# Thermodynamics

- 1. Among the following the state function(s) is 7. (are)
  - (i) Internal energy
  - (ii) Irreversible expansion work
  - (iii) Reversible expansion work
  - (iv) Molar enthalpy
  - (a) (ii) and (iii) (b) (i), (ii) and (iii)
  - (c) (i) and (iv) (iv)(d) (i) only
- 2. If a reaction involves only solids and liquids which of the following is true?

(a)  $\Delta H < \Delta E$ (b)  $\Delta H = \Delta E$ (c)  $\Delta H > \Delta E$ (d)  $\Delta H = \Delta E + \Delta nRT$ 

- One mole of a non-ideal gas undergoes a change 3. of state (2.0 atm, 3.0 L, 95 K)  $\rightarrow$  (4.0 atm, 5.0 L, 245 K) with a change in internal energy,  $\Delta U = 30.0 L$  atm. The change in enthalpy  $\Delta H$ of the process in L atm is. Tricky
  - (a) 40.0
  - (b) 42.3
  - (c) 44.0
  - (d) Not defined because pressure is not constant
- 4. If bond enthalpies of  $N \equiv N$ , H –H and N –H bonds are  $x_1$ ,  $x_2$  and  $x_3$  respectively,  $\Delta H_f^0$  for NH, will be
  - (a)  $x_1 + 3x_2 6x_3$  (b)  $1/2x_1 + 3/2x_2 3x_3$ (c)  $3x_3 - 1/2x_1 - 3/2x_2(d) = 6x_3 - x_1 - 3x_2$
- Heat of neutralization of a strong acid HA 5. and a weaker acid HB with KOH are - 13.7 and -12.7 k cal mol<sup>-1</sup>. When 1 mole of KOH was added to a mixture containing 1 mole each of HA and HB, the heat change was -13.5 kcal. In what ratio is the base distributed between HA and HB.

(a) 
$$3:1$$
 (b)  $1:3$  (c)  $4:1$  (d)  $1:4$   
**6.** A gas expands adiabatically at constant pressure  
such that T V<sup>-1/2</sup>. The value of  $\gamma$  (C<sub>p,m</sub>/C<sub>v,m</sub>)  
of the gas will be:  
(a) 1.30 (b) 1.50 (c) 1.70 (d) 2

One mole of an ideal gas at 300 K is expanded isothermally from an initial volume of 1 litre to 10 litres. The  $\Delta E$  for this process is (R = 2 cal  $mol^{-1} K^{-1}$ )

(a) 163.7 cal (b) zero

(c) 1381.1 cal (d) 9 lit atm

- 8. The latent heat of vapourization of a liquid at 500 K and 1 atm pressure is 10.0 kcal/mol. What will be the change in internal energy ( $\Delta U$ ) of 3 moles of liquid at the same temperature
  - (a) 13.0 kcal/mol (b) -13.0 kcal/mol
  - (c) 27.0 kcal (d) -7.0 kcal/mol
- 9. Equal volumes of methanoic acid and sodium hydroxide are mixed. If x is the heat of formation of water, then heat evolved on neutralization is
  - (a) more than x (b) equal to x

(c) less than x (d) twice x.

10. A cyclic process ABCD is shown in P-V diagram for an ideal gas. Which of the following diagram represents the same process?

Tricky



**11.** What is the value of change in internal energy at 1 atm in the process? Critical Thinking

$$H_2O 1,323 K \longrightarrow H_2O g,423 K$$

Given : 
$$C_{v,m}$$
 (H<sub>2</sub>O, 1) = 75.0 JK<sup>-1</sup> mol<sup>-1</sup>;

 $C_{nm}$  (H<sub>2</sub>O, g) = 33.314 JK<sup>-1</sup> mol<sup>-1</sup>

 $\Delta H_{vap}$  at 373 K = 40.7 kJ/mol

- (b) 43086 kJ/mol (a) 42.91 kJ/mol
- (c) 42.6 kJ/mol (d) 49.6 kJ/mol
- 12. Which of the following statements/relationships is **not** correct in thermodynamic changes?
  - (a)  $\Delta U =$  (isothermal reversible expansion of a gas)

(b) 
$$w = -nRT \ln \frac{V_2}{V_1}$$
 (isothermal reversible

expansion of an ideal gas)

(c) w = nRT ln 
$$\frac{V_2}{V_1}$$
 (isothermal reversible

expansion of an ideal gas)

- (d) For a system of constant volume heat involved directly changes to internal energy.
- 13. The heat of atomization of methane and ethane are 360 kJ/mol and 620 kJ/mol, respectively. The longest wavelength of light capable of breaking the C - C bond is (Avogadro number  $= 6.02 \times 10^{23} \text{ mol}^{-1}$ , h =  $6.62 \times 10^{-34} \text{ J s}$ ) :

#### Toughnut

(a) 
$$2.48 \times 10^4$$
 nm (b)  $1.49 \times 10^3$  nm

c) 
$$2.48 \times 10^3$$
 nm (d)  $1.49 \times 10^4$  nm

14. Following reaction occurrs in an automobile

 $2\mathrm{C}_8\mathrm{H}_{18}$  g  $+\,25\mathrm{O}_2$  g  $\rightarrow 16\mathrm{CO}_2$  g  $-18\mathrm{H}_2\mathrm{O}$  g .

The sign of  $\Delta H$ ,  $\Delta S$  and  $\Delta G$  would be

### Tricky

(a) +,-,+ (b) -,+,- (c) -,+,+ (d) +,+,-15. A heat engine carries one mole of an ideal mono-atomic gas around the cycle as shown in the figure. Select the correctoption:



- (a)  $q_{AB} = 450 \text{ R}$  and  $q_{CA} = -450 \text{ R}$
- (b)  $q_{AB} = 450 \text{ R}$  and  $q_{CA} = -225 \text{ R}$ (c)  $q_{AB} = 450 \text{ R}$  and  $q_{CA} = -375 \text{ R}$
- (d)  $q_{AB} = 375 \text{ R} \text{ and } q_{CA} = -450 \text{ R}$
- 16. The standard enthalpy of formation of NH<sub>3</sub> is - 46.0 kJ/mol. If the enthalpy of formation of  $H_2$  from its atoms is -436 kJ/mol and that of  $N_2$ is - 712 kJ/mol, the average bond enthalpy of N - H bond in NH, is:

(a) 
$$-1102 \text{ kJ/mol}$$
 (b)  $-964 \text{ kJ/mol}$ 

(c) 
$$+ 352 \text{ kJ/mol}$$
 (d)  $+ 1056 \text{ kJ/mol}$ 

- The standard enthalpy of formation  $(\Delta_f H^{\circ}_{298})$ 17. for methane,  $CH_4$  is -74.9 kJ mol<sup>-1</sup>. In order to calculate the average energy given out in the formation of a C - H bond from this it is necessary to know which one of the following?
  - (a) The dissociation energy of the hydrogen molecule, H<sub>2</sub>.
  - (b) The first four ionisation energies of carbon.
  - (c) The dissociation energy of H<sub>2</sub> and enthalpy of sublimation of carbon (graphite).
  - The first four ionisation energies of carbon (d) and electron affinity of hydrogen.
- 18. 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°C, (given : molar enthalpy of vapourisation of water at 1 bar and 373 K = 41 kJ mol<sup>-1</sup> and  $R = 8.3 \text{ J mol}^{-1} \text{ K}^{-1}$ ) will be
  - (a)  $41.00 \text{ kJ mol}^{-1}$ (b) 4.100 kJ mol<sup>-1</sup>
  - (c)  $3.7904 \text{ kJ mol}^{-1}$ (d)  $37.904 \text{ kJ mol}^{-1}$
- 19. An ideal gas expands against a constant external pressure of 2.0 atmosphere from 20 litre to 40 litre and absorbs 10 kJ of heat from surrounding. What is the change in internal energy of the system?
  - (given : 1atm-litre = 101.3 J)
  - (b) 5948 J (a) 4052 J

(c) 
$$14052 J$$
 (d)  $9940 J$ 

- 20. For which one of the processes represented by the following equations the enthalpy (heat) change is likely to be negative
  - (a)  $Cl^{-}(g)$  aq  $\rightarrow Cl^{-}(aq)$
  - (b)  $Cl(g) \rightarrow Cl^+(g) + e^-$
  - (c)  $1/2Cl_2(g) \rightarrow Cl(g)$
  - (d)  $Cl_2(l) \rightarrow Cl_2(g)$

- 21. The 'thermite reaction' involving the reaction between ferric oxide and metallic aluminium produces molten iron. Given that
  2A1 3/2O<sub>2</sub> → Al<sub>2</sub>O<sub>3</sub>; ΔH<sub>1</sub> -400 kcal/ mol 2Fe 3/2O<sub>2</sub> → Fe<sub>2</sub>O<sub>3</sub>; ΔH<sub>2</sub> -200 kcal/mol. What is ΔH for the formation of 1 mole of iron?
  (a) -100 kcal
  (b) -200 kcal
  (c) +100 kcal
  (d) +200 kcal
- **22.** Given :

23.

