Chapter 16

Sample Exercise Writing Equilibrium-Constant Expressions
Write the equilibrium expression, K_c, for the following reactions:
$2O_3(g) \rightleftharpoons 3O_2(g)$ $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$ $Ag^+(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)$

$K_c = \frac{[O_2]^3}{[O_3]^2}$ $K_c = \frac{[NOCl]^2}{[NO]^2[Cl_2]}$ $K_c = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2}$

homogeneous equilibrium

Sample Exercise Writing Equilibrium-Constant Expressions for Heterogeneous Reactions
Write the equilibrium-constant expression, K_c, for each of the following reactions:
$Ni(OH)_2(s) \rightleftharpoons Ni^{2+}(aq) + 2OH^-(aq)$ $H_2O(l) \rightleftharpoons H_2O(g)$ $HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$

exclude liquids and solids

$K_c = [Ni^{2+}][OH^-]^2$ $K_c = [H_2O(g)]$ $K_c = \frac{[H_3O^+][F^-]}{[HF]}$

Practice Writing Equilibrium-Constant Expressions
1) Write the expressions for K_c for the following reactions, and indicate whether the reaction is homogeneous or heterogeneous.

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

$K_c = \frac{[HI]^2}{[H_2][I_2]}$

ans: homogeneous $K_c = \frac{[HI]^2}{[H_2][I_2]}$

$Cd^{2+}(aq) + 4Br^-(aq) \rightleftharpoons CdBr_4^{2-}(aq)$ homogeneous

$K_c = \frac{[CdBr_4^{2-}]}{[Cd^{2+}][Br^-]^4}$

ans: homogeneous $k_c = \frac{[CdBr_4^{2-}]}{[Cd^{2+}][Br^-]^4}$

$Ni(CO)_4(g) \rightleftharpoons Ni(s) + 4CO(g)$ heterogeneous

$K_c = \frac{[CO]^4}{[Ni(CO)_4]}$

ans: heterogeneous $K_c = \frac{[CO]^4}{[Ni(CO)_4]}$

$2Ag(s) + Zn^{2+}(aq) \rightleftharpoons 2Ag^+(aq) + Zn(s)$ heterogeneous

$K_c = \frac{[Ag^+]^2}{[Zn^{2+}]}$

ans: heterogeneous $K_c = \frac{[Ag^+]^2}{[Zn^{2+}]}$

Sample Exercise Converting between K_c and K_p
In the synthesis of ammonia from nitrogen and hydrogen:
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
$K_c = 9.60$ at 300 °C. Calculate K_p for this reaction at this temperature.

$K_p = K_c(RT)^{\Delta n}$ Δn = # gas moles Prod − # gas moles Reactants

$9.6(.08206 \times (300 + 273))^{-2}$ $2-(3+1)$

$2 - 4$

-2

$K_p = .0043$

Practice Converting between K_c and K_p.

1) For the equilibrium $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$, K_c is 4.08×10^{-3} at 1000 K. Calculate the value for K_p. **ans: 0.335**

$K_p = K_c(RT)^{\Delta N}$ $K_p = (4.08 \times 10^{-3})(.08206(1000))^1$

0.335

2) If $K_c = 0.042$ for $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$ at 500 K, what is the value of K_p for this reaction at this temperature? **ans: 1.0×10^{-3}**

$K_p = K_c(RT)^{\Delta N}$ $K_p = (.042)(.08206(500))^{-1}$

1.0×10^{-3}

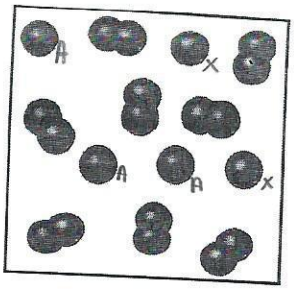
3) Calculate K_c at 303 K for $SO_2(g) + Cl_2(g) \rightleftharpoons SO_2Cl_2(g)$ if $K_p = 34.5$ at this temperature. **ans: 858**

$K_p = K_c(RT)^{\Delta N}$ $34.5 = K_c(.08206(303))^{-1}$

858

Sample Exercise: Interpreting the Magnitude of an Equilibrium Constant

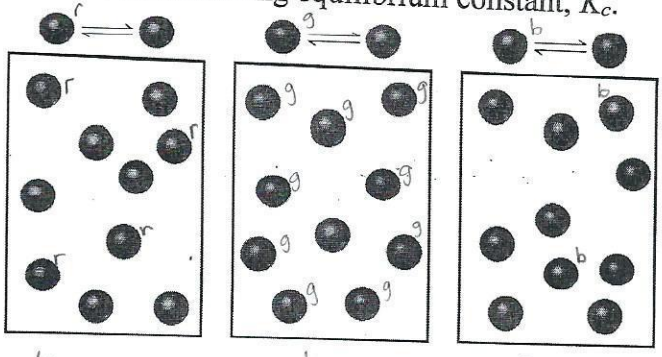
The diagram represents an equilibrium mixture produced for a reaction of the type $A + X \rightleftharpoons AX$. If the volume is 1 L, is K greater or less than 1?



$K = \frac{P}{R}$ $= \frac{8}{3(2)}$ $\frac{8}{6}$ greater

Sample Exercise: Interpreting the Magnitude of an Equilibrium Constant

This diagram represents three different systems at equilibrium, all in the same size containers. Rank the three systems in order of increasing equilibrium constant, K_c.



