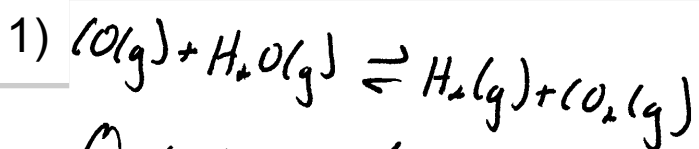


CH 302H Spring 2016 HW 4 key



Qualitatively: There are equal moles of gas on each side of the equation, so nothing happens when you increase pressure

Quantitatively:

$$K_p = \frac{\left(\frac{P_{\text{H}_2}}{p^\circ}\right)^{\nu_{\text{H}_2}} \left(\frac{P_{\text{CO}_2}}{p^\circ}\right)^{\nu_{\text{CO}_2}}}{\left(\frac{P_{\text{CO}}}{p^\circ}\right)^{\nu_{\text{CO}}} \left(\frac{P_{\text{H}_2\text{O}}}{p^\circ}\right)^{\nu_{\text{H}_2\text{O}}}}$$

but $P_{\text{H}_2\text{O}} = X_{\text{H}_2\text{O}} P_{\text{TOT}}$
 $P_{\text{CO}_2} = X_{\text{CO}_2} P_{\text{TOT}}$
 etc...

$$\Rightarrow K_p = \frac{\left(\frac{X_{\text{H}_2} P_{\text{TOT}}}{p^\circ}\right)^{\nu_{\text{H}_2}} \left(\frac{X_{\text{CO}_2} P_{\text{TOT}}}{p^\circ}\right)^{\nu_{\text{CO}_2}}}{\left(\frac{X_{\text{CO}} P_{\text{TOT}}}{p^\circ}\right)^{\nu_{\text{CO}}} \left(\frac{X_{\text{H}_2\text{O}} P_{\text{TOT}}}{p^\circ}\right)^{\nu_{\text{H}_2\text{O}}}}$$

→

$$\text{define } K_x = \frac{X_{H_2}^{v_{H_2}} X_{CO_2}^{v_{CO_2}}}{X_{CO}^{v_{CO}} X_{H_2O}^{v_{H_2O}}} = \prod_c X_c^{v_c}$$

$$K_p = K_x \left(\frac{P_{\text{Tot}}}{p^0} \right)^{v_{H_2} + v_{CO_2} - v_{CO} - v_{H_2O}} = K_x \left(\frac{P_{\text{Tot}}}{p^0} \right)^{+1-1-1} = K_x \frac{P_{\text{Tot}}}{p^0}$$

$$\underline{K_p = 1(K_x)}$$

No change in K_x is necessary to keep K_p constant, so nothing happens as pressure increases.

$$2) k_p(2100\text{K}) = 2k_p(2000\text{K})$$

$$\ln\left(\frac{k_p(2100\text{K})}{k_p(2000\text{K})}\right) = \frac{-\Delta H_{rxn}^\circ}{R} \left(\frac{1}{2100\text{K}} - \frac{1}{2000\text{K}} \right)$$

$$\text{Solve for } \Delta H_{rxn}^\circ = \frac{-R \ln\left(\frac{k_p(2100\text{K})}{k_p(2000\text{K})}\right)}{\left(\frac{1}{2100\text{K}} - \frac{1}{2000\text{K}}\right)} = \frac{(-8.314\text{ J/mol}) \ln(2)}{\left(\frac{1}{2100\text{K}} - \frac{1}{2000\text{K}}\right)}$$

$$\Delta H_{rxn}^\circ = 242\text{ kJ/mol}$$



P: qualitative: there are two moles of gas on both sides of the equation, so there will be no change in the location of equilibrium as pressure changes

quantitative: $K_p = K_x P_{\text{TOT}}^{\sum \nu_i} = K_x P_{\text{TOT}}^{1+1-2} = K_x P_{\text{TOT}}^0 = K_x (1)$

So no change in K_x to keep K_p constant as P_{TOT} changes

T: We have to do a bit more work:

