

# Thermodynamics

## CHAPTER 6

- If an endothermic reaction is non-spontaneous at freezing point of water and becomes feasible at its boiling point, then [2002]
  - $\Delta H$  is -ve,  $\Delta S$  is +ve
  - $\Delta H$  and  $\Delta S$  both are +ve
  - $\Delta H$  and  $\Delta S$  both are -ve
  - $\Delta H$  is +ve,  $\Delta S$  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]
  - violates 1<sup>st</sup> law of thermodynamics
  - violates 1<sup>st</sup> law of thermodynamics if  $Q_1$  is -ve
  - violates 1<sup>st</sup> law of thermodynamics if  $Q_2$  is -ve
  - does not violate 1<sup>st</sup> law of thermodynamics.
- For the reactions, [2002]
 
$$2C + O_2 \rightarrow 2CO_2; \quad \Delta H = -393 \text{ J}$$

$$2Zn + O_2 \rightarrow 2ZnO; \quad \Delta H = -412 \text{ J}$$
  - carbon can oxidise Zn
  - oxidation of carbon is not feasible
  - oxidation of Zn is not feasible
  - Zn can oxidise carbon.
- The heat required to raise the temperature of body by 1 K is called [2002]
  - specific heat
  - thermal capacity
  - water equivalent
  - 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]
  - > 40 kJ
  - < 40 kJ
  - Zero
  - 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<sup>-1</sup>, 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]
  - 250 kJ
  - +125 kJ
  - 125 kJ
  - +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]
  - $(dS)_{V,E} > 0, (dG)_{T,P} < 0$
  - $(dS)_{V,E} = 0, (dG)_{T,P} = 0$
  - $(dS)_{V,E} = 0, (dG)_{T,P} > 0$
  - $(dS)_{V,E} < 0, (dG)_{T,P} < 0$
- The correct relationship between free energy change in a reaction and the corresponding equilibrium constant  $K_c$  is [2003]
  - $-\Delta G = RT \ln K_c$
  - $\Delta G^\circ = RT \ln K_c$
  - $-\Delta G^\circ = RT \ln K_c$
  - $\Delta G = RT \ln K_c$
- The enthalpy change for a reaction does **not** depend upon [2003]
  - use of different reactants for the same product
  - the nature of intermediate reaction steps
  - the differences in initial or final temperatures of involved substances
  - the physical states of reactants and products
- An ideal gas expands in volume from  $1 \times 10^{-3}$  to  $1 \times 10^{-2}$  m<sup>3</sup> at 300 K against a constant pressure of  $1 \times 10^5$  Nm<sup>-2</sup>. The work done is [2004]
  - 270 kJ
  - 900 kJ
  - 900
  - 900 kJ
- The enthalpies of combustion of carbon and carbon monoxide are -393.5 and -283 kJ mol<sup>-1</sup> respectively. The enthalpy of formation of carbon monoxide per mole is [2004]

