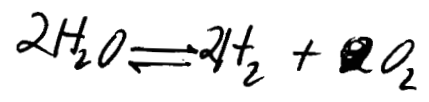


| | H_2O | H_2 | O_2 |
|-------------------|---|--|---|
| Initial: | 2 | | |
| Amount in eq.: | $(1-\alpha) \cdot 2$ | $\alpha \cdot 2$ | $\frac{1}{2} \alpha \cdot 2$ |
| Mole fraction: | $\frac{1-\alpha}{1+\frac{1}{2}\alpha}$ | $\frac{\alpha}{1+\frac{1}{2}\alpha}$ | $\frac{\frac{1}{2}\alpha}{1+\frac{1}{2}\alpha}$ |
| Partial pressure: | $\frac{(1-\alpha)p}{1+\frac{1}{2}\alpha}$ | $\frac{\alpha p}{1+\frac{1}{2}\alpha}$ | $\frac{\frac{1}{2}\alpha p}{1+\frac{1}{2}\alpha}$ |



a) $K = \left(\frac{P_i}{P^\circ} \right)^{\nu_i}$ eq. $a_i = \frac{P_i}{P^\circ}$

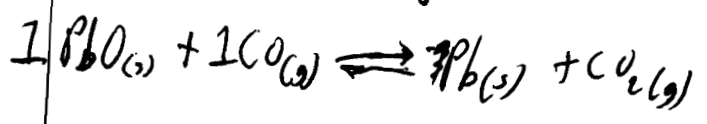
$$K = \frac{\left(\frac{P_{H_2}}{P^\circ} \right)^2 \left(\frac{P_{O_2}}{P^\circ} \right)}{\left(\frac{P_{H_2O}}{P^\circ} \right)^2} = \frac{\left(\frac{\alpha p}{(1+\frac{1}{2}\alpha)P^\circ} \right)^2 \left(\frac{\frac{1}{2}\alpha p}{(1+\frac{1}{2}\alpha)P^\circ} \right)}{\left(\frac{(1-\alpha)p}{(1+\frac{1}{2}\alpha)P^\circ} \right)^2}$$

simplify: $\frac{\alpha^3 p}{2(1-\alpha)^2 (1+\frac{1}{2}\alpha) P^\circ} = \frac{(0.01773)^3}{2(1-0.01773)^2 (1+\frac{1}{2} \cdot 0.01773)} = \boxed{2.85 \times 10^{-6}}$

b) $\Delta G^\circ = -RT \ln K = -(8.314 \text{ J/Kmol}) (2257 \text{ K}) \ln(2.85 \times 10^{-6})$
 $= \boxed{2.40 \times 10^5 \text{ J/mol}} = 240 \text{ kJ/mol}$

c) $\Delta_r G = 0$ because reaction in equilibrium

7.3 a) a) $\Delta_r G^\circ = \sum \nu_i \Delta_f G^\circ(i) = 0$



$$0 = Pb(s) + CO_2(g) - PbO(s) - CO(g)$$

$$\Delta_r G = \Delta_f G^\circ(Pb(s)) + \Delta_f G^\circ(CO_2(g)) - \Delta_f G^\circ(PbO(s)) - \Delta_f G^\circ(CO(g))$$

$$= -394.36 \text{ kJ/mol} - (-137.17 \text{ kJ/mol}) - (-188.93 \text{ kJ/mol})$$

$$= \boxed{-68.26 \text{ kJ/mol}}$$

$$\ln K = \frac{-\Delta_r G^\circ}{RT} = \frac{68.26 \times 10^3 \text{ J/mol}}{(8.314 \text{ J/Kmol})(298 \text{ K})} = 27.55$$

$$e^{27.55} = \boxed{K = 9.2 \times 10^{11}}$$

b) ~~At 400 K~~ $\ln K_{400} = \ln K_{298} - \frac{\Delta_r H^\circ}{R} \left(\frac{1}{400 \text{ K}} - \frac{1}{298 \text{ K}} \right)$

