

product concentrations appear in the numerator and the reactant concentrations in the denominator. Each concentration is raised to the power of its stoichiometric coefficient in the balanced equation.

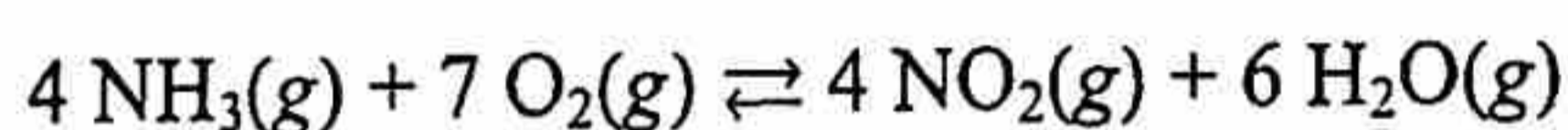
- [] indicates concentration in Molarity (mol/L)
- K_c is for concentration (aqueous)
- K_p is for partial pressure (gases)
- "K" values are often written without units

- USING EQUILIBRIUM CONSTANT EXPRESSIONS
- Pure solids--do not appear in expression—you'll see this in K_{sp} problems soon!
- Pure liquids--do not appear in expression— $H_2O(l)$ is pure, so leave it out of the calculation
- Water--as a pure liquid or reactant, does not appear in the expression. (55.5 M will not change significantly)
 - Weak acid and weak base equations are heterogeneous [multi-states of matter; pure liquid and aqueous components] equilibria.
 - Solubility of salts also fits into this category. The initial solid component has a constant concentration and is therefore left out of the equilibrium expression.

Exercise 1

Writing Equilibrium Expressions

Write the equilibrium expression for the following reaction:



$$K = \frac{[\text{NO}_2]^4 [\text{H}_2\text{O}]^6}{[\text{NH}_3]^4 [\text{O}_2]^7}$$

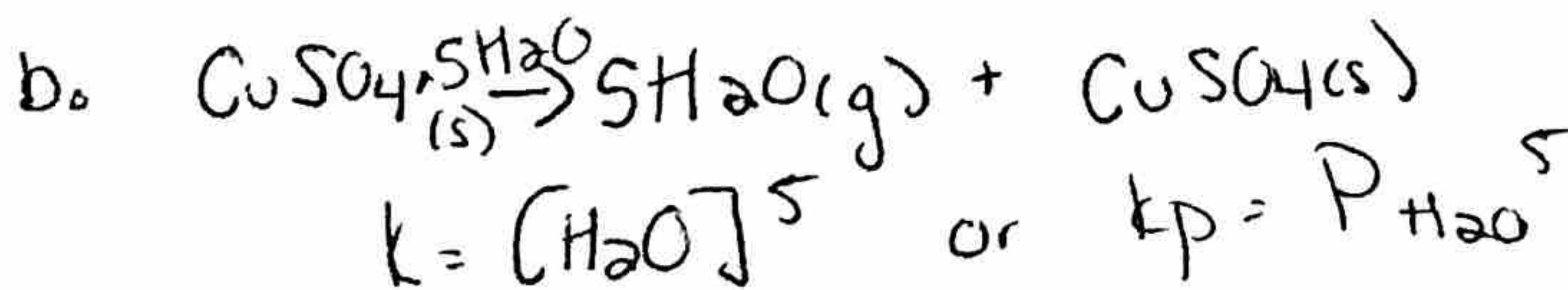
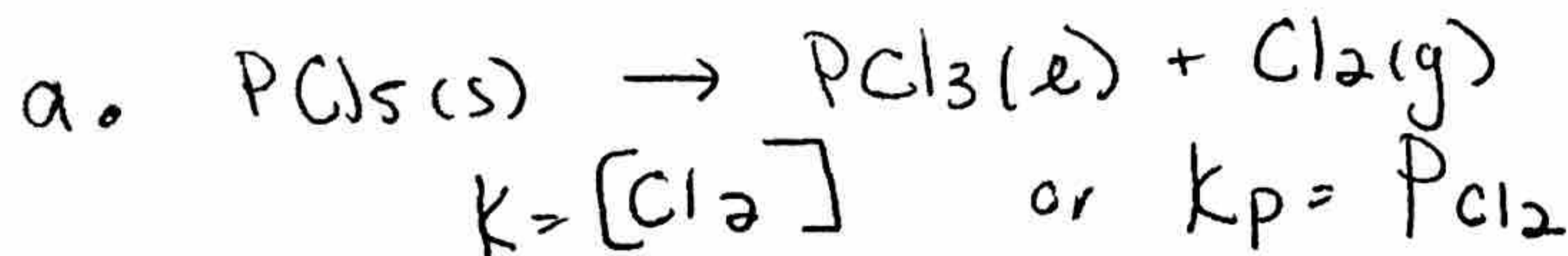
$$K = \frac{[\text{NO}_2]^4 [\text{H}_2\text{O}]^6}{[\text{NH}_3]^4 [\text{O}_2]^7}$$