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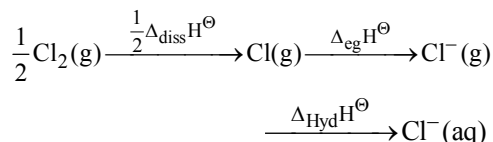
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- (a)  $-676.5 \text{ kJ}$  (b)  $676.5 \text{ kJ}$   
(c)  $110.5 \text{ kJ}$  (d)  $-110.5 \text{ kJ}$
12. Consider the reaction :  $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$  carried out at constant temperature and pressure. If  $\Delta H$  and  $\Delta U$  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)  $\Delta H = 0$
13. If the bond dissociation energies of XY,  $\text{X}_2$  and  $\text{Y}_2$  (all diatomic molecules) are in the ratio of 1 : 1 : 0.5 and  $\Delta H_f^\circ$  for the formation of XY is  $-200 \text{ kJ mole}^{-1}$ . The bond dissociation energy of  $\text{X}_2$  will be [2005]  
(a)  $400 \text{ kJ mol}^{-1}$  (b)  $300 \text{ kJ mol}^{-1}$   
(c)  $200 \text{ kJ mol}^{-1}$  (d)  $100 \text{ kJ mol}^{-1}$
14. 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]  
(a)  $(T_f)_{\text{rev}} = (T_f)_{\text{irrev}}$   
(b)  $T_f = T_i$  for both reversible and irreversible processes  
(c)  $(T_f)_{\text{irrev}} > (T_f)_{\text{rev}}$   
(d)  $T_f > T_i$  for reversible process but  $T_f = T_i$  for irreversible process
15. 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]  
(a) the first four ionization energies of carbon and electron gain enthalpy of hydrogen  
(b) the dissociation energy of hydrogen molecule,  $\text{H}_2$   
(c) the dissociation energy of  $\text{H}_2$  and enthalpy of sublimation of carbon  
(d) latent heat of vapourization of methane
16. The enthalpy changes for the following processes are listed below : [2006]
- $\text{Cl}_2(\text{g}) = 2\text{Cl}(\text{g}), \quad 242.3 \text{ kJ mol}^{-1}$   
 $\text{I}_2(\text{g}) = 2\text{I}(\text{g}), \quad 151.0 \text{ kJ mol}^{-1}$   
 $\text{ICl}(\text{g}) = \text{I}(\text{g}) + \text{Cl}(\text{g}), \quad 211.3 \text{ kJ mol}^{-1}$   
 $\text{I}_2(\text{s}) = \text{I}_2(\text{g}), \quad 62.76 \text{ kJ mol}^{-1}$
- 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]  
(a)  $+16.8 \text{ kJ mol}^{-1}$  (b)  $+244.8 \text{ kJ mol}^{-1}$   
(c)  $-14.6 \text{ kJ mol}^{-1}$  (d)  $-16.8 \text{ kJ mol}^{-1}$
17.  $(\Delta H - \Delta U)$  for the formation of carbon monoxide (CO) from its elements at 298 K is [2006] ( $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ )  
(a)  $-2477.57 \text{ J mol}^{-1}$  (b)  $2477.57 \text{ J mol}^{-1}$   
(c)  $-1238.78 \text{ J mol}^{-1}$  (d)  $1238.78 \text{ J mol}^{-1}$
18. 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  $\Delta H^\circ$  and  $\Delta S^\circ$  are  $+179.1 \text{ kJ mol}^{-1}$  and  $160.2 \text{ J/K}$  respectively at 298 K and 1 bar. Assuming that  $\Delta H^\circ$  and  $\Delta S^\circ$  do not change with temperature, temperature above which conversion of limestone to lime will be spontaneous is [2007]  
(a) 1118 K (b) 1008 K  
(c) 1200 K (d) 845 K.
19. Assuming that water vapour is an ideal gas, the internal energy change ( $\Delta U$ ) when 1 mol of water is vapourised at 1 bar pressure and  $100^\circ\text{C}$ , (given : molar enthalpy of vapourisation of water at 1 bar and 373 K =  $41 \text{ kJ mol}^{-1}$  and  $R = 8.3 \text{ J mol}^{-1} \text{ K}^{-1}$ ) will be [2007]  
(a)  $41.00 \text{ kJ mol}^{-1}$  (b)  $4.100 \text{ kJ mol}^{-1}$   
(c)  $3.7904 \text{ kJ mol}^{-1}$  (d)  $37.904 \text{ kJ mol}^{-1}$
20. Identify the correct statement regarding a spontaneous process: [2007]  
(a) Lowering of energy in the process is the only criterion for spontaneity.  
(b) For a spontaneous process in an isolated system, the change in entropy is positive.  
(c) Endothermic processes are never spontaneous.  
(d) Exothermic processes are always spontaneous.
21. Oxidising power of chlorine in aqueous solution

