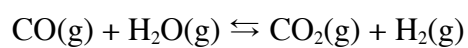


Chemical Equilibrium:

Chemical Reactions reach a state of dynamic equilibrium in which “*The rate of the forward and reverse reaction are equal*” and there is no net change in composition.

Reversible Reactions

Consider the following reaction in the gas phase:



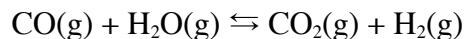
Let's graph the reaction rates:

Let's graph the concentrations:

Le Chatelier's Principle

When a system at equilibrium is subjected to a stress, the equilibrium will shift to relieve the stress. What is a stress?

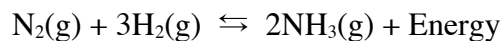
Consider adding and removing certain species.



Which direction does the equilibrium shift if we:

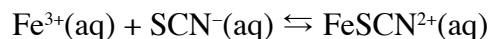
- a) Add CO
- b) Add water
- c) Add carbon dioxide
- d) Remove Hydrogen gas
- e) Remove CO

Consider changing things other than the concentrations of reactants and products.



- a) The volume is increased
- b) The pressure is decreased
- c) The temperature is increased
- d) The system is compressed
- e) It is placed into an ice bath
- f) A catalyst is added

A classic example of Le Chatelier's Principle is the iron (III) thiocyanate equilibrium:



By starting with a dilute solution of $\text{Fe}^{3+}(\text{aq})$ and adding a drop or two of $\text{SCN}^{-}(\text{aq})$ you get a "Brick Red" solution. The equilibrium system can be "Stressed" by adding solutions that contain common ions.

Laboratory Data

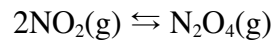
Solution Added	What two ions are in this solution?	Did it get darker or lighter?	How does the $[\text{FeSCN}^{2+}]$ Change?	What ion caused the change?
FeCl_3		Darker		
KSCN		Darker		
NaSCN		Darker		
NaCl		Little Change		
$\text{Fe}(\text{NO}_3)_3$		Darker		
NH_4NO_3		Little Change		
Na_2CO_3		Substantially Lighter		
KBr		Little Change		
NH_4SCN		Darker		
NaOH		Substantially Lighter		
CaCl_2		Substantially Lighter		

What are the spectator ions?

How does solubility play a role in this?

Classic Equilibrium Demonstrations

Consider the reaction:

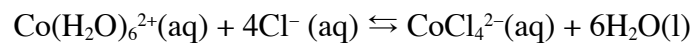


We have seen previously that N_2O_4 is a dimer held together with a bond between two NO_2 molecules. NO_2 is brown and N_2O_4 is clear.

Draw a picture of two beakers:

Is this reaction exothermic or endothermic as written above?

Now consider the reaction of Cobalt Chloride



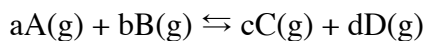
Draw a picture of three beakers:

Is this reaction exothermic or endothermic as written above?

Equilibrium Constants

What is an equilibrium constant?

How do you write an equilibrium constant?



What is included in an equilibrium constant?

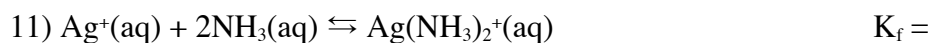
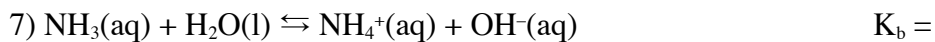
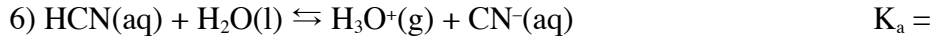
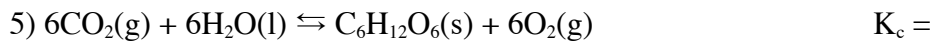
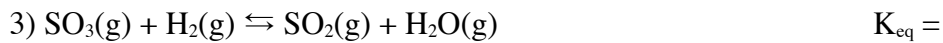
Why not solids and pure liquids? What is the physical difference?

Rate Laws

What are the special cases of the equilibrium constant?

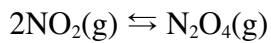


Write the equilibrium constant expression for the following reactions:



How do you calculate an equilibrium constant?