Reaction

(I) 
$$H_2(g) + \frac{1}{2}O_2(g) \to H_2O(l);$$
  
 $\Delta H_{298K} - 285.9 \text{kJ mol}^{-1}$ 

(II) 
$$H_2(g) + \frac{1}{2}O_2(g) \to H_2O(g);$$

$$\Delta H_{298K} -241.8 \text{ kJ mol}^{-1}$$

The molar enthalpy of vapourisation of water will be :

(a)	241.8 kJ mol <sup>-1</sup>	(b)	22.0 kJ mol <sup>-1</sup>
(c)	44.1 kJ mol <sup>-1</sup>	(d)	527.7 kJ mol <sup>-1</sup>
Giv	en		

**Energy Change** 

(in kJ) Li(s)  $\rightarrow$  Li(g) 161 Li(g)  $\rightarrow$  Li<sup>+</sup>(g) 520  $\frac{1}{2}F_2(g) \rightarrow F(g)$  77 F(g) + e<sup>-</sup>  $\rightarrow$  F<sup>-</sup>(g) (Electron gain enthalpy) Li<sup>+</sup>(g) + F<sup>-</sup>(g)  $\rightarrow$  Li F(s) - 1047 Li (s) +  $\frac{1}{2}F_2(g) \rightarrow$  Li F(s) - 617

Based on data provided, the value of electron gain enthalpy of fluorine would be :



(a)  $-300 \text{ kJ mol}^{-1}$  (b)  $-350 \text{ kJ mol}^{-1}$ (c)  $-328 \text{ kJ mol}^{-1}$  (d)  $-228 \text{ kJ mol}^{-1}$ 

- 24. Fixed mass of an ideal gas contained in a 24.63 L sealed rigid vessel at 1 atm is heated from – 73°C to 27°C. Calculate change in gibb's energy if entropy of gas is a function of temperature as  $S = 2 + 10^{-2} T (J/K)$ : (Use 1 atm L = 0.1 kJ) (a) 1231.5 J (b) 1281.5 J (c) 781.5 J (d) 0
- 25. For the reaction taking place at certain temperature  $NH_2COONH_4(s) \Longrightarrow 2NH_3(g) \quad CO_2(g),$

if equilibrium pressure is 3X bar then  $\Delta_r G^\circ$ would be **Tricky** 

- (a)  $RT \ln 9 3RT \ln X$
- (b) RT  $\ln 4 3$ RT  $\ln X$
- (c)  $-3RT \ln X$

- 26. Standard Gibb's free energy change for isomerization reaction
  - cis-2-pentene  $\rightleftharpoons$  trans-2-pentene

is -3.67 kJ/mol at 400 K. If more trans-2pentene is added to the reaction vessel, then

- (a) more cis-2-pentene is formed
- (b) equilibrium remains unaffected
- (c) additional trans-2-pentene is formed
- (d) equilibrium is shifted in forward direction
- 27. The dissolution of KCl in water is endothermic yet it dissolves in water spontaneously. Which one of the following best explains this behaviour?
  - (a) Endothermic processes are energetically favoured.
  - (b) The electrostatic bonds between the ions are not too strong.
  - (c) Energy changes have nothing to do with the dissolution processes.
  - (d) The entropy driving force causes the dissolution.
- 28. Hydrogen has an ionisation energy of 1311 kJ mol<sup>-1</sup> and for chlorine it is 1256 kJ mol<sup>-1</sup>. Hydrogen forms H<sup>+</sup> (aq) ions but chlorine does not form Cl<sup>+</sup> (aq) ions because
  - (a) H<sup>+</sup> has lower hydration enthalpy
  - (b) Cl<sup>+</sup> has lower hydration enthalpy
  - (c) Cl has high electron affinity
  - (d) Cl has high electronegativity
- **29.** At 25°C, when 1 mole of MgSO<sub>4</sub> was dissolved in water, the heat evolved was found to be 91.2 kJ. One mole of MgSO<sub>4</sub> . 7H<sub>2</sub>O on dissolution gives a solution of the same composition accompanied by an absorption of 13.8 kJ. The enthalpy of hydration, i.e.,  $\Delta H_h$ for the reaction

 $MgSO_4(s) + 7H_2O(l) \longrightarrow MgSO_4.7H_2O(s)$ 

is:

Toughnut

- (a) -105 kJ/mol (b) -77.4 kJ/mol
- (c) 105 kJ/mol (d) None of these

**30.** Calculate the heat produced (in kJ) when 224 g of CaO is completely converted to CaCO<sub>2</sub> by reaction with CO<sub>2</sub> at 27°C in a container of fixed volume.

Critical Thinking

Given :  $\Delta H_f$  (CaCO<sub>3</sub>,s) = - 1207 kJ/mol;

 $\Delta H_f$  (CaO,s) = -635 kJ/mol,  $\Delta H_f$  (CO<sub>2</sub>,g) =

- [Use  $R = 8.3 \text{ JK}^{-1} \text{ mol}^{-1}$ ] - 394 kJ/mol;
- (a) 702.04 kJ (b) 721.96 kJ
- (c) 712 kJ (d) 721 kJ
- **31.** Given that:
  - (i)  $\Delta_{\rm f} H$  of N<sub>2</sub>O is 82 kJ mol<sup>-1</sup>
  - (ii) Bond energies of  $N \equiv N, N = N, O = O$ and N = O are 946, 418, 498 and 607 kJ mol<sup>-1</sup> respectively,

The resonance energy of N<sub>2</sub>O is : (a) -88kJ (b) -66kJ (c) -62kJ (d) -44kJ

**32.** The difference between the reaction enthalpy change ( $\Delta_r$ H) and reaction internal energy change ( $\Delta_r U$ ) for the reaction:

$$2C_6H_6(l) + 15O_2(g) \longrightarrow 12CO_2(g) \quad 6H_2O(l)$$

- at 300 K is  $(R = 8.314 \text{ J mol}^{-1}\text{K}^{-1})$
- (a)  $0 \text{ J mol}^{-1}$ (b) 2490 J mol<sup>-1</sup> (c)  $-2490 \text{ J mol}^{-1}$ (d) -7482 J mol<sup>-1</sup>
- **33.** From given following equations and  $\Delta H^{\circ}$ values, determine the enthalpy of reaction at 298 K for the reaction :

 $C_2H_4(g) + 6F_2(g) \longrightarrow 2 CF_4(g) \quad 4HF(g)$ 

 $H_2(g) + F_2(g) \longrightarrow 2HF(g); \Delta H_1 = -537 \text{ kJ}$ 

 $C(s) + 2F_2(g) \longrightarrow CF_4(g); \Delta H_2 = -680 \text{ kJ}$ 

$$\begin{array}{rrrr} 2C(s) + 2H_2(g) &\longrightarrow & C_2H_4(g); \Delta H_3 & 52 \text{ kJ} \\ (a) & -1165 & (b) & -2486 \\ (c) & +1165 & (d) & +2486 \end{array}$$

34. Substance  $A_2B(g)$  can undergoes decomposition to form two set of products : Tricky

 $A_{2}B(g) \longrightarrow A_{2}(g) \quad B(g); \Delta H \quad 40 \text{ kJ/mol}$ 

50 kJ/mol If the molar ratio of  $A_2(g)$  to A(g) is 5 : 3 in a set of product gases, then the energy involved in the decomposition of 1 mole of  $A_2B(g)$  is : (a) 48.75 kJ/mol (b) 43.73 kJ/mol

- 36 mL of pure water takes 100 sec to evaporate 35. from a vessel and heater connected to an electric source which delivers 806 watt. The  $\Delta H_{yap}$  of  $H_{2}O$  is :
  - (a) 40.3 kJ/mol (b) 43.2 kJ/mol (c) 4.03 kJ/mol(d) None of these
- 36. For the combustion reaction at 298 K  $2Ag(s) + 1/2O_2(g) \longrightarrow 2Ag_2O(s)$

Which of the following alternatives is correct?



- (a)  $\Delta H = \Delta U$
- (b)  $\Delta H > \Delta U$
- (c)  $\Delta H < \Delta U$
- (d)  $\Delta H$  and  $\Delta U$  has no relation with each other
- A gas undergoes change from state A to state B. In this process, the heat absorbed and work done by the gas is 5 J and 8 J, respectively. Now gas is brought back to A by another process during which 3 J of heat is evolved. In this reverse process of B to A :
  - (a) 10 J of the work will be done by the gas.
  - (b) 6 J of the work will be done by the gas.
  - 10 J of the work will be done by the (c) surrounding on gas.
  - (d) 6 J of the work will be done by the surrounding on gas.
- The amount of energy released when 20 mL of 38. 0.5 M NaOH are mixed with 100 mL of 0.1 M HCl is x kJ. The heat of neutralisation (in kJ mol<sup>-1</sup>) is
  - (a) -100x (b) -50x
  - (c) +100 x(d) +50x
- **39.** Which of the following value of  $\Delta_f H$  represent that the product is least stable ?
  - (a)  $-94.0 \text{ kcal mol}^{-1}$  (b)  $-231.6 \text{ kcal mol}^{-1}$ (c) +21.4 kcal mol<sup>-1</sup> (d) +64.8 kcal mol<sup>-1</sup>
- Enthalpy of neutralisation of HCl with NaOH 40. is x. The heat evolved when 500 mL of 2 N HCl are mixed with 250 mL of 4N NaOH will be. (a)  $500 \times (b) 100 \times (c) \times (c) = 100 \times (c) \times (c$ (d) 10 x
- 41. The enthalpy of neutralisation of NH<sub>4</sub>OH with HCl is -51.46 kJ mol<sup>-1</sup> and the enthalpy of neutralisation of NaOH with HCl is -55.90 kJ mol<sup>-1</sup>. The enthalpy of ionisation of NH<sub>4</sub>OH

- (a)  $-107.36 \text{ kJ mol}^{-1}$  (b)  $-4.44 \text{ kJ mol}^{-1}$
- (c)  $+ 107.36 \text{ kJ mol}^{-1}$  (d)  $+ 4.44 \text{ kJ mol}^{-1}$
- (c) 46.25 kJ/mol (d) None of these

37.

- **42.** The molar heat capacity  $(C_p)$  of  $CD_2O$  is 10 cals at 1000 K. The change in entropy associated with cooling of 32 g of CD<sub>2</sub>O vapour from 1000 K to 100 K at constant pressure will be: (D = deuterium, atomic mass = 2 u)(a)  $23.03 \text{ cal } \text{deg}^{-1}$ (b) -23.03 cal deg<sup>-1</sup> (c)  $2.303 \text{ cal deg}^{-1}$ (d) -2.303 cal deg<sup>-1</sup>
- **43.** The  $(S^{\circ})$  of the following substances are: CH<sub>4</sub> (g) 186.2 JK<sup>-1</sup> mol<sup>-1</sup>  $O_{2}(g) 205.2 \text{ JK}^{-1} \text{ mol}^{-1}$  $CO_{2}$  (g) 213.6 JK<sup>-1</sup> mol<sup>-1</sup>  $H_{2}O(g) 69.9.JK^{-1} mol^{-1}$ The entropy change ( $\Delta S^{\circ}$ ) for the reaction  $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$  is:



- (a)  $-312.5 \text{ J K}^{-1} \text{ mol}^{-1}$
- (b)  $-242.8 \text{ J K}^{-1} \text{ mol}^{-1}$
- (c)  $-108.1 \text{ J K}^{-1} \text{ mol}^{-1}$
- (d)  $-37.6 \text{ J K}^{-1} \text{ mol}^{-1}$
- 44. The enthalpy of the reaction forming PbO according to the following equation is 438 kJ. What heat energy (kJ) is released in formation of 22.3 g PbO(s)?

