction is the enthalpy change for a reaction when all the participating substances are in their standard states. The standard state of a substance at a specified temperature is its

pure form at 1 bar. For example, the standard state of liquid ethanol at 298 K is pure liquid ethanol at 1 bar. Standard state of solid iron at 500 K is pure iron at 1

33. (d)

34. (a)
$$\Delta C_n = 2 \times 25.1 + 3 \times 75.3 - [103.8 + 3 \times 28.8]$$

$$= 85.9 \text{ J K}^{-1} \text{mol}^{-1}$$

$$\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta C_p;$$

$$\frac{\Delta H_2 - (-33290)}{358 - 298} = 85.9$$

$$\Delta H = -28136 \text{ Imol}^{-1}$$

$$=-28.136 \text{ kJ mol}^{-1}$$

35. (b) The enthalpy of ionisation of weak acid is given by AHion (HA)

 $=\Delta H_{N(weak acid/strong base)} - \Delta H_{N(strong acid/strong base)}$

$$=-56.1 - (-57.3) = 1.2 \text{ kJ mol}^{-1}$$

 $\Delta H_{(ionisation)} = 1.5 \text{ kJ mol}^{-1}$

Hence % ionisation in 1 M solution

$$=\frac{(1.5-1.2)}{1.5}\times100=20$$

36. (d)
$$\frac{1}{2}$$
N₂(g) + $\frac{3}{2}$ F₂(g) \longrightarrow NF₃; Δ H = -113 kJ

or
$$\Delta H_{N\equiv N}$$
 + $\frac{3}{2}$ ΔH_{F-F} -3 ΔH_{N-F} = -113 kJ

Let x kJ mol-1 be the bond energy of F-F bond then bond energy of $N \equiv N$ bond = 6x

$$\therefore \frac{1}{2} \times 6x + \frac{3}{2} \times x - 3 \times 273 = -113 \text{ kJ}$$

On solving,

$$x = 156.9 \text{ kJmol}^{-1}$$
 and

 $N \equiv N \text{ bond energy} = 6 \times 156.9 = 941.4 \text{ kJ mol}^{-1}$

37. (b) Given ΔH

$$\frac{1}{2}A \longrightarrow B + 150$$
 ...(1)

$$3B \longrightarrow 2C + D$$
 -125 ...(2)

$$E + A \longrightarrow 2D \qquad +350 \qquad \qquad ...(3)$$

To calculate ΔH operate

$$2 \times eq. (1) + eq. (2) - eq. (3)$$

 $\Delta H = 300 - 125 - 350 = -175$

38. (a)
$$q = -W = 2.303 \text{nRT} \log \frac{V_2}{V_1}$$

(c)

40. (a) The first reaction is exothermic and the second reaction is endothermic. On passing the mixture of O2 and H2O (steam) over coke while keeping the temperature constant ΔH of both the reactions must be same. Moles of O2 needed to evolve 132 kJ

$$=\frac{0.5\times132}{110}=0.6$$

Hence steam: O2 ratio must be 1:0.6

41. (a) The greater the (negative value) of heat of neutralisation, the more is the strength of the acid. Hence,

- 42. (b) Dissolution of KNO, is endothermic, hence heat is absorbed and cooling is observed.
- The positive sign expresses when work is done on the system. Similarly, negative sign expresses when work is done by the system.
- 44. (b) This is combustion reaction, which is always exothermic hence

$$\Delta H = -vc$$

As the no. of gaseous molecules are increasing hence entropy increases so $\Delta S = +ve$.

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

For a spontaneous reaction

which is possible in this case as $\Delta H = -ve$ and $\Delta S = +ve$.

45. (c) ΔS has negative value if number of gaseous moles decreases during a reaction, $\Delta n_g = -ve$ For the reaction

$$2SO_2 + O_2 \rightarrow 2SO_3$$

$$\Delta n_g = 2 - 3 = -1$$