1. **(a) From vapor pressure data 1350 K the following data has been found for the Cu- Fe liquid solution (metastable). Complete the table.**

**Solution:**

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| item | data | | | | | | | |
| X\_Cu | 1.0000 | 0.9000 | 0.8000 | 0.6000 | 0.4000 | 0.2000 | 0.1000 | 0.0000 |
| p\_Cu, Pa | 55.80 | 51.50 | 49.10 | 46.87 | 44.64 | 39.06 | 30.13 | 000 |
| a\_Cu w.r.t. pure liq | 1 | 0.9229 | 0.8799 | 0.8400 | 0.8000 | 0.7000 | 0.5400 | 0 |
| a\_Cu w.r.t. liq/X\_Cu | 1 | 1.025 | 1.100 | 1.400 | 2.000 | 3.500 | 5.400 | 0/0  Obtain by limit operation  (extrapolation) |
| GCu in sol – GCu, liq## | 0 | -900.5 | -1436 | -1957 | -2505 | -4003 | -6916 | -∞ |
| a\_Cu w.r.t. Cu in 40at.% soln\*. | 1.25 | 1.154 | 1.100 | 1.050 | 1.0 | 0.8750 | 0.6750 | 0 |

\* aCu = fCu /f­Cuo = pCU/pCu0 ( assumed to be ideal at ths high temperature and low pressure).

## GCu in sol – GoCu = RT ln aCu ; GoCu refers to the reference state for the activity definition.

**(b) Can you reduce NiO(s) by Cu(l) at 1350 K to give Ni(s) and Cu2­O(s)? Use the data (Gaskell) :**

4Cu(l) + O2(g) = 2Cu2O(s); ΔG0 = -376600+176.96 T, J/mol.;

NiO(s) = Ni(s) +1/2 O2(g), ΔG0 = 235600-86.0T, J/mol.

**Solution :**

Connect the two reactions by consuming the oxygen produced by one reaction by the other reaction.

2Cu(l) + ½ O2(g) = Cu2O(s); ΔG0 = −137700 J/mol

\_\_\_\_\_NiO(s) = Ni(s) +1/2 O2(g), ΔG0 = 119500 J/mol\_\_\_\_\_

NiO(s) + 2Cu(l) = Ni(s) + Cu2O(s); ΔG0 = -18200 J/mol

Since all the reactants and the products are in the same state as in the reference (standard) reaction, all activities are unity. Hence ΔG = ΔG0 + RT ln 1 = ΔG0 =-18200. Negative, hence copper reduces NiO.

**(c) Will the reduction by Cu still take pace if it is in solution in iron with atom fraction of 0.1 ?**

**Solution :**

Here copper has an activity of 0.54 w.r.t.Cu(l); Other activities are unity. Then:

ΔG = ΔG0 + RT ln Q = ΔG0 + RT ln (aNi.aCu2O/(aNiO.aCu) = ΔG0 + RT ln (1x1/(1x0.54)

= -18200 + 8.314x1350 ln 1.852 = - 11283 J/mol.

Still negative, hence copper in solution too will reduce NiO(s).

[ Later we will learn the real situation:

1. Ni produced will go into solution in Cu(l) decreasing the activity for both Cu and Ni. The extent of reaction will depend on mass balance : How much of NiO and the metallic solution you took initially.
2. Iron in the Cu-Fe solution may actually perform the reduction rather than Cu. ]
3. (a) At 25C, water has an equilibrium vapour pressure of 0.03126 atm. at 25C (i.e., liquid water and pure steam vapour are in equilibrium with each other at this pressure and temperature). What is the free energy change when one kg of water at 1atm. is converted into steam (i) at 0.03126atm. and 25C (ii) at 1 atm. and 25C (metastable).

Assume density of water to be constant at 1000 kg/m3, and steam to be ideal gas.

**Solution :**

(b) In a water ethanol mixture, mole fraction of water being 0.40, the vapour pressure of water has been measured to be 0.0243 atm. at 25C. What is the (i) activity and (ii) activity coefficient of water in the solution with respect to pure water (liquid).

Solution :

Reversible; eqbm

ΔG = 0

ΔG negligible,

Condensed phase#

steam at 25C;

0.03126 atm.

Water at 25C;

0.03126 atm.

Water at 25C;

1atm.

(i)

Water at 25C;

1atm.

steam at 25C;

0.03126 atm.

ΔG = RT ln (1/0.03126)

steam at 25C;

0.03126 atm.

ΔG = 0

Water at 25C;

0.03126 atm.

ΔG ~0

ΔG = RT ln (1/0.03126) = 8590 J/mol; for 1 kg water = 477230 J/kg

*# density of water – 1000kg/m3, that is molar volume VH2O = 1.8x10-5 m3/mol.*

*= 1.8x10-5 (-0.96874)105 ~1.7 J/mol. Negligible compared to 8590 for steam expansion*