(Atomic masses : Pb = 207, O = 16.0)

(b)  $Cl_{2}(g)$ 

 $2Pb(s) + O_2(g) \longrightarrow 2PbO(s)$ 

(a) 21.9 (b) 28.7 (c) 14.6 (d) 34.2

- 45. The species which by definition has zero standard molar enthalpy of formation at 298 K is
  - (a)  $Br_{2}(g)$
  - (c)  $H_{2}O(g)$ (d)  $CH_4(g)$
- What is  $\Delta n_{gas}$  for the combustion of 1 mole of 46. benzene, when both the reactants and the products are at 298 K?

(a) 0 (b) 1/2 (c) 3/2(d) -3/2

47. The enthalpy of neutralisation of  $NH_4OH$  and CH<sub>3</sub>COOH is -10.5 kcal mol<sup>-1</sup> and enthalpy of neutralisation of CH<sub>2</sub>COOH with strong base is -12.5 kcal mol<sup>-1</sup>. The enthalpy of ionisation of NH<sub>4</sub>OH will be

> (a)  $3.2 \text{ kcal mol}^{-1}$ (b)  $2.0 \text{ kcal mol}^{-1}$

- (c)  $3.0 \text{ kcal mol}^{-1}$ (d)  $4.0 \text{ kcal mol}^{-1}$
- If for a given substance melting point is  $T_{\rm B}$  and **48**. freezing point is T<sub>A</sub>, then correct variation shown by, graph between entropy change and

temperature is





- 49. What is the free energy change for the conversion of 1 mole of water into steam at 373.2 K. The heat of vaporization ( $\Delta H_{..}$ ) of water of 373.2 K is 9.1 kcal mol<sup>-1</sup>. The entropy change is 25.5 cal/mol deg.
  - (a) -401.6 cal/mol (b) -416.6 cal/mol (c) 516.5 cal/mol (d) -516.5 cal/mol
- A certain reaction is non spontaneous at 298K. 50. The entropy change during the reaction is 121  $JK^{-1}$ . Is the reaction is endothermic or exothermic ? The minimum value of  $\Delta H$  for the reaction is
  - (a) endothermic,  $\Delta H = 36.06 \text{ kJ}$
  - (b) exothermic,  $\Delta H = -36.06 \text{ kJ}$
  - endothermic,  $\Delta H = 60.12 \text{ kJ}$ (c)
  - (d) exothermic,  $\Delta H = -60.12 \text{ kJ}$
- 51. The entropy of a sample of a certain substance increases by 0.836 J K<sup>-1</sup> on adding reversibly 0.3344 J of heat at constant temperature. The temperature of the sample is:
  - (a) 2.5 K (b) 0.3 K
  - (d) 0.4 K (c) 0.016 K
- 52. One mole of an ideal gas is expanded isothermally and reversibly to half of its initial pressure.  $\Delta S$  for the process in J K<sup>-1</sup> mol<sup>-1</sup> is  $[\ell n \ 2 = 0.693 \text{ and } R = 8.314, \text{ J/(mol K)}]$ (a) 6.76 (b) 5.76 (c) 10.76 (d) 8.03
- 53. The enthalpy of hydrogenation of cyclohexene is – 119.5 kJ mol<sup>-1</sup>. If resonance energy of benzene is -150.4 kJ mol<sup>-1</sup>, its enthalpy of hydrogenation would be

(a)  $-208.1 \text{ kg mol}^{-1}$  (b)  $-269.9 \text{ kg mol}^{-1}$ (c)  $-358.5 \text{ kg mol}^{-1}$  (d)  $-508.9 \text{ kg mol}^{-1}$  54. The enthalpies of formation of  $Al_2O_3$  and  $Cr_2O_3$ are -1596 kJ and -1134 kJ respectively.  $\Delta H$  for the reaction  $2Al + Cr_2O_3 \rightarrow 2Cr \quad Al_2O_3$  is

## Critical Thinking

- (a) -2730 kJ (b) -462 kJ
- (c) -1365 kJ (d) +2730 kJ
- **55.** The favourable conditions for a spontaneous reaction are
  - (a)  $T\Delta S$   $\Delta H$ ,  $\Delta H$  ve,  $\Delta S$  ve (b)  $T\Delta S$   $\Delta H$ ,  $\Delta H$  ve,  $\Delta S$  -ve (c)  $T\Delta S$   $\Delta H$ ,  $\Delta H$  -ve,  $\Delta S$  -ve
  - (d) T $\Delta$ S  $\Delta$ H,  $\Delta$ H ve,  $\Delta$ S ve
- 56. The standard Gibb's free energy change,  $\Delta G^{\circ}$  is related to equilibrium constant,  $K_{p}$  as

(a) 
$$K_{P} = -RT \ln \Delta G^{\circ}$$
 (b)  $K_{P} \left[ \frac{e}{RT} \right]^{\Delta G^{\circ}}$   
(c)  $K_{P} = -\frac{\Delta G}{RT}$  (d)  $K_{P} e^{-\Delta G^{\circ}/RT}$ 

- **57.** Which of the following salts should cause maximum cooling when 1 mole of it is dissolved in the same volume of water ?
  - (a) NaCl;  $\Delta H^{\circ} = 5.35 \text{ kJ mol}^{-1}$
  - (b) KNO<sub>3</sub>;  $\Delta H^{\circ} = 53.5 \text{ kJ mol}^{-1}$
  - (c) KOH;  $\Delta H^{\circ} = -56.0 \text{ kJ mol}^{-1}$
  - (d) HBr;  $\Delta H^{\circ} = -83.3 \text{ kJ mol}^{-1}$
- **58.** The molar enthalpies of combustion of isobutane and n-butane are  $-2870 \text{ kJ mol}^{-1}$  and  $-2875 \text{ kJ mol}^{-1}$  respectively at 298 K and 1 atm. Calculate  $\Delta H^{\circ}$  for the conversion of 1 mole of n-butane to 1 mole of isobutane

(a) 
$$-8 \text{ kJ mol}^{-1}$$
 (b)  $+8 \text{ kJ mol}^{-1}$ 

(c) 
$$-5748 \text{ kJ mol}^{-1}$$
 (d)  $+5748 \text{ kJ mol}^{-1}$ 

**59.** The enthalpy of atomisation of  $CH_4$  and  $C_2H_6$  are 360 and 620 kcal mol<sup>-1</sup> respectively. The C - C bond energy is expected to be



(a)	$210 \text{ kcal mol}^{-1}$	(b)	80 kcal mol <sup>-1</sup>						
< >	1001 1 11	(1)	1001 1 1	1					

- (c)  $130 \text{ kcal mol}^{-1}$  (d)  $180 \text{ kcal mol}^{-1}$
- **60.** Boron can undergo the following reactions with the given enthalpy changes :

$$2B(s) + \frac{3}{2}O_2(g) \longrightarrow B_2O_3(s); \Delta H = -1260 \text{ kJ}$$
  

$$2B(s) + 3H_2(g) \longrightarrow B_2H_6(g); \Delta H = 30 \text{ kJ}$$
  
Assume no other reactions are occurring.

If in a container (operating at constant pressure) which is isolated from the surrounding, mixture of  $H_2$  (gas) and  $O_2$  (gas) are passed over excess of B(s), then calculate the molar ratio ( $O_2 : H_2$ ) so that temperature of the container do n o t change :

(a) 15:3 (b) 42:1 (c) 1:42 (d) 1:8461. Combustion of sucrose is used by aerobic organisms for providing energy for the life sustaining processes. If all the capturing of energy from the reaction is done through electrical process (non P–V work) then calculate maximum available energy which can be captured by combustion of 34.2 g of sucrose Given :  $\Delta H_{combustion}$  (sucrose) = -6000 kJ mol<sup>-1</sup>

 $\Delta S_{\text{combustion}} = 180 \text{ J/Kmol}$  and body temperature is 300 K **Toughnut** 

- (a) 600 kJ (b) 594.6 kJ
- (c) 5.4 kJ (d) 605.4 kJ
- 62. The factor of  $\Delta G$  values is important in metallurgy. The  $\Delta G$  values for the following reactions at 800°C are given as :

 $S_2(s) + 2O_2(g) \longrightarrow 2SO_2(g); \Delta G = -544 \text{ kJ}$ 

 $2Zn(s) + S_2(s) \longrightarrow 2ZnS(s); \Delta G = -293 \text{ kJ}$ 

 $2Zn(s) + O_2(g) \longrightarrow 2ZnO(s); \Delta G = -480 \text{ kJ}$ 

Then  $\Delta G$  for the reaction :

will be :

**63**.

 $2ZnS(s) + 3O_2(g) \longrightarrow 2ZnO(s) \quad 2SO_2(g)$ 

#### Tricky

- (a) -357 kJ (b) -731 kJ(c) -773 kJ (d) -229 kJ
- 1 gram equivalent of  $H_2SO_4$  is treated with 112 g of KOH for complete neutralization. Which of the following statements correct?
  - (a) 13.7 kcal of heat is evolved with the formation of 87 g of  $K_2SO_4$ , leaving no KOH.
  - (b) 27.4 kcal of heat is evolved with the formation of 87 g of  $K_2SO_4$ , leaving 4 gram equivalent of KOH.
  - (c) 15.7 kcal of heat is evolved with the formation of 1 gram equivalent of  $K_2SO_4$ , leaving 56 g of KOH.
  - (d) 13.7 kcal of heat is evolved with the formation of 87g of  $K_2SO_4$ , leaving 1 gram equivalent of KOH.

**64.** From the following data  $\Delta H$  of the following reactions

$$C(s) + \frac{1}{2}O_{2}(g) \longrightarrow CO(g);$$
  

$$\Delta H = -110 \text{ kJ and}$$
  

$$C(s) + H_{2}O(g) \longrightarrow CO(g) + H_{2}(g);$$
  

$$\Delta H = 132 \text{ kJ}$$

Calculate the mole composition of the mixture of steam and oxygen on being passes over coke at 1273 K, keeping the temperature constant. (a) 1: 0.6 (b) 0.6: 1 (c) 2: 3 (d) 3: 2

**65.** Gasoline has an enthalpy of combustion 24000 kJ/ gallon. When gasoline burns in an automobile engine, approximately 30% of the energy released is used to produce mechanical work. The remainder is lost as heat transfer to the engine's cooling system. As a start on estimating how much heat transfer is required, calculate what mass of water could be heated from 25°C to 75°C by the combustion of 1.0 gallon of gasoline in an automobile?