~~$\ln K = 27.55 + \dots$~~

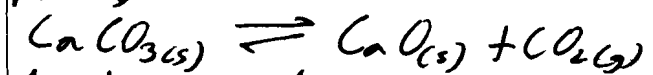
$$\begin{aligned} \Delta_r H^\circ &= \Delta_f H^\circ(\text{Pb, s}) + \Delta_f H^\circ(\text{CO}_2) - \Delta_f H^\circ(\text{PbO}) - \Delta_f H^\circ(\text{CO}) \\ &= -393.51 \text{ kJ/mol} - (-218.99 \text{ kJ/mol}) - (-110.53 \text{ kJ/mol}) \\ &= \cancel{-163.99} \text{ 63.99 kJ/mol} \end{aligned}$$

$$\ln K = 27.55 - \left(\frac{-63.99 \text{ kJ/mol}}{8.314 \text{ J/Kmol}} \right) \left(-8.56 \times 10^{-4} \text{ K}^{-1} \right) = \boxed{20.96}$$

$$K = e^{20.96} = \boxed{1.3 \times 10^9}$$

$$\begin{aligned} \Delta_r G^\circ(400 \text{ K}) &= -RT \ln K = -(8.314 \text{ J/Kmol})(400 \text{ K})(20.96) \\ &= \boxed{-69.7 \text{ kJ/mol}} \end{aligned}$$

7.12a)



$K=1$, for the purpose of this exercise.
 $\ln K=0$, and $\Delta_r G^\circ=0$

$$\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ = 0$$

$$\Delta_r H^\circ = T\Delta_r S^\circ$$

$$T = \frac{\Delta_r H^\circ}{\Delta_r S^\circ}$$



$$\Delta_r H^\circ = -635.09 + -393.51 - (-1206.9) = 178.3 \text{ kJ/mol}$$

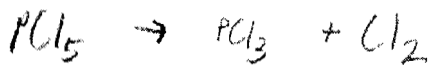
$$\Delta_r S^\circ = 39.75 + 213.74 - 92.9 = 160.6 \text{ J/K mol}$$

$$T = \frac{178.3 \times 10^3 \text{ J/mol}}{160.6 \text{ J/K mol}} = \boxed{1110 \text{ K}} = \boxed{840^\circ \text{C}}$$

1) find K @ 298 K I.G

favors products or reactants

$$\Delta_r G^\circ = \sum_{\text{prod}} \nu \Delta_f G^\circ - \sum_{\text{react}} \nu \Delta_f G^\circ$$



$$\Delta_r G^\circ = 1 \Delta_f G^\circ(\text{PCl}_3) + 1 \Delta_f G^\circ(\text{Cl}_2) - 1 \Delta_f G^\circ(\text{PCl}_5) = \frac{-267.8 \text{ kJ}}{\text{mole}} + 0 - \left(\frac{-305.0 \text{ kJ}}{\text{mole}} \right)$$

$$\Delta_r G^\circ = \frac{37.2 \text{ kJ}}{\text{mole}}$$

$$\Delta_r G^\circ = -RT \ln K$$

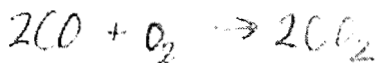
$$e^{\left(\frac{-\Delta_r G^\circ}{RT} \right)} = K$$

$$R = \frac{8.314 \text{ J}}{\text{mole} \cdot \text{K}} \cdot \frac{\text{K}}{1000}$$

$$K = \frac{8.314 \times 10^{-3} \text{ kJ}}{\text{mole} \cdot \text{K}}$$

$$K = 3.01 \times 10^{-7} \checkmark$$

favors reactants



$$\Delta_r G^\circ = 2(\Delta_f G^\circ(\text{CO}_2)) - (2\Delta_f G^\circ(\text{CO}) + \Delta_f G^\circ(\text{O}_2)) = 2\left(\frac{-394.36 \text{ kJ}}{\text{mole}} \right) - (2(-137.12) + 0) = \frac{-514.38 \text{ kJ}}{\text{mole}}$$

$$\Delta_r G^\circ = \frac{-514.38 \text{ kJ}}{\text{mole}}$$

$$K = 1.47 \times 10^{90}$$

favors products



$$\Delta_r G^\circ = 2 \Delta_f G^\circ \text{O}_3 - 3 \Delta_f G^\circ \text{O}_2 = 2\left(\frac{163.2 \text{ kJ}}{\text{mole}} \right) - 0 = \frac{326.4 \text{ kJ}}{\text{mole}}$$