Exercise 2

Equilibrium Expressions for Heterogeneous Equilibria

Write the expressions for K and K_p for the following processes:

- The decomposition of solid phosphorus pentachloride to liquid phosphorus trichloride and chlorine gas.
- Deep blue solid copper(II) sulfate pentahydrate is heated to drive off water vapor to form white solid copper(II) sulfate.



$$\begin{aligned} \text{A: } K &= [\text{Cl}_2] \\ K_p &= P_{\text{Cl}_2} \\ \text{B: } K &= [\text{H}_2\text{O}]^5 \\ K_p &= P_{\text{H}_2\text{O}}^5 \end{aligned}$$

when the stoichiometric coefficients of a balanced equation are multiplied by some factor, the K raised to the power of the multiplication factor (K^n). Thus, $2x$ is K squared; $3x$ is K cubed; etc.

- REVERSING EQUATIONS
take the reciprocal of K ($1/K$)
- ADDING EQUATIONS
multiply respective K s ($K_1 \times K_2 \times K_3 \dots$)

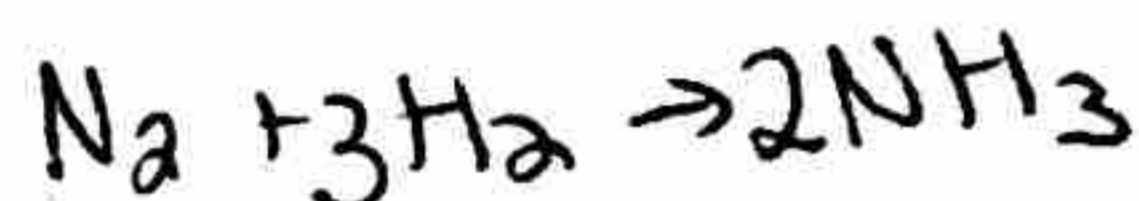
Exercise 3

Calculating the Values of K

The following equilibrium concentrations were observed for the Haber process at 127°C :

~~with~~

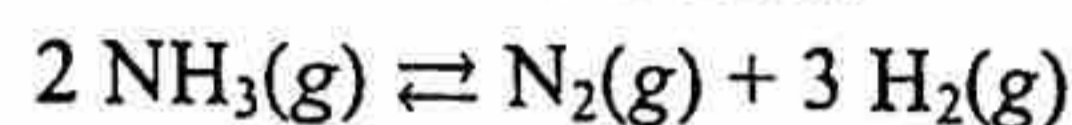
$$\begin{aligned} [\text{NH}_3] &= 3.1 \times 10^{-2} \text{ mol/L} \\ [\text{N}_2] &= 8.5 \times 10^{-1} \text{ mol/L} \\ [\text{H}_2] &= 3.1 \times 10^{-3} \text{ mol/L} \end{aligned}$$



a. Calculate the value of K at 127°C for this reaction.

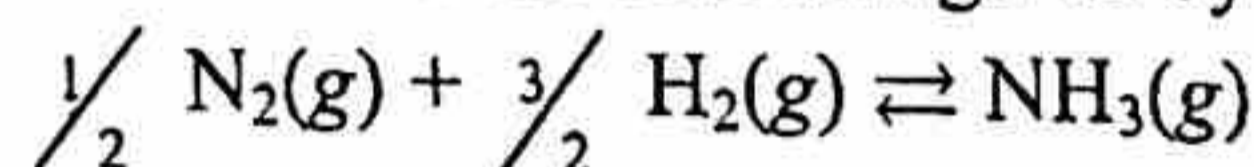
$$K = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{[3.1 \times 10^{-2}]^2}{[8.5 \times 10^{-1}][3.1 \times 10^{-3}]^3} = 3.8 \times 10^4$$

b. Calculate the value of the equilibrium constant at 127°C for the reaction:



$$K = \frac{[\text{N}_2][\text{H}_2]^3}{[\text{NH}_3]^2} = \frac{[8.5 \times 10^{-1}][3.1 \times 10^{-3}]^3}{[3.1 \times 10^{-2}]^2} = 2.6 \times 10^{-5}$$

c. Calculate the value of the equilibrium constant at 127°C for the reaction given by the equation:

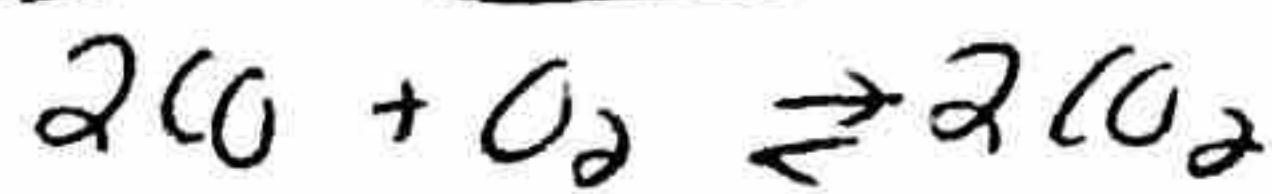


$$K = \frac{[\text{NH}_3]}{[\text{N}_2]^{1/2}[\text{H}_2]^{3/2}} = \frac{[3.1 \times 10^{-2}]}{[8.5 \times 10^{-1}]^{1/2}[3.1 \times 10^{-3}]^{3/2}} = 1.9 \times 10^2$$

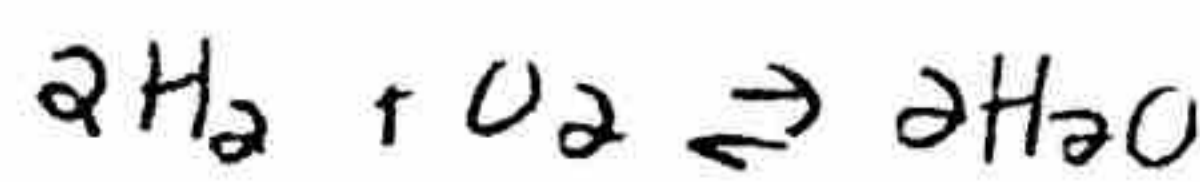
1.031

A: $K = 3.8 \times 10^4$
B: $K = 2.6 \times 10^{-5}$
C: $K = 1.9 \times 10^2$

Don't worry
about
this \rightarrow



$$K_c = 3.3 \times 10^9$$

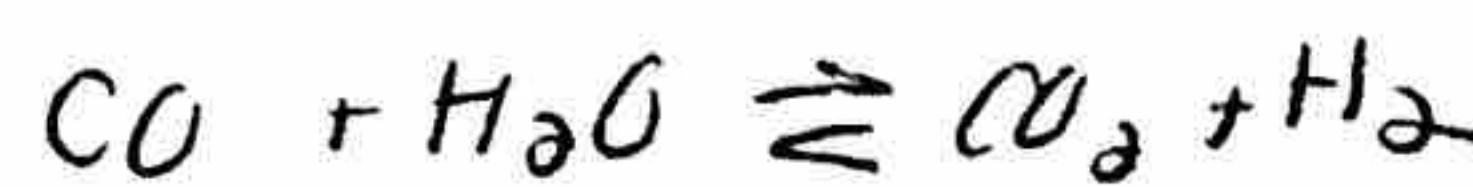


$$K_c = 9.1 \times 10^{80}$$

reverse

square root
both b/c not
coefficients

calculate K_c for



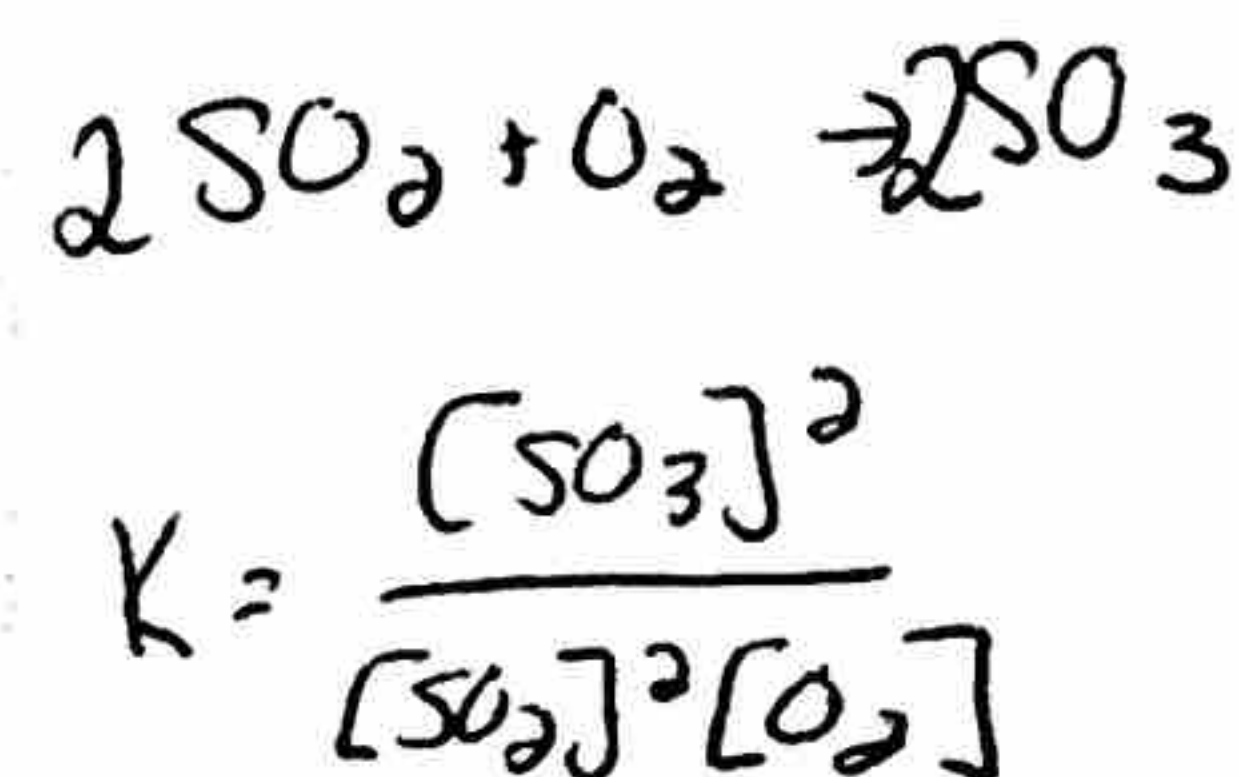
$$\left(\sqrt{3.3 \times 10^9} \right) \left(\frac{1}{\sqrt{9.1 \times 10^{80}}} \right)$$

$$(5.7 \times 10^4) (3.3 \times 10^{-41})$$

$$1.9 \times 10^5$$

The following results were collected for two experiments involving the reaction at 600°C between gaseous sulfur dioxide and oxygen to form gaseous sulfur trioxide:

Experiment 1		Experiment 2	
Initial	Equilibrium	Initial	Equilibrium
$[\text{SO}_2]_0 = 2.00 \text{ M}$	$[\text{SO}_2] = 1.50 \text{ M}$	$[\text{SO}_2]_0 = 0.500 \text{ M}$	$[\text{SO}_2] = 0.590 \text{ M}$
$[\text{O}_2]_0 = 1.50 \text{ M}$	$[\text{O}_2] = 1.25 \text{ M}$	$[\text{O}_2]_0 = 0$	$[\text{O}_2] = 0.0450 \text{ M}$
$[\text{SO}_3]_0 = 3.00 \text{ M}$	$[\text{SO}_3] = 3.50 \text{ M}$	$[\text{SO}_3]_0 = 0.350 \text{ M}$	$[\text{SO}_3] = 0.260 \text{ M}$



Show that the equilibrium constant is the same in both cases.

