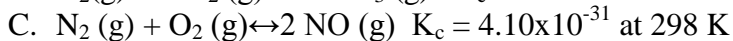
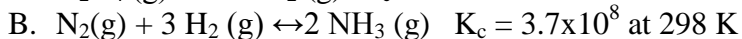
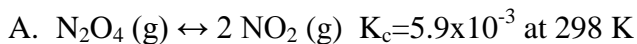


Chapter 14: 12, 18, 22, 24, 28, 32, 36, 44, 72

14.12 Calculate  $K_p$  for each reaction:



SOLUTION:

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

A.

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

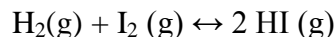
B.

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

C.

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

14.18 Consider the reaction:



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

T (°C)	[H <sub>2</sub> ]	[I <sub>2</sub> ]	[HI]	K <sub>c</sub>
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

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$

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:

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

$$[HI]^2 = 0.114$$

$$[HI] = 0.338 \text{ M}$$

T (°C)	[H <sub>2</sub> ]	[I <sub>2</sub> ]	[HI]	K <sub>c</sub>
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:



A reaction mixture is made containing an initial [SO<sub>2</sub>Cl<sub>2</sub>] of 0.020 M. At equilibrium, [Cl<sub>2</sub>]=1.2x10<sup>-2</sup> M. Calculate the value of the equilibrium constant (K<sub>c</sub>).

SOLUTION:

All equilibrium problems have THREE parts!

1. Balanced equation:



2. Equilibrium constant expression (K equation)

$$K_c = \frac{[\text{SO}_2\text{Cl}_2]}{[\text{Cl}_2][\text{SO}_2]}$$

### 3. ICE chart

	SO <sub>2</sub> Cl <sub>2</sub>	↔	Cl <sub>2</sub> (g)	SO <sub>2</sub> (g)
I	0.020 M		0	0
C	-x		+x	+x
E	0.020-x		0.012 M	x

From the Cl<sub>2</sub>:

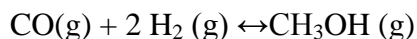
$$0+x=0.012 \text{ M}$$

$$x=0.012 \text{ M}$$

	SO <sub>2</sub> Cl <sub>2</sub>	↔	Cl <sub>2</sub> (g)	SO <sub>2</sub> (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:

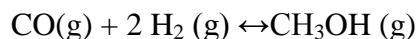


A reaction mixture in a 5.19 L flask at a certain temperature contains 26.9 g CO and 2.34 g H<sub>2</sub>. At equilibrium, the flask contains 8.65 g CH<sub>3</sub>OH. Calculate the equilibrium constant (K<sub>c</sub>) for the reaction at this temperature.

SOLUTION:

All equilibrium problems have THREE parts!

4. Balanced equation:



5. Equilibrium constant expression (K equation)

$$K_c = \frac{[\text{CH}_3\text{OH}]}{[\text{CO}][\text{H}_2]^2}$$

### 6. ICE chart

	CO (g) +	2 H <sub>2</sub> (g)	↔	CH <sub>3</sub> OH (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.

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

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

$$2.34 \text{ g H}_2 \frac{1 \text{ mol H}_2}{2.016 \text{ g}} = 1.161 \text{ mol H}_2$$

$$\frac{1.161 \text{ mol H}_2}{5.19 \text{ L}} = 0.224 \text{ M H}_2$$

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$$8.65 \text{ g H}_2 \frac{1 \text{ mol CH}_3\text{OH}}{32.04 \text{ g}} = 0.254 \text{ mol CH}_3\text{OH}$$

$$\frac{0.254 \text{ mol CH}_3\text{OH}}{5.19 \text{ L}} = 0.0489 \text{ M CH}_3\text{OH}$$

	CO (g) +	2 H <sub>2</sub> (g)	↔	CH <sub>3</sub> OH (g)
I	0.185 M	0.224 M		0
C	-x	-2x		+x
E	0.185-x	0.224-2x		0+x=0.0489M

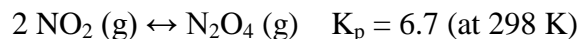
From the methanol (CH<sub>3</sub>OH), we know that x=0.0489 M

	CO (g) +	2 H <sub>2</sub> (g)	↔	CH <sub>3</sub> OH (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

$$K_c = \frac{[\text{CH}_3\text{OH}]}{[\text{CO}][\text{H}_2]^2} = \frac{(0.0489 \text{ M})}{(0.136)(0.126)^2} = 22.6$$

14.28 Nitrogen dioxide dimerizes according to the reaction:



A 2.25 L container contains 0.055 mol of  $\text{NO}_2$  and 0.082 mol of  $\text{N}_2\text{O}_4$  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  $K$ .

$$Q = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2}$$

Since we have  $K_p$ , we should use atmospheres.

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

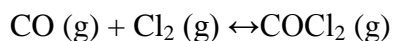
$$P = \frac{0.055R(298)}{2.25 \text{ L}} = 0.598 \text{ atm}$$

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

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

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.

