Chapter 14: 12, 18, 22, 24, 28, 32, 36, 44, 72

14.12 Calculate K_p for each reaction:

A. N_2O_4 (g) ↔ 2 NO_2 (g) K_c=5.9x10^{-3} at 298 K
B. N_2(g) + 3 H_2 (g) ↔2 NH_3 (g) K_c = 3.7x10^{8} at 298 K
C. N_2 (g) + O_2 (g)↔2 NO (g) K_c = 4.10x10^{-31} at 298 K

SOLUTION:

$$K_p = K_c(RT)^{\Delta n}$$

A.

$$K_p = K_c(RT)^{\Delta n} = (5.9 \times 10^{-3})(0.082058\frac{L\ atm}{mol\ K}298)^{2-1} = 0.144$$

B.

$$K_p = K_c(RT)^{\Delta n} = (3.7 \times 10^{8})(0.082058\frac{L\ atm}{mol\ K}298)^{2-(3+1)} = 6.2 \times 10^{5}$$

C.

$$K_p = K_c(RT)^{\Delta n} = (4.10 \times 10^{-31})(0.082058\frac{L\ atm}{mol\ K}298)^{2-2} = 4.10 \times 10^{-31}$$

14.18 Consider the reaction:

H_2(g) + I_2 (g) ↔ 2 HI (g)

Complete the table. Assume all the concentrations are equilibrium concentrations in M.

T (ºC)	[H_2]	[I_2]	[HI]	K_c
25	0.0355	0.0388	0.922	
340		0.0455	0.387	9.6
445	0.0485	0.0468		50.2

SOLUTION:

It's just all about K

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

At 25C:

$$K_c = \frac{[0.922]^2}{[0.0355][0.0388]} = 617$$

At 340C:

$$K_c = \frac{[0.387]^2}{[H_2][0.0455]} = 9.6$$
$$\frac{[0.387]^2}{[9.6][0.0455]} = [H_2] = 0.343$$

At 445 C:

$$K_c = \frac{[HI]^2}{[0.0485][0.0468]} = 50.2$$

$$[HI]^2 = 0.114$$

$$[HI] = 0.338\ M$$

T (ºC)	$[H_2]$	$[I_2]$	[HI]	K_c
25	0.0355	0.0388	0.922	617
340	0.343	0.0455	0.387	9.6
445	0.0485	0.0468	0.338	50.2

14.22 Consider the reaction:

SO_2Cl_2 (g) ↔SO_2 (g) + Cl_2 (g)

A reaction mixture is made containing an initial [SO_2Cl_2] of 0.020 M. At equilibrium, [Cl_2]=$1.2x10^{-2}$ M. Calculate the value of the equilibrium constant (K_c).

SOLUTION:

All equilibrium problems have THREE parts!

1. Balanced equation:

SO_2Cl_2 (g) ↔SO_2 (g) + Cl_2 (g)

2. Equilibrium constant expression (K equation)

$$K_c = \frac{[SO_2Cl_2\ ]}{[Cl_2]\{SO_2\ ]}$$

3. ICE chart

	SO_2Cl_2	↔	Cl_2 (g)	SO_2 (g)
I	0.020 M		0	0
C	-x		+x	+x
E	0.020-x		0.012 M	x

From the Cl_2:

0+x=0.012 M
x=0.012 M

	SO_2Cl_2	↔	Cl_2 (g)	SO_2 (g)
I	0.020 M		0	0
C	-0.012		+0.012 M	+0.012 M
E	0.008 M		0.012 M	0.012 M

$$K_c = \frac{(0.012)(0.012)}{0.008} = 0.018$$

14.24 Consider the reaction:

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

A reaction mixture in a 5.19 L flask at a certain temperature contains 26.9 g CO and 2.34 g H_2. At equilibrium, the flask contains 8.65 g CH_3OH. Calculate the equilibrium constant (K_c) for the reaction at this temperature.

SOLUTION:

All equilibrium problems have THREE parts!

4. Balanced equation:

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

5. Equilibrium constant expression (K equation)

$$K_c = \frac{[CH_3OH]}{[CO]\{H_2\ ]^2}$$

6. ICE chart

	CO (g) +	2 H_2 (g)	↔	CH_3OH (g)
I				
C	-x	-2x		+x
E				

Since I'm looking for K_c, easiest to just do the ICE chart in molarity from the beginning.