Experiment 1

$$K = \frac{[3.50]^2}{[1.50]^2[1.25]}$$

$$= \frac{12.25}{2.8125}$$

$$K = 4.36$$

Experiment 2

$$K = \frac{[0.260]^2}{[0.590]^2[0.0450]}$$

$$= \frac{0.0676}{0.01566}$$

$$K = 4.32$$

$$K_1 = 4.36$$

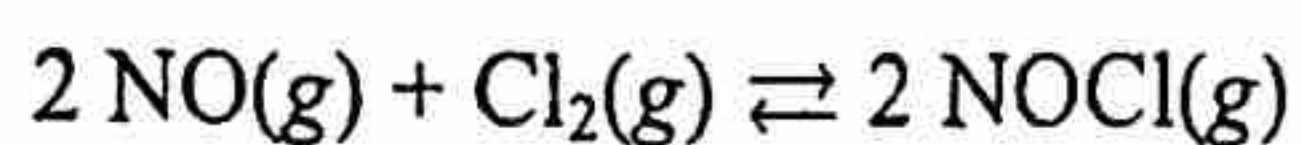
$$K_2 = 4.32$$

- K_c & K_p —NOT INTERCHANGEABLE! $K_p = K_c(RT)^{\Delta n}$
where Δn is the change in the number of moles of gas going from reactants to products:
- $\Delta n = \text{total moles gas produced} - \text{total moles gas reacting}$
 - $R = \text{universal gas law constant } 0.0821 \text{ L atm/mol K}$
 - $T = \text{temperature in Kelvin}$
- ✦ • $K_c = K_p$ if the number of moles of gaseous product = number of moles of gaseous reactant since $(RT)^{\Delta n} = (RT)^0 = 1$
- $K_p = K_c(RT)^{\Delta n}$ is often referred to as the “politically correct” (pc) equation to help you remember the order of the K s in the equation!

Exercise 5

Calculating Values of K_p

The reaction for the formation of nitrosyl chloride



was studied at 25°C. The pressures at equilibrium were found to be

$$\begin{aligned} P_{\text{NOCl}} &= 1.2 \text{ atm} \\ P_{\text{NO}} &= 5.0 \times 10^{-2} \text{ atm} \\ P_{\text{Cl}_2} &= 3.0 \times 10^{-1} \text{ atm} \end{aligned}$$

Calculate the value of K_p for this reaction at 25°C.

$$K_p = \frac{P_{\text{NOCl}}^2}{P_{\text{NO}}^2 \cdot P_{\text{Cl}_2}} = \frac{1.2^2}{(5.0 \times 10^{-2})^2 (3.0 \times 10^{-1})} = \frac{1.44}{.00075}$$

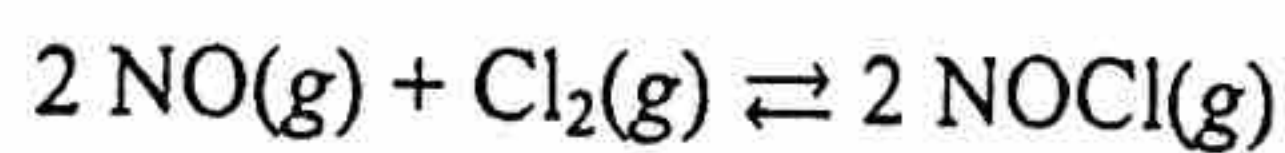
$$K_p = 1.9 \times 10^3$$

$$= 1.9 \times 10^3$$

Exercise 6

Calculating K from K_p

Using the value of K_p obtained in Sample Exercise 13.4, calculate the value of K at 25°C for the reaction:



→ 298

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

$$1.9 \times 10^3 = K_c (0.08206)(298K)^{2-3-1}$$

$$K_c = 4.6 \times 10^4$$

$$= 4.6 \times 10^4$$

- **MAGNITUDE OF K** --what does it mean anyway? When greater than one, formation of products is favored. When less than one, formation of reactants is favored.

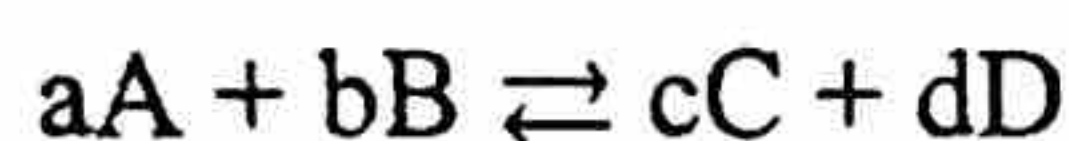
Can you...

1. ...write an equilibrium constant expression?
2. ...tell how K is changed if the stoichiometric coefficients are changed on an equation?
3. ... tell how to find K for a summary equation?
4. ...tell how K depends on the way equilibrium concentrations are expressed and how to convert K in terms of K_c vs. K_p ?
5. ...explain what K is telling you about a reaction?

THE REACTION QUOTIENT

For use when the system is NOT at equilibrium.

For the general reaction



$$\text{Reaction quotient} = Q_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

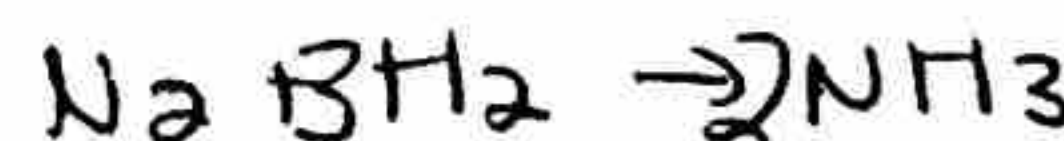
Q_c has the appearance of K but the concentrations are *not necessarily* at equilibrium.