Toughnut

(Given : C (H<sub>2</sub>O) =  $4.18 \text{ J/g}^{\circ}$ C) (a) 34.45 kg (b) 80.383 kg

(c) 22 kg (d) 224 kg

- 66. 2 moles of an ideal gas at 27 °C temperature is expanded reversibly from 2 L to 20 L. Find entropy change (R = 2 cal/mol K)
  (a) 92.1 (b) 0 (c) 4 (d) 9.2
- 67. One mole of solid iron was vaporized in an oven at its boiling point of 3433 K and enthalpy of vaporization of iron is  $344.3 \text{ kJ mol}^{-1}$ . The value of entropy vaporization (in J mol<sup>-1</sup>) of iron is (a) 100 (b) 10 (c) -100 (d) 110
- **68.** A reaction is spontaneous at low temperature but non-spontaneous at high temperature. Which of the following is true for the reaction?

### Tricky

- (a)  $\Delta H > 0, \Delta S > 0$  (b)  $\Delta H < 0, \Delta S > 0$
- (c)  $\Delta H > 0$ ,  $\Delta S = 0$  (d)  $\Delta H < 0$ ,  $\Delta S < 0$
- **69.** Which of the following pairs of processes is certain to occur in a spontaneous chemical reaction?
  - (a) Exothermic and increasing disorder
  - (b) Exothermic and decreasing disorder
  - (c) Endothermic and increasing disorder
  - (d) Endothermic and decreasing disorder

- 70. For the reaction  $2C_6H_5CO_2H(s)+15O_2(g) \longrightarrow$ 
  - $\begin{array}{rl} 14 \text{CO}_2(\text{g}) & 6 \text{H}_2 \text{O}(\text{g}) \\ \Delta \text{U}^\circ = -772.7 \text{ kJ mol}^{-1} \text{ at } 298 \text{ K. Calculate } \Delta \text{H}^\circ \\ (\text{a}) & +760.3 \text{ kJ mol}^{-1} & (\text{b}) & -760.3 \text{ kJ mol}^{-1} \\ (\text{c}) & +670.3 \text{ kJ mol}^{-1} & (\text{d}) & -790.3 \text{ kJ mol}^{-1} \end{array}$
- **71.**  $\Delta H_{f}^{o}$  of water is 285.8 kJ mol<sup>-1</sup>. If enthalpy of neutralisation of monoacidic strong base is

 $-57.3 \text{ kJmol}^{-1}$ .  $\Delta H_f^o$  of  $OH^-$  ion will be



- (a)  $-114.25 \text{ kJ mol}^{-1}$  (b)  $114.25 \text{ kJ mol}^{-1}$ (c)  $228.5 \text{ kJ mol}^{-1}$  (d)  $-228.5 \text{ kJ mol}^{-1}$
- 72. The heat of atomization of  $PH_3(g)$  is 228 kcal mol<sup>-1</sup> and that of  $P_2H_4(g)$  is 335 kcal mol<sup>-1</sup>. The energy of the P–P bond is
  - (a)  $102 \text{ kcal mol}^{-1}$  (b)  $51 \text{ kcal mol}^{-1}$
  - (c)  $26 \text{ kcal mol}^{-1}$  (d)  $204 \text{ kcal mol}^{-1}$
- **73.** For the reaction

 $CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g), \Delta H, \text{ and } \Delta S$ 

are -283 kJ and -87 JK<sup>-1</sup>, respectively. It was intended to carry out this reaction at 1000, 1500, 3000 and 3500 K. At which of these temperatures would this reaction be thermodynamically spontaneous?

- (a) 1500 and 3500 K
- (b) 3000 and 3500 K
- (c) 1000, 1500 and 3000 K
- (d) 1500, 3000 and 3500 K
- 74. The molar entropies of HI (g) and I (g) at 298 K are 206.5, 114.6, and 180.7 J mol<sup>-1</sup> K<sup>-1</sup> respectively. Using the  $\Delta G^{\circ}$  given Below, calculate the bond energy of HI.

HI g 
$$\longrightarrow$$
 H g I g ;  $\Delta G^{\circ} = 271.8 \text{ kJ}$   
(a) 282.4 kJ mol<sup>-1</sup> (b) 298.3 kJ mol<sup>-1</sup>  
(c) 290.1 kJ mol<sup>-1</sup> (d) 315.4 kJ mol<sup>-1</sup>

**75.** What is the equilibrium constant if ATP hydrolysis by water produce standard free energy of -50 kJ/mol under normal body conditions ?

Tricky

(a)	2.66	$\times 10^8$	(b)	5.81	$\times 10^{8}$
(c)	1.18	$\times 10^{7}$	(d)	1.98	$\times 10^{8}$

76. 0.5 mole each of two ideal gases

A $\left(C_{v,m} - \frac{5}{2}R\right)$  and B ( $C_{v,m} = 3R$ ) are taken in a container and expanded reversibly and adiabatically, during this process temperature of gaseous mixture decreased from 350 K to 250 K. Find  $\Delta$ H (in cal/mol) for the process:

Toughnut

- (a) -100 R (b) -137.5 R(c) -375 R (d) None of these
- 77. What is the free energy change '∆G' when 1.0 mole of water at 100 °C and 1 atm pressure is converted into steam at 100 °C and 1 atm. pressure
  - (a) 540 cal (b) -9800 ca
  - (c) 9800 cal (d) 0 cal
- **78.** 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
  - (a)  $(\Delta S)_{VF} > 0, (\Delta G)_{TP} < 0$
  - (b)  $(\Delta S)_{V,E} = 0, (\Delta G)_{T,P} = 0$
  - (c)  $(\Delta S)_{V,E} = 0, (\Delta G)_{T,P} > 0$

(d) 
$$(\Delta S)_{VF} < 0, (\Delta G)_{TP} < 0$$

79. For the auto-ionization of water at 25°C,

H<sub>2</sub>O 1  $\implies$  H<sup>+</sup> aq OH<sup>-</sup> aq equilibrium constant is 10<sup>-14</sup>. What is ΔG° for the process? (a)  $\approx 8 \times 10^4$  J mol<sup>-1</sup> (b)  $\approx 3.5 \times 10^4$  J mol<sup>-1</sup>

- (c)  $\simeq 2 \times 10^4 \text{ J} \text{ mol}^{-1} \text{ (d)}$  None of these
- **80.** For which of the following process,  $\Delta S$  is negative?
  - (a)  $H_2(g) \longrightarrow 2H(g)$
  - (b)  $2SO_3(g) \longrightarrow 2SO_2(g) + O_2(g)$
  - (c)  $N_2(4l) \xrightarrow{\text{compressed}} N_2(2l)$

(d) C(diamond)  $\longrightarrow$  C(graphite)

81. What is the entropy change (in JK<sup>-1</sup> mol<sup>-1</sup>) when one mole of ice is converted into water at 0° C? (The enthalpy change for the conversion of ice to liquid water is 6.0 kJ mol<sup>-1</sup> at 0 °C) (a) 21.98 (b) 20.13 (c) 2.013 (d) 2.198

- 82. Temperature of 5 moles of a gas is decreased by 2K at constant pressure. Indicate the correct statementTricky
  - (a) Work done by gas is = 5 R
  - (b) Work done over the gas is = 10 R
  - (c) Work done by the gas = 10 R
  - (d) Work done = 0
- **83.** An ideal gas occuping a volume of 2dm<sup>3</sup> and a pressure of 5 bar undergoes isothermal and irreversible expansion against external pressure of 1 bar. The final volume of the system and the work involved in the process is
  - (a)  $10 \text{ dm}^3$ , 1000 J (b)  $8 \text{ dm}^3$ , -800 J
  - (c)  $10 \text{ dm}^3$ , -800 J (d)  $10 \text{ dm}^3$ , -1000 J
- **84.** 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:
  - $(R = 8.314 \text{ J/mol K}) (\ln 7.5 = 2.01)$
  - (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
- 85. The heats of neutralisation of CH<sub>3</sub>COOH, HCOOH, HCN and H<sub>2</sub>S are 13.2, 13.4, 2.9 and 3.8 kcal per equivalent respectively. Arrange the acids in increasing order of strength
  - (a)  $HCOOH > CH_3COOH > H_2S > HCN$
  - (b)  $CH_3COOH > HCOOH > H_2S > HCN$
  - (c)  $H_2S > HCOOH > CH_3COOH > HCN$
  - (d)  $HCOOH > H_2S > CH_3COOH > HCN$
- 86. The enthalpy of neutralisation of a weak acid in 1 M solution with a strong base is 56.1 kcal mol<sup>-1</sup>. If the enthalpy of ionisation of acid is 1.5 kcal mol<sup>-1</sup> and enthalpy of neutralisation of the strong acid with a strong base is 57.3 kJ eq<sup>-1</sup>. What is the % ionisation of the weak acid in molar solution (assume the acid is



**87.** The free energy change for the following reactions are given below,

$$C_2H_2(g) + \frac{5}{2}O_2(g) \rightarrow$$
  
2CO<sub>2</sub>(g) + H<sub>2</sub>O(l); ΔG −1234kJ

$$C(s) + O_2(g) \rightarrow CO_2(g); \Delta G = -394 kJ$$

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l); \Delta G = -237 kJ$$

What is the standard free energy change for the reaction  $H_2(g) + 2C(s) \longrightarrow C_2H_2(g)$ (a) -209 kJ (b) -2259 kJ

(c) 
$$+ 2259 \text{ kJ}$$
 (d)  $209 \text{ kJ}$ 

88. For the reaction  

$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) \quad 4H_2O(l)$$

at constant temperature,  $\Delta H - \Delta E$  is

- (a) -RT (b) +RT (c) -3 RT (d) +3 RT
  89. Among the following, the intensive properties are
  - (i) molar conductivity
  - (ii) electromotive force
  - (iii) resistance
  - (iv) heat capacity

(c) (i) and (iv) (d) (i) only

**90.** What is the normal boiling point of mercury?  
Given : 
$$\Delta H_f$$
 (Hg, l) = 0; S°(Hg, l) = 77.4 J/K-  
mol  $\Delta H_f$  (Hg, g) = 60.8 kJ/mol; S°(Hg, g) =  
174.4 J/K-mol