$\frac{6}{4}$ $\frac{1}{9}$ $\frac{8}{2}$

2 1 3

Sample Exercise: Interpreting the Magnitude of an Equilibrium Constant
When the following reactions come to equilibrium, does the equilibrium mixture contain mostly reactants or mostly products?

$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $K_c = 1.5 \times 10^{-10}$ reactants
.000000000015

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ $K_p = 2.5 \times 10^{9}$ products
2500000000

Practice: Interpreting Equilibrium Constants
1) The following reactions occur at 500 K. Arrange them in order of increasing tendency to proceed to completion (least completion → greatest completion). **ans: 3 < 4 < 1 < 2**

1) $2NOCl \rightleftharpoons 2NO + Cl_2$ $K_p = 1.7 \times 10^{-2}$ .017 3
2) $N_2O_4 \rightleftharpoons 2NO_2$ $K_p = 1.5 \times 10^{3}$ 1500 4
3) $2SO_3 \rightleftharpoons 2SO_2 + O_2$ $K_p = 1.3 \times 10^{-5}$ .000013 1
4) $2NO_2 \rightleftharpoons 2NO + O_2$ $K_p = 5.9 \times 10^{-5}$ .000059 2

Sample Exercise Calculating *K* When All Equilibrium Concentrations Are Known
A mixture of hydrogen and nitrogen in a reaction vessel is allowed to attain equilibrium at 472 °C. The equilibrium mixture of gases was analyzed and found to contain 7.38 atm H_2, 2.46 atm N_2, and 0.166 atm NH_3. From these data, calculate the equilibrium constant K_p for the reaction:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

$K_p = \frac{(P_{NH_3})^2}{(P_{N_2})(P_{H_2})^3}$ at Eq: 2.46 7.38 .166

$= \frac{(.166)^2}{(2.46)(7.38)^3}$

$= 2.79 \times 10^{-3}$

Practice Calculating K
1) Phosphorous pentachloride decomposes according to the following equation.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

At 250 °C, the equilibrium $[PCl_5] = 1.271$ M, $[PCl_3] = 0.229$ M, and $[Cl_2] = 0.229$ M. What is the value of K_c? **ans: 0.0413**

$K_c = \frac{[P_{PCl_3}][Cl_2]}{[PCl_5]}$ $\frac{(.229)(.229)}{(1.271)} = .0413$

2) For each of the following hypothetical reactions, write the expression for the equilibrium constant and calculate its value. Assume that all components are gaseous.

a) $A + B \rightleftharpoons 2C$
At equilibrium, [A] = [B] = 7.02×10^{-3} M, and [C] = 2.16×10^{-2} M ans: $K_c = 9.47$

$K_C = \frac{[C]^2}{[A][B]}$ $K_c = \frac{(2.16 \times 10^{-2})^2}{(7.02 \times 10^{-3})(7.02 \times 10^{-3})} = 9.47$

b) $2A \rightleftharpoons 2C + D$
At equilibrium, [A] = 6.59×10^{-4} M, [C] = 4.06×10^{-3} M, and [D] = 2.03×10^{-3} M.
ans: $K_c = 7.71 \times 10^{-2}$

$K_C = \frac{[C]^2[D]}{[A]^2} = \frac{(4.06 \times 10^{-3})^2 (2.03 \times 10^{-3})}{(6.59 \times 10^{-4})^2} = 7.71 \times 10^{-2}$

c) $2A + B \rightleftharpoons 2C$
At equilibrium, [A] = 5.50×10^{-3} M, [B] = 2.25×10^{-3} M, and [C] = 1.02×10^{-2} M.
ans: $K_c = 1.53 \times 10^3$

$K_c = \frac{[C]^2}{[A]^2[B]} = \frac{(1.02 \times 10^{-2})^2}{(5.5 \times 10^{-3})^2 (2.25 \times 10^{-3})} = 1.53 \times 10^3$

3) Gaseous hydrogen iodide is placed in a closed container at 425 °C, where it partially decomposes to hydrogen and iodine:

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

At equilibrium it is found that [HI] = 3.53×10^{-3} M, [H_2] = 4.79×10^{-4} M, and [I_2] = 4.79×10^{-4} M. What is the value of Kc at this temperature? ans: $K_c = 1.84 \times 10^{-2}$

$K_C = \frac{[H_2][I_2]}{[HI]^2} = \frac{(4.79 \times 10^{-4})(4.79 \times 10^{-4})}{(3.53 \times 10^{-3})^2} = 1.84 \times 10^{-2}$

4) The equilibrium $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$ is established at 500 K. An equilibrium mixture of the three gases has partial pressures of 0.095 atm for NO, 0.171 atm for Cl_2, and 0.28 atm for NOCl. Calculate Kp for this reaction at 500 K. **ans: Kp = 51**

$K_p = \frac{[NOCl]^2}{[NO]^2[Cl_2]} = \frac{(.28)^2}{(.095)^2(.171)} = 51$

5) The following equilibrium reaction is used in the manufacture of methanol. The equilibrium constant at 400 K for the reaction is 1.609.