1. If $Q < K$, the system is not at equilibrium: Reactants \rightarrow products to make $Q = K$ at equil.
 2. If $Q = K$, the system is at equilibrium.
 3. If $Q > K$, the system is not at equilibrium: Reactants \leftarrow products to make $Q = K$ at equil.
- Quite useful for predicting what will happen under special conditions.*

Exercise 7

Using the Reaction Quotient

For the synthesis of ammonia at 500°C , the equilibrium constant is 6.0×10^{-2} . Predict the direction in which the system will shift to reach equilibrium in each of the following cases:



a. $[\text{NH}_3]_0 = 1.0 \times 10^{-3} \text{ M}$; $[\text{N}_2]_0 = 1.0 \times 10^{-5} \text{ M}$; $[\text{H}_2]_0 = 2.0 \times 10^{-3} \text{ M}$

$$Q = \frac{[1.0 \times 10^{-3}]^2}{[1.0 \times 10^{-5}][2.0 \times 10^{-3}]^3} = 1.3 \times 10^7 \text{ vs } 6.0 \times 10^{-2}$$

\uparrow
Q is larger (shift to the left)

b. $[\text{NH}_3]_0 = 2.00 \times 10^{-4} \text{ M}$; $[\text{N}_2]_0 = 1.50 \times 10^{-5} \text{ M}$; $[\text{H}_2]_0 = 3.54 \times 10^{-1} \text{ M}$

$$Q = \frac{[2.00 \times 10^{-4}]^2}{[1.5 \times 10^{-5}][3.54 \times 10^{-1}]^3} = \frac{4 \times 10^{-8}}{6.65 \times 10^{-7}} = .0601 = 6.0 \times 10^{-2}$$

(No shift)

c. $[\text{NH}_3]_0 = 1.0 \times 10^{-4} \text{ M}$; $[\text{N}_2]_0 = 5.0 \text{ M}$; $[\text{H}_2]_0 = 1.0 \times 10^{-2} \text{ M}$

$$Q = \frac{[1.0 \times 10^{-4}]^2}{[5.0][1.0 \times 10^{-2}]^3} = \frac{1 \times 10^{-8}}{5 \times 10^{-6}} = .002 \text{ vs } 6.0 \times 10^{-2}$$

\uparrow
Q is smaller (shift to the right)

- A: shift left
B: no shift
C: shift right

SOME CALCULATIONS WITH THE EQUILIBRIUM CONSTANT

General steps for solving equilibrium problems.

1. Set up "RICE" TABLE—write a balanced reaction, place initial concentrations into the table, determine the change in initial concentrations in terms of x , calculate the equilibrium concentration expressions ($0.25 M - x$).

R = write a balanced reaction for the predominant reacting species

I = fill in the initial concentrations

C = determine the change that is taking in place in terms of x

E = express the equilibrium concentrations in terms of x

2. Set up the equilibrium expression and set it equal to its value, if given.
3. Celebrate if you are given equilibrium concentrations! Just skip down to the "E" line and fill them in. You may be asked to work backwards to determine the "change" in equilibrium.
4. If you are given a K value, then use it to solve for x and use x to calculate the equilibrium concentrations.

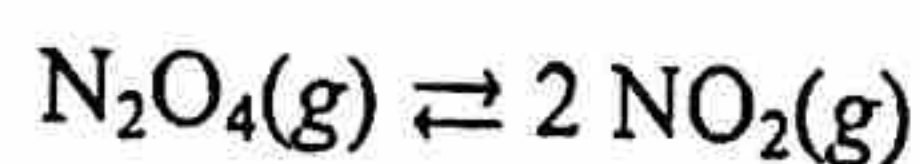
Hints:

- Look for very small K values (where $K < 10^{-5}$), " x " may be negligible.
- If " x " is large enough to impact the equilibrium values, then you must subtract it from the initial concentration. Your math will be simplified if the problem is a perfect square. If not, you must use the quadratic formula. You are allowed to use your calculator with a solver or program for solving the quadratic.
- If none of the initial concentrations are zero, then Q must be calculated first to determine the direction of the shift before following the above general steps.