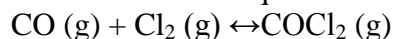


If a reaction mixture initially contains a CO concentration of 0.1500 M and a  $\text{Cl}_2$  concentration of 0.175 M at 1000 K, what are the equilibrium concentrations of CO,  $\text{Cl}_2$  and  $\text{COCl}_2$  at 1000 K?

SOLUTION:

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

1. Balanced Equation



2. Equilibrium Expression

$$K_c = 255 = \frac{[\text{COCl}_2]}{[\text{CO}][\text{Cl}_2]}$$

### 3. ICE Chart

	CO (g) +	Cl <sub>2</sub> (g)	↔	COCl <sub>2</sub> (g)
I	0.150 M	0.175 M		0
C	-x	-x		+x
E	0.150-x	0.175-x		x

$$K_c = 255 = \frac{[\text{COCl}_2]}{[\text{CO}][\text{Cl}_2]}$$

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

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:

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

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

$$x=0.193 \text{ or } x=0.136$$

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

	CO (g) +	Cl <sub>2</sub> (g)	↔	COCl <sub>2</sub> (g)
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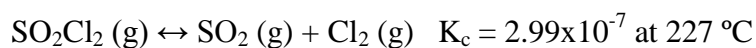
I	0.150 M	0.175 M		0
C	-0.136	-0.136		+0.136
E	0.014	0.039		0.136

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:



If a reaction mixture initially contains 0.175 M  $\text{SO}_2\text{Cl}_2$ , what is the equilibrium concentration of  $\text{Cl}_2$  at  $227^\circ\text{C}$ ?

SOLUTION:

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

1. Balanced Equation



2. Equilibrium Expression

$$K_c = 2.99 \times 10^{-7} = \frac{[\text{SO}_2][\text{Cl}_2]}{[\text{SO}_2\text{Cl}_2]}$$

3. ICE chart

	$\text{SO}_2\text{Cl}_2 (\text{g})$	$\leftrightarrow$	$\text{SO}_2 (\text{g})$	$+\text{Cl}_2 (\text{g})$
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:

$$0.175 \ll x$$

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

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

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

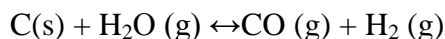
$$\frac{2.288 \times 10^{-4}}{0.175} \times 100 = 0.1\% \text{ GREAT assumption}$$

	SO <sub>2</sub> Cl <sub>2</sub> (g)	↔	SO <sub>2</sub> (g)	+Cl <sub>2</sub> (g)
I	0.175 M		0	0
C	-2.288 × 10 <sup>-4</sup>		+2.288 × 10 <sup>-4</sup>	+2.288 × 10 <sup>-4</sup>
E	0.175		2.288 × 10 <sup>-4</sup>	2.288 × 10 <sup>-4</sup>

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:



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

- C is added to the reaction mixture.
- H<sub>2</sub>O is condensed and removed from the reaction mixture.
- CO is added to the reaction mixture.
- H<sub>2</sub> 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:

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

- 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.
- If I remove water from the reaction, I have fewer reactants than I should. The reaction shifts left to make more reactants.
- CO is a product. If I add some, I have too much product so the reaction shifts left to lower the amount of products.
- H<sub>2</sub> 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:

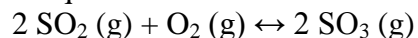


A 2.75 L reaction vessel at 950 K initially contains 0.100 mol of  $\text{SO}_2$  and 0.100 mol of  $\text{O}_2$ . Calculate the total pressure (in atmospheres) in the reaction vessel when equilibrium is reached.

SOLUTION:

All equilibrium problems have 3 parts:

1. Balanced equation



2. Equilibrium constant expression:

$$K_p = 0.355 = \frac{P_{\text{SO}_3}^2}{P_{\text{SO}_2}^2 P_{\text{O}_2}}$$

3. ICE chart

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

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

	2 $\text{SO}_2$ (g) +	$\text{O}_2$ (g)	$\leftrightarrow$	2 $\text{SO}_3$ (g)
I	2.835 atm	2.835 atm		0
C	-2x	-x		+2x
E	2.835 atm-2x	2.835 atm-x		2x

$$K_p = 0.355 = \frac{P_{\text{SO}_3}^2}{P_{\text{SO}_2}^2 P_{\text{O}_2}} = \frac{(2x)^2}{(2.835 - 2x)^2 (2.835 - x)}$$

When in doubt, try the assumption:  $2x \ll 2.835$

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

$x = 1.4$  *bad assumption*

So, I need to do some algebra or type it into my graphing calculator. I typed it into [www.wolframalpha.com](http://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

	$2 \text{ SO}_2 (\text{g}) +$	$\text{O}_2 (\text{g})$	$\leftrightarrow$	$2 \text{ SO}_3 (\text{g})$
I	2.835 atm	2.835 atm		0
C	-2(0.663)	-0.663		+2(0.663)
E	1.509	2.172		1.326

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