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

At equilibrium, the concentration of CH_3OH in the reaction vessel is 0.818 M and the concentration of CO is 1.402 M. What is the concentration of H_2 in the vessel? **ans: 0.602 M**

$K_C = \frac{[CH_3OH]}{[CO][H_2]^2}$ $1.609 = \frac{.818}{(1.402)(x^2)}$ $1.609(1.402x^2) = .818$

$2.25x^2 = .818$ $x^2 = .3626$ $x = .602\ M$

6) At 700 K, the equilibrium constant is 3.164×10^3 for the following reaction system for the hydrogenation of ethene, C_2H_4, to ethane, C_2H_6.

$$C_2H_4(g) + H_2(g) \rightleftharpoons C_2H_6(g)$$

What will be the equilibrium concentration of ethene if the concentration of H_2 is 0.0619 M and the concentration of C_2H_6 is 1.055 M? **ans: 5.39×10^{-3} M**

$3.164 \times 10^3 = \frac{1.055}{(.0619)(x)}$ $195.85x = 1.055$

$x = 5.39 \times 10^{-3}\ M$

7) When nitrogen monoxide gas comes in contact with air, it oxidizes to the brown gas nitrogen dioxide according to the following equation:

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

a) The equilibrium constant for this reaction at 500 K is 1.671×10^4. What concentration of NO_2 is present at equilibrium if [NO] = 6.200×10^{-2} M and $[O_2] = 8.305 \times 10^{-3}$ M? **ans: 0.7034 M**

$1.671 \times 10^4 = \frac{x^2}{(6.2 \times 10^{-2})^2 (8.305 \times 10^{-3})}$

$.533 = x^2$ $x = .7304\ M$

b) At 1000 K, the equilibrium constant for this reaction is 1.315×10^{-2}. If the concentrations for NO and O_2 are the same as in (a), what will be the concentration of NO_2? **ans: 6.479×10^{-4} M**

$1.315 \times 10^{-2} = \frac{x^2}{(6.2 \times 10^{-2})^2 (8.305 \times 10^{-3})}$

$4.20 \times 10^{-7} = x^2$

$6.479 \times 10^{-4}\ M = x$

Sample Exercise Calculating *K* from Initial and Equilibrium Concentrations
A closed system initially containing 1.000×10^{-3} *M* H_2 and 2.000×10^{-3} M I_2 at 448 °C is allowed to reach equilibrium. Analysis of the equilibrium mixture shows that the concentration of HI is 1.87×10^{-3} *M*. Calculate K_c.

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

	H_2	I_2	$2HI$
Initial Molarity	1.000×10^{-3}	2.000×10^{-3}	0
change	$-x$	$-x$	$+2x$
Equilibrium	$1.000 \times 10^{-3} - x$	$2.000 \times 10^{-3} - x$	$2x = 1.87 \times 10^{-3}$
	$1.000 \times 10^{-3} - 9.35 \times 10^{-4}$		$x = 9.35 \times 10^{-4}$

eq. constant: 6.5×10^{-5} $\quad 1.06 \times 10^{-3}$

$$K_c = \frac{[HI]^2}{[H_2][I_2]} \rightarrow K_c = \frac{(1.87 \times 10^{-3})^2}{(6.5 \times 10^{-5})(1.06 \times 10^{-3})} = 50.5$$

Sample Exercise Calculating *K* from Initial and Equilibrium Concentrations
Sulfur trioxide decomposes at high temperature in a sealed container:

$$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$$

Initially, the vessel is charged at 1000 K with $SO_3(g)$ at 0.500 atm. At equilibrium the SO_3 is 0.200 atm. Calculate K_p.

	SO_3	SO_2	O_2
Initial	.5	0	0
Concentration	$-2x$	$+2x$	x
Equilibrium	.2	$2x$	x
		.3	.15

$.5 - 2x = .2$
$-.2x = -.3$
$x = .15$

$$K_p = \frac{(P_{SO_2})^2 (P_{O_2})}{(P_{SO_3})^2}$$

$$K_p = \frac{(.3)^2 (.15)}{(.2)^2} = .3375$$

Sample Exercise Calculating *K* from Initial and Equilibrium Concentrations
1.25 moles of NOCl were placed in a 2.50 L reaction chamber at 427°C. After equilibrium was reached, 1.10 moles of NOCl remained. Calculate the equilibrium constant, K_c, for the reaction

$$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g).$$

$$K_c = \frac{[NO]^2[Cl_2]}{[NOCl]^2}$$

Always in [ ] mol/L

	$2NOCl$	$2NO$	Cl_2
I	1.25	0	0
C	$-2x$	$+2x$	$+x$
E	1.10	$+2x$	$+x$
		$2(.075)$	.075
		.15	

$1.25 - 2x = 1.10$
$-2x = -.15$
$x = .075$

$$K_c = \frac{\left[\frac{.15}{2.5}\right]^2 \left[\frac{.075}{2.5}\right]}{\left[\frac{1.10}{2.5}\right]^2}$$

$K_c = 5.578 \times 10^{-4}$

Practice Calculating K from Initial and Equilibrium Concentrations

1) A mixture of 0.100 mol of NO, 0.050 mol of H_2, and 0.100 mol of H_2O is placed in a 1.0 L vessel at 300 K. The following equilibrium is established:

$$2NO(g) + 2H_2(g) \rightleftharpoons N_2(g) + 2H_2O(g)$$

At equilibrium, [NO] = 0.062 M. Calculate K_c. **ans: 6.5 x10²**

I	.1	.05	0	.1
C	-2x	-2x	+x	+2x
E	.1-2x	.05-2x	x	.1+2x

.1 - 2x = .062
x = .019

$$K_c = \frac{[N_2][H_2O]^2}{[NO]^2[H_2]^2} = \frac{(.019)(.1+2(.019))^2}{(.1-2(.019))^2(.05-2(.019))^2} = 6.5 \times 10^2$$