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can be determined by the parameters indicated below:



(using the data,

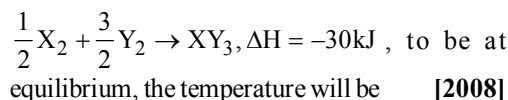
$$\Delta_{\text{diss}}H^\ominus_{\text{Cl}_2} = 240 \text{ kJ mol}^{-1},$$

$$\Delta_{\text{eg}}H^\ominus_{\text{Cl}} = -349 \text{ kJ mol}^{-1},$$

$$\Delta_{\text{hyd}}H^\ominus_{\text{Cl}^-} = -381 \text{ kJ mol}^{-1}), \text{ will be } \quad [2008]$$

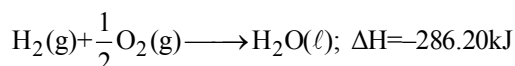
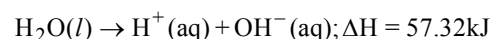
- (a) +152 kJ mol<sup>-1</sup>      (b) -610 kJ mol<sup>-1</sup>  
(c) -850 kJ mol<sup>-1</sup>      (d) +120 kJ mol<sup>-1</sup>

22. Standard entropy of X<sub>2</sub>, Y<sub>2</sub> and X Y<sub>3</sub> are 60, 40 and 50 J K<sup>-1</sup> mol<sup>-1</sup>, respectively. For the reaction,



- (a) 1250 K      (b) 500 K  
(c) 750 K      (d) 1000 K

23. On the basis of the following thermochemical data : ( $\Delta_f G^\ominus H^\oplus_{(\text{aq})} = 0$ )      [2009]



The value of enthalpy of formation of OH<sup>-</sup> ion at 25° C is:

- (a) -228.88 kJ      (b) +228.88 kJ  
(c) -343.52 kJ      (d) -22.88 kJ

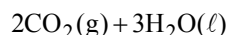
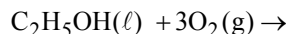
24. The standard enthalpy of formation of NH<sub>3</sub> is -46.0 kJ mol<sup>-1</sup>. If the enthalpy of formation of H<sub>2</sub> from its atoms is -436 kJ mol<sup>-1</sup> and that of N<sub>2</sub> is -712 kJ mol<sup>-1</sup>, the average bond enthalpy of N-H bond in NH<sub>3</sub> is      [2010]

- (a) -964 kJ mol<sup>-1</sup>      (b) +352 kJ mol<sup>-1</sup>  
(c) +1056 kJ mol<sup>-1</sup>      (d) -1102 kJ mol<sup>-1</sup>

25. For a particular reversible reaction at temperature T,  $\Delta H$  and  $\Delta S$  were found to be both +ve. If T<sub>e</sub> is the temperature at equilibrium, the reaction would be spontaneous when

- (a) T<sub>e</sub> > T      (b) T > T<sub>e</sub>      [2010]  
(c) T<sub>e</sub> is 5 times T      (d) T = T<sub>e</sub>

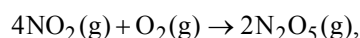
26. The value of enthalpy change ( $\Delta H$ ) for the reaction



at 27° C is -1366.5 kJ mol<sup>-1</sup>. The value of internal energy change for the above reaction at this temperature will be :      [2011RS]

- (a) -1369.0 kJ      (b) -1364.0 kJ  
(c) -1361.5 kJ      (d) -1371.5 kJ

27. Consider the reaction :



$$\Delta_r H = -111 \text{ kJ}.$$

If N<sub>2</sub>O<sub>5</sub>(s) is formed instead of N<sub>2</sub>O<sub>5</sub>(g) in the above reaction, the  $\Delta_r H$  value will be :

(given,  $\Delta H$  of sublimation for N<sub>2</sub>O<sub>5</sub> is 54 kJ mol<sup>-1</sup>)      [2011RS]

