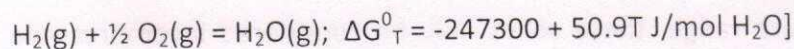amount of oxygen will form after equilibrium is reached. Is it true? If so what is the p_{O2}?

[**Do not use equilibrium constant concept.** Instead use the concept that $G_{O2, P} - G_{O2, 1 atm} = \int_1^P V dP = RT \ln P/1$.

$$H_2(g) + \tfrac{1}{2} O_2(g) = H_2O(g); \quad \Delta G^0_T = -247300 + 50.9T \text{ J/mol } H_2O]$$

Assume here that the partial pressures of H_2 and H_2O remain at more or less at 1 atm. each. Further G_{H2} and G_{H2O} remain that for pure gases even though they are in a mixture: that is

$G_{H2 \text{ pure, 1 atm}} = G^0_{H2, \text{ mixture, pH2: 1atm}}$.

$G_{H2O \text{ pure, 1 atm}} = G^0_{H2O, \text{ mixture, pH2O: 1atm}}$.

(b) Will this gas (50:50 mixture of H2 and H₂O), oxidize iron(pure solid) to wustite (pure solid) at 1000K ?

$$x\, Fe(s) + \tfrac{1}{2} O_2(g) = Fe_xO(s); \quad \Delta G^0_T = -263700 + 64.3T \text{ J/mol}$$
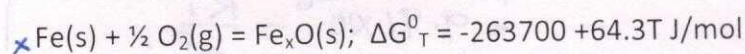
Neglect the change in G of condensed phases. **Again, Do not use equilibrium constant concept.**

Solution: ΔG^0 is only a data stored. For physical interpretation, one needs to find ΔG when the reactants and products are in conditions that are given.

Here H_2 and H_2O are at 1 atm pr. Oxygen partial pressure is low; let it be P.

Then:

$$H_{2, 1 atm} \quad H_2(g)_{,\, pH_2 = 1 \text{ in mixture}} + \tfrac{1}{2} O_2{}_{pO_2} = P = H_2O(g)_{,\, pH_2O = 1 atm}.$$

At equilibrium:

$$\Delta G = G_{H_2O}^{\text{in mixture},\, pH_2O = 1atm} - G_{H2O}^{\text{in mixture},\, pH_2 = 1atm} - \tfrac{1}{2} G_{O_2}{}_{pO_2 = P atm}. \quad (ii)$$

All at 1000K

$$= G^0_{H_2O} - G^0_{H_2} - \tfrac{1}{2} G_{O_2}{}_{pO_2 = P} = 0.$$

$$= G^0_{H2O} - G^0_{H_2} - \tfrac{1}{2} G^0_{O_2} - \tfrac{1}{2} \left(G_{O_2, P atm} - G^0_{O_2} \right)$$

$$= \Delta G^0 - \tfrac{1}{2} \left(RT \ln \tfrac{P}{1} \right) = 0.$$

$$\ln P = \frac{2 \times (-196400)}{R \times 1000} = -47.246; \quad P = 3.03 \times 10^{-21} \text{ atm} \quad \text{(2 by atm.?)}$$

(b) Note that $G_{O_2, P} - G^0_{O_2} = 2 \times -196400 = -392800$.
use this here:

$$\Delta G = G^0_{FeO}{}_{1000} - x G^0_{Fe} - \tfrac{1}{2} G^0_{O_2} - \tfrac{1}{2} \left(G_{O_2, 3.03 \times 10^{-21} atm} - G^0_{O_2} \right)$$

$$= -198700 - \tfrac{1}{2} (-392800) = -2300 \text{ J/mol}.$$

$\Delta G_{P,T} < 0$. Hence reduction takes place

2. What is the free energy change for the oxidation with pure oxygen of pure iron to pure wustite at 1000K if the pressure is raised from 1 atm. pressure to (i) 100 atm. (ii) 10^{-9} atm. Density of iron and wustite are respectively 7800 and 4000 kg/m³. (data from problem 1 (b))

[In this pressure range, these solids may be considered incompressible as an approximation. Oxygen obeys ideal gas law].

$$x\,Fe(s) + \tfrac{1}{2}O_2(g) = Fe_xO(g)\ ;\ \Delta G^0_{1000} = -198700\ J/mol\ .$$
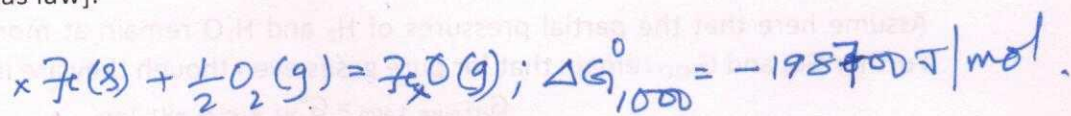
$$\left(\frac{\partial \Delta G}{\partial P}\right)_T = V_{Fe_xO} - x\,V_{Fe} - \tfrac{1}{2}V_{O_2}$$

$$V_{Fe_{0.95}O} = \frac{1}{4000} \times \frac{69.2}{1000}$$

$$= 1.73 \times 10^{-5}\ m^3/mol\ .$$

$$V_{FeO} = \frac{1}{7200} \times \frac{56}{1000}$$

$$= 7.778 \times 10^{-6}\ m^3/mol$$

$$= 9.91 \times 10^{-6} - \frac{RT}{2P}\ .$$

$$\Delta G_P - \Delta G_{1atm} = \int_1^P \Delta V\, dP$$

$$= 9.91 \times 10^{-6} \times 1.013 \times 10^5 (P-1)$$

$$- \frac{RT}{2}\ln P\ .$$ P in atm.

$$= 1.004\,(P-1) - \frac{RT}{2}\ln P\ .$$

Hence (i) $P = 100$ atm,

$$\Delta G_P - \Delta G_{1atm} = \frac{99.4}{100.4} - 19144 = -19044\ J/mol\ .$$

$$\Delta G_P = -217744\ J/m\ .$$

(ii) $P = 10^{-9}$ atm.

$$\Delta G_P - \Delta G_{1atm} = 1.004 \times (-1) + 86147 = +86145\ J/mol.$$

$$\Delta G_P = -112554\ J/mol$$