Equilibrium

Reactions are reversible

- A + B ⟶ C + D (forward)
- C + D ⟶ A + B (reverse)
- Initially there is only A and B so only the forward reaction is possible
- As C and D build up, the reverse reaction speeds up while the forward reaction slows down.
- Eventually the rates are equal

Forward Reaction

Reaction Rate

Equilibrium

Reverse reaction

Time
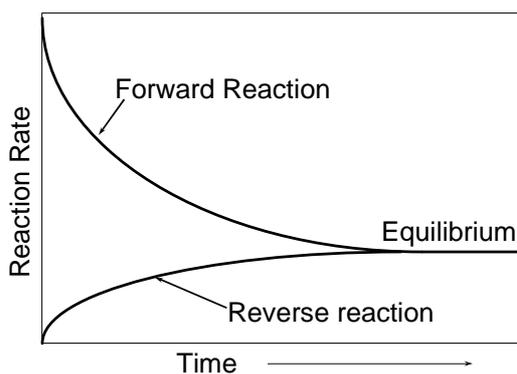
What is equal at Equilibrium?

- Rates are equal
- Concentrations are not.
- Rates are determined by concentrations and activation energy.
- The concentrations do not change at equilibrium.
- or if the reaction is verrrry slooooow.

Law of Mass Action

- For any reaction
- $jA + kB \rightleftharpoons lC + mD$
- $K = \dfrac{[C]^l[D]^m}{[A]^j[B]^k}$ $\dfrac{\text{PRODUCTS}^{power}}{\text{REACTANTS}^{power}}$
- K is called the equilibrium constant.
- $\rightleftharpoons$ is how we indicate a reversible reaction

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Playing with K

- If we write the reaction in reverse.
- $lC + mD \rightleftharpoons jA + kB$
- Then the new equilibrium constant is
- $K' = \dfrac{[A]^j[B]^k}{[C]^l[D]^m} = 1/K$

Playing with K

◌ If we multiply the equation by a constant

◌ $njA + nkB \rightleftharpoons nlC + nmD$
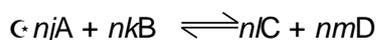
◌ Then the equilibrium constant is

◌ $K' = \dfrac{[C]^{nl}[D]^{nm}}{[A]^{nj}[B]^{nk}} = \dfrac{([C]^{l}[D]^{m})^{n}}{([A]^{j}[B]^{k})^{n}} = K^{n}$

The units for K

◌ Are determined by the various powers and units of concentrations.

◌ They depend on the reaction.

K is CONSTANT

◌ At any temperature.

◌ Temperature affects rate.

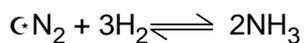◌ The equilibrium concentrations don't have to be the same, only K.

◌ Equilibrium position is a set of concentrations at equilibrium.

◌ There are an unlimited number.

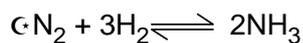## Equilibrium Constant

One for each Temperature

Calculate K

◌ $N_2 + 3H_2 \rightleftharpoons 2NH_3$

◌ Initial   At Equilibrium

◌ $[N_2]_0 = 1.000$ M $[N_2] = 0.921$ M

◌ $[H_2]_0 = 1.000$ M $[H_2] = 0.763$ M

◌ $[NH_3]_0 = 0$ M $[NH_3] = 0.157$ M

Calculate K

◌ $N_2 + 3H_2 \rightleftharpoons 2NH_3$

◌ Initial   At Equilibrium

◌ $[N_2]_0 = 0$ M $[N_2] = 0.399$ M

◌ $[H_2]_0 = 0$ M $[H_2] = 1.197$ M

◌ $[NH_3]_0 = 1.000$ M $[NH_3] = 0.203$ M

◌ K is the same no matter what the amount of starting materials

Equilibrium and Pressure

- Some reactions are gaseous
- $PV = nRT$
- $P = (n/V)RT$
- $P = CRT$
- C is a concentration in moles/Liter
- $C = P/RT$