- (a) +54 kJ      (b) +219 kJ  
(c) -219 J      (d) -165 kJ

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)  $\ln K = \frac{\Delta H^\ominus - T\Delta S^\ominus}{RT}$

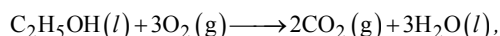
(d)  $K = e^{-\Delta G^\ominus/RT}$

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:      [2013]

$$(R = 8.314 \text{ J/mol K}) (\ln 7.5 = 2.01)$$

- (a) q = +208 J, w = -208 J  
(b) q = -208 J, w = -208 J  
(c) q = -208 J, w = +208 J  
(d) q = +208 J, w = +208 J

30. For complete combustion of ethanol,



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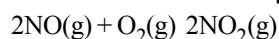
the amount of heat produced as measured in bomb calorimeter, is  $1364.47 \text{ kJ mol}^{-1}$  at  $25^\circ\text{C}$ . Assuming ideality the enthalpy of combustion,  $\Delta_c H$ , for the reaction will be:

( $R = 8.314 \text{ kJ mol}^{-1}$ ) [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 following reaction is performed at  $298 \text{ K}$ .

[JEE M 2015]



The standard free energy of formation of  $\text{NO}(\text{g})$  is  $86.6 \text{ kJ/mol}$  at  $298 \text{ K}$ . What is the standard free energy of formation of  $\text{NO}_2(\text{g})$  at  $298 \text{ K}$ ?

( $K_p = 1.6 \times 10^{12}$ )

- (a)  $86600 -$   
 (b)  $0.5[2 \times 86,600 - R(298) \ln(1.6 \times 10^{12})]$   
 (c)  $R(298) \ln(1.6 \times 10^{12}) - 86600$   
 (d)  $86600 + R(298) \ln(1.6 \times 10^{12})$

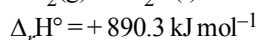
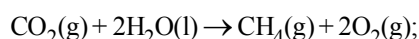
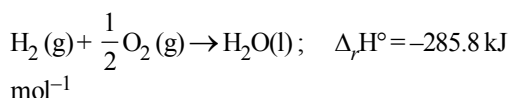
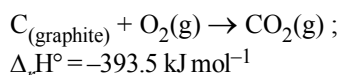
32. The heats of combustion of carbon and carbon monoxide are  $-393.5$  and  $-283.5 \text{ kJ mol}^{-1}$ , respectively. The heat of formation (in  $\text{kJ}$ ) of carbon monoxide per mole is: [JEE M 2016]

- (a)  $-676.5$  (b)  $-110.5$   
 (c)  $110.5$  (d)  $676.5$

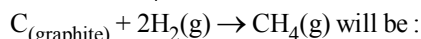
33.  $\Delta U$  is equal to [JEE M 2017]

- (a) Isochoric work (b) Isobaric work  
 (c) Adiabatic work (d) Isothermal work

34. Given [JEE M 2017]



Based on the above thermochemical equations, the value of  $\Delta_r H^\circ$  at  $298 \text{ K}$  for the reaction



- (a)  $+74.8 \text{ kJ mol}^{-1}$  (b)  $+144.0 \text{ kJ mol}^{-1}$   
 (c)  $-74.8 \text{ kJ mol}^{-1}$  (d)  $-144.0 \text{ kJ mol}^{-1}$

### Answer Key

| 1   | 2   | 3   | 4   | 5   | 6   | 7   | 8   | 9   | 10  | 11  | 12  | 13  | 14  | 15  |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| (b) | (a) | (d) | (b) | (c) | (c) | (a) | (c) | (b) | (c) | (d) | (b) | (N) | (c) | (c) |
| 16  | 17  | 18  | 19  | 20  | 21  | 22  | 23  | 24  | 25  | 26  | 27  | 28  | 29  | 30  |
| (a) | (d) | (a) | (d) | (b) | (b) | (c) | (a) | (b) | (b) | (b) | (d) | (c) | (a) | (a) |
| 31  | 32  | 33  | 34  |     |     |     |     |     |     |     |     |     |     |     |
| (b) | (b) | (c) | (c) |     |     |     |     |     |     |     |     |     |     |     |