- (c) 636.8 K (d) None of these
- **91.** When 1 mole of oxalic acid is treated with excess of NaOH in dilute aqueous solution, 106 kJ of heat is liberated. Predict the enthalpy of

ionisation of the acid **Critical** 

Thinking

(a)	4.3 kJ mol <sup>-1</sup>	(b)	- 4.3 kJ mol <sup>-1</sup>
(c)	8.6 kJ mol <sup>-1</sup>	(d)	– 8.6 kJ mol <sup>-1</sup>

- **92.** The lattice energy of solid NaCl is 180 kcal  $mol^{-1}$  and enthalpy of solution is 1 kcal  $mol^{-1}$ . If the hydration energies of Na and Cl<sup>-</sup> ions are in the ratio 3 : 2, what is the enthalpy of hydration of sodium ion ?
  - (a)  $-107.4 \text{ kcal mol}^{-1}$  (b)  $107.4 \text{ kcal mol}^{-1}$
  - (c) 71.6 kcal mol<sup>-1</sup> (d) -71.6 kcal mol<sup>-1</sup>

**93.** Standard enthalpy of combustion of  $CH_4$  is  $-890 \text{ kJ} \text{ mol}^{-1}$  and standard enthalpy of vaporisation of water is 40.5 kJ mol<sup>-1</sup>. The enthalpy change of the reaction

$$CH_4 (g) + 2 O_2 (g) \longrightarrow CO_2 (g) + H_2 O (g)$$
  
(a) - 809.5 kJ mol<sup>-1</sup> (b) - 890 kJ mol<sup>-1</sup>  
(c) 809 kJ mol<sup>-1</sup> (d) - 971 kJ mol<sup>-1</sup>

94. Standard enthalpy and standard entropy changes for the oxidation of ammonia at 298 K are – 382.64 kJ mol<sup>-1</sup> and – 45.6 JK<sup>-1</sup> mol<sup>-1</sup>, respectively. Standard Gibb's energy change for the same reaction at 298 K is

(a) 
$$-22.1 \text{ kJ mol}^{-1}$$
 (b)  $-339.3 \text{ kJ mol}^{-1}$ 

(c) 
$$-439.3 \text{ kJ mol}^{-1}$$
 (d)  $-523.2 \text{ kJ mol}^{-1}$ 

- **95.**  $\Delta G$  in  $Ag_2O \rightarrow 2 Ag + 1/2O_2$  at a certain temperature is  $-10 \text{ kJ mol}^{-1}$ . Pick the correct statement
  - (a)  $Ag_2O$  decomposes to Ag and  $O_2$
  - (b) Ag and  $O_2$  combines to form Ag<sub>2</sub>O
  - (c) Reaction is in equilibrium
  - (d) Reaction does not take place

96. For complete combustion of ethanol,

 $C_2H_5OH \ 1 + 3O_2 \ g \longrightarrow 2CO_2 \ g \ 3H_2O \ 1$ , the amount of heat produced as measured in bomb calorimeter, is 1364.47 kJ mol<sup>-1</sup> at 25°C. Assuming ideality the enthalpy of combustion,

 $\Delta_{c}$ H, for the reaction will be: **Toughnut** 

 $(R = 8.314 \text{ kJ mol}^{-1})$ 

- (a)  $-1366.95 \text{ kJ mol}^{-1}$
- (b)  $-1361.95 \text{ kJ mol}^{-1}$
- (c)  $-1460.95 \text{ kJ mol}^{-1}$
- (d)  $-1350.50 \text{ kJ mol}^{-1}$

97. Diborane is a potential rocket fuel which  
undergoes combustion according to the equation  
$$B_2H_6(g)+3O_2(s)\longrightarrow B_2O_3(s) \quad 3H_2O(g)$$
  
Calculate the enthalpy change for the  
combustion of diborane. Given Critical  
Thinking

(i) 
$$2B(s) + \frac{3}{2}O_2(g) \longrightarrow B_2O_3(s);$$
  
 $\Delta H = -1273 \text{ kJ per mol}$ 

(ii) 
$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l);$$

 $\Delta H = -286 \text{ kJ per mol}$ 

(iii)  $H_2O(l) \longrightarrow H_2O(g);$ 

(iv) 
$$2B(s) + 3H_2(g) \longrightarrow B_2H_6(g);$$

- $\Delta H = 36 \text{ kJ per mol}$
- (a) +2035 kJ per mol (b) -2035 kJ per mol
- (c) +2167 kJ per mol(d) -2167 kJ per mol
- 98. What is the amount of heat (in Joules) absorbed by 18 g of water initially at room temperature heated to 100°C? If 10 g of Cu is added to this water, than decrease in temperature (in Kelvin) of water was found to be? C (p,m) for water 75.32 J/mol K ; C (p,m) for Cu = 24.47 J/mol K.

- (a) 5649, 369 (b) 5544, 324 (c) 5278, 342
  - (d) 3425, 425

99. How many molecules of ATP, undergo hydrolysis to raise the temperature of 180 kg of water which was originally at room temperature by 1°C? C{P,m} water = 75.32 J/mol/K,  $\Delta$ H{P} for ATP hydrolysis = 7 kcal/mol



**100.** Consider the  $\Delta G_f$  and  $\Delta H_f$  (kJ/mol) for the following oxides. Which oxide can be most easily decomposed to form the metal and oxygen gas?

(a)  $1.5 \times 10^{25}$ 

(c)  $3.4 \times 10^{25}$ 

- (a) ZnO ( $\Delta G^{\circ} = -318.4, \Delta H^{\circ} = -348.3$ )
- (b)  $Cu_2O (\Delta G^\circ = -146.0, \Delta H^\circ = -168.8)$
- (c) HgO ( $\Delta G^{\circ} = -58.5$ ,  $\Delta H^{\circ} = -90.8$ )
- (d) PbO ( $\Delta G^{\circ} = -187.9$ ,  $\Delta H^{\circ} = -217.3$ )



## **Answer KEY**

1	(c)	11	(c)	21	(a)	31	(a)	41	(d)	51	(d)	61	(d)	71	(d)	81	(a)	91	(c)
2	(b)	12	(c)	22	(c)	32	(d)	42	(b)	52	(b)	62	(b)	72	(b)	82	(b)	92	(a)
3	(c)	13	(b)	23	(c)	33	(b)	43	(b)	53	(a)	63	(d)	73	(c)	83	(c)	93	(a)
4	(b)	14	(b)	24	(c)	34	(b)	44	(a)	54	(b)	64	(a)	74	(b)	84	(a)	94	(b)
5	(c)	15	(c)	25	(d)	35	(a)	45	(b)	55	(a)	65	(b)	75	(a)	85	(a)	95	(a)
6	(b)	16	(b)	26	(a)	36	(c)	46	(d)	56	(d)	66	(d)	76	(c)	86	(b)	96	(a)
7	(b)	17	(c)	27	(d)	37	(d)	47	(b)	57	(b)	67	(a)	77	(d)	87	(d)	97	(b)
8	(c)	18	(d)	28	(b)	38	(a)	48	(a)	58	(a)	68	(d)	78	(a)	88	(c)	98	(a)
9	(c)	19	(b)	29	(a)	39	(d)	49	(b)	59	(b)	69	(a)	79	(a)	89	(a)	99	(a)
10	(c)	20	(a)	30	(a)	40	(c)	50	(a)	60	(d)	70	(b)	80	(c)	90	(b)	100	(c)



# **Hints & Solutions**

13.



- 1. (c) Internal energy and molar enthalpy are state functions. Work (reversible or irreversible) is a path function.
- 2. (b)  $\Delta H \Delta E P \Delta V$ , for solid and liquid,  $\Delta V = 0$ or  $\Delta H = \Delta E + \Delta n RT$ , for solids and liquids  $\Delta n = 0$
- 3. (c)  $\Delta H = H_2 H_1$  (E<sub>2</sub> P<sub>2</sub>V<sub>2</sub>) (E<sub>1</sub> P<sub>1</sub>V<sub>1</sub>) = (E<sub>2</sub> - E<sub>1</sub>) + (P<sub>2</sub>V<sub>2</sub> - P<sub>1</sub>V<sub>1</sub>) 30 (4×5-2×3) 44L atm

4. **(b)** 
$$\frac{1}{2}$$
 N<sub>2</sub> +  $\frac{3}{2}$  H<sub>2</sub>  $\longrightarrow$  NH<sub>3</sub>  
 $\frac{1}{2}$ x<sub>1</sub> +  $\frac{3}{2}$ x<sub>2</sub> - 3x<sub>3</sub>

5. (c) Let x mole of KOH be neutralized by the strong acid HA. Then, moles neutralized by HB = 1 - xHence,  $-13.7 \times x + (-12.7) \times (1-x) = -13.5$  $\Rightarrow x = 0.8; \frac{x}{1-x} \frac{0.8}{0.2} \frac{4}{1} 4 : 1$ 6. (b) T  $\frac{1}{\sqrt{V}}$ ; TV<sup>1/2</sup> constant

For adiabatic process,

 $TV^{\gamma-1}$  constant

$$\therefore \gamma - 1 = \frac{1}{2}, \gamma = \frac{3}{2}$$

7. (b) For a finite change  $\Delta E = C_v \Delta T$ . For an isothermal process  $\Delta T = 0$ . Hence  $\Delta E = 0$ 

8. (c)  $3H_2O(l) \rightarrow 3H_2O(g)$ ;

$$\Delta n = 3, \Delta E = \Delta H - \Delta n R T$$

$$=30-3\times\frac{2}{1000}\times500$$
 27 kcal

- 9. (c) Neutralisation of weak acid with strong base hence < x. Extra heat is utilised to effect the ionisation of weak acid.</li>
- **10.** (c) AB : Isobaric expansion

BC : Isothermal expansion CD : Isochoric DA : Isothermal compression

....

11. (c) 
$$H_2O(1, 323 \text{ K}) \xrightarrow{\Delta U_1} H_2O(1, 373 \text{ K})$$
  
 $\downarrow^{\Delta U_2}$   
 $H_2O(g, 323 \text{ K}) \xleftarrow{\Delta U_3} H_2O(1, 373 \text{ K})$   
 $C_{v,m}(H_2O, g) = 33.314 - 8.314$   
 $= 25 \text{ J/K mol}$   
 $\Delta U_2 = \Delta H_2 - \Delta n_g \text{RT} = 37.6$   
 $\Delta U_{\text{total}} = \Delta u_1 + \Delta u_2 + \Delta u_3$   
 $= C_{v,m}(1)\Delta T + \Delta V_{vap} + C_{v,m}(g)\Delta T$   
 $\frac{75 \times 50}{1000} 37.6 \frac{25 \times 50}{1000}$   
 $= 42.6 \text{ kJ/mol}$   
12. (c) For isothermal reversible expansion.

