

Problem Set 6 Solutions
CHM 3400, Fall 2011, Dr. Chatfield

1. (Atkins 7.2)

$$(a) \quad K = \frac{a_{\text{COCl}_2} a_{\text{Cl}_2}}{a_{\text{CO}} a_{\text{Cl}_2}} \approx \frac{P_{\text{COCl}_2} P_{\text{Cl}_2}}{P_{\text{CO}} P_{\text{Cl}_2}}$$

$$(b) \quad K = \frac{a_{\text{SO}_3}^2}{a_{\text{SO}_2}^2 a_{\text{O}_2}} \approx \frac{P_{\text{SO}_3}^2}{P_{\text{SO}_2}^2 P_{\text{O}_2}}$$

$$(c) \quad K = \frac{a_{\text{HBr}}^2}{a_{\text{H}_2} a_{\text{Br}_2}} \approx \frac{P_{\text{HBr}}^2}{P_{\text{H}_2} P_{\text{Br}_2}}$$

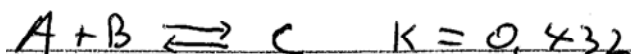
$$(d) \quad K = \frac{a_{\text{O}_2}^3}{a_{\text{O}_3}^2} \approx \frac{P_{\text{O}_2}^3}{P_{\text{O}_3}^2}$$

In the approximate expressions, partial pressures must be in bar, and units are ignored.

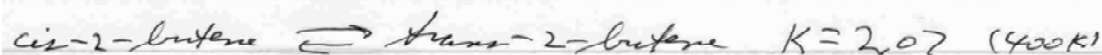
Alternatively, each partial pressure can be replaced with the ratio over p^\ominus , e.g.

$$P_{\text{COCl}_2} \rightarrow \frac{P_{\text{COCl}_2}}{p^\ominus}$$

2. (Atkins 7.4)



3. (Atkins 7.6)



$$\Delta_r G^\ominus = -RT \ln K = -2419 \text{ J/mol} = -2.419 \text{ kJ/mol}$$

4. (Atkins 7.9)

$$1^{\text{st}} \text{ reactions } \Delta_r G^\circ(1) = -250 \text{ kJ/mol}$$

$$K(1) = e^{-\Delta_r G^\circ(1)/RT} \leftarrow \text{assume } 298 \text{ K (same)}$$

$$= 6,61 \times 10^{43}$$

$$2^{\text{nd}} \text{ reactions: } K(2) = \frac{1}{8.4} K(1) = 7,87 \times 10^{42}$$

$$\Delta_r G^\circ(2) = -RT \ln K(2) = -245 \text{ kJ/mol}$$

5. (Atkins 7.17)

$$\ln K' - \ln K = \frac{\Delta_r H^\circ}{R} \left(\frac{1}{T} - \frac{1}{T'} \right)$$

$$\Delta_r H^\circ = +224 \text{ kJ/mol}$$

$$\text{At } T = 1200 \text{ K, } \Delta_r G^\circ = +33 \text{ kJ/mol} \Rightarrow K = e^{-\Delta_r G^\circ/RT} = 0,04$$

$$+33 \text{ kJ/mol}$$

$$\leftarrow \begin{matrix} \Delta_r G^\circ \\ -\Delta_r G^\circ/RT \end{matrix} \leftarrow 1200 \text{ K}$$

$$= 0,04$$

$$K' = 1, \text{ want to solve for } T'$$

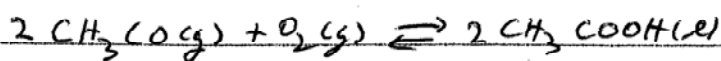
$$\ln(1) - \ln(0,0450) = \frac{+224 \text{ kJ/mol}}{R} \left(\frac{1}{1200 \text{ K}} - \frac{1}{T'} \right)$$

$$T' = 1501 \text{ K}$$

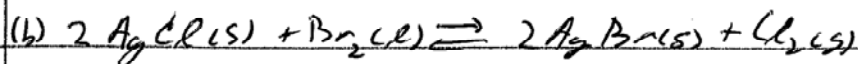
6. (Atkins 7.22)

$$K > 1 \text{ if } \Delta_r G^\circ < 0$$

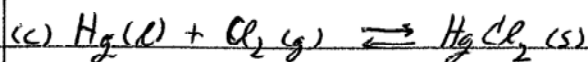
$$(a) \Delta_r G^\circ = \sum_{\text{prod.}} \nu_i \Delta_f G^\circ - \sum_{\text{react}} \nu_i \Delta_f G^\circ$$



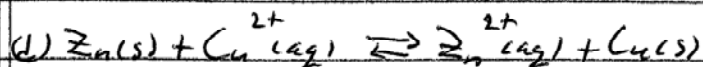
$$\Delta_r G^\circ = 2(-389.9) - 2(-128.86) + 0 = -522.08 \text{ kJ/mol}$$