## SOLUTIONS

1. (b) **TIPS / Formulae**  $\Delta G = \Delta H - T\Delta S$   
 Since  $\Delta G = \Delta H - T\Delta S$  for an endothermic reaction,  
 $\Delta H = +ve$  and at low temperature  $\Delta S = +ve$   
 Hence  $\Delta G = (+)\Delta H - T(+)\Delta S$   
 and if  $T\Delta S < \Delta H$  (at low temp)  
 $\Delta G = +ve$  (non spontaneous)  
 But at high temperature, reaction becomes spontaneous i.e.  $\Delta G = -ve$ .  
 because at higher temperature  $T\Delta S > \Delta H$ .

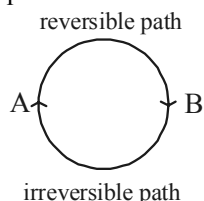
2. (a) According to first law of thermodynamics energy can neither be created nor destroyed although it can be converted from one form to another.

**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.

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3. (d)  $\Delta H$  negative shows that the reaction is spontaneous. Higher negative value for Zn shows that the reaction is more feasible.
4. (b) The heat required to raise the temperature of body by 1K is called thermal capacity or heat capacity.
5. (c) For a cyclic process the net change in the internal energy is zero because the change in internal energy does not depend on the path.



6. (c)  $\text{CH}_2=\text{CH}_2(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{CH}_3-\text{CH}_3$   
Enthalpy change = Bond energy of reactants - Bond energy of products.  
 $\Delta H = 1(\text{C}=\text{C}) + 4(\text{C}-\text{H}) + 1(\text{H}-\text{H}) - 1(\text{C}-\text{C}) - 6(\text{C}-\text{H})$   
 $= 1(\text{C}=\text{C}) + 1(\text{H}-\text{H}) - 1(\text{C}-\text{C}) - 2(\text{C}-\text{H})$   
 $= 615 + 435 - 347 - 2 \times 414 = 1050 - 1175 = -125 \text{ kJ}$
7. (a) For spontaneous reaction,  $dS > 0$  and  $dG$  should be negative i.e.  $< 0$ .
8. (c)  $\Delta G^\circ = -RT \ln K_c$  or  $-\Delta G^\circ = RT \ln K_c$
9. (b) Enthalpy change for a reaction does not depend upon the nature of intermediate reaction steps.
10. (c)  $w = -P\Delta V = -10^{-5}(1 \times 10^{-2} - 1 \times 10^{-3})$   
 $= -900 \text{ J}$
11. (d) (i)  $\text{C} + \text{O}_2 \rightleftharpoons \text{CO}_2, \Delta H = -393.5 \text{ kJ mol}^{-1}$   
(ii)  $\text{CO} + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{CO}_2, \Delta H = -283.0 \text{ kJ mol}^{-1}$   
Operating (i) - (ii), we have  
 $\text{C} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO} \quad \Delta H = -110.5 \text{ kJ mol}^{-1}$
12. (b)  $\Delta H = \Delta U + \Delta nRT$  for  
 $\text{N}_2 + 3\text{H}_2 \longrightarrow 2\text{NH}_3$   
 $\Delta n_g = 2 - 4 = -2$   
 $\therefore \Delta H = \Delta U - 2RT$  or  $\Delta U$   
 $= \Delta H + 2RT \therefore \Delta U > \Delta H$