2) A mixture of 4.103 atm of CO_2, 2.052 atm of H_2, and 3.282 atm H_2O is placed in a 2.000 L vessel. The following equilibrium is established at 500.0 K

$$CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$$

At equilibrium, P_{H_2O} = 3.510 atm. Calculate K_p. **ans: K_p.= 0.1132**

3.282 + x = 3.51
x = .228

I	4.103	2.052	0	3.282
C	-x	-x	+x	+x
E	4.103-x	2.052-x	x	3.282+x

$$K_p = \frac{(P_{CO})(P_{H_2O})}{(P_{CO_2})(P_{H_2})} = \frac{(.228)(3.282+.228)}{(4.103-.228)(2.052-.228)} = .1132$$

3) The reaction A(g) + 2B(g) ⇌ C(g) was allowed to come to equilibrium. The initial amounts of reactants placed into a 5.00 L vessel were 1.0 mol A and 1.8 mol B. After the reaction reached equilibrium, 1.0 mol of B was found. Calculate K_c for this reaction. **ans: 17**

I	1	1.8	0
C	-x	-2x	+x
E	1-x	1.8-2x	x

1.8 - 2x = 1
x = .4

$$K_c = \frac{[C]}{[A][B]^2} = \frac{\left(\frac{.4}{5}\right)}{\left(\frac{1-.4}{5}\right)\left(\frac{1.8-2(.4)}{5}\right)^2} = \frac{.08}{(.12)(.04)}$$

$$= 17$$

4) The brown gas NO_2 and the colorless gas N_2O_4 exist in equilibrium, $2NO_2 \rightleftharpoons N_2O_4$. In an experiment, 0.625 mole of N_2O_4 was introduced into a 5.00 L vessel and was allowed to decompose until equilibrium was reached. The concentration of N_2O_4 at equilibrium was 0.0750 M. Calculate K_c for the reaction. **ans: 7.5**

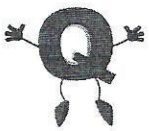
	$2NO_2$	$\rightleftharpoons$	N_2O_4
I	0		.625
C	-2x		+x
E	0-2x		.625 + x

$.625 + x = .0750$

$x = -.55$

$$K_c = \frac{[N_2O_4]}{[NO_2]^2} = \frac{\left[\frac{.625 + -.55}{5}\right]}{\left[\frac{-2(-.55)}{5}\right]^2} = \frac{.015}{.0484} =$$

Sample Exercise Predicting the Direction of Approach to Equilibrium



At 448 °C the equilibrium constant K_c for the reaction

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

K ↘

is 50.5. Predict in which direction the reaction will proceed if we start with 2.0×10^{-2} mol of HI, 1.0×10^{-2} mol of H_2, and 3.0×10^{-2} mol of I_2 in a 2.00-L container.

$Q = \frac{[HI]^2}{[H_2][I_2]}$ All initial concentrations

$$\frac{\left(\frac{2.0 \times 10^{-2}\ mol}{2L}\right)^2}{\left(\frac{1 \times 10^{-2}\ mol}{2L}\right)\left(\frac{3.0 \times 10^{-2}\ mol}{2L}\right)} = 1.3$$

$1.3 < 50.5$

$Q < K$ moves right

Practice Using Q, the Reaction Quotient.

1) At 100 °C the equilibrium constant for the reaction $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$ has the value $K_c = 2.19 \times 10^{-10}$. Are the following mixtures at equilibrium? If not, indicate the direction that the reaction must proceed to achieve equilibrium.

a) $[COCl_2] = 2.00 \times 10^{-3}$ M, $[CO] = 3.3 \times 10^{-6}$ M, $[Cl_2] = 6.62 \times 10^{-6}$ M **ans: Q = 1.1×10^{-8}, shift left**

$$Q = \frac{[CO][Cl_2]}{[COCl_2]} = \frac{(3.3 \times 10^{-6})(6.62 \times 10^{-6})}{2 \times 10^{-3}} = 1.1 \times 10^{-8}$$

$Q > K$ shifts left

b) $[COCl_2] = 4.50 \times 10^{-2}$ M, $[CO] = 1.1 \times 10^{-7}$ M, $[Cl_2] = 2.25 \times 10^{-6}$ M **ans: Q = 5.5×10^{-12}, shift right**

$$Q = \frac{(1.1 \times 10^{-7})(2.25 \times 10^{-6})}{4.5 \times 10^{-2}} = 5.5 \times 10^{-12}$$

$Q < K$ Shifts right

c) $[COCl_2] = 0.010$ M, $[CO] = [Cl_2] = 1.48 \times 10^{-6}$ M **ans: Q = 2.2×10^{-10}, the mixture is at equilibrium**

$Q = \frac{(1.48 \times 10^{-6})^2}{.010} = 2.19 \times 10^{-10}$

equilibrium

Sample Exercise Using Le Châtelier's Principle to Predict shifts in Equilibrium
Consider the equilibrium

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \quad \Delta H = 58.0 \text{ kJ}$$

endothermic

In which direction will the equilibrium shift when

(a) N_2O_4 is added to the right

(b) NO_2 is removed to the right

(c) the total pressure is increased by addition of $N_2(g)$ no effect

(d) the volume is increased to the right

(e) the temperature is decreased to the left

Practice Using Le Châtelier's Principle to Predict shifts in Equilibrium
Consider the following equilibrium, for which $\Delta H < 0$ exothermic

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) + \text{heat}$$

How will each of the following changes affect an equilibrium mixture of these three gasses?

a) O_2 is added to the system to the right

b) the reaction mixture is heated to the left

c) the volume of the reaction vessel is doubled to the left

d) a catalyst is added to the mixture no effect

e) the total pressure of the system is increased by adding helium no effect

f) SO_3 is removed from the system to the right

Sample Exercise Calculating Equilibrium Concentrations from Initial Concentrations
A 1.000-L flask is filled with 1.000 mol of H_2 and 2.000 mol of I_2 at 448 °C. The value of the equilibrium constant K_c for the reaction

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

is 50.5. What are the equilibrium concentrations of H_2, I_2, and HI in moles per liter?

