USE OF FREE ENERGY IN CHEMICAL EQUILIBRIA

1 MARK

HARD

1. In a certain process 678 J of heat is absorbed by a system while 290 J of work is done on the system. What is the change in internal energy for the process?

968 J

MODERATE

1. State one application of first law of thermodynamics.

Hess's law is an application of first law of thermodynamics.

2. For the reaction $2Al_2O_3 = 4Al\ (s) + 3O_2(g)$, $\Delta H = 334 kJ$, what is the enthalpy of formation of Al_2O_3 ?

-1670 kJ

3. What is the amount of free energy change for a reversible process?

Free energy change for a reversible process is equal to zero.

Easy

1. Give one example of State Function

Enthalpy.

2. Write one process where entropy decreases.

The conversion of CO_2 into dry ice, here entropy decreases.

3. At inversion temperature what is the Value of Joule – Thomson coefficient?

At inversion temperature Joule Thomson Coefficient value is Zero.

4. Give one example of intensive property.

Density.

5 marks

Easy:

1.(a) Explain the term chemical potential. 1

(b) Derive the relation of EMF of cell with ΔG and ΔH. 4

For a pure substance chemical potential is equal to molar Gibbs free energy. In a system of variable composition chemical potential of a substance is equal to the rate of change of the Gibbs free energy G of the system with respect to the moles of i added at constant T, P and other mole numbers. Thus for a two component mixture chemical potential of the component 1 is μ_1 and is given by,

$$\mu = \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n2}$$

(b) Relation between ΔG and EMF of a cell (E).

The relation between ΔG and E is $\Delta G_{T,P} = -nFE$. Electrical work is produced at the cost of decreade in Gibbs free energy.

Relation between ΔH and E

We know at constant T, P, $\Delta G = \Delta H - T\Delta S$

From Gibbs – Helmholtz equation for a reaction

$$\Delta S = \left[\frac{\partial(\Delta G)}{\partial T}\right]_P = -\left[\frac{\partial(-nFE)}{\partial T}\right]_P = nF\left(\frac{\partial E}{\partial T}\right)_P$$

We have, $\Delta H = \Delta G + T\Delta S$

Therefore, $\Delta H = -nFE + TnF\left(\frac{\partial E}{\partial T}\right)_P = -nF\left[E - T\left(\frac{\partial E}{\partial T}\right)_P\right]$

2. How many types of hardness is possible? Why hard water is not suitable for boiler use? 3 + 2

Hardness of water is of two types.

(i) Temporary Hardness : It is caused due to presence of bicarbonates of calcium and magnesium. It can be removed easily by boiling.

(ii) Permanent Hardness: It is caused due to presence of chlorides and sulphates of calcium and magnesium salts. It cannot be removed by boiling.

Huge quantity of water is used in boilers for generation of steam. If hard water is used in the boiler, a number of difficulties arise which are as follows:

Scale and sludge formation

Boiler Corrosion

Priming and foaming

Caustic embrittlement.

Moderate:

1. Show that, entropy of mixing of ideal gases $\Delta S_{mix} > 0$. 5

Mixing of two or more gases are spontaneous process, hence it should be accompanied by increase in entropy.

Let n_1 moles of ideal gas A_1 and n_2 moles of gas A_2 having volume V_1 and V_2 at constant pressure P and temperature T be separated by a partition. After removing the partition, these two gas mixed spontaneously when the total pressure P and the final temperature T remain constant and both gas occupying the entire volume, $V = V_1 + V_2$ of the cylinder.

Hence the entropy change $\Delta S_1 = n_1R \ln (V_1 + V_2) / V_1$

Similarly for gas A_2 $\Delta S_2 = n_2R \ln (V_1 + V_2) / V_2$

Since gases are ideal, each gas acts independently of the other. Hence entropy change of mixing ΔS_{mix} is equal to the sum of the entropy change due to their individual isothermal volume expansion.

$\Delta S_{mix} = \Delta S_1 + \Delta S_2 = n_1R \ln\frac{(V_1+V_2)}{V_1} + n_2R \ln\frac{(V_1+V_2)}{V_2} = -n_1Rln\frac{V_1}{V_1+V_2} - n_2Rln\frac{V_2}{V_1+V_2}$

If X_1 and X_2 are the mole fraction of gas A_1 and A_2 respectively in the mixture, then,

$X_1 = n_1/(n_1 + n_2) = n_1 / n = V_1 / (V_1 + V_2)$

$X_2 = n_2/(n_1 + n_2) = n_2 / n = V_2 / (V_1 + V_2)$

Entropy of mixing:

$\Delta S_{mix} = - n_1R \ln X_1 - n_2R \ln X_2 = -nR(n_1/n \ln X_1 + n_2/n \ln X_2) = -nR(X_1 \ln X_1 + X_2 \ln X_2)$

The equation may be generalise to the mixing of N ideal gases,

$\Delta S_{mix} = -nR\sum_{i=1}^{N} X_i lnX_i$

Molar entropy of mixing

$(\Delta S_{mix})_{mix} = -R\sum_{i=1}^{N} X_i lnX_i$

Since mole fraction X_i of gas always less than 1, hence $\ln X_i$ always less than zero. So ΔS_{mix} is always > 0.