Exercise 8

Calculating Equilibrium Pressures I

Dinitrogen tetroxide in its liquid state was used as one of the fuels on the lunar lander for the NASA Apollo missions. In the gas phase it decomposes to gaseous nitrogen dioxide:



Consider an experiment in which gaseous N_2O_4 was placed in a flask and allowed to reach equilibrium at a temperature where $K_p = 0.133$. At equilibrium, the pressure of N_2O_4 was found to be 2.71 atm. Calculate the equilibrium pressure of

$$K_p = \frac{(\text{NO}_2(\text{g}))^2}{\text{P}_{\text{N}_2\text{O}_4}}$$

$$0.133 = \frac{x^2}{2.71}$$

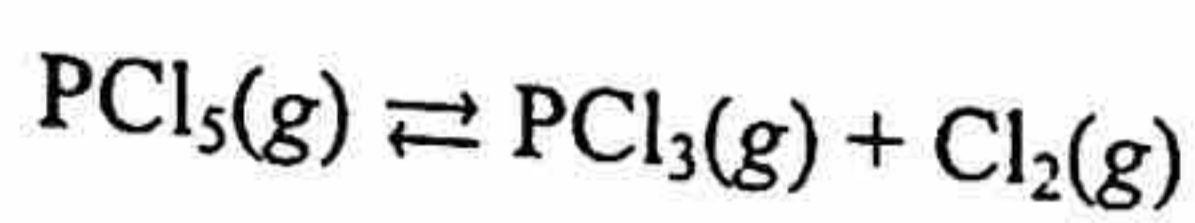
$$x = .600 \text{ atm}$$

$$= 0.600 \text{ atm}$$

Exercise 9

Calculating Equilibrium Pressures II

At a certain temperature a 1.00-L flask initially contained 0.298 mol $\text{PCl}_3(\text{g})$ and 8.70×10^{-3} mol $\text{PCl}_5(\text{g})$. After the system had reached equilibrium, 2.00×10^{-3} mol $\text{Cl}_2(\text{g})$ was found in the flask. Gaseous PCl_5 decomposes according to the reaction



$$K = \frac{[\text{Cl}_2][\text{PCl}_3]}{[\text{PCl}_5]}$$

Calculate the equilibrium concentrations of all species and the value of K .

	$\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$			
I	8.70×10^{-3}	0.298	0	$x = 2.00 \times 10^{-3}$
C	-x	+x	+x	
E	0.0067	0.300	2.00×10^{-3}	

$$K = \frac{[2.00 \times 10^{-3}][0.300]}{0.0067}$$

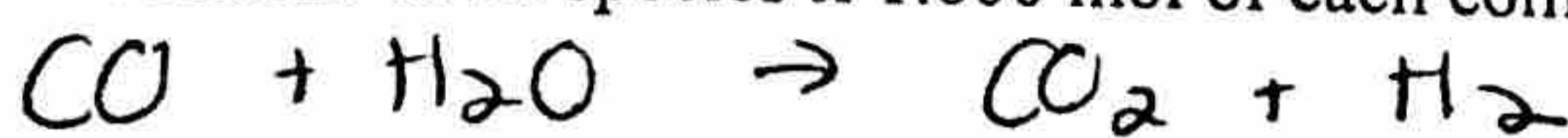
$$K = 0.0896$$

$$\begin{aligned} [\text{Cl}_2] &= 2.00 \times 10^{-3} \text{ M} \\ [\text{PCl}_3] &= 0.300 \text{ M} \\ [\text{PCl}_5] &= 6.70 \times 10^{-3} \text{ M} \\ K &= 8.96 \times 10^{-2} \end{aligned}$$

Exercise 10

Calculating Equilibrium Concentrations I

Carbon monoxide reacts with steam to produce carbon dioxide and hydrogen. At 700 K the equilibrium constant is 5.10. Calculate the equilibrium concentrations of all species if 1.000 mol of each component is mixed in a 1.000-L flask.



$$K = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]} = 5.10$$

$$Q = \frac{(1)(1)}{(1)(1)} = 1 \quad Q < K \quad \text{Shift towards products}$$