(c) For isomerimal reversion expansion:  

$$w = -nRT \ln \frac{V_2}{V_1}$$
(b) In CH<sub>4</sub>, 4 × BE<sub>(C-H)</sub> = 360 kJ/mol  

$$\therefore BE_{(C-H)} = 90 kJ/mol$$
In C<sub>2</sub>H<sub>6</sub>, BE<sub>(C-C)</sub>+6 × BE<sub>(C-H)</sub>=620 kJ/mol  

$$\therefore BE_{(C-C)} = 80 kJ/mol$$

$$\therefore BE_{(C-C)} = \frac{80 \times 10^3}{6.023 \times 10^{23}} J/molecule$$
Now, E  $\frac{hc}{\lambda}$   

$$\therefore \lambda = \frac{6.626 \times 10^{-34} \times 3 \times 10^8 \times 6.023 \times 10^{23}}{80 \times 10^3}$$

$$\therefore \lambda = 1.49 \times 10^3 \text{ nm}$$

- 14. (b) For combustion reaction,  $\Delta H$  is negative,  $\Delta n \quad 16 \quad 18 \quad -25 \quad 2 \quad 7$ , so  $\Delta S$  is + ve, reaction is spontaneous, hence  $\Delta G$  is -ve.
- **15.** (c) For monoatomic gas  $C_v = \frac{3}{2} R C_p = \frac{5}{2} R$ At constant volume,  $\Delta U = q_v = nC_{v,m} \Delta T$ At constant pressure,  $\Delta H = q_p = nC_{p,m} \Delta T$
- **16.** (b) Given  $\frac{1}{2}N_2 = \frac{3}{2}H_2 \implies NH_3;$

16. (b) Given 
$$\frac{1}{2}N_2$$
  $\frac{3}{2}H_2 \Longrightarrow NH_3$ ;  
 $\Delta H_f = -46.0 \text{ kJ/mol}$   
 $H + H \Longrightarrow H_2$ ;  $\Delta H_f = -436 \text{ kJ/mol}$   
 $N + N \Longrightarrow N_2$ ;  $\Delta H_f = -712 \text{ kJ/mol}$   
 $\Delta H_f NH_3 = \frac{1}{2}\Delta H_{N-N} + \frac{3}{2}\Delta H_{H-H} - \Delta H_{N-F}$   
 $-46 = \frac{1}{2} -712 + \frac{3}{2} -436 - \Delta H_{N-F}$   
On calculation  
 $\Delta H_{N-F} = -964 \text{ kJ/mol}$   
17. (c) To calculate average enthalpy of C - H  
bond in methane following informations  
are needed  
(i) dissociation energy of H<sub>2</sub> i.e.  
 $\frac{1}{2}H_2(g) \longrightarrow H(g)$ ;  $\Delta H$  x suppose  
(ii) Sublimation energy of C(graphite) to C(g)  
 $C(graphite) \longrightarrow C(g)$ ;  $\Delta H$  y Suppose  
Given  
 $C(graphite) + 2H_2(g) \longrightarrow CH_4(g)$ ;  
 $\Delta H -75 \text{ kJ mol}^{-1}$ 

- 18. (d) Given  $\Delta H = 41 \text{ kJ mol}^{-1} = 41000 \text{ J mol}^{-1}$   $T = 100^{\circ}C = 273 + 100 = 373 \text{ K}$   $\Delta n = 1$   $\Delta U = \Delta H - \Delta nRT = 41000 - (1 \times 8.314 \times 373)$  $= 37898.88 \text{ J mol}^{-1} \simeq 37.9 \text{ kJmol}^{-1}$
- **19.** (b)  $\Delta U = q + w$ =10 × 1000 - 2 × (20) × 101.3 = 5948 J
- 20. (a) Gaseous ions, when dissolved in water, get hydrated and heat is evolved (heat of hydration).

 $Cl^{-}(g) + aq \rightarrow Cl^{-}(aq)$  is such reaction.

- 21. (a) I II, gives,  $2AI + Fe_2O_3 \rightarrow 2Fe \quad Al_2O_3$ we have  $-400 - (-200) \quad -200$ ; For one mole of iron the value is -100 cal
- 22. (c) Given

$$\mathrm{H}_{2}(\mathbf{g}) + \frac{1}{2} \mathrm{O}_{2}(\mathbf{g}) \longrightarrow \mathrm{H}_{2}\mathrm{O}(l) ;$$

- $\Delta H^{\circ} = -285.9 \text{ kJ mol}^{-1} \dots (1)$   $H_{2}(g) + \frac{1}{2}O_{2}(g) \longrightarrow H_{2}O(g);$   $\Delta H^{\circ} = -241.8 \text{ kJ mol}^{-1} \dots (2)$ We have to calculate  $H_{2}O(l) \longrightarrow H_{2}O(g); \Delta H^{\circ} = ?$ On substracting eqn. (2) from eqn. (1) we get  $H_{2}O(l) \longrightarrow H_{2}O(g);$   $\Delta H^{\circ} = -241.8 (-285.9)$   $= 44.1 \text{ kJ mol}^{-1}$ 23. (c) Applying Hess's Law
  - $\Delta_{f}H \quad \Delta_{sub}H + \frac{1}{2}\Delta_{diss}H \quad I.E. \quad E.A \quad \Delta_{lattice}H$ -617 161 520 77 E.A. (-1047) E.A. = -617 + 289 = -328 kJ mol<sup>-1</sup>  $\therefore$  electron affinity of fluorine = -328 kJ mol<sup>-1</sup>
- 24. (c) At constant volume,  $\frac{P_1}{T_1} = \frac{P_2}{T_2}$   $\Rightarrow P_2 = 1 \times \frac{300}{200} = \frac{3}{2}$ and  $V_1 = 24.63$  L for single phase  $\therefore dG = Vdp - SdT$   $\Delta G = V\Delta P - \int 2 = 10^{-2}$ T dT  $= 1231.5 - 200 - \left(\frac{10^{-2} \times 50,000}{2}\right)$ = 781.5 J
- 25. (d)  $\Delta G^{\circ} = -RT \ln K_{p}; K_{p} = (2x)^{2} X = 4x^{3}$   $\Delta G^{\circ} = -RT \ln (4X^{3})$  $\Delta G^{\circ} = -RT \ln 4 - 3RT \ln X$
- 26. (a) If more trans-2-pentene is added, then its concentration in right hand side will increase. But in order to maintain the K constant, concentration of cis-2-pentene will also increase. Therefore more cis-2-pentene will be formed.

27 (d)

28. (b) Hydration energy of Cl<sup>+</sup> is very less than H<sup>+</sup>, hence it doesn't form Cl<sup>+</sup> (aq) ion.

35. (a) 1 watt = 1 J/sec  
Total heat supplied for 36 mL H<sub>2</sub>O  
= 806 × 100  
= 80600 J  

$$\Delta H_{vap} = \frac{80600}{36} \times 18$$
  
= 40300 J or 40.3 kJ/mol  
36. (c)  $\Delta H = \Delta U + \Delta nRT$   
 $\Delta n = n_p - n_R$   
Now,  $\Delta n = 2 - \frac{5}{2} = -\frac{1}{2}$   
 $\therefore \Delta H = \Delta U - \frac{1}{2}RT$   
Thus,  $\Delta U = \Delta H$   $\frac{1}{2}RT$   
 $\therefore \Delta U > \Delta H$   
37. (d)  $A \xrightarrow{q = 5, w - 8J} A \longrightarrow B$   
 $\Delta U_{AB} = q w = 5 (-8) = -3$   
 $q = -3, \Delta U_{BA} = 3$   
 $\Delta U_{BA} = q w$   
 $\Rightarrow 3 = -3 + w \Rightarrow w = 6 J$  (work done on the system).  
38. (a) In question 0.01 gev of NaOH is being neutralised by 0.01 gev of HCl and value is x kJ, for 1 gev the value is -100x (exothermic process).  
39. (d) As  $\Delta_r H$  increases stability decreases.

- 40. (c) Enthalpy of neutralisation of HCl with
  - NaOH is x. In question gev of HCl

$$\left(\frac{500 \times 2}{1000} \quad \text{1gev}\right)$$
 and NaOH  $\left(\frac{250 \times 4}{1000} \quad \text{1gev}\right)$   
hence the value x.

**41.** (d) 
$$\underset{\text{Strong acid}}{\text{HCl}} \xrightarrow{H} \underset{\text{(Complete ionisation)}}{\text{Cl}^{-}} \qquad \dots(i)$$

$$NH_4OH \xrightarrow{Weak base} NH_4 OH^-$$
$$\Delta H = x \text{ kJ mol}^{-1} \dots (ii)$$

$$H + OH^{-} \longrightarrow H_2O$$
  
$$\Delta H = -55.90 \text{ kJ mol}^{-1} \qquad \dots (iii)$$

(from neutralisation of strong acid and strong base)

From equation (i), (ii) and (iii)  $NH_4OH + HCl \longrightarrow NH_4 \quad Cl^- \quad H_2O$  $\Delta H = -51.46 \text{ kJ mol}^{-1}$ x + (-55.90) = -51.46*.*.. x = -51.46 + 55.90 $= 4.44 \text{ kJ mol}^{-1}$ : Enthalpy of ionisation of NH<sub>4</sub>OH is  $\Rightarrow$  4.44 kJ mol<sup>-1</sup> **42.** (b) Given,  $C_p = 10$  cals at 1000 K  $T_1 = 1000$  K.  $T_2 = 100$  K m = 32 g $\Delta S = ?$ at constant pressure  $\Delta S \quad C_p \ln \frac{T_2}{T_1}$  $= 2.303 \times C_p \log \frac{T_2}{T_1}$ 

$$= 2.303 \times 10 \log \frac{100}{1000}$$
$$= -23.03 \text{ cal deg}^{-1}$$

**43.** (b) 
$$\Delta S = S_{CO_2} = 2 \times S^{\circ}_{H_2O} - S_{CH_4} = 2 \times S_{O_2}$$
  
= (213.6 + 2 × 69.9) - (186.2 + 2 × 205.2)  
= -242.8 J K<sup>-1</sup> mol<sup>-1</sup>.