$$26.9\ g\ CO\,\frac{1\ mol\ CO}{28.011\ g} = 0.960\ mol\ CO$$

$$\frac{0.960\ mol\ CO}{5.19\ L} = 0.185\ M\ CO$$

$$2.34\ g\ H_2\,\frac{1\ mol\ H_2}{2.016\ g} = 1.161\ mol\ H_2$$

$$\frac{1.161\ mol\ H_2}{5.19\ L} = 0.224\ M\ H_2$$

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$$8.65\ g\ H_2\,\frac{1\ mol\ CH_eOH}{32.04\ g} = 0.254\ mol\ CH_3OH$$

$$\frac{0.254\ mol\ CH_3OH}{5.19\ L} = 0.0489\ M\ CH_3OH$$

	CO (g) +	2 H_2 (g)	↔	CH_3OH (g)
I	0.185 M	0.224 M		0
C	-x	-2x		+x
E	0.185-x	0.224-2x		0+x=0.0489M

From the methanol (CH_3OH), we know that x=0.0489 M

	CO (g) +	2 H_2 (g)	↔	CH_3OH (g)
I	0.185 M	0.224 M		0
C	-0.0489	-2*(0.0489)		+0.0489
E	0.136	0.126		0.0489M

Then I just plug it into the K-equation

$$K_c = \frac{[CH_3OH]}{[CO]\{H_2\ ]^2} = \frac{(0.0489\ M)}{(0.136)(0.126)^2} = 22.6$$

14.28 Nitrogen dioxide dimerizes according to the reaction:

$2\ NO_2\ (g) \leftrightarrow N_2O_4\ (g) \quad K_p = 6.7$ (at 298 K)

A 2.25 L container contains 0.055 mol of NO_2 and 0.082 mol of N_2O_4 at 298 K. Is the reaction at equilibrium? If not, in what direction will the reaction proceed?

SOLUTION:

This is just a question of Q versus K.

$$Q = \frac{[N_2O_4]}{[NO_2]^2}$$

Since we have K_p, we should use atmospheres.

$$P = \frac{nRT}{V}$$

$$P = \frac{0.055R(298)}{2.25\ L} = 0.598\ atm$$

$$P = \frac{0.082R(298)}{2.25\ L} = 0.891\ atm$$

$$Q = \frac{0.891}{(0.598)^2} = 2.49$$

Since $Q_p < K_p$, the reaction is not at equilibrium. Q is too small, meaning not enough products (or too many reactants), so the reaction must proceed to the right to make more product to get to equilibrium.

14.32 For the reaction, K_c=255 at 1000 K.

$CO\ (g) + Cl_2\ (g) \leftrightarrow COCl_2\ (g)$

If a reaction mixture initially contains a CO concentration of 0.1500 M and a Cl_2 concentration of 0.175 M at 1000 K, what are the equilibrium concentrations of CO, Cl_2 and $COCl_2$ at 1000 K?

SOLUTION:

Hey, you know what? All equilibrium problems have THREE PARTS!

1. Balanced Equation

$CO\ (g) + Cl_2\ (g) \leftrightarrow COCl_2\ (g)$

2. Equilibrium Expression

$$K_c = 255 = \frac{[COCl_2]}{[CO][Cl_2]}$$

3. ICE Chart

	CO (g) +	Cl_2 (g)	↔	$COCl_2$ (g)
I	0.150 M	0.175 M		0
C	-x	-x		+x
E	0.150-x	0.175-x		x

$$K_c = 255 = \frac{[COCl_2]}{[CO][Cl_2]}$$

$$255 = \frac{[x]}{[0.150 - x][0.175 - x]}$$

Try the assumption, but it won't work here. So…some algebra.

$$255 = \frac{[x]}{0.02625 - 0.325x + x^2}$$

$$255(0.02625 - 0.325x + x^2) = x$$

$$255x^2 - 82.875x + 6.69375 = x$$

$$255x^2 - 83.875x + 6.69375 = 0$$

Quadratic equation:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{- -83.875 \pm \sqrt{(83.875)^2 - 4(255)(6.69375)}}{2(255)}$$

$$x = \frac{83.875 \pm 14.401}{510}$$

x=0.193 or x=0.136

If x=0.193, I get nonsense in the ICE chart (negative concentrations) so x=0.136

	CO (g) +	Cl_2 (g)	↔	$COCl_2$ (g)

I	0.150 M	0.175 M		0
C	-0.136	-0.136		+.136
E	0.014	0.039		0.136

I can check my result by putting the values back into K

$$\frac{0.136}{(0.014)(0.039)} = 249$$

Since I rounded to 2 sig figs, I only expect 2 sig figs in K, which is what I have.

14.36 Consider the reaction:

SO_2Cl_2 (g) ↔ SO_2 (g) + Cl_2 (g) $K_c = 2.99 \times 10^{-7}$ at 227 ºC

If a reaction mixture initially contains 0.175 M SO_2Cl_2, what is the equilibrium concentration of Cl_2 at 227ºC?

SOLUTION:

Hmmm…I think there's 3 parts to this problem.