	$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$			
I	1.000	1.000	1.000	1.000
C	-x	-x	+x	+x
E	$1.000 - x$	$1.000 - x$	$1 + x$	$1 + x$

$$\sqrt{5.10} = \sqrt{\frac{(1.000 + x)^2}{(1.000 - x)^2}}$$

$$2.26 = \frac{1.000 + x}{1.000 - x}$$

$$[\text{CO}] = [\text{H}_2\text{O}] = 0.613 \text{ M}$$

$$[\text{CO}_2] = [\text{H}_2] = 1.387 \text{ M}$$

$$2.26 - 2.26x = 1.000 + x - 1.000$$

$$1.26 - 2.26x = x$$

$$+ 2.26x$$

$$1.26 = 3.26x$$

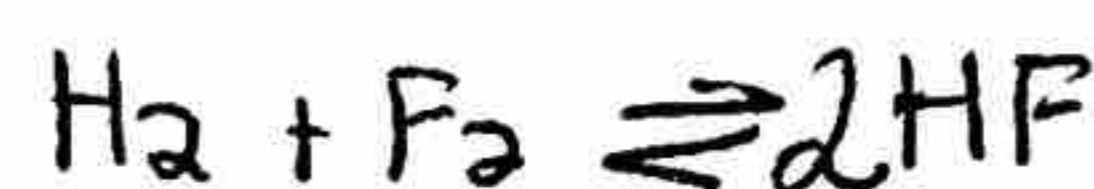
$$x = 0.387 \text{ M}$$

Exercise 11

Calculating Equilibrium Concentrations II

Assume that the reaction for the formation of gaseous hydrogen fluoride from hydrogen and fluorine has an equilibrium constant of 1.15×10^2 at a certain temperature. In a particular experiment, 3.000 mol of each component was added to a 1.500-L flask. Calculate the equilibrium concentrations of all species.

$$K = \frac{[HF]^2}{[H_2][F_2]} = 1.15 \times 10^2$$



$$Q = \frac{[2]^2}{2 \cdot 2} = 1 \quad \text{smaller so shift to the right}$$

	H_2	F_2	$2HF$
I	2	2	2
C	-x	-x	+2x
E	2-x	2-x	2+2x

$$\sqrt{1.15 \times 10^2} = \frac{[2+2x]^2}{(2-x)(2-x)}$$

$$10.7 = \frac{2+2x}{2-x}$$

$$21.45 - 10.7x = 2 + 2x$$

$$19.45 - 10.7x = 2x$$

$$19.45 = 12.7x$$

$$\frac{19.45}{12.7} = \frac{12.7x}{12.7}$$

$$1.528 = x$$

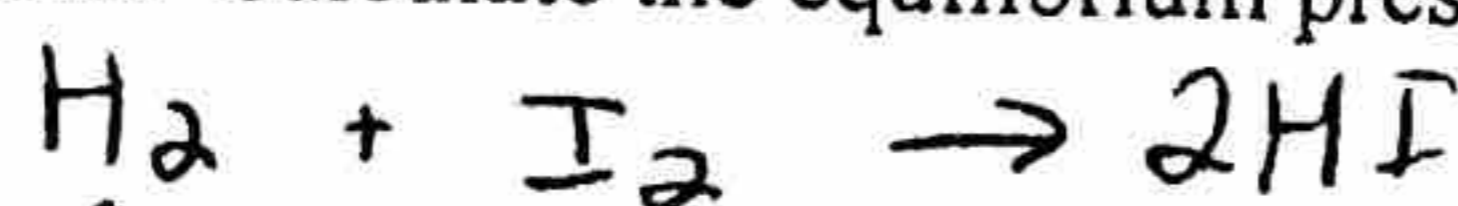
$$[H_2] = [F_2] = 0.472 M$$

$$[HF] = 5.056 M$$

Exercise 12

Calculating Equilibrium Pressures

Assume that gaseous hydrogen iodide is synthesized from hydrogen gas and iodine vapor at a temperature where the equilibrium constant is 1.00×10^2 . Suppose HI at 5.000×10^{-1} atm, H_2 at 1.000×10^{-2} atm, and I_2 at 5.000×10^{-3} atm are mixed in a 5.000-L flask. Calculate the equilibrium pressures of all species.



$$K_p = \frac{P_{HI}^2}{P_{H_2}P_{I_2}}$$

$$Q = \frac{(5.000 \times 10^{-1})^2}{(1.000 \times 10^{-2})(5.000 \times 10^{-3})} = 5000 \text{ vs. } 1.00 \times 10^2$$

shift to the left



	H_2	I_2	$2HI$
I	.005	.01	.5
C	-x	-x	+2x
E	.005-x	.01-x	.5+2x

$$K_p = \frac{(0.5+2x)^2}{(0.005-x)(0.01-x)}$$

$$P_{HI} = 4.29 \times 10^{-1} \text{ atm}$$

$$P_{H_2} = 4.55 \times 10^{-2} \text{ atm}$$

$$P_{I_2} = 4.05 \times 10^{-2} \text{ atm}$$