Equilibrium and Pressure

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

- $Kp = \dfrac{(P_{SO3})^2}{(P_{SO2})^2\,(P_{O2})}$

- $K = \dfrac{[SO_3]^2}{[SO_2]^2\,[O_2]}$

Equilibrium and Pressure

- $K = \dfrac{(P_{SO3}/RT)^2}{(P_{SO2}/RT)^2(P_{O2}/RT)}$

- $K = \dfrac{(P_{SO3})^2\,\,(1/RT)^2}{(P_{SO2})^2(P_{O2})\,(1/RT)^3}$

- $K = Kp\,\dfrac{(1/RT)^2}{(1/RT)^3} = Kp\,RT$

General Equation

- $jA + kB \rightleftharpoons lC + mD$
- $K_p = \dfrac{(P_C)^l\,(P_D)^m}{(P_A)^j\,(P_B)^k} = \dfrac{(C_C \times RT)^l\,(C_D \times RT)^m}{(C_A \times RT)^j(C_B \times RT)^k}$
- $K_p = \dfrac{(C_C)^l\,(C_D)^m \times (RT)^{l+m}}{(C_A)^j(C_B)^k \times (RT)^{j+k}}$
- $K_p = K\,(RT)^{(l+m)-(j+k)} = K\,(RT)^{\Delta n}$
- $\Delta n = (l+m)-(j+k) = $ Change in moles of gas

Homogeneous Equilibria

- So far every example dealt with reactants and products where all were in the same phase.
- We can use K in terms of either concentration or pressure.
- Units depend on reaction.

Heterogeneous Equilibria

- If the reaction involves pure solids or pure liquids the concentration of the solid or the liquid doesn't change.
- As long as they are not used up we can leave them out of the equilibrium expression.
- For example

For Example

☞ $H_2(g) + I_2(s) \rightleftharpoons 2HI(g)$
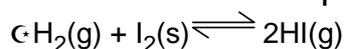
☞ $K = \dfrac{[HI]^2}{[H_2][I_2]}$

☞ But the concentration of I_2 does not change.

☞ $K[I_2] = \dfrac{[HI]^2}{[H_2]} = K'$

Write the equilibrium constant for the heterogeneous reaction

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The Reaction Quotient

☞ Tells you the direction the reaction will go to reach equilibrium

☞ Calculated the same as the equilibrium constant, but for a system not at equilibrium

☞ $Q = \dfrac{[Products]^{coefficient}}{[Reactants]^{coefficient}}$

☞ Compare value to equilibrium constant

What Q tells us

☞ If Q<K
  - 💻 Not enough products
  - 💻 Shift to right

☞ If Q>K
  - 💻 Too many products
 - 💻 Shift to left

☞ If Q=K system is at equilibrium

Example

☞ for the reaction

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

☞ $K = 1.55 \times 10^{-5}$ M at 35ºC

☞ In an experiment 0.10 mol NOCl, 0.0010 mol NO(g) and 0.00010 mol Cl_2 are mixed in 2.0 L flask.

☞ Which direction will the reaction proceed to reach equilibrium?

Solving Equilibrium Problems

☞ Given the starting concentrations and one equilibrium concentration.

☞ Use stoichiometry to figure out other concentrations and K.

☞ Learn to create a table of initial and final conditions.

☞ Consider the following reaction at 600ºC

☞ $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
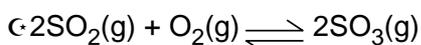
☞ In a certain experiment 2.00 mol of SO_2, 1.50 mol of O_2 and 3.00 mol of SO_3 were placed in a 1.00 L flask. At equilibrium 3.50 mol of SO_3 were found to be present. Calculate

☞ The equilibrium concentrations of O_2 and SO_2, K and K_P

☞ Consider the same reaction at 600ºC
$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

☞ In a different experiment .500 mol SO_2 and .350 mol SO_3 were placed in a 1.000 L container. When the system reaches equilibrium 0.045 mol of O_2 are present.

