Homework 10 Key

1.

	SCl_2	+	$2\,C_2H_4$	⇌	$S(CH_2CH_2Cl)_2$
I	0.675		0.973		0
C	$-x$		$-2x$		$+x$
E	$0.675-x$		$0.973-2x$		$+x$

$$K_c = \frac{[S(CH_2CH_2Cl)_2]}{[C_2H_4]^2[SCl_2]}$$

↑ equals 0.350 M

$[SCl_2]_{eq} = 0.675 - 0.350 = 0.325\,M$
$[C_2H_4]_{eq} = 0.973 - 2(0.350) = 0.273\,M$
$[S(CH_2CH_2Cl)_2]_{eq} = 0.350\,M$

$$K_c = \frac{0.350}{(0.273)^2(0.325)} = 14.45$$

$$K_p = K_c\left(\frac{c^\circ RT}{P^\circ}\right)^{V_{S(CH_2CH_2Cl)_2} - V_{SCl_2} - V_{C_2H_4}}$$

$$K_p = 14.45\left(\frac{1\,\frac{\cancel{mol}}{\cancel{L}}\cdot 0.08314\,\frac{\cancel{L}\cdot\cancel{bar}}{\cancel{mol}\cdot\cancel{K}}\cdot 293\,\cancel{K}}{1\,\cancel{bar}}\right)^{1-1-2}$$

$$K_p = 0.024$$

$V_{S(CH_2CH_2Cl)_2} = 1$
$V_{SCl_2} = 1$
$V_{C_2H_4} = 2$
$c^\circ = 1\ mol/L$
$R = 0.08314\ \frac{L\cdot bar}{mol\cdot K}$
$T = 293\ K$
$P^\circ = 1\ bar$

2. a) Shift in equilibrium position to favor reactants (K_p decreases)
b) Shift in equilibrium position to favor products (no change in K_p)
c) No change to equilibrium position or K_p

3.

	$2NOCl_{(g)}$	⇌	$2NO$	+	Cl_2
I	n_0		0		0
C	-2ξ		$+2\xi$		$+\xi$
E	$n_0-2\xi$		$+2\xi$		$+\xi$

total # moles: $n_0 - \cancel{2\xi} + \cancel{2\xi} + \xi$
$= n_0 + \xi$

$$K_p = \frac{P_{NO}^2 P_{Cl_2}}{P_{NOCl}^2} = \frac{(X_{NO}^2 \cancel{P_{tot}})^{\cancel{2}} X_{Cl_2} P_{tot}}{X_{NOCl}^2 \cancel{P_{tot}^2}}$$

$X_{NO} = \frac{2\xi}{n_0+\xi}$

$X_{Cl_2} = \xi / n_0+\xi$

$X_{NOCl} = \frac{n_0-2\xi}{n_0+\xi}$

3(cont)

$$K_p = \left(\frac{2\xi}{\cancel{n_0+\xi}}\right)^2\left(\frac{\xi}{n_0+\xi}\right)\left(\frac{\cancel{n_0+\xi}}{(n_0-2\xi)}\right)^2 P_{tot}$$

$$= \frac{4\xi^2\cdot\xi}{(n_0+\xi)(n_0-2\xi)^2} P_{tot}$$

$$= \frac{4\xi^3}{(n_0+\xi)(n_0-2\xi)^2} P_{tot}$$ ~~[illegible]~~

~~$$= \frac{4(\xi/n_0)^3}{(1+\xi/n_0)(1-2\xi/n_0)^2} P_{tot}$$~~

4. a) $N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$

$$\Delta_r G^\circ = 2\,\Delta G_f^\circ(NO_2) - \Delta G_f^\circ(N_2O_4)$$
$$= 2(51.258) - 97.787$$
$$= 4.729\ \text{kJ/mol} = 4729\ \text{J/mol}$$

$K_p = e^{-\Delta_r G^\circ/RT}$ $T = 298\,K$, $R = 8.314\ \text{J/mol}\cdot K$

$= 0.148$

b) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

$$\Delta_r G^\circ = 2\,\Delta G_f^\circ(HI) - \Delta G_f^\circ(I_2) - \Delta G_f^\circ(H_2)$$
$$= 2(1.560) - 19.325 - 0$$
$$= -16.205\ \text{kJ/mol} = -16205\ \text{J/mol}$$
$$K_p = e^{-\Delta_r G^\circ/RT}$$
$$= 692$$