$$K = 6.1 \times 10^{-58}$$

favors reactant



$$\Delta_r G^\circ = 2\Delta_f G^\circ \text{NO} - (\Delta_f G^\circ(\text{N}_2) + \Delta_f G^\circ(\text{O}_2)) = 2\left(\frac{26.51 \text{ kJ}}{\text{mole}}\right) - 0 = \frac{173.1 \text{ kJ}}{\text{mole}}$$

$$K = 4.54 \times 10^{-31}$$

favors reactants

* because the earth's atmosphere is composed of ~20% O_2 and 70% N_2 , so if for the reactions $3\text{O}_2 \rightarrow 2\text{O}_3$ and $\text{N}_2 + \text{O}_2 \rightarrow 2\text{NO}$ the products were favored then the atmosphere would be mostly composed of NO and O_3 but as mentioned this is not the case thus we know the reactants are favored

for the rxn $\text{CO} + \text{O}_2 \rightarrow \text{CO}_2$ we see that the product, CO_2 is favored however, this is simply the thermodynamic result and doesn't tell us about the rate of the rxn, in fact gas rxns typically occur at slow rate due to the low density and collision rates of the molecules so the rxn occurs slowly, and the detector so you can evacuate and allow sufficient time for the rxn to occur but eventually the CO will be converted to CO_2



$$\Delta_r H^\circ = \sum_{\text{prod}} \nu \Delta_f H^\circ - \sum_{\text{react}} \nu \Delta_f H^\circ = \Delta_f H^\circ(\text{H}_2\text{O}) + \Delta_f H^\circ(\text{CO}) - (\Delta_f H^\circ(\text{H}_2) + \Delta_f H^\circ(\text{CO}_2))$$

numbers eg for $\Delta_f H^\circ$ use in the entropies and free energy from the internet!

$$\Delta_r H^\circ = \frac{-241.82 \text{ kJ}}{\text{mole}} + \frac{-110.53 \text{ kJ}}{\text{mole}} - \left(0 + \frac{-393.51 \text{ kJ}}{\text{mole}} \right) = \frac{41.16 \text{ kJ}}{\text{mole}}$$

$$\Delta_r G^\circ = \frac{-228.57 \text{ kJ}}{\text{mole}} + \frac{-137.17 \text{ kJ}}{\text{mole}} - \left(0 + \frac{-394.36 \text{ kJ}}{\text{mole}} \right) = \frac{28.62 \text{ kJ}}{\text{mole}}$$

K @ 298 K

$$\Delta_r G^\circ = -RT \ln K \quad \left(\frac{\Delta_r G^\circ}{-RT} \right) = K$$

$$K = 9.62 \times 10^{-6}$$

~~XXXXXXXXXX~~ !!!

$$\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ$$

$$\Delta_r S^\circ = \frac{188.83 \text{ J}}{\text{K} \cdot \text{mole}} + \frac{197.67 \text{ J}}{\text{K} \cdot \text{mole}}$$

$$- \left(130.66 + 213.74 \right) - \frac{42.08 \text{ J}}{\text{K} \cdot \text{mole}}$$

$$\Delta_r C_p = \sum \nu C_p - \sum \nu C_p$$

prod react

$$\frac{33.58 \text{ J}}{\text{K} \cdot \text{mole}} + \frac{29.14 \text{ J}}{\text{K} \cdot \text{mole}} - \left(37.11 + 28.824 \right) = \frac{-3.214 \text{ J}}{\text{K} \cdot \text{mole}}$$

$$\Delta_r H^\circ(T_2) = \Delta_r H^\circ(T_1) + \int_{T_1}^{T_2} \Delta_r C_p dT = \frac{41.16 \text{ kJ}}{\text{mole}} \left(\frac{1000 \text{ J}}{\text{kJ}} \right) + \int_{298}^{1000} \frac{-3.214 \text{ J}}{\text{K} \cdot \text{mole}} dT$$

$$\Delta_r S^\circ(1000\text{K}) = \Delta_r S^\circ(298) + \int_{298}^{1000} \frac{\Delta_r C_p}{T} dT$$

$$\frac{41160 \text{ J}}{\text{mole}} + \frac{-3.214 \text{ J}}{\text{K} \cdot \text{mole}} (1000 \text{ K} - 298 \text{ K})$$