$K_c = \frac{[HI]^2}{[H_2][I_2]} = 50.5$

	H_2	I_2	$2HI$
Initial	1	2	0
Concentration	$-x$	$-x$	$+2x$
Equilibrium	$1-x$	$2-x$	$2x$

$\frac{(2x)^2}{(1-x)(2-x)} = 50.5$

$\frac{4x^2}{2-x-2x+x^2} = 50.5$

$50.5(2-3x+x^2) = 4x^2$

$101 - 151x + 50.5x^2 = 4x^2$

$46.5x^2 - 151x + 101 = 0$

$x = \frac{-b \pm \sqrt{b^2-4ac}}{2a}$

$x = \frac{151 \pm \sqrt{(-151)^2 - 4(101)(46.5)}}{2(46.5)}$

$x = .937$ or 3.378

can't be a conc. can't be negative (with $1-x$ or $2-x$)

$H_2 = .063$
$I_2 = 1.063$
$2HI = 1.8734$

Practice Calculating Equilibrium Concentrations from Initial Concentrations
1) Carbon monoxide reacts with steam to form carbon dioxide and hydrogen. At 700 K the equilibrium constant, Kc, is 5.10. Calculate the equilibrium concentrations of all species if 1.00 mole of CO(g) and 1.00 mol of $H_2O(g)$ are placed in a 1.00 L flask.
ans: [CO(g)] = [H_2O(g)] = 0.307 M, [CO_2(g)] = [H_2(g)] = 0.693 M

$K_c = \frac{[CO_2][H_2]}{[CO][H_2O]} = 5.10$

$\frac{(x^2)}{(1-x)^2} = 5.10$

$\frac{x}{1-x} = \sqrt{5.10}$

$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$

I	1	1	0	0
C	$-x$	$-x$	$+x$	$+x$
E	$1-x$	$1-x$	x	x

$2.258 = \frac{x}{1-x}$

$2.258 - 2.258x = x$

$2.258 = 3.258x$

$x = .693$

$1 - .693 = .307$ CO, H_2O

H_2, CO_2: .693

2) At 200 °C the equilibrium constant for the reaction

$$2NO(g) \rightleftharpoons N_2(g) + O_2(g)$$

is Kc = 2.4×10^3. If the initial concentration of NO is 0.200 M, what are the equilibrium concentrations of NO, N_2, and O_2? **ans: [NO] = 0.0020 M, [N_2] = [O_2] = 0.099 M**

I	.2	0	0
C	$-2x$	$+x$	$+x$
E	$.2-2x$	x	x

$K_c = \frac{[N_2][O_2]}{[NO]^2} = 2.4 \times 10^3$

$\frac{x^2}{(.2-2x)^2} = 2.4 \times 10^3$

$\frac{x^2}{.04 - .8x + 4x^2} = 2.4 \times 10^3$

$x^2 = 2.4 \times 10^3 (.04 - .8x + 4x^2)$

$x^2 = 96 - 1920x + 9600x^2$

$0 = 9599x^2 - 1920x + 96$

$x = \frac{-b \pm \sqrt{b^2-4ac}}{2a}$

$0 = \frac{1920 \pm \sqrt{1920^2 - 4(9599)(96)}}{2(9599)}$

$x = .101$ or $.0989$

$.2 - 2(.0989)$

$[NO] = .0020$ M

$[N_2] = .099$ M

$[O_2] = .099$ M

3) At 250°C, the equilibrium constant K_p for the reaction $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ is 1.80. Sufficient PCl_5 is put into a reaction vessel to give an initial pressure of 2.74 atm at 250°C. Calculate the pressure of PCl_5 after the system has reached equilibrium. **ans: 1.24 atm**

$K_P = \frac{(P_{PCl_3})(P_{Cl_2})}{(P_{PCl_5})} = 1.8$

	PCl_5	PCl_3	Cl_2
I	2.74	0	0
C	$-x$	$+x$	$+x$
E	$2.74-x$	x	x

$\frac{x^2}{2.74-x} = 1.8$

$x^2 = 1.8(2.74-x)$

$x^2 = 4.932 - 1.8x$

$x^2 + 1.8x - 4.932 = 0$

$x = \frac{-b \pm \sqrt{b^2-4ac}}{2a}$

$x = \frac{-1.8 \pm \sqrt{1.8^2 - 4(1)(-4.932)}}{2(1)}$

$x = 1.49$ or -3.29

$2.74 - 1.49 = 1.24$ atm

4) For the reaction $SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$, the equilibrium constant is 18.0 at 1,200°C. If 1.0 mole of SO_2 and 2.0 moles of NO_2 are placed in a 20. L container, what concentration of SO_3 will be present at equilibrium? **ans: 5.4 x10^{-3} M** .048