**44.** (a) 
$$Q = \frac{1}{2} 438 \times \frac{22.3}{223}$$
 21.9

45. (b) The species in its elemental form has zero standard molar enthalpy of formation at 298 K. At 298K, Cl<sub>2</sub> is gas while Br<sub>2</sub> is liquid.

**46.** (d) 
$$C_6H_6(l) + \frac{15}{2}O_2(g) \rightarrow$$

$$6CO_2$$
 (g)  $3H_2O$  (l)

kJ

$$\Delta n = 6 - 15/2 = -3/2$$
47. (b)  $\Delta_{neu}H$  for strong base and strong acid  

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

$$\Delta H_{\text{ion}} (CH_3COOH)$$

$$= -12.5 - (-13.7) = 1.2 \text{ kcal mol}^{-1}$$

$$\Delta H_{\text{ion}} (NH_4OH)$$

 $= -10.5 - (-13.7) - \Delta H_{ion} (CH_3COOH)$ = 13.7 - 10.5 - 1.2 = 2 kcalmol<sup>-1</sup>

**48.** (a) For a pure substance T<sub>A</sub> and T<sub>B</sub> represent the same temperature. Hence A is a correct choice.

**49.** (b) 
$$\Delta G = \Delta H - T\Delta S$$
  
 $\therefore \Delta G = 9100 - 373.2 \times 25.5 = -416.6 \text{ cal} \text{mol}^{-1}$ 

- 50. (a) For non spontaneous reaction
  - $\Delta G = + ve$   $\Delta G = \Delta H - T \Delta S \text{ and}$   $\Delta S = 121 \text{ JK}^{-1}$ For  $\Delta G = + ve$  $\Delta H \text{ has to be positive. Hence fit$

 $\Delta H$  has to be positive. Hence the reaction is endothermic.

The minimum value of  $\Delta H$  can be obtained by putting  $\Delta G = 0$  $\Delta H = T\Delta S = 298 \times 121 \text{ J}$ 

$$= 36.06 \text{ kJ}$$

**51.** (d) 
$$\Delta S = \frac{\Delta H}{T}$$
;  $T = \frac{\Delta H}{\Delta S} = \frac{0.3344}{0.836} = 0.4$ K

**52.** (b) For isothermal process  $(\Delta T = 0)$ 

$$\Delta S \quad R \, \ell n \, \frac{P_1}{P_2} = 8.314 \, \ell n \, 2$$
  
= 8.314 × 0.693 = 5.76  
53. (a) + H<sub>2</sub> ;  $\Delta H = -119.5 \, \text{kJ}$   
+ 3H<sub>2</sub> ;  $\Delta H = 3(-119.5)$ 

= -358.5 kJ

The resonance energy provides extra stability to the benzene molecule so it has to be overcome for hydrogenation to take place. So

 $\Delta H = -358.5 - (-150.4) = -208.1 \text{ kJ}$ 

54. (b) 
$$2Al + \frac{3}{2}O_2 \rightarrow Al_2O_3$$
,  $\Delta H = -1596 \text{ kJ}$   
.....(i)  
 $2Cr + \frac{3}{2}O_2 \rightarrow Cr_2O_3$ ,  $\Delta H = -1134 \text{ kJ}$   
....(ii)  
 $By (i) - (ii)$   
 $2Al + Cr_2O_3 \rightarrow 2Cr + Al_2O_3$ ,  $\Delta H = -462 \text{ kJ}$ .

- 55. (a)  $\Delta G = \Delta H T \Delta S$ ,  $\Delta H$  is +ve,  $\Delta S$  is + ve; T $\Delta S > \Delta H$ for spontaneous process. It will make  $\Delta G$ , –ve 56. (d)  $\Delta G = -RT \ln K_p \text{ or } K_p = e^{-\Delta G/RT}$
- 57. (b) Dissolution of  $KNO_3$  is endothermic, hence heat is absorbed and cooling is observed.
- Isobutane + oxygen  $\rightarrow$  CO<sub>2</sub> H<sub>2</sub>O 58. (a)

 $\Delta H = -2870 \text{ kJ mol}^{-1} \dots (i)$ 

n-butane + oxygen  $\rightarrow CO_2$  H<sub>2</sub>O

$$\Delta H = -2878 \text{ kJ mol}^{-1} \dots (ii)$$

- (ii) (i); n-butane Isobutane,  $\Delta H = (-2878 + 2870)$  $= -8 \text{ kJ mol}^{-1}$ .
- **59.** (b) Atomisation of methane  $CH_4(g) \longrightarrow C(g) + 4H(g);$  $\Delta H = 360 \text{ kcal}$   $\therefore \text{ C} - \text{H bond energy} = \frac{360}{4}$  $= 90 \text{ kcal mol}^{-1}$  $C_2H_6(g) \longrightarrow 2C(g) + 6H(g);$  $\Delta H = 620 \text{ kcal}$ or  $H_{C-C} + 6 H_{C-H} = 620$  $H_{C-C} = 620 - 6 H_{C-H}$ *:*..  $= 620 - 6 \times 90 = 80 \text{ kcal mol}^{-1}$ 60. (d) No. of moles of  $O_2$  required to supplied 30 kJ heat to second reaction  $=\frac{30}{1260}\times\frac{3}{2}$   $\frac{1}{28}$  $n_{O_2}$  :  $n_{H_2} = \frac{1}{28}$  : 3 or 1 : 84

61. (d) No. of moles of sucrose 
$$\frac{34.2}{342}$$
 0.1  
 $-(\Delta G)_{T,P} = \text{useful work done by the system}$   
 $-\Delta G = -\Delta H + T\Delta S$   
 $= + (6000 \times 0.1) + \frac{180 \times 0.1 \times 300}{1000}$   
 $= 605.4 \text{ kJ}$   
62. (b) For the reaction  
 $2 \text{ ZnS} \rightarrow 2 \text{ Zn} + \text{S}_2$ ;  $\Delta G_1^{\circ} = 293 \text{ kJ}$   
......(i)  
 $2 \text{ Zn} + \text{O}_2 \rightarrow 2 \text{ ZnO}$ ;  $\Delta G_2^{\circ} = -480 \text{ kJ}$   
......(ii)  
 $S_2 + 2 \text{ O}_2 \rightarrow 2 \text{ SO}_2$ ;  $\Delta G_3^{\circ} = -544 \text{ kJ}$   
......(iii)  
 $\Delta G^{\circ}$  for the reaction  
 $2 \text{ ZnS} + 3 \text{ O}_2 \rightarrow 2 \text{ ZnO} + 2 \text{ SO}_2$   
can be obtained by adding eqn. (i), (ii) and  
(iii)  
 $\Rightarrow \Delta G^{\circ} = 293 - 480 - 544 = -731 \text{ kJ}$   
63. (d)  $H_2 \text{SO}_4 \ 2\text{KOH} \rightarrow \text{K}_2 \text{SO}_4 \ 2\text{H}_2 \text{O}$   
 $\frac{98}{49} \ \frac{112}{56} \ \frac{174}{87} \ \frac{2 \text{ mole}}{1 \text{ mole}}$ 

13.7 kcal is the heat evolved when 1 gev of strong acid is neutralised by 1 gev of strong base.

2 mole

64. (a) The first reaction is exothermic and the second reaction is endothermic. If on passing the mixture of O<sub>2</sub> and H<sub>2</sub>O (steam) over coke while keeping the temperature constant  $\Delta H$  of both the reactions must be same.

Moles of O<sub>2</sub> needed to evolve 132 kJ

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

Hence steam :  $O_2$  ratio must be 1 : 0.6

- **65.** (b)  $q = m \times c \times \Delta T$ ,  $m = q/(c \times \Delta T)$  $=(24 \times 10^{6} \times 0.7)/(4.18 \times 50)$ = 80383 g or 80.383 kg
- (d) Entropy change at constant temperature 66.

= 2.303nR log 
$$\frac{V_1}{V_2}$$
 = 2.303 × 2 × 2 log  $\frac{20}{2}$   
= 9.2 cal K<sup>-1</sup> mol<sup>-1</sup>

67. (a) 
$$\Delta S = \frac{\Delta H}{T} = \frac{344.3 \times 10^3}{3443} = 100 \text{ J mol}^{-1}$$

- **68.** (d) We know that  $\Delta G = \Delta H T\Delta S$ When  $\Delta H < 0$  and  $\Delta S < 0$  then  $\Delta G$  will be negative at low temperatures (positive at high temperature) and the reaction will be spontaneous.
- 69. (a) Measure of disorder of a system is nothing but entropy. For a spontaneous reaction,  $\Delta G < 0$ . As per Gibbs Helmholtz equation,  $\Delta G = \Delta H - T\Delta S$ Thus  $\Delta G$  is -ve only when  $\Delta H = -ve$  (exothermic) and  $\Delta S = +ve$  (increasing disorder)
- 70. (b)  $\Delta H^{\circ} \Delta U^{\circ} \Delta nRT$

 $= -760.3 \text{ kJ mol}^{-1}$ 

$$\Delta H^{\circ} = -772.7 \quad \frac{5 \times 8.314 \times 298}{1000}$$

71. (d) 
$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l);$$
  
 $\Delta H = -285.8 \text{ kJ} \qquad \dots (i)$   
 $H (aq) + OH^-(aq) \longrightarrow H_2O(l);$   
 $\Delta H = -57.3 \text{ kJ} \qquad \dots (ii)$   
 $\frac{1}{2}H_2(g) + aq \longrightarrow H (aq) + e^-; \Delta H = 0$   
(by convention)  $\qquad \dots (iii)$   
 $(i) - (ii) - (iii)$  gives,  
 $\frac{1}{2}H_2(g) + \frac{1}{2}O_2(g) + e^- + aq \longrightarrow$ 

$$\Delta H = -285.8 + 57.3 = -228.5 \text{ kJ}$$
72. (b) Bond dissociation energy of  

$$PH_{3}(g) = 228 \text{ kcal mol}^{-1}$$

$$P - H \text{ bond energy} = \frac{228}{3} \quad 76 \text{ kcal mol}^{-1}$$

$$H \longrightarrow P - P \longrightarrow H$$
Bond energy of 4 (P - H) + (P - P)