1. Balanced Equation

SO_2Cl_2 (g) ↔ SO_2 (g) + Cl_2 (g)

2. Equilibrium Expression

$$K_c = 2.99 \times 10^{-7} = \frac{[SO_2][Cl_2]}{[SO_2Cl_2]}$$

3. ICE chart

	SO_2Cl_2 (g)	↔	SO_2 (g)	+Cl_2 (g)
I	0.175 M		0	0
C	-x		+x	+x
E	0.175-x		x	x

$$2.99 \times 10^{-7} = \frac{[x][x]}{[0.175 - x]}$$

Let's try our assumption:

0.175<<x

$$2.99 \times 10^{-7} = \frac{[x][x]}{[0.175]}$$

$$5.2325 \times 10^{-8} = x^2$$

$$x = \sqrt{5.2325 \times 10^{-8}} = 2.288 \times 10^{-4}$$

$$\frac{2.288 \times 10^{-4}}{0.175} \times 100 = 0.1\% \ \ GREAT\ assumption$$

	SO_2Cl_2 (g)	$\leftrightarrow$	SO_2 (g)	$+Cl_2$ (g)
I	0.175 M		0	0
C	-2.288×10^{-4}		$+2.288 \times 10^{-4}$	$+2.288 \times 10^{-4}$
E	0.175		2.288×10^{-4}	2.288×10^{-4}

If we check our result:

$$K = \frac{(2.288 \times 10^{-4})(2.288 \times 10^{-4})}{0.175} = 2.99 \times 10^{-7}$$

14.44 Consider the reaction at equilibrium:

$C(s) + H_2O\ (g) \leftrightarrow CO\ (g) + H_2\ (g)$

Predict whether the reaction will shift left, shift right, or remain unchanged upon each disturbance.

a. C is added to the reaction mixture.
b. H_2O is condensed and removed from the reaction mixture.
c. CO is added to the reaction mixture.
d. H_2 is removed from the reaction mixture.

SOLUTION: LeChatelier's principle says that a system when stressed will respond to alleviate that stress. To be at equilibrium, the equilibrium constant must be satisfied:

$$K = \frac{[products]}{[reactants]} = some\ number$$

a. If I add C to the reaction, I have more reactants than I should. I need to lower the amount of reactants which causes the reaction to shift right.
b. If I remove water from the reaction, I have fewer reactants than I should. The reaction shifts left to make more reactants.
c. CO is a product. If I add some, I have too much product so the reaction shifts left to lower the amount of products.
d. H_2 is a product. If I remove it, I have too little product and need to make more. The

reaction shifts to the right.

14.72 Consider the reaction:

$2\ SO_2\ (g) + O_2\ (g) \leftrightarrow 2\ SO_3\ (g)$ K_p=0.355 at 950 K

A 2.75 L reaction vessel at 950 K initially contains 0.100 mol of SO_2 and 0.100 mol of O_2. Calculate the total pressure (in atmospheres) in the reaction vessel when equilibrium is reached.

SOLUTION:

All equilibrium problems have 3 parts:

1. Balanced equation
   $2\ SO_2\ (g) + O_2\ (g) \leftrightarrow 2\ SO_3\ (g)$

2. Equilibrium constant expression:

$$K_p = 0.355 = \frac{P_{SO_3}^2}{P_{SO_2}^2 P_{O_2}}$$

3. ICE chart

Since I have K_p, it's easiest to just do the ICE chart in atmospheres.

$$P = \frac{nRT}{V} = \frac{0.100\ mol\ (0.082058\ \frac{L\ atm}{mol\ K})(950\ K)}{2.75\ L}$$

	$2\ SO_2$ (g) +	O_2 (g)	$\leftrightarrow$	$2\ SO_3$ (g)
I	2.835 atm	2.835 atm		0
C	-2x	-x		+2x
E	2.835 atm-2x	2.835 atm-x		2x

$$K_p = 0.355 = \frac{P_{SO_3}^2}{P_{SO_2}^2 P_{O_2}} = \frac{(2x)^2}{(2.835-2x)^2(2.835-x)}$$

When in doubt, try the assumption: 2x<<2.835

$$0.355 = \frac{(2x)^2}{(2.835)^2(2.835)} = \frac{4x^2}{22.786}$$
$$x = 1.4\ \ bad\ assumption$$

So, I need to do some algebra or type it into my graphing calculator. I typed it into www.wolframalpha.com

The solution was x=0.663 atm.

I plug this back into my ICE chart and then check my result against K

	$2\ SO_2$ (g) +	O_2 (g)	$\leftrightarrow$	$2\ SO_3$ (g)
I	2.835 atm	2.835 atm		0
C	-2(0.663)	-0.663		+2(0.663)
E	1.509	2.172		1.326

$$K = \frac{(1.326)^2}{(1.509)^2(2.172)} = 0.356\ \ \textit{It checks}!$$