☞ Calculate the final concentrations of SO_2 and SO_3 and K

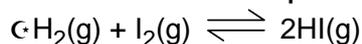
Solving Equilibrium Problems

Type 1

What if you're not given equilibrium concentration?

☞ The size of K will determine what approach to take.

☞ First let's look at the case of a LARGE value of K (>100).

☞ Allows us to make simplifying assumptions.

Example

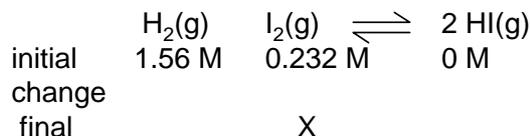☞ $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

☞ $K = 7.1 \times 10^2$ at 25ºC

☞ Calculate the equilibrium concentrations if a 5.00 L container initially contains 15.8 g of H_2 294 g I_2 .
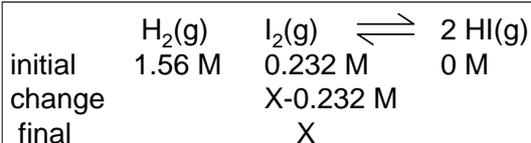
☞ $[H_2]_0 = (15.8g/2.02)/5.00 \text{ L} = 1.56 \text{ M}$

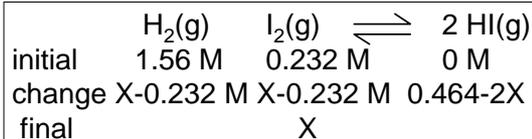☞ $[I_2]_0 = (294g/253.8)/5.00L = 0.232 \text{ M}$

☞ $[HI]_0 = 0$

☞ Q= 0<K so more product will be formed.

☞ Set up table of initial, final and change in concentrations.

☞ Assumption since K is large- reaction will almost go to completion.

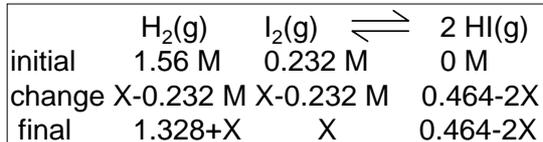☞ Stoichiometry tells us I_2 is LR, it will be smallest at equilibrium let it be x

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$$H_2(g) \quad I_2(g) \rightleftharpoons 2\,HI(g)$$

	$H_2(g)$	$I_2(g)$	$2\,HI(g)$
initial	1.56 M	0.232 M	0 M
change			
final		X	

☞ Choose X so it is small.

☞ For I_2 the change in X must be X-.232 M

☞ Final must = initial + change

$$H_2(g) \quad I_2(g) \rightleftharpoons 2\,HI(g)$$

	$H_2(g)$	$I_2(g)$	$2\,HI(g)$
initial	1.56 M	0.232 M	0 M
change		X-0.232 M	
final		X	

☞ Using to stoichiometry we can find

☞ Change in H_2 = X-0.232 M

☞ Change in HI = -twice change in H_2

☞ Change in HI = 0.464-2X

$$H_2(g) \quad I_2(g) \rightleftharpoons 2\,HI(g)$$

	$H_2(g)$	$I_2(g)$	$2\,HI(g)$
initial	1.56 M	0.232 M	0 M
change	X-0.232 M	X-0.232 M	0.464-2X
final		X	

☞ Now we can determine the final concentrations by adding.

$$H_2(g) \quad I_2(g) \rightleftharpoons 2\,HI(g)$$

	$H_2(g)$	$I_2(g)$	$2\,HI(g)$
initial	1.56 M	0.232 M	0 M
change	X-0.232 M	X-0.232 M	0.464-2X
final	1.328+X	X	0.464-2X