ΔG_f°	CH_3OH	$(\text{CH}_3)_2\text{O}$	H_2O
ΔG_f°	-166.4 kJ/mol	-112.7 kJ/mol	-228.6 kJ/mol
ΔH_f°	-238.7 kJ/mol	-184.1 kJ/mol	-241.8 kJ/mol

$$\begin{aligned} \Delta H_{\text{rxn}}^\circ &= \Delta H_f^\circ(\text{H}_2\text{O}) + \Delta H_f^\circ((\text{CH}_3)_2\text{O}) - 2\Delta H_f^\circ(\text{CH}_3\text{OH}) \\ &= (-241.8 \text{ kJ/mol}) - 184.1 \text{ kJ/mol} - (2)(-238.7 \text{ kJ/mol}) \end{aligned}$$

$$\underline{\Delta H_{\text{rxn}}^\circ = 50.9 \text{ kJ/mol}}$$

$$\begin{aligned} \Delta G_{\text{rxn}}^\circ &= \Delta G_f^\circ(\text{H}_2\text{O}) + \Delta G_f^\circ((\text{CH}_3)_2\text{O}) - 2\Delta G_f^\circ(\text{CH}_3\text{OH}) \\ &= -228.6 \text{ kJ/mol} + (-112.7 \text{ kJ/mol}) - (2)(-166.4 \text{ kJ/mol}) \end{aligned}$$

$$\underline{\Delta G_{\text{rxn}}^\circ = -8.5 \text{ kJ/mol}}$$

$$K_p = \exp \left[\frac{-(-8.5 \times 10^3 \text{ J/mol})}{(8.314 \text{ J/Kmol})(298 \text{ K})} \right] = \underline{30} = K_p$$



qualitative: Since $\Delta H_{rxn} > 0$, if we increase T , the rxn will move to products.

quantitative: Since $k_p = 31$, at 298k, Products will be 30x reactants. Let's say I want to make $k_p = 1000$, so products are 1000x reactants:

$$\ln \left(\frac{k_p(T_2)}{k_p(298k)} \right) = \frac{-\Delta H_{rxn}}{R} \left(\frac{1}{T_2} - \frac{1}{298k} \right)$$

$$\begin{aligned} \text{Solve for } T_2: \quad \frac{1}{T_2} &= \frac{-R}{\Delta H_{rxn}} \left[\ln \left(\frac{k_p(T_2)}{k_p(298k)} \right) \right] + \frac{1}{298k} \\ &= \frac{-(8.314 \text{ J/kmol})}{(50.9 \times 10^3 \text{ J/mol})} \left[\ln \left(\frac{1000}{30} \right) \right] + \frac{1}{298k} \\ \frac{1}{T_2} &= 0.0032 \text{ 1/k} \end{aligned}$$

$$\boxed{T_2 = 317 \text{ K}}$$

So we heat it up by not too much to push the rxn to products.



b) $K = \frac{P_{\text{HI}}^2}{P_{\text{H}_2} P_{\text{I}_2}}$

c) First, determine the value of K from ΔG_{rxn}

$$\Delta G_{\text{rxn}} = \Delta H_{\text{rxn}} - T\Delta S_{\text{rxn}}$$

$$\Delta H_{\text{rxn}} = 2(\Delta H_f[\text{HI}]) - \Delta H_f(\text{H}_2) - \Delta H_f(\text{I}_2)$$

$$= 2(26.48 \frac{\text{kJ}}{\text{mol}}) - 0 - 62.44 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta H_{\text{rxn}} = -9.48 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta S_{\text{rxn}} = 2(206.48 \frac{\text{J}}{\text{K}\cdot\text{mol}}) - 130.57 \frac{\text{J}}{\text{K}\cdot\text{mol}} - 260.58 \frac{\text{J}}{\text{K}\cdot\text{mol}}$$

$$\Delta S_{\text{rxn}} = 21.81 \frac{\text{J}}{\text{K}\cdot\text{mol}}$$

$$\Delta G_{\text{rxn}}(600\text{K}) = -9.48 \times 10^3 \frac{\text{J}}{\text{mol}} - 600\text{K} (21.81 \frac{\text{J}}{\text{K}\cdot\text{mol}})$$

$$\Delta G_{\text{rxn}} = -22.57 \frac{\text{J}}{\text{mol}}$$

$$\therefore K = \exp\left[\frac{-\Delta G}{RT}\right] = \exp\left[\frac{22.57 \frac{\text{J}}{\text{mol}}}{8.314 \frac{\text{J}}{\text{K}\cdot\text{mol}} \cdot 600\text{K}}\right] = \underline{92.6}$$