$K_C = \frac{[SO_3][NO]}{[SO_2][NO_2]} = 18$

	SO_2	NO_2	SO_3	NO
I	1	2	0	0
C	$-x$	$-x$	$+x$	$+x$
E	$1-x$	$2-x$	x	x

$\frac{\left(\frac{x}{20}\right)\left(\frac{x}{20}\right)}{\left(\frac{1-x}{20}\right)\left(\frac{2-x}{20}\right)} = 18$

$\frac{\left(\frac{x}{20}\right)^2}{\left(\frac{1-x}{20}\right)} = 18\left(\frac{2-x}{20}\right)$

$\frac{(x)^2}{(20)} = \left(\frac{36-18x}{20}\right)\left(\frac{1-x}{20}\right)$

$\frac{x^2}{400} = \frac{36 - 36x - 18x + 18x^2}{400}$

$0 = 17x^2 - 54x + 36$

$x = \frac{54 \pm \sqrt{54^2 - 4(17)(36)}}{2(17)}$

$x = 2.22$ or $.9519$

$\frac{.9519}{20} = .048$

Sample Exercise Calculating K_{sp} from Molar Solubility ← that many moles of $BaSO_4(s)$ dissociate and dissolve in water
The molar solubility of barium sulfate is 1.05 x10^{-5} M. Calculate the Ksp for barium sulfate.

$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$

$S = 1.05\times10^{-5}$ $S = 1.05\times10^{-5}$

$K_{sp} = [Ba^{2+}][SO_4^{2-}]$

$= (1.05\times10^{-5})(1.05\times10^{-5}) = 1.1025\times10^{-10}$

Sample Exercise Calculating K_{sp} from Molar Solubility
The molar solubility of Ag_2CrO_4 is 6.5 x10^{-5} M. Calculate the Ksp for silver chromate.

$Ag_2CrO_4(s) \rightleftharpoons 2Ag^+(aq) + CrO_4^{2-}(aq)$

S $2S$ S

$(2)(6.5\times10^{-5})$ (6.5×10^{-5})

$K_{sp} = [Ag^+]^2[CrO_4^{2-}]$

$(2s)^2$ (s)

$4s^2$ s

$(2\times6.5\times10^{-5})^2(6.5\times10^{-5})$

$= 1.1\times10^{-12}$

Practice Calculating K_{sp} from Molar Solubility

1) The molar solubility of CaF_2 at 35 °C is 1.24×10^{-3} mol/L. What is the Ksp at this temperature? **ans: $K_{sp} = 7.63 \times 10^{-9}$**

$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$

S S 2S

1.24×10^{-3} $2(1.24 \times 10^{-3})$

$K_{sp} = [Ca^{2+}][F^-]^2$

$(1.24 \times 10^{-3})(2 \times (1.24 \times 10^{-3}))^2 = 7.63 \times 10^{-9}$

2) The molar solubility of $PbBr_2$ at 25 °C is 1.0×10^{-2} mol/L. Calculate K_{sp}. **ans: $K_{sp} = 4.0 \times 10^{-6}$**

$PbBr_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Br^-(aq)$

S S 2S

1.0×10^{-2} $2(1.0 \times 10^{-2})$

$K_{sp} = [Pb^{2+}][Br^-]^2 = (1.0 \times 10^{-2})(2(1.0 \times 10^{-2}))^2 = 4.0 \times 10^{-6}$

Sample Exercise Calculating K_{sp} from Solubility

A saturated solution of MgF_2 contains 0.00741 g of dissolved MgF_2 per 1.00×10^2 mL at 25 °C. What is the K_{sp} for MgF_2?

change to mol/L

$.00741\ g\ MgF_2 \mid \frac{mol\ MgF_2}{62.305\ g}$

$.1\ L$

$= 1.189 \times 10^{-3}\ M$

$MgF_2(s) \rightleftharpoons Mg^{2+}(aq) + 2F^-(aq)$

S S 2S

$K_{sp} = [Mg^{2+}][F^-]^2$

$= (1.189 \times 10^{-3})(2(1.189 \times 10^{-3}))^2$

$= 6.72 \times 10^{-9}$

Practice Calculating K_{sp} from Solubility

1) Silver bromate, $AgBrO_3$, is slightly soluble in water. A saturated solution is found to contain 0.276 g $AgBrO_3$ dissolved in 150.0 mL of water. Calculate Ksp for silver bromate. **ans: $K_{sp} = 6.09 \times 10^{-5}$**

$.276\ g \mid \frac{mol\ AgBrO_3}{235.77\ g}$

$.15\ L = 7.804 \times 10^{-3}$

$AgBrO_3(s) \rightleftharpoons Ag^{+1}(aq) + BrO_3^-(aq)$

S S

$K_{sp} = [Ag^{+1}][BrO_3^-] = 6.09 \times 10^{-5}$

2) 2.50 L of a saturated solution of calcium fluoride leaves a residue of 0.0427 g of CaF_2 when evaporated to dryness. Calculate the Ksp of CaF_2. **ans: Ksp = 4.20×10^{-11}**