☞ Now plug these values into the equilibrium expression

☞ $K = \dfrac{(0.464-2X)^2}{(1.328+X)(X)} = 7.1 \times 10^2$

Why we chose X

☞ $K = \dfrac{(0.464-2X)^2}{(1.328+X)(X)} = 7.1 \times 10^2$

☞ Since X is going to be small, we can ignore it in relation to 0.464 and 1.328

☞ So we can rewrite the equation

☞ $7.1 \times 10^2 = \dfrac{(0.464)^2}{(1.328)(X)}$

☞ Makes the algebra easy

	$H_2(g)$	$I_2(g)$	$\rightleftharpoons$	2 HI(g)
initial	1.56 M	0.232 M		0 M
change	X-0.232 M	X-0.232 M		0.464-2X
final	1.328+X	X		0.464-2X

☾ When we solve for X we get 2.3×10^{-4}

☾ So we can find the other concentrations

☾ $I_2 = 2.3 \times 10^{-4}$ M

☾ $H_2 = 1.328$ M

☾ HI = 0.464 M

Checking the assumption

☾ The rule of thumb is that if the value of X is less than 5% of all the smallest concentrations, our assumption was valid.

☾ If not we would have had to use the quadratic equation

☾ More on this later.

☾ Our assumption was valid.

Practice

☾ For the reaction $Cl_2 + O_2 \rightleftharpoons 2ClO(g)$ K = 156

☾ In an experiment 0.100 mol ClO, 1.00 mol O_2 and 0.0100 mol Cl_2 are mixed in a 4.00 L flask.

☾ If the reaction is not at equilibrium, which way will it shift?

☾ Calculate the equilibrium concentrations.

At an elevated temperature, the reaction:

has a value of $K_{eq} = 944$. If 0.234 mol IBr is placed in a 1.00 L. flask and allowed to reach equilibrium, what is the equilibrium concentration in M. of I_2?
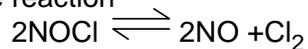

Type 2
Problems with small K

K< .01

Process is the same

☾ Set up table of initial, change, and final concentrations.

☾ Choose X to be small.

☾ For this case it will be a product.

☾ For a small K the product concentration is small.

For example

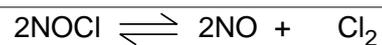- For the reaction
$$2NOCl \rightleftharpoons 2NO + Cl_2$$
- $K = 1.6 \times 10^{-5}$
- If 1.20 mol NOCl, 0.45 mol of NO and 0.87 mol Cl_2 are mixed in a 1 L container
- What are the equilibrium concentrations
- $Q = \dfrac{[NO]^2[Cl_2]}{[NOCl]^2} = \dfrac{(0.45)^2(0.87)}{(1.20)^2} = 0.15\ M$

$$2NOCl \rightleftharpoons 2NO + Cl_2$$

	2NOCl	2NO	Cl₂
Initial	1.20	0.45	0.87
Change			
Final			

- Choose X to be small
- NO will be LR
- Choose NO to be X

$$2NOCl \rightleftharpoons 2NO + Cl_2$$
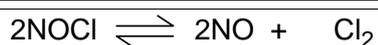
	2NOCl	2NO	Cl₂
Initial	1.20	0.45	0.87
Change			
Final		X	

- Figure out change in NO
- Change = final - initial
- change = X-0.45

$$2NOCl \rightleftharpoons 2NO + Cl_2$$
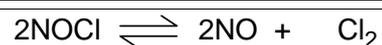
	2NOCl	2NO	Cl₂
Initial	1.20	0.45	0.87
Change		X-.45	
Final		X	

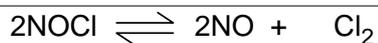- Now figure out the other changes
- Use stoichiometry
- Change in Cl_2 is 1/2 change in NO
- Change in NOCl is - change in NO