Calculate the equilibrium constants for the following reactions:

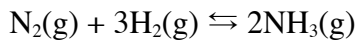


K=

Experiment	[NO ₂]	[N ₂ O ₄]
1.	0.052	0.595
2.	0.024	0.127
3.	0.068	1.02

Show work here

Show answers here

K₁= =K₂= =K₃= =

K=

Experiment	[N ₂]	[H ₂]	[NH ₃]
1.	0.921	0.763	0.157
2.	0.399	1.197	0.203
3.	2.59	2.77	1.82

Show work here

Show answers here

K₁= =K₂= =K₃= =

Manipulating the equilibrium constant

1) For the following reaction:



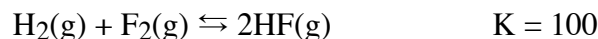
Write the following reactions and their equilibrium constants:

Reverse Reaction

Twice the forward reaction

Half the forward reaction

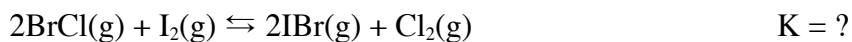
2) Give numerical values for K in the following situations dealing with:



3) Consider the following reactions:



Find the equilibrium constant for:

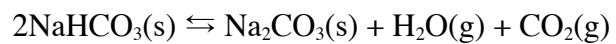


K_p versus K_c

Let's think about how we measure the concentration using the ideal gas law.

Now apply this to the idea of equilibrium constants:

Consider the reaction:



In an isolated flask the total pressure of the equilibrium mixture at 110°C is 1.648 atm.
What is the value of K_p and K_c for this reaction?

The Reaction Quotient

Solving Equilibrium Problems

Steps to solving an equilibrium problem.

1)

2)

3)

4)

5)

6)

7)

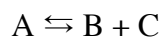
The Quadratic Equation.

For an equation of the form:

$$ax^2+bx+c=0$$

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

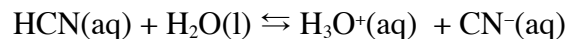
1) For the reaction:



the equilibrium constant is 3.0×10^{-6} . What is the concentration of B at equilibrium if A was originally 0.10 M?

ICE Boxes

2) The K_a for the reaction of HCN in water is 6.3×10^{-10} , as in the following reaction:

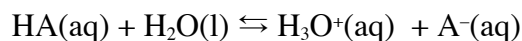


What is the concentration of cyanide ion at equilibrium if you start with 0.100 M HCN?

3) For the reaction of acetic acid in water the K_{eq} is 1.75×10^{-5} . What is the remaining concentration of acetic acid if the original concentration was 0.10 M?

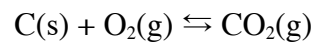


4) If a 0.10 M solution of an acid HA has an $[\text{H}_3\text{O}^+]$ of 4.0×10^{-4} what is the equilibrium constant K_a for the reaction?



K_p and K_c

5) An equilibrium mixture contains oxygen gas at 2.9 atm and carbon dioxide at 2.6 atm.



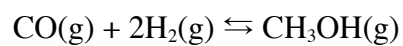
Calculate K_p and K_c at for this system at 289 Kelvin.

6) Given



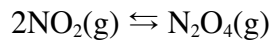
Find the value of K_c at 2000 K.

7) What is the ratio of K_c/K_p for the reaction at 25°C:



Reaction Quotients

8) For the equilibrium system:



the equilibrium constant is 170 at room temperature. Assume a 1.00 liter container contains 0.005 moles of nitrogen dioxide and 0.005 moles of dinitrogen tetroxide. Is this system at equilibrium? Which direction will it shift to reach equilibrium?

9) At some unspecified temperature



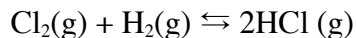
Which way will the system shift to achieve equilibrium if the concentration of Br is 0.100 M and the concentration of Br_2 is also 0.100 M?

10) For the reaction



Which way will the equilibrium shift if you start with $[\text{Br}_2] = [\text{Cl}_2] = 0.0100 \text{ M}$ and $[\text{BrCl}] = 10.0 \text{ M}$?

11)



For the reaction above, the value of the equilibrium constant, K_p is 193 at 2500. K.

a) Write the expression for the equilibrium constant K_p , for the reaction.

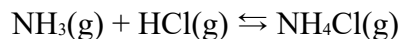
b) Assume the initial partial pressures of the gases are as follows:

$P_{\text{H}_2} = 0.766 \text{ atm}$, $P_{\text{Cl}_2} = 0.393 \text{ atm}$, and $P_{\text{HCl}} = 0.921 \text{ atm}$

(i) Calculate the value of the reaction quotient, Q , at these initial conditions.

(ii) Predict the direction in which the reaction will proceed at 2500. K if the initial partial pressures are those given above. Justify your answer.

c) The value of K_p for the reaction represented below is 1.5×10^3 at 2500. K.



Calculate the value of K_p at 2500. K for each of the reactions represented below:

(i) $\text{NH}_4\text{Cl}(\text{g}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{HCl}(\text{g})$

(ii) $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) + 2\text{NH}_3(\text{g}) \rightleftharpoons 2\text{NH}_4\text{Cl}(\text{g})$

