

UWO **CHEM 1302**

Fall 2024, Chapter 7 Notes



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7. The Equilibrium Constant

7.1

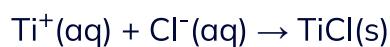
7.1 Intro to Equilibrium + characteristics of dynamic equilibrium

7.1.1

Introduction to Equilibrium

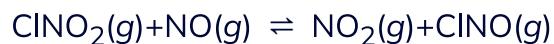
Some chemical systems react to completion.

Example:



But other reactions form an **equilibrium**. These reactions are **reversible** and go in both directions.

Example:

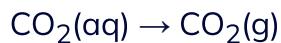


Equilibrium is when the **rate of the forward reaction = the rate of the reverse reaction**

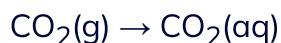
- Is this stationary or dynamic? _____
- There is **no net change