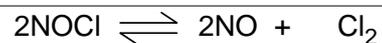$$2NOCl \rightleftharpoons 2NO + Cl_2$$

	2NOCl	2NO	Cl₂
Initial	1.20	0.45	0.87
Change	0.45-X	X-.45	0.5X -.225
Final		X	

- Now we can determine final concentrations
- Add

$$2NOCl \rightleftharpoons 2NO + Cl_2$$

	2NOCl	2NO	Cl₂
Initial	1.20	0.45	0.87
Change	0.45-X	X-.45	0.5X -.225
Final	1.65-X	X	0.5 X +0.645

- Now we can write equilibrium constant
- $K = \dfrac{(X)^2(0.5X+0.645)}{(1.65-X)^2}$
- Now we can test our assumption X is small ignore it in + and -

	2NOCl	$\rightleftharpoons$	2NO	+	Cl$_2$
Initial	1.20		0.45		0.87
Change	0.45-X		X-.45		0.5X -.225
Final	1.65-X		X		0.5 X +0.645

- $K = \dfrac{(X)^2(0.645)}{(1.65)^2} = 1.6 \times 10^{-5}$
- $X = 8.2 \times 10^{-3}$
- Figure out final concentrations

	2NOCl	$\rightleftharpoons$	2NO	+	Cl$_2$
Initial	1.20		0.45		0.87
Change	0.45-X		X-.45		0.5X -.225
Final	1.65-X		X		0.5 X +0.645

- [NOCl] = 1.64
- [Cl$_2$] = 0.649
- Check assumptions
- .0082/.649 = 1.2 % OKAY!!!

Practice Problem

☞ For the reaction
$2ClO(g) \rightleftharpoons Cl_2 (g) + O_2 (g)$
☞ K = 6.4×10^{-3}
☞ In an experiment 0.100 mol ClO(g), 1.00 mol O$_2$ and 1.00×10^{-2} mol Cl$_2$ are mixed in a 4.00 L container.
☞ What are the equilibrium concentrations?

Type 3
Mid-range K's

.01<K<10

No Simplification

☞ Choose X to be small.
☞ Can't simplify so we will have to solve the quadratic (we hope)
☞ $H_2(g) + I_2 (g) \rightleftharpoons 2HI(g)$ K=38.6
☞ What is the equilibrium concentrations if 1.800 mol H$_2$, 1.600 mol I$_2$ and 2.600 mol HI are mixed in a 2.000 L container?

Problems Involving Pressure

☞ Solved exactly the same, with same rules for choosing X depending on K$_P$
☞ For the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ K$_P$ = .131 atm. What are the equilibrium pressures if a flask initially contains 1.000 atm N$_2$O$_4$?

Le Châtelier's Principle

- If a stress is applied to a system at equilibrium, the position of the equilibrium will shift to reduce the stress.
- 3 Types of stress
  - Concentration
  - Pressure
  - Temperature

Change amounts of reactants and/or products

- Adding product makes Q>K ⟵
- Removing reactant makes Q>K ⟵
- Adding reactant makes Q<K ⟶
- Removing product makes Q<K ⟶
- Determine the effect on Q, will tell you the direction of shift

Change Pressure

- By changing volume
- System will move in the direction that has the least moles of gas.
- Because partial pressures (and concentrations) change, a new equilibrium must be reached.
- System tries to minimize the moles of gas if volume is reduced
- And visa versa

Change in Pressure

- By adding an inert gas
- Partial pressures of reactants and product are not changed
- No effect on equilibrium position

Change in Temperature

- Affects the <u>rates</u> of both the forward and reverse reactions.
- Doesn't just change the equilibrium position, changes the equilibrium constant.
- The direction of the shift depends on whether it is exo- or endothermic

Exothermic

- $\Delta H < 0$
- Releases heat
- Think of heat as a product
- Raising temperature push toward reactants.
- Shifts to left.

Endothermic

- $\Delta H > 0$
- Produces heat
- Think of heat as a reactant
- Raising temperature push toward products.
- Shifts to right.