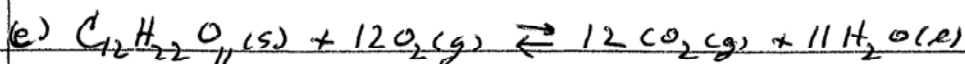
$$\Delta_r G^\circ = 2(96.90) + 0 - 2(-109.79) - 0 = +25.78 \text{ kJ/mol}$$



$$\Delta_r G^\circ = -178.6 - 0 - 0 = -178.6 \text{ kJ/mol}$$



$$\Delta_r G^\circ = -147.06 + 0 - 0 - 65.49 = -212.55 \text{ kJ/mol}$$



$$\Delta_r G^\circ = 12(-394.36) + 11(-237.13) - (-1543) - 0 = -5798 \text{ kJ/mol}$$

$K > 1$ for a, c, d, e. Note $K > 1$ means products are favored.

7. (Atkins 7.37)

This is gas phase reaction, so activities are approximately equal to partial pressures and $K_p \approx K_c$. However, problem asks for concentration, so it will be to convert to K_c and work in terms of molar based concentration.

$$K_c = K_p \left(\frac{c^\ominus RT}{p^\ominus} \right)^{-\Delta n_{\text{gas}}} \quad \text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$$

$\Delta n_{\text{gas}} = +1$

$K_c = 0.0108 \quad 0.0831447 \text{ L}\cdot\text{bar}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$

$$M(\text{PCl}_5) = 30.97 + 5(35.45) = 208.22 \text{ g/mol}$$

$$n_{\text{PCl}_5} = 1.5 \text{ g} / 208.22 \text{ g/mol} = 0.007204 \text{ mol}$$

	initial	change	final	final []
PCl ₅	0.007204	-x	0.007204 - x	4(0.007204 - x)
PCl ₃	-	x	x	4x
Cl ₂	-	x	x	4x

$V = 0.250 \text{ L}$

$$K_c = 0.0108 = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = \frac{16x^2}{0.028816 - 4x}$$

$$16x^2 + 0.0433x - 0.000312 = 0$$

$$x = \frac{-0.0433 \pm \sqrt{0.0433^2 + 4(16)(0.000312)}}{2(16)} = 0.00327, -0.00597$$

unphysical
↓

x cannot be negative because it represented the final number of moles of PCl₃ and Cl₂.
Therefore x = 0.00327 is the only acceptable solution.

$$\text{Final } n(\text{PCl}_5) = 0.007204 - 0.00327 = 0.00393 \text{ mol}$$

$$n(\text{PCl}_3) = n(\text{Cl}_2) = 0.00327 \text{ mol}$$

$$[\text{PCl}_5] = \frac{n(\text{PCl}_5)}{0.250 \text{ L}} = 0.0157 \text{ M}$$

$$[\text{PCl}_3] = [\text{Cl}_2] = 0.0131 \text{ M}$$

$$\% \text{ decomposition of PCl}_5 = \frac{0.00327 \text{ mol}}{0.007204 \text{ mol}} \cdot 100\% = 45.4\%$$

8. (Atkins 7.38)



$$\text{Initial: } P_{\text{N}_2} = 0.020 \text{ bar} \quad P_{\text{H}_2} = 0.020 \text{ bar} \quad P_{\text{NH}_3} = 0$$

	Initial	change	Final
P_{N_2}	0.020	-x	0.020-x
P_{H_2}	0.020	-3x	0.020-3x
P_{NH_3}	0	+2x	+2x

$$K = 0.036 = \left(\frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} P_{\text{H}_2}^3} \right)_{\text{final}} = \frac{(2x)^2}{(0.020-x)(0.020-3x)^3}$$

This will lead to a difficult-to-solve quartic equation. Therefore we will make the approximation that x and 3x are small compared to 0.020 and neglect them in the denominator. Later we will test the assumption.

$$K \approx \frac{(2x)^2}{(0.020)(0.020)^3} = 2.5 \times 10^7 x^2 = 0.036$$

$$x = \sqrt{\frac{0.036}{2.5 \times 10^7}} = 3.8 \times 10^{-5}$$

Check: Is x small compared to 0.020 (<5%)? yes
 \Rightarrow approximation OK

$$\begin{aligned} \text{At equilibrium: } P_{\text{N}_2} &= 0.020 - x = 0.019962 \text{ bar} \\ P_{\text{H}_2} &= 0.020 - 3x = 0.019886 \text{ bar} \\ P_{\text{NH}_3} &= 2x = 7.6 \times 10^{-5} \text{ bar} \end{aligned}$$