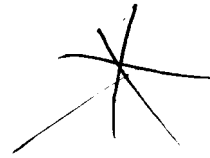
$$\frac{42.08 \text{ J}}{\text{K} \cdot \text{mole}} + \frac{-3.214 \text{ J}}{\text{mole} \cdot \text{K}} \ln \left(\frac{1000 \text{ K}}{298 \text{ K}} \right)$$

$$\Delta_r H^\circ(1000\text{K}) = \frac{38.94 \text{ kJ}}{\text{mole}}$$

$$\Delta_r S^\circ(1000\text{K}) = 38.2 \text{ J/mole} \cdot \text{K}$$

$$\Delta_r G^\circ(1000\text{K}) = 38900 \frac{\text{J}}{\text{mole}} - 1000\text{K} \left(\frac{39.2\text{ J}}{\text{mole}\cdot\text{K}} \right)$$

$$\Delta_r G^\circ(1000\text{K}) = 700 \frac{\text{J}}{\text{mole}}$$



$$K_2 = 0.75 \quad *$$

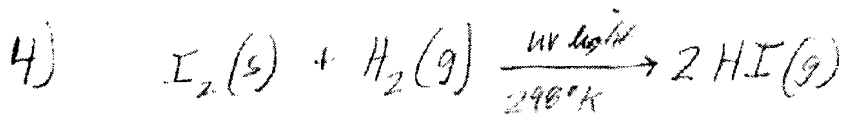
$$\ln \left(\frac{K_2}{K_1} \right) = \frac{-\Delta_r H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln K_2 = \frac{-38.9\text{ kJ}\cdot\text{mole}\cdot\text{K}}{\text{mole}\cdot 0.008314\text{ kJ}} \left(\frac{1}{1259\text{K}} - \frac{1}{1000\text{K}} \right) + \ln(0.75)$$

$$\ln K_2 = 0.67 \quad e^{0.67} = K_2$$

$$K_2 = 1.95$$

experimental K is 1.60 the calc. K is 1.95 this is off by 0.32
 reasons for this are likely that we have assumed the $\Delta_r G^\circ$ is independent
 of T in the calc of $\Delta_r H^\circ$ and $\Delta_r S^\circ$ and also that $\Delta_r H^\circ$ is constant w/ T from
 1000 K to 1259 K, however $\Delta_r G^\circ$ and $\Delta_r H^\circ$ are not independent of T



39% HI 61% H₂ @ 300K and 1 bar

$$\Delta_r G^\circ \quad Y_{\text{HI}} = 0.39 \quad Y_{\text{H}_2} = 0.61 \quad Y = \frac{P}{P_0}$$

$P_0 = 1 \text{ bar}$

$$K = \frac{a_{\text{HI}}^2}{a_{\text{I}_2} a_{\text{H}_2}} = \frac{\left(\frac{P_{\text{HI}}}{P_0}\right)^2}{\left(\frac{P_{\text{H}_2}}{P_0}\right)} = \frac{P_{\text{HI}}^2}{P_{\text{H}_2}} = \frac{(0.39)^2}{(0.61)} = 0.25$$

$$\Delta_r G^\circ = -RT \ln K = -\frac{8314 \text{ J}}{\text{mole} \cdot \text{K}} (300 \text{ K}) \ln 0.25 = 3457.7 \frac{\text{J}}{\text{mole}}$$

$$\Delta_r G^\circ = 3.5 \text{ kJ} / \text{mole}$$

| | I ₂ | H ₂ | HI | total gas |
|----------------|-------------------------|----------------|----------------------|-----------|
| initial | 0.5 | 0.5 | 0 | 0.5 |
| equil | 0.5-x | 0.5-x | 2x | 0.5+x |
| P _i | $\frac{0.5-x}{0.5+x} P$ | | $\frac{2x}{0.5+x} P$ | |

