UNIVERSITY OF ROCHESTER
COLLEGE OF ARTS AND SCIENCE
DEPARTMENT OF CHEMISTRY

CHEM131 HOMEWORK #10 KEY

6-25. PCl_5 --> $PCl_3 + Cl_2$ We know the initial pressure of PCl_5, before the dissociation reaction begins, is $P_{PCl5} = 0.50$ and the equilibrium pressure is $P_{eq} = 0.84$. If the equilibrium pressure of PCl_3 is $P_{PCL3} = X$, then $P_{Cl2} = X$, and $P_{PCl5} = 0.50 - X$. The final pressure is just the sum of the three component pressures, 0.84 = 0.50 - X + X + X and X = 0.34. So P_{PCL3} = 0.34 atm, P_{Cl2} = 0.34 atm, and P_{PCl5} = 0.16 atm.

K_p = 0.34_0.34/0.16 = 0.72 atm; $K = K_p/(RT)^{\Delta n} = K_p/RT$, since $\Delta n = 1$ (see previous homework set)

K = 0.72/(0.8206*523) = 0.017 mol/L

6-28. This question requires calculating numerous reaction quotients. Units of both mol/L and pressure are used, but since Δn is 0, $K = K_P$. If the reaction quotient, Q, is larger than K, the reaction goes to the left; if Q < K, the rxn goes to the right; if Q = K, the rxn is at equilibrium.

6-28a. $Q = 2.0*2.6/(0.024)^2 = 9*10^3 > K$ and the reaction shifts to the left.

6-28b. $Q = 0.62*2.0/(0.016)^2 = 2.4*10^3 = K$ and the reaction is at equilibrium.

6-28c. $Q = 0.80*0.57/(0.020)^2 = 1.1*10^3 < K$ and the reaction shifts to the right.

6-28d. $Q = 0.11*2.0/(0.010)^2 = 2.2*10^3 < K$ and the reaction shifts to the right.

6-28e. $0.36*0.67/(0.0078)^2 = 4.0*10^3 > K$ and the reaction shifts to the left.

6-28f. $Q = 0.51*0.18/(0.0062)^2 = 2.4*10^3 = K$ and the reaction is at equilibrium.

6-29. If the reaction quotient, Q, is larger than K, the reaction goes to the left and $[H_2O]$ decreases; if Q < K, the rxn goes to the right and $[H_2O]$ increases; if Q = K, $[H_2O]$ stays the same. So you have more Q's to calculate.

a. Q = (0.22*0.10)/(0.010*0.010) = 220 > K, $[H_2O]$ decreases

b. Q = 2.2 = K, $[H_2O]$ constant

c. Q = 0.40 < K, $[H_2O]$ increases

d. Q = 2.2 = K, $[H_2O]$ constant

e. $K = 2.2 = 2.0[H_2O]/(0.10*5.0)$, $[H_2O]$ = 0.55 M

f. Since water is not the solvent, the concentration of water changes as the reaction proceeds and must be included in K.

6-31. a. First we need the number of moles of Cl_2O and H_2O present. 1.0/18.0 = 5.6810^{-2} mol H_2O, 2.0/86.9 = $2.3*10^{-2}$ mol Cl_2O.

	H_2O	+	Cl_2O	⇔	2HOCl
initial	5.6810^{-2}		2.3_10^{-2}		0
change	-X		-X		2X
equil.	5.6810^{-2} - X		2.3_10^{-2} - X		2X

$K = 4X^2/\{(5.6810^{-2} - X)(2.3*10^{-2} - X)\} = 0.090$, unfortunately this is a quadratic equation. See PRACTICE.xls on the ChemLab web page for using Excel to solve quadratic equations.

$3.91X^2 + 7.11*10^{-3} - 1.16*10^{-4} = 0$; applying X = [-b ± (b^2 - 4ac)–]/2a gives X = $4.6*10^{-3}$ M or $-6.4*10^{-3}$ M

Clearly the positive result is the only one that is possible.