$.0427\ g\ CaF_2 \mid \frac{mol\ CaF_2}{78.074\ g}$

$2.5\ L = 2.1876 \times 10^{-4}$

$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$

S S 2S

$K_{sp} = [Ca^{2+}][F^-]^2$

$K_{sp} = (2.1876 \times 10^{-4})(2(2.1876 \times 10^{-4}))^2$

$K_{sp} = 4.20 \times 10^{-11}$

3) It is found that 1.1 x10^{-2} g of SrF_2 dissolves per 100.0 mL of aqueous solution at 25 °C. Calculate the solubility product constant for strontium fluoride. **ans: Ksp = 2.7 x10^{-9}**

$SrF_2(s) \rightleftharpoons Sr^{2+}(aq) + 2F^-(aq)$

S 2S

.011g SrF_2 | 1 mol / 125.616 g = 8.76 x10^{-4} / .1 L

$K_{sp} = (8.76 \times 10^{-4})(2 \times (8.76 \times 10^{-4}))^2$

$K_{sp} = 2.7 \times 10^{-9}$

Sample Exercise Calculating Solubility from K_{sp}

What is the molar solubility of AgBr? Calculate the concentration of all species in solution.

use the handout $K_{sp} = 5.0 \times 10^{-13}$

$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$

S S S

$K_{sp} = [Ag^+][Br^-]$

$5.0 \times 10^{-13} = s^2$

$\sqrt{5.0 \times 10^{-13}} = s$

$7.1 \times 10^{-7}\ M = s$

$[Ag^+] = 7.1 \times 10^{-7}$

$[Br^-] = 7.1 \times 10^{-7}$

Sample Exercise Calculating Solubility from K_{sp}

What is the molar solubility of $PbCl_2$? Calculate the concentration of all species in solution.

$K_{sp} = 1.7 \times 10^{-5}$

$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$

S S 2S

$K_{sp} = [Pb^{2+}][Cl^-]^2$

$1.7 \times 10^{-5} = (s)(2s)^2$

$1.7 \times 10^{-5} = 4s^3$

$\sqrt[3]{\frac{1.7 \times 10^{-5}}{4}} = s = 1.6 \times 10^{-2}\ M$

$[Pb^{2+}] = 1.6 \times 10^{-2}\ M$

$[Cl^-] = 2(1.6 \times 10^{-2}) = 3.2 \times 10^{-2}\ M$

Sample Exercise Calculating Solubility from K_{sp}

What is the molar solubility of calcium phosphate? Calculate the concentration of all species in solution.

$K_{sp} = 2.0 \times 10^{-29}$

$Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$

S 3S 2S

$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2$

$(3s)^3(2s)^2$

$(27s^3)(4s^2)$

$2.0 \times 10^{-29} = 108\ s^5$

$\sqrt[5]{\frac{2.0 \times 10^{-29}}{108}} = s = 7.1 \times 10^{-7}$

$[Ca^{2+}] = 3(7.1 \times 10^{-7}) = 2.1 \times 10^{-6}\ M$

$[PO_4^{3-}] = 1.4 \times 10^{-6}\ M$

Sample Exercise Calculating pH from K_{sp}
Calculate the molar solubility of magnesium hydroxide and the pH of a saturated solution of magnesium hydroxide.

$K_{sp} = 1.8 \times 10^{-11}$

$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$

S S 2S

$k_{sp} = (s)(2s)^2$

$1.8 \times 10^{-11} = 4s^3$

$\sqrt[3]{\frac{1.8 \times 10^{-11}}{4}} = s = 1.65 \times 10^{-4}$

$[Mg^{2+}] = 1.65 \times 10^{-4}$

$[OH^-] = 3.3 \times 10^{-4}$

to get pH: $-\log[OH^-] = pOH = -\log 3.3 \times 10^{-4}$

$= 3.48$

$pH = 14 - 3.48 = 10.52$

Sample Exercise Calculating Solubility with Varying pH.
Calculate the molar solubility of magnesium hydroxide in a buffered solution where pH = 7.00

$K_{sp} = 1.8 \times 10^{-11}$

$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$ pH won't change, stays at 7

I	—	0	10^{-7}
C	—	+S	+2S
E	—	S	$10^{-7} + 2s$
			$\approx 10^{-7}$

$K_{sp} = [Mg^{2+}][OH^-]^2$

$= (s)(10^{-7} + 2s)^2$

$1.8 \times 10^{-11} \approx (s)(10^{-7})^2$

$1.8 \times 10^{-11} = (s)(10^{-14})$

$\frac{1.8 \times 10^{-11}}{10^{-14}} = S = 1.8 \times 10^3$

Practice Molar Solubility
1) Calculate the molar solubility of calcium sulfate. **ans: 4.9 x10^{-3} mol/L**

$K_{sp} = 2.4 \times 10^{-5}$ $CaSO_4(s) \rightleftharpoons Ca^{2+}(aq) + SO_4^{2-}(aq)$

$2.4 \times 10^{-5} = s^2$

$\sqrt{2.4 \times 10^{-5}} = s$

4.9×10^{-3} mol/L

2) What is the molar solubility of $Ca(OH)_2$? What is the pH of a saturated solution of $Ca(OH)_2$?
ans: solubility = 0.012 mol/L, pH = 12.37

$K_{sp} = 6.5 \times 10^{-6}$

$Ca(OH)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2OH^-(aq)$

S 2S

$6.5 \times 10^{-6} = 4s^3$

$\sqrt[3]{\frac{6.5 \times 10^{-6}}{4}} = s$

0.012 mol/L

$2(0.012) = .023$

$-\log(.023) = 1.62$

$14 - 1.62 = 12.37$

3) What is the solubility of LaF_3? **ans: 9 x10^{-6} mol/L**

$K_{sp} = 2 \times 10^{-19}$ $\quad LaF_3\ (s) \rightleftharpoons La^{3+}\ (aq) + 3F^-\ (aq)$ $\quad s \quad 3s$