P = 1 bar

$$K = \frac{P_{\text{HI}}^2}{P_{\text{H}_2}} = \frac{\left(\frac{2x}{0.5+x} P\right)^2}{\left(\frac{0.5-x}{0.5+x} P\right)} = \frac{(2x)^2}{(0.5-x)(0.5+x)} = \frac{4x^2}{(0.25-x^2)} = 0.25$$

$$4x^2 = 0.25(0.25-x^2) = 0.0625 - 0.25x^2 = 4x^2 + 0.25x^2$$

$$4.25x^2 = 0.0625$$

$$x^2 = 0.015$$

$$x = 0.12$$

$$\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ$$

$$\Delta_r G^\circ = \frac{3502 - 2650}{\text{mole}} = \frac{852}{\text{mole}}$$

$$\Delta_r S^\circ = 0.077 \text{ kJ} / \text{K} \cdot \text{mole}$$

$$\Delta H = 6.62 \text{ kJ}$$

$$\Delta H = n \times \Delta_r H^\circ \quad n = 0.12$$

$$\frac{\Delta H}{n} = \frac{6.62 \text{ kJ}}{0.12} = 55.2 \text{ kJ/mole}$$

$$\Delta_r H^\circ = 55.2 \text{ kJ/mole}$$



$$Q = \frac{a_{\text{H}_2(l)}^{2 \rightarrow 1} a_{\text{O}_2(g)}^{1 \rightarrow 1}}{a_{\text{H}_2\text{O}}^{2 \rightarrow 1}} = a_{\text{O}_2(g)} = \frac{p_{\text{O}_2}}{p^0} = p_{\text{O}_2}$$

$p^0: 1 \text{ bar}$

$$\Delta_r G^\circ = -RT \ln K$$

$$\Delta_r G^\circ = 2 \Delta_f G^\circ \text{H}_2(l) + \Delta_f G^\circ \text{O}_2(g) - 2 \Delta_f G^\circ \text{H}_2\text{O}(s)$$

$$2(0) + 0 - 2(-58.54 \text{ kJ/mole}) = 117.08 \text{ kJ/mole}$$

$$e^{\frac{\Delta_r G^\circ}{-RT}} = K$$

$T @ 298 \text{ K}$
 $K = 3 \times 10^{-21}$

$$Q = p_{\text{O}_2}$$

w/ 20% of the air in the atmosphere being oxygen $Q \approx 0.2$ and then $Q > K$ so the rxn is also favoring the reactant because of the large amount of O_2 in the earth's atmosphere then the reaction will not occur except at high T or in an environment w/ much less O_2

| | 7. A(s) | B(g) | + C(s) | + D(m) | Total Gas |
|---------|--------------------|---------------------|--------------------|-------------------|-----------|
| initial | | 4 | 1 | 0 | 5 |
| equal | | 4-2x | 1+x | 3x | 5+2x |
| P: | | $\frac{4-2x}{5+2x}$ | $\frac{1+x}{5+2x}$ | $\frac{3x}{5+2x}$ | |

$$P_C = P_D \therefore 3x = 1+x \quad \therefore P_B = \frac{1}{2} \quad P_C = \frac{1}{4} \quad P_D = \frac{1}{4}$$

$$x = 0.5$$

$$K = \frac{\frac{P_C}{P^\circ} \cdot \frac{P_D^3}{P^\circ{}^3}}{\frac{P_B^2}{P^\circ{}^2}} = \frac{P_C \cdot P_D^3}{P_B^2 \cdot P^\circ{}^2} = \frac{1/4 \cdot 1/64}{1/4 \cdot 3^2} = \frac{1}{576}$$

$$\Delta_r G^\circ = -RT \ln [K]$$

$$= -8.314 \cdot 300 \cdot \ln \left[\frac{1}{576} \right]$$

$$= 15.9 \text{ kJ/mole}$$

$$q = \Delta_r H \cdot x = +1 \text{ kJ}$$

$$w = -\Delta n RT = 2x \cdot 8.314 \cdot 300 = -2.49 \text{ kJ}$$

$$\Delta U = q + w = 1 \text{ kJ} + (-2.49 \text{ kJ})$$

$$= -1.49 \text{ kJ}$$