H_2O = 0.051, Cl_2O = 0.0.018, HOCl = $0.079.2*10^{-3}$ M

b. We can carry on the same table,

initial	0	0	1.0/2.0 = 0.50
change	X	X	-2X
equil.	X	X	.50 - 2X

$K = (.50 - 2X)^2/X^2 = 0.090$; $(.50 - 2X)/X = 0.30$; $2.30X = 0.50$; $X = 0.217$

H_2O = 0.22, Cl_2O = 0.22, HOCl = 0.07 M

6-33. This is a very important atmospheric reaction because $SO_3 + H_2O \rightarrow H_2SO_4$, a major component of acid rain. This reaction is catalyzed by particulate matter and aerosols that are also part of air pollution. First set up the ICE table:

initial	0.50	0.50	0
change	-2X	-X	+2X
equilibrium	0.50 - 2X	0.50 - X	2X

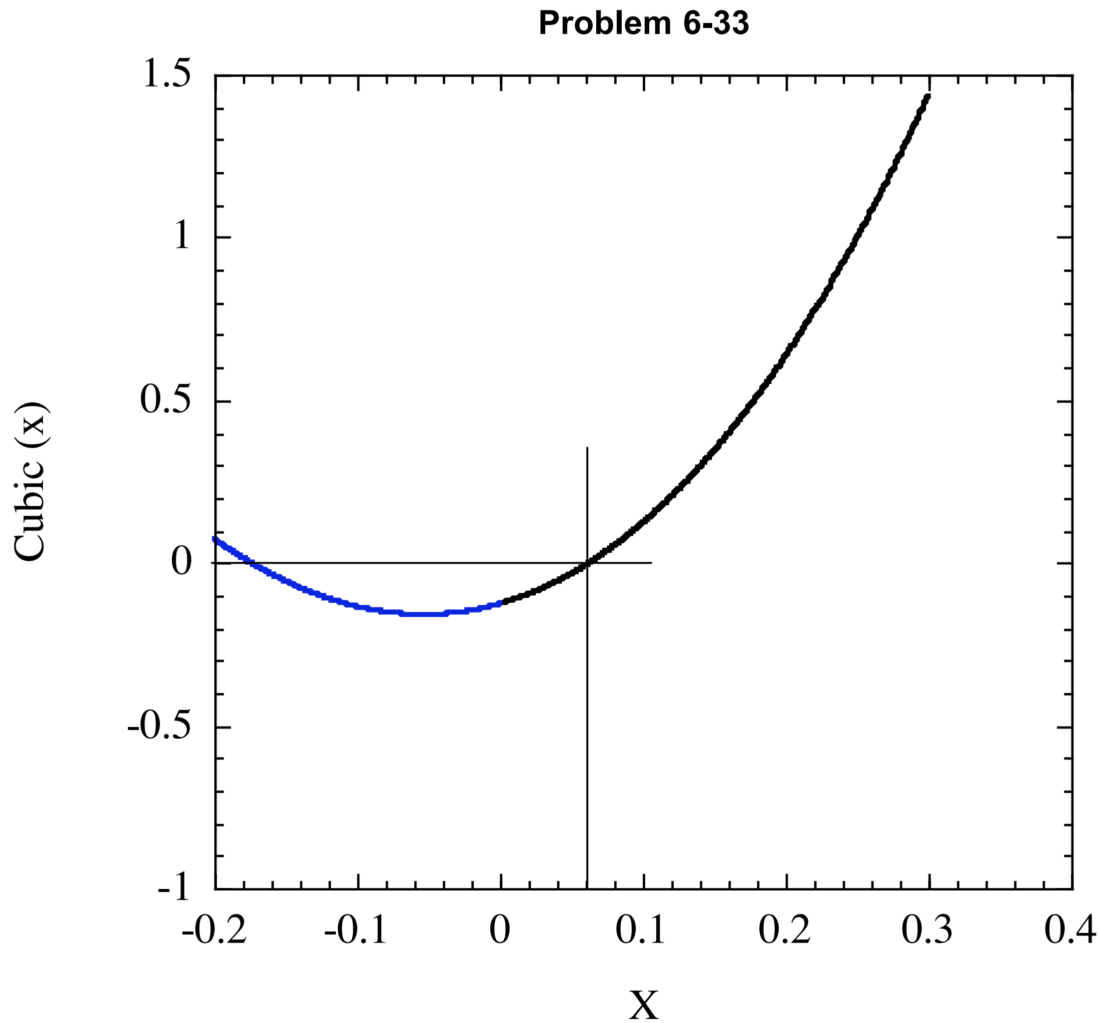
$K_P = 0.25 = 4X^2/\{(0.50 - 2X)^2(0.50 - X)\}$ This is a cubic equation, so you HOPE that leaving the 2X and X terms out of the denominator will give a value for X that is small relative to 0.50. Sometimes you win and sometimes you lose, and this time you lose. Successive approximations are required and now is the perfect time to use the first sheet of Eq&Absorption.xls Excel Project from ChemLab. See page 113 of your Lab Manual.