Let's assume that the flask was filled at 25°C , then the partial pressures of the gases is:

$$P_{\text{H}_2}(600\text{K}) = 1.32 \text{ atm} \left(\frac{600\text{K}}{298\text{K}}\right) = 2.66 \text{ atm}$$

$$P_{\text{I}_2}(600\text{K}) = 1.140 \text{ atm} \left(\frac{600\text{K}}{298\text{K}}\right) = 2.30 \text{ atm}$$

Set up an ICE table to write an expression for K in terms of the equilibrium partial pressures.

	H_2	I_2	HI
I	2.66	2.30	0
Δ	-x	-x	+2x
E	2.66-x	2.30-x	2x



4 (cont.)

$$K = \frac{(2x)^2}{(2.66-x)(2.30-x)} = 92.6$$

multiply and collect terms...

$$88.6x^2 - 459.30x + 566.56 = 0$$

$$x = \frac{459.30 \pm \sqrt{(459.30)^2 - 4(88.6)(566.56)}}{2(88.6)}$$

gives negative pressures, so not physical

$$x = \cancel{3.16}, 2.02$$

$$P_{HI} = 2 \cdot 2.02 \text{ atm} = \boxed{4.04 \text{ atm}}$$

$$P_{H_2} = 2.66 \text{ atm} - 2.02 \text{ atm} = \boxed{0.64 \text{ atm}}$$

$$P_{I_2} = 2.3 \text{ atm} - 2.02 \text{ atm} = \boxed{0.28 \text{ atm}}$$

$$d) \text{ percent reacted} = \frac{2.30 \text{ atm} - 0.28 \text{ atm}}{2.30 \text{ atm}} \times 100\% = \boxed{87.8\% \text{ reacted}}$$

$$\textcircled{5} \quad \text{a) } K = \frac{(P_{\text{H}_2\text{S(g)}})^8}{(P_{\text{H}_2\text{(g)}})^8}$$

$$\text{b) } K = \frac{P_{\text{COCl}_2\text{(g)}} P_{\text{H}_2\text{(g)}}}{P_{\text{Cl}_2\text{(g)}}}$$

$$\text{c) } K = P_{\text{CO}_2\text{(g)}}$$

$$\text{d) } K = \frac{1}{(P_{\text{C}_2\text{H}_2\text{(g)}})^3}$$

⑥

$$K_1 = \frac{P_{XeOF_4} (P_{HF})^2}{P_{XeF_6} P_{H_2O}}$$

$$K_2 = \frac{P_{XeOF_4} P_{XeO_3F_2}}{P_{XeO_4} P_{XeF_6}}$$

$$K_3 = \frac{P_{XeO_3F_2} P_{H_2O}}{P_{XeO_4} (P_{HF})^2}$$

There are several ways to do this. Here is one:

a) Use K_1 expression to solve for P_{XeOF_4} :

$$P_{XeOF_4} = \frac{K_1 P_{XeF_6} P_{H_2O}}{(P_{HF})^2}$$

b) Use K_2 expression to solve for $P_{XeO_3F_2}$:

$$P_{XeO_3F_2} = \frac{K_2 P_{XeO_4} P_{XeF_6}}{P_{XeOF_4}}$$

c) Plug results from a) and b) into expression for K_3 and cancel terms:

$$K_3 = \frac{K_2 \cancel{P_{XeO_4}} \cancel{P_{XeF_6}} \cancel{P_{H_2O}} \cancel{(P_{HF})^2}}{\cancel{P_{XeO_4}} \cdot K_1 \cdot \cancel{P_{XeF_6}} \cancel{P_{H_2O}} \cancel{(P_{HF})^2}}$$

$$K_3 = \frac{K_2}{K_1}$$