5. $2H_2(g) + CO(g) \rightleftharpoons CH_3OH(g)$

$$Q = \frac{P_{CH_3OH}}{P_{CO}P_{H_2}^2} = \frac{10.0\ \text{bar}/1\ \text{bar}}{\left(\frac{0.005\ \text{bar}}{1\ \text{bar}}\right)\left(\frac{0.10\ \text{bar}}{1\ \text{bar}}\right)^2} = 2\times10^5$$

$K_p = 2.21\times10^4$

$Q > K_p$ Rxn will proceed toward left (make more H_2+CO ~~[illegible]~~)

(Also $\Delta_r G = RT\ln Q/K_p$, here $\Delta_r G > 0$ so rxn isn't spontaneous as written

6. $H_{2\,(g)} + I_{2\,(g)} \rightleftharpoons 2HI_{(g)}$ $\Delta_r H^\circ = -12.93$ KJ/mol

a) $k_p(1000K) = 29.1$

Van't Hoff Eq

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

$$\ln\left(\frac{29.1}{k_p(700)}\right) = -\frac{-12.93\times 1000 \text{ J/mol}}{8.314 \text{ J/mol}\cdot\text{K}}\left(\frac{1}{1000} - \frac{1}{700}\right)$$

$$\ln\left(\frac{29.1}{k_p}\right) = -0.664$$

$$\frac{29.1}{k_p} = e^{-0.664}$$

$$k_p = 56.7 \quad @\ 700\,K$$

b) k_p decreases as a function of increasing temperature because this is a exothermic reaction.

$$K_p = \frac{[HI]^2}{[H_2][I_2]}$$ so more HI when k_p is bigger... more HI at 700K.

c) $k_p(1000K)$ is bigger for endothermic rxn

7. $$CaF_{2\,(s)} \rightleftharpoons Ca^{2+}_{(aq)} + 2F^-_{(aq)}$$

$$K_{sp} = a_{Ca^{2+}}\, a_{F^-}^2 = C_{Ca^{2+}} C_{F^-}^2 \gamma_\pm^3 = 3.9\times 10^{-11}$$

$$\text{so } C_{Ca^{2+}} C_{F^-}^2 = \frac{3.9\times 10^{-11}}{\gamma_\pm^3}$$

Step 1 Let $\gamma_\pm = 1$ and $s = C_{Ca^{2+}}$

so $C_{F^-} = 2s$

$$(s)(2s)^2 = 3.9\times 10^{-11} / \cancel{\gamma_\pm^3}^{\,1}$$

$$4s^3 = 3.9\times 10^{-11} \qquad s = 2.136\times 10^{-4}\ M$$

Step 2 Ionic Strength

$$I_c = \frac{1}{2}\left(z_+^2 c_{Ca^{2+}} + (z_-)^2 c_{F^-}\right)$$

$$= \frac{1}{2}\left(2^2 \cdot s + (-1)^2 \cdot 2s\right.$$ $s = 2.136 \times 10^{-4}$ M

$$\left. + 2^2 \cdot 0.015 + (-2)^2 0.015\right)$$ MgSO$_4$

$$= 0.0606 \text{ M}$$

Step 3 Extended Debye-Huckel for $\gamma_\pm$

$$\ln \gamma_\pm = \frac{-1.173 |z_+ z_-| I_c^{1/2}}{1 + I_c^{1/2}}$$

$I_c = 0.0606$ M
$z_+ = 2$
$z_- = -1$

$$= -0.463$$

$$\gamma_\pm = 0.629$$

Step 4 Repeat Step 1 w/ $\gamma_\pm = 0.629$

$$4s^3 = 3.9 \times 10^{-11} / (0.629)^3 \quad s = 3.396 \times 10^{-4} \text{ M}$$

Step 5 Repeat Step 2 w/ ~~γ~~ new $s = 3.396 \times 10^{-4}$ M

$$I_c = \frac{1}{2}\left(2^2 s + (-1)^2 \cdot 2s + 2^2 \cdot 0.015 + (-2)^2 0.015\right)$$

$$= 0.0610 \text{ M}$$

Step 6 Repeat Step 3 w/ new I_c

$$\ln \gamma_\pm = \frac{-1.173 |z_+ z_-| I_c^{1/2}}{1 + I_c^{1/2}} = -0.4647$$

$$\gamma_\pm = 0.628$$

Repeat Cycle (steps 1-3)

w/ new $\gamma_\pm$, $s = 3.402 \times 10^{-4}$ M
w/ new s, $I_c = 0.0610$ M
w/ new I_c, $\gamma_\pm = 0.628$
w/ $\gamma_\pm$, $s = 3.402 \times 10^{-4}$ M $\boxed{\text{converged}}$

Without using activities, s was 2.14×10^{-4} M but it really is 3.40×10^{-4} M!