Alternatively, you can use some little grey cells to get the answer another way. The cubic equation is: $4x^3+12x^2+1.25x-0.125 = 0$. This has three roots, but we know some things about the physical root: a) our x is positive, and b) our x is < 0.25 or else we run out of SO_2. SO, we can graph the cubic using your favorite program and look for where it crosses zero somewhere Between $0<x<0.25$. (see next page) The answer is x = 0.06. SO,

P_{SO2}= 0.5-2x =0.38 atm

P_{H2O}= 0.5-x =0.44 atm

P_{SO3}= 2x =0.12 atm



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6-39a. $K_P = K(RT)^{\Delta n}$ and $\Delta n = -1$, so $K_P = 4.5*10^9/(0.08206*373) = 1.5*10^8$ atm^{-1}.

6-39b. Begin with an ICE table: Since K is very large effectively all of the material ENDS as $COCl_2$ so that we can say at equilibrium (approximately of course) P_{COCl2}= 5.0 atm. Let Y = partial pressures of CO and Cl_2 initially. (remember = moles means = pressures)

initial	Y	Y	0.0
change	-X	-X	+X
equilibrium	Y-X	Y-X	X

$K_P = 1.5*10^8 = X/(Y-X)^2$. Since K_P is so large, the equilibrium state of the reaction lies far to the right and X ~ 5 atm. So solve $1.5*10^8 = 5.0/(Y-X)^2$ to get Y-X = $1.8*10^{-4}$, which is indeed very much less than 5. (5% rule holds). At equilibrium $P_{CO} = P_{Cl2}$= Y-X = $1.8*10^{-4}$ atm.

6-41. Since ethanol is a reactant, the larger the ethanol concentration the farther to the right will be the equilibrium result. Water is a product so any water pushes the reaction to the left. So pure ethanol is the best choice.

6-46. The water vapor in the air under humid conditions favors rain and also pushes this reaction to the right, or pink side.

6-49. a) Adding H_2 (*g*) shifts the equilibrium to the LEFT.
b) Removing I_2 (*g*) shifts the equilibrium to the RIGHT.
c) Removing HI (*g*) shifts the equilibrium to the LEFT.
d) Adding Ar (*g*) does NOT shift the equilibrium. (no change in partial pressures)
e) Doubling the volume of the container does NOT shift the equilibrium. (convince yourself by writing out K in terms of mol/V and double V.
f) The reaction is exothermic – meaning Heat can be thought of as a product. Decreasing the temperature shifts the equilibrium to the RIGHT (to make more heat).

6-60. $PCl_5 \leftrightharpoons PCl_3 + Cl_2$ $K_p = 11.5$ atm

a. PV = nRT; n = 2.540/208.22 = 1.220_10^{-2} mol; P = nRT/V = $1.220*10^{-2}$ * 0.08206 * 600/0.500 = 1.16 atm

b. initial	1.16	0	0
change	-X	X	X
equil.	1.16 - X	X	X

$K_p = X^2/1.16\text{-}X = 11.5$; $X^2 + 11.5X - 13.3 = 0$; Use $X = [-b \pm (b^2 - 4ac)^{1/2]}/2a$

X = +1.06 or -12.6 atm and obviously +1.06 atm is correct, and $X = P_{PCl3} = P_{Cl2}$

$P_{PCl5} = 1.16 - 1.06 = 0.10$ atm

c. Just add the three partial pressures, $P_{tot} = 0.10 + 1.06 + 1.06 = 2.22$ atm

d. X is the amount of PCl_5 that dissociated, 1.16 is the total amount of PCl_5 so % dissoc. = 100*1.06/1.16 = 91.6% (Note that partial pressures are used here rather than concentrations but this is OK for assumed ideal gas behavior.

Next H.W.: Ch. 7: 22,31,33,39, 43,59,72,73