13. (N)  $\text{X}_2 + \text{Y}_2 \longrightarrow 2\text{XY}, \Delta H = 2(-200)$ .  
Let  $x$  be the bond dissociation energy of  $\text{X}_2$ . Then  
 $\Delta H = -400 = \xi_{x-x} + \xi_{y-y} - 2\xi_{x-y}$   
 $= x + 0.5x - 2x = -0.5x$   
or  $x = \frac{400}{0.5} = 800 \text{ kJ mol}^{-1}$   
(In the question paper, this option was not mentioned. So the answer has been marked 'N')
14. (c) **NOTE** In a reversible process the work done is greater than in irreversible process. Hence the heat absorbed in reversible process would be greater than in the latter case. So  
 $T_f(\text{rev.}) < T_f(\text{irr.})$
15. (c) The standard enthalpy of formation of  $\text{CH}_4$  is given by the equation :  
 $\text{C}(\text{s}) + 2\text{H}_2(\text{g}) \longrightarrow \text{CH}_4(\text{g})$   
Hence, dissociation energy of hydrogen and enthalpy of sublimation of carbon is required.
16. (a)  $\text{I}_2(\text{s}) + \text{Cl}_2(\text{g}) \longrightarrow 2\text{ICl}(\text{g})$   
 $\Delta A = [\Delta H_{\text{I}_2(\text{s}) \rightarrow \text{I}_2(\text{g})} + \Delta H_{\text{I-I}} + \Delta H_{\text{Cl-Cl}}] - [\Delta H_{\text{I-Cl}}]$   
 $= 151.0 + 242.3 + 62.76 - 2 \times 211.3 = 33.46$   
 $\Delta H_f^\circ(\text{ICl}) = \frac{33.46}{2} = 16.73 \text{ kJ / mol}$
17. (d) For the reaction,  $\text{C}(\text{s}) + \frac{1}{2}\text{O}_{2(\text{g})} \longrightarrow \text{CO}$   
 $\Delta H = \Delta U + \Delta nRT$  or  $\Delta H - \Delta U = \Delta nRT$   
 $\Delta n = 1 - \frac{1}{2} = \frac{1}{2}$ ;  
 $\Delta H - \Delta U = \frac{1}{2} \times 8.314 \times 298$   
 $= 1238.78 \text{ J mol}^{-1}$
18. (a)  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$   
For a spontaneous reaction  $\Delta G^\circ < 0$   
or  $\Delta H^\circ - T\Delta S^\circ < 0 \Rightarrow T > \frac{\Delta H^\circ}{\Delta S^\circ}$   
 $\Rightarrow T > \frac{179.3 \times 10^3}{160.2} > 1117.9 \text{ K} \approx 1118 \text{ K}$
19. (d) Given  $\Delta H = 41 \text{ kJ mol}^{-1} = 41000 \text{ J mol}^{-1}$   
 $T = 100^\circ\text{C} = 273 + 100 = 373 \text{ K}$   
 $n = 1$

c-30

Chemistry

$$\Delta U = \Delta H - \Delta nRT = 41000 - (2 \times 8.314 \times 373) \\ = 37898.88 \text{ J mol}^{-1} \approx 37.9 \text{ kJ mol}^{-1}$$

20. (b) Spontaneity of reaction depends on tendency to acquire minimum energy state and maximum randomness. For a spontaneous process in an isolated system the change in entropy is positive.

21. (b) The energy involved in the conversion of

$$\frac{1}{2} \text{Cl}_2(\text{g}) \text{ to } \text{Cl}^{-1}(\text{aq}) \text{ is given by}$$

$$\Delta H = \frac{1}{2} \Delta_{\text{diss}} H_{\text{Cl}_2}^{(-)} + \Delta_{\text{eg}} H_{\text{Cl}}^{(-)} + \Delta_{\text{hyd}} H_{\text{Cl}}^{(-)}$$

Substituting various values from given data, we get

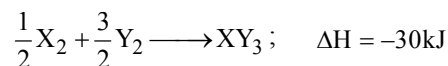
$$\Delta H = \left( \frac{1}{2} \times 240 \right) + (-349) + (-381) \text{ kJ mol}^{-1} \\ = (120 - 349 - 381) \text{ kJ mol}^{-1} = -610 \text{ kJ mol}^{-1} \\ \text{i.e., the correct answer is (b)}$$