$2 \times 10^{-19} = (s)(3s)^3$

$2 \times 10^{-19} = 27s^4$

9×10^{-6} mol/L

4) What is the molar solubility of Ag_2S? **ans: 1 x10^{-17} mol/L**

$K_{sp} = 6 \times 10^{-51}$ $\quad Ag_2S\ (s) \rightleftharpoons 2Ag^+\ (aq) + S^{2-}\ (aq)$ $\quad 2s \quad s$

$6 \times 10^{-51} = 4s^3$

1×10^{-17} mol/L

5) Calculate the molar solubility and the concentration of each species for each of the following

a) barium bromate, $Ba(BrO_3)_2$, Ksp = 2.43 x10^{-4}
ans: 3.93 x10^{-2} M, [Ba^{2+}] = 3.93 x10^{-2}, [BrO_3^-] = 7.86 x10^{-2} M

$Ba(BrO_3)_2\ (s) \rightleftharpoons Ba^{2+}\ (aq) + 2BrO_3^-\ (aq)$ $\quad s \quad 2s$

$2.43 \times 10^{-4} = 4s^3$

3.93×10^{-2} M

$[Ba^{2+}] = 3.93 \times 10^{-2}$ M

$[BrO_3^-] = 7.86 \times 10^{-2}$ M

b) lithium phosphate, Li_3PO_4, Ksp = 2.37 x10^{-4}
ans: 5.44 x10^{-2}M, [Li+] = 0.163 M, [PO_4^{3-}] = 5.44 x10^{-2} M

$Li_3PO_4\ (s) \rightleftharpoons 3Li^+\ (aq) + PO_4^{3-}\ (aq)$ $\quad 3s \quad s$

$2.37 \times 10^{-4} = 27s^4$

5.44×10^{-2} M

$[PO_4^{3-}] = 5.44 \times 10^{-2}$ M

$[Li^+] = .163$ M

c) magnesium phosphate, $Mg_3(PO_4)_2$, Ksp = 1.04 x10^{-24}
ans: 6.26 x10^{-6} M, [Mg^{2+}] = 1.88 x10^{-5} M, [PO_4^{3-}] = 1.25 x10^{-5} M

$Mg_3(PO_4)_2\ (s) \rightleftharpoons 3Mg^{2+}\ (aq) + 2PO_4^{3-}\ (aq)$ $\quad 3s \quad 2s$

$1.04 \times 10^{-24} = (27s^3)(4s^2)$

$1.04 \times 10^{-24} = 108s^5$

6.26×10^{-6} M

$[PO_4^{3-}] = 1.88 \times 10^{-5}$ M

$[Mg^{2+}] = 1.25 \times 10^{-5}$ M

d) bismuth(III) sulfide, Bi_2S_3, Ksp = 1.0×10^{-97}
ans: zero for all practical purposes or on my TI-30 calculator. But if you have an expensive calculator: 1.6×10^{-20} M, $[Bi^{3+}] = 3.1 \times 10^{-20}$ M, $[S^{2-}] = 4.7 \times 10^{-20}$ M

$Bi_2S_3(s) \rightleftharpoons 2Bi^{3+}(aq) + 3S^{2-}(aq)$
$2s \quad 3s$
$1 \times 10^{-97} = 108s^5$
0

e) zinc arsenate, $Zn_3(AsO_4)_2$, Ksp = 2.8×10^{-28}
ans: 1.2×10^{-6} M, $[Zn^{2+}] = 3.6 \times 10^{-6}$ M, $[AsO_4^{3-}] = 2.4 \times 10^{-6}$ M

$Zn_3(AsO_4)_2(s) \rightleftharpoons 3Zn^{2+}(aq) + 2AsO_4^{3-}(aq)$
$3s \quad 2s$
$2.8 \times 10^{-28} = 108s^5$
1.2×10^{-6} m
$[Zn^{2+}] = 3.6 \times 10^{-6}$
$[AsO_4^{3-}] = 2.4 \times 10^{-6}$

88.99

6) Calculate the solubility of $Mn(OH)_2$, Ksp = 1.6×10^{-13}, in grams per liter when buffered at

a) pH = 7.00 **ans: 1400 g/L**

$Mn(OH)_2(s) \rightleftharpoons Mn^{2+}(aq) + 2OH^-(aq)$

I	0		10^{-7}
C	s		2s
E	s		$10^{-7} + 2s$

$1.6 \times 10^{-13} = (s)(10^{-7})^2$
$1.6 \times 10^{-13} = s + 10^{-14}$
$1.5 \times 10^{-13} = s$

b) pH = 9.50 **ans: 0.014 g/L**

I	0		$10^{-4.5}$
C	s		2s
E	s		$10^{-4.5} + 2s$

$1.6 \times 10^{-13} = s(10^{-4.5})^2$
$s + 10^{-10}$
$-9.9 \times 10^{-11} = s$

c) pH = 11.80 **ans: 3.6×10^{-7} g/L**

I	0		$10^{-2.2}$
C	s		2s
E	s		$10^{-2.2} + 2s$

$1.6 \times 10^{-13} = s(10^{-2.2})^2$
$s + 10^{-4.4}$
$-3.9 \times 10^{-5} = s$