OH<sup>-</sup> (aq)

= 355 kcal mol<sup>-1</sup> or  $4 \times 76 + (P - P) = 355$  kcal mol<sup>-1</sup> P-P bond energy = 51 kcal mol<sup>-1</sup>

- 73. (c) ∴ ΔG=ΔH-T×ΔS For a spontaneous reaction, ΔG should be negative ΔH = -238 kJ, ΔS = -87 JK<sup>-1</sup> Hence, reaction will be spontaneous when ΔH>T×ΔS. Therefore, at 1000, 1500 and 3000 K the reaction would be spontaneous.
- 74. (b)  $\Delta S^{\circ} = -206.5 + 114.6 + 180.7 = 88.8$   $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$   $\Delta H^{\circ} = 271.8 + 298 \times 88.8 \times 10^{-3}$  $\Delta H^{\circ} = 298.3 \text{ kJ mol}^{-1}$

75. (a) 
$$\Delta G = -RT \ln K_{eq}$$
:  
Normal body temperature = 37°C  
 $\Rightarrow -50 \frac{kJ}{mol} = 8.314 \frac{J}{K mol} \times 310 \ln K_{eq}$ 

$$\Rightarrow 19.39 = \ln K_{eq}$$
$$\Rightarrow K_{eq} = 2.6 \times 10^{8}$$

76. (c) 
$$\Delta H = (n_1 C_{p,m_1} + n_2 C_{p,m_2}) \Delta T$$
  
=  $\left( 0.5 \times \frac{7}{2} R + 0.5 \times 4 R \right) -100$   
=  $-375 R$ 

77. (d) Condition of equilibrium, hence  $\Delta G = 0$ 

**78.** (a) For spontaneous reaction, 
$$dS > 0$$
 and  $\Delta G$  and  $\Delta G$  should be negative i.e. < 0.

- 79. (a)  $\Delta G = -RT \ln K$ = -8.314JK<sup>-1</sup>mol<sup>-1</sup> × 298 K × 2.303log 10<sup>-14</sup> = 7.98 × 10<sup>4</sup>  $\simeq$  8 × 10<sup>4</sup> J mol<sup>-1</sup>
- 80. (c) When gas is compressed, its entropy decreases so,  $\Delta S$  is negative.

81. (a) 
$$\Delta S = \frac{\Delta H}{T}$$
  
 $\Delta S(\text{per mole}) = \frac{\Delta H \text{ per mole}}{T} = \frac{6000}{273}$   
 $21.98 \text{ JK}^{-1} \text{mol}^{-1}$ 

82. (b) For 5 moles of gas at temperature T,  $PV_1 = 5RT$ For 5 moles of gas at temperature T - 2,  $PV_2 = 5R(T - 2)$ 

$$\therefore P(V_2 - V_1) = 5R(T - 2 - T);$$

$$P\Delta V = -10R,$$

$$- P\Delta V = 10R$$
When  $\Delta V$  is negative, W is + ve.  
83. (c)  $P_1V_1 = P_2V_2$ 

$$\therefore \qquad V = \frac{5bar \times 2dm^3}{1bar} = 10 \ dm^3$$
  
Work, W = - P<sub>ext</sub> ((V<sub>final</sub> - V<sub>initial</sub>))  
= -1 bar (10 - 2)  
= -1 × 10<sup>5</sup> Pa × 8 × 10<sup>-3</sup> m<sup>3</sup>  
= -800 J

- 84. (a) Process is isothermal reversible expansion, hence  $\Delta U = 0$ , therefore q = -w. Since q = +208 J, W = -208 J
- 85. (a) The greater the (negative value) of heat of neutralisation, the more is the strength of the acid. Hence,

 $HCOOH > CH_3COOH > H_2S > HCN$ 

- **86.** (b) The enthalpy of ionisation of weak acid is given by
  - $\Delta H_{\text{ion}}(\text{HA})$

 $= \Delta H_N$  (weak acid / strong base) -

 $\Delta H_N$  (strong acid / strong base)

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

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

Hence % ionisation in 1 M solution

$$=\frac{(1.5-1.2)}{1.5}\times 100=20\%$$

- 87. (d) By  $2 \times (ii) (i) + (iii)$ H<sub>2</sub>(g) + 2C(s)  $\rightarrow$  C<sub>2</sub>H<sub>2</sub>(g),  $\Delta$ G° = 209 kJ
- 88. (c)  $\Delta H = \Delta E + \Delta nRT$   $\Delta n = 3 - (1 + 5)$  = 3 - 6 = -3 $\Delta H - \Delta E$  (-3RT)
- 89. (a) Mass independent properties (molar conductivity and electromotive force) are intensive properties. Resistance and heat

capacity are mass dependent, hence extensive properties.

90. (b) Hg 1 
$$\Longrightarrow$$
 Hg g ,  
 $\Delta_R S^\circ = 174.4 - 77.4 = 97 \text{ J/K-mol}$   
 $\therefore \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 0$   
T  $\frac{\Delta H}{\Delta S}$   
 $\frac{60.8 \times 1000}{97}$  626.8 K

91. (c) 
$$H^{+}(aq) + OH^{-}(aq) \longrightarrow H_2O(l);$$
  
 $\Delta H = -57.3 \text{ kJ} \qquad \dots (i)$   
 $H_2C_2O_4 + 2OH^{-} \longleftarrow$   
 $C_2O_4^{--} + 2H_2O; \Delta H = -106 \text{ kJ}$ 

.... (ii) For the second reaction the value should have been  $2 \times (-57.3) = -114.6 \text{ kJ}$ The difference

 $(114.6 - 106) = 8.6 \text{ kJmol}^{-1}$  is used to effect of the ionisation of oxalic acid.

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

 $= 1 - 180 = -179 \text{ kcalmol}^{-1}$ 

Then  $\Delta H_{hyd.}$  (Na ) +  $\Delta H_{hyd.}$  (Cl<sup>-</sup>) = -179

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

or  $\Delta H_{hyd.}(Na) = -107.4 \text{ kcalmol}^{-1}$ 

(a) 
$$CH_4(g) + 2O_2(g) \longrightarrow$$

93.

$$\mathrm{CO}_{2}(\mathrm{g})+2\,\mathrm{H}_{2}\mathrm{O}\left(l\right)$$

$$\Delta H = -890 \text{ kJ}$$
 .... (i)

$$2 \text{ H}_2\text{O} (l) \longrightarrow 2 \text{ H}_2\text{O} (g);$$
  

$$\Delta \text{H} = 2 \times 40.5 = 81 \text{ kJ} \qquad \dots \text{ (ii)}$$
  
From (i) + (ii), we get  

$$C\text{H}_4 (g) + 2 \text{ O}_2 (g) \longrightarrow$$
  

$$C\text{O}_2 (g) + 2 \text{ H}_2\text{O} (g)$$

 $\Delta H = -\ 890 + 81 = -\ 809 \ kJ$ 

94. (b)  $\Delta G \quad \Delta H - T \Delta S$  $-382.64 - (298 \times 145.6 \times 10^{-3})$ -339.3 kJ mol<sup>-1</sup> 95. (a)  $\Delta G = -ve$  means the process is spontaneous. 96. (a)  $C_2H_5OH(1) + 3O_2(g) \longrightarrow$  $2CO_2(g) 3H_2O(l)$ Bomb calorimeter gives  $\Delta U$  of the reaction Given,  $\Delta U = -1364.47 \text{ kJ mol}^{-1}$ 

$$\Delta n_g = -1$$
  

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

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

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

- 97. (b) For the equation
  - $B_2H_6(g) + 3O_2(g) \longrightarrow B_2O_3(g) \quad 3H_2O(g)$ Eqs. (i) + 3 (ii) + 3 (iii) – (iv)  $\Delta H = -1273 + 3(-286) + 3(44) - 36$ = -1273 - 858 + 132 - 36= -2035 kJ/mol
- **98.** (a) 18gm of water at 100°C 10gm of Cu at 25°C is added.

$$q_{p} = C_{p,m} dT$$

$$= 75.32 \times \frac{J}{K \text{ mol}} \times \frac{18g}{18g / \text{ mol}} (373 - 298) K$$

$$= 75.32 \frac{J}{K} \times 75 K$$

$$= 5.649 \times 10^{3} J$$
If now 10g of copper is added  
 $C_{p,m} = 24.47 \text{ J/ mol K}$ 

Amount of heat gained by Cu

= 24.47 
$$\frac{J}{K \text{ mol}} \times \frac{10g}{63g / \text{ mol}} (373 - 298) \text{ K}$$
  
= 291.3 J  
Heat lost by water = 291.30 J  
- 291.30 J = 75.32  $\frac{J}{K} \times (T_2 - 373 \text{ K})$   
 $\Rightarrow -3.947 \text{ K} = T_2 - 373 \text{ K}$   
 $\Rightarrow T_2 = 369.05 \text{ K}$ 

**99.** (a) 
$$q_p = \Delta H = C_p dT$$

$$\Rightarrow q_p = 75.32 \frac{J}{K \text{ mol}} \times (299 - 298) K$$
$$\Rightarrow q_p = 75.32 \frac{J}{K \text{ mol}}$$

For 180 kg of water, no. of moles of water

$$=\frac{180 \times 10^3 \text{ g}}{18 \text{ g / mol}} = 10^4 \text{ g moles}$$

$$q_{p} = 75.32 \frac{J}{mol} \times 10^{4} \text{ moles}$$

$$= 753.2 \times 10^{3} \text{ J} = 753.2 \text{ kJ}$$

$$\Delta H \text{ for ATP} = 7 \text{ kcal / mol}$$

$$= 7 \times 4.184 \text{ kJ/mol}$$

$$= 29.2 \text{ kJ/mol}$$

$$6.022 \times 10^{23} \text{ molecules of ATP produce}$$

$$= 29.2 \text{ kJ}$$

$$29.2 \text{ kJ produced from}$$

$$6.022 \times 10^{23} \text{ molecules}$$

$$753.2 \text{ kJ produced from}$$

$$6.022 \times 10^{23} \times \frac{75.8}{29.2}$$

$$= 1.5 \times 10^{25}$$
 molecules

**100.** (c)  $\Delta G^{\circ} = -RT \ln K$ ;

K ↑ stability of reactant  $\downarrow$