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

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

$$\text{or } \Delta H = T\Delta S$$

For the reaction



(given)

Calculating  $\Delta S$  for the above reaction, we get

$$\Delta S = 50 - \left[ \frac{1}{2} \times 60 + \frac{3}{2} \times 40 \right] \text{ JK}^{-1} \\ = 50 - (30 + 60) \text{ JK}^{-1} = -40 \text{ JK}^{-1}$$

$$\text{At equilibrium, } T\Delta S = \Delta H$$

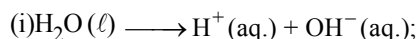
$$[\because \Delta G = 0]$$

$\therefore$

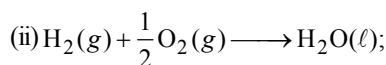
$$T \times (-40) = -30 \times 1000 [\because 1 \text{ kJ} = 1000 \text{ J}]$$

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

23. (a) Given, for reaction



$$\Delta H_r = 57.32 \text{ kJ}$$



$$\Delta H_r = -286.20 \text{ kJ}$$

For reaction (i)

$$\Delta H_r = \Delta H_f^\circ(\text{H}^+, \text{aq.}) + \Delta H_f^\circ(\text{OH}^-, \text{aq.}) - \\ \Delta H_f^\circ(\text{H}_2\text{O}, \ell)$$

$$57.32 = 0 + \Delta H_f^\circ(\text{OH}^-, \text{aq.}) - \Delta H_f^\circ(\text{H}_2\text{O}, \ell) \dots \text{(iii)}$$

For reaction (ii)

$$\Delta H_r = \Delta H_f^\circ(\text{H}_2\text{O}, \ell) -$$

$$\Delta H_f^\circ(\text{H}_2, \text{g}) - \frac{1}{2} \Delta H_f^\circ(\text{O}_2, \text{g})$$

$$-286.20 = \Delta H_f^\circ(\text{H}_2\text{O}, \ell)$$

On replacing this value in equ. (iii) we have

$$57.32 = \Delta H_f^\circ(\text{OH}^-, \text{aq.}) - (-286.20)$$

$$\Delta H_f^\circ = -286.20 + 57.32$$

$$= -228.88 \text{ kJ}$$

24. (b)  $\text{N}_2 + 3\text{H}_2 \longrightarrow 2\text{NH}_3 \quad \Delta H = 2 \times -46.0 \text{ kJ mol}^{-1}$

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 be taken as positive.]

$$\Delta H = \Sigma \text{Bond energies of products} - \Sigma \text{Bond energies of reactants}$$

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

$$-92 = 2020 - 6x$$

$$6x = 2020 + 92$$

$$6x = 2112$$

$$x = +352 \text{ kJ/mol}$$

25. (b) At equilibrium  $\Delta G = 0$

$$\text{Hence, } \Delta G = \Delta H - T_e \Delta S = 0$$

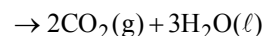
$$\therefore \Delta H = T_e \Delta S \quad \text{or} \quad T_e = \frac{\Delta H}{\Delta S}$$

For a spontaneous reaction

$\Delta G$  must be negative which is possible only if  $\Delta H < T\Delta S$

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

26. (b)  $\text{C}_2\text{H}_5\text{OH}(\ell) + 3\text{O}_2(\text{g})$



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

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

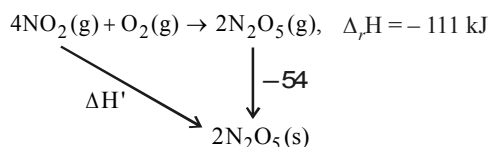


Thermodynamics

c-31

$$\begin{aligned}
 &= -1366.5 - (-1) \\
 &= -1366.5 - (1) \times \frac{8.314}{10^3} \times 300 \\
 &= -1366.5 + 0.8314 \times 3 = -1364 \text{ kJ}
 \end{aligned}$$