Hard

1. 'All adiabatic reversible expansions lead to a fall of temperature.' – Comment or Justify. 5

   From 1st law of thermodynamics $\Delta U = Q + W$ where W is negative for expansion process. In adiabatic process $Q = 0$. So, for adiabatic process $\Delta U = W$. In reversible expansion appreciable work is produced and ΔU is negative for a adiabatic reversible expansion since W is negative in expansion process. For ideal gas internal energy (U) depends only on temperature and $\Delta U = C_v\Delta T$. Since in adiabatic reversible expansion ΔU is negative it is seen that for this process ΔT is negative (because C_V is always positive) $\Delta T = T_{final} - T_{initial}$. For adiabatic reversible expansion of ideal gas $T_f < T_i$.. For adiabatic reversible expansion there occurs a fall of temperature. (For real gases volume increase has negligible effect on ΔU and there is cooling effect in adiabatic reversible expansion in all cases).

15 Marks

Easy

1. (a) What is the condition of spontaneity in terms of entropy? The condition of spontaneity : $\Delta G_{x,\,y} < 0$; $\Delta A_{p,r} < 0$, where G is the Gibbs Free Energy and A is the Helmholtz free energy. Identify x, y, p and r. 2 + 4
   (b) State whether the following properties are extensive or intensive properties:
   Pressure, Concentration, Entropy, Viscosity, Temperature. 5
   (c) For a reaction both ΔH and ΔS are positive. Under what conditions will the reaction be spontaneous? What is state function? Give example. 2 + 2

   (a) Condition of spontaneity in terms of entropy for isolated system $\Delta S > 0$.
   Condition of spontaneity in terms of entropy for non-isolated system $\Delta S_{total} > 0$
   $\Delta S_{total} = \Delta S_{universe} = \Delta S_{system} + \Delta S_{surrounding} > 0$
   Condition of spontaneity in constant T, P process is $\Delta G_{T,\,P} < 0$.
   Condition of spontaneity in constant T, V process is $\Delta A_{T,\,V} < 0$.
   (b) Pressure : intensive property
   Concentration : intensive property
   Entropy: extensive property
   Viscosity : intensive property
   Temperature: intensive property.
   (c) If $T\Delta S > \Delta H$ the reaction will be spontaneous. If ΔS and ΔH both are positive, then T must be high for the spontaneity of the reaction.
   A state function is a property that depends only on the state of the system and not on how the system has been achieved. Example: Enthalpy, Entropy etc.

Moderate

1. (a) Write the Nernst equation for the cell reaction in the Daniel cell. How will the E_{cell} effected when the concentration of Zn^{2+} is increased?

(b) What do you mean by hardness of water? Explain how hard water fails to form lather with soap? What is alkalinity of water? 5

(c) Define corrosion. What are different types of corrosion? 5

(a) Daniel Cell is represented as $Zn\,|\,(s)\;\; Zn^{2+}\,||\,(aq)\;\; Cu^{2+}\,|\,(aq)\;\; Cu\,(s)$

The cell reaction for 2F electricity drawn is $Zn\,(s) + Cu^{2+}\,(aq) = Zn^{2+}\,(aq) + Cu\,(s)$

Nernst equation for the cell reaction is

$$E = E^0 - \frac{RT}{2F}\ln(a_{Zn^{+2}} \times a_{Cu})/\,(a_{Zn^{+2}} \times a_{Cu})$$

$$= E^0 - \frac{RT}{2F}\ln C_{Zn^{+2}}/C_{Cu^{+2}}$$

Assuming activity if ion equal to concentration of the ion and activity of solid = 1.

The Nernst equation shows that if concentration of Zn^{2+} is increased cell potential E decreases. [$\Delta G_{T, P}$ = -nFE. For spontaneous reaction E is positive and ΔG is negative. Decrease of E with increase of concentration of Zn^{2+} makes ΔG less negative. The tendency of forward reaction is diminished and this is an accord with Le – Chatelir principle that if a product species is added the reaction is shifted to the left side.]

(b) Hardness is the characteristic of water which prevents formation of lather with soap. This is due to the presence of certain salts of calcium, magnesium and other heavy metals dissolved in it. The salts are calcium chloride, calcium carbonate, calcium bicarbonate, magnesium chloride, magnesium carbonate, magnesium bicarbonate etc.

Hard water, when treated with soap (sodium or potassium salt of higher fatty acid like oleic, palmitic or stearic) does not produce lather, but forms scum or precipitate. The reactions of soap (sodium stearate) with calcium and magnesium salts are depicted below.

$$2\ C_{17}H_{35}COONa + CaSO_4 \longrightarrow (C_{17}H_{35}COO)_2\ Ca \downarrow + 2Na_2SO_4$$

$$2\ C_{17}H_{35}COONa + MgCl_2 \longrightarrow (C_{17}H_{35}COO)_2\ Mg \downarrow + 2NaCl$$

When all the Ca & Mg removed then hard water getting soft and it produces lather.

The alkalinity of natural water is ordinarily due to presence of carbonates, bicarbonates of calcium and magnesium. The alkalinity of water can be considered mainly due to Hydroxide, Carbonates and Bicarbonates.

The alkalinity of water can be estimated separately by titration against standard acid solution.

Corrosion may be defined as the process of slow deterioration of surface of metal due to direct attack by atmospheric gases, moisture present in the atmosphere or by any other chemical or electrochemical environment.

Different type of corrosion:

Dry Corrosion

Liquid – metal corrosion

Wet Corrosion (Electrochemical corrosion)

(i) Wet corrosion of metal with evolution of H_2gas

(ii) Wet corrosion of metal by absorption of O_2.