27. (d)



$$-111 - 54 = \Delta H'$$

$$\Delta H' = -165 \text{ kJ}$$

28. (c)  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$$-RT \ln K = \Delta H^\circ - T\Delta S^\circ$$

$$\ln K = -\frac{\Delta H^\circ - T\Delta S^\circ}{RT}$$

29. (a) Process is isothermal reversible expansion, hence

$$\Delta U = 0, \text{ therefore } q = -w.$$

$$\text{Since } q = +208 \text{ J, } w = -208 \text{ J}$$

30. (a)  $\text{C}_2\text{H}_5\text{OH}(\ell) + 3\text{O}_2(\text{g}) \longrightarrow 2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\ell)$

Bomb calorimeter gives  $\Delta U$  of the reaction

$$\text{Given, } \Delta U = -1364.47 \text{ kJ mol}^{-1}$$

$$\Delta n_g = -1$$

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

$$-1364.47 - \frac{1 \times 8.314 \times 298}{1000}$$

$$= -1366.93 \text{ kJ mol}^{-1}$$

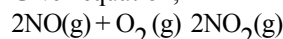
31. (b)  $\Delta G^\circ_{\text{NO}(\text{g})} = 86.6 \text{ kJ/mol} = 86600 \text{ J/mol}$

$$= x \text{ J/mol}$$

$$T = 298, K_p = 1.6 \times 10^{12}$$

$$\Delta G^\circ = -RT \ln K_p$$

Given equation,



$$\therefore 2\Delta G^\circ_{\text{NO}_2} - 2\Delta G^\circ_{\text{NO}} = -R(298) \ln(1.6 \times 10^{12})$$

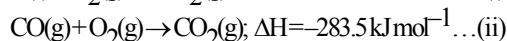
$$2\Delta G^\circ_{\text{NO}_2} - 2 \times 86600 = -R(298) \ln(1.6 \times 10^{12})$$

$$2\Delta G^\circ_{\text{NO}_2} = 2 \times 86600 - R(298) \ln(1.6 \times 10^{12})$$

$$\Delta G^\circ_{\text{NO}_2} = [2 \times 86600 - R(298) \ln(1.6 \times 10^{12})]$$

$$= 0.5 [2 \times 86600 - R(298) \ln(1.6 \times 10^{12})]$$

32. (b) Given



$\therefore$  Heat of formation of CO = eqn(i) - eqn(ii)

$$= -393.5 - (-283.5)$$

$$= -110 \text{ kJ}$$

33. (c) From 1<sup>st</sup> law of thermodynamics

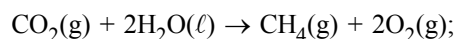
$$\Delta U = q + w$$

For adiabatic process :

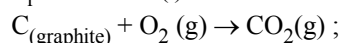
$$q = 0$$

$$\therefore \Delta U = w$$

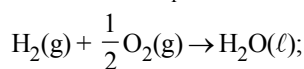
34. (c) Given



$$\Delta_f H^\circ = 890.3 \dots (i)$$



$$\Delta_f H^\circ = -393.5 \text{ kJ mol}^{-1} \dots (ii)$$



$$\Delta_f H^\circ = -285.8 \text{ kJ mol}^{-1} \dots (iii)$$

$$\Delta_r H^\circ = \sum (\Delta_f H^\circ)_{\text{products}} - \sum (\Delta_f H^\circ)_{\text{Reactants}}$$

$$890.3 = [1 \times (\Delta_f H^\circ)_{\text{CH}_4} + 2 \times 0] - [1 \times (-393.5) + 2 \times (-285.8)]$$

$$(\Delta_f H^\circ)_{\text{CH}_4} = 890.3 - 965.1 = -74.8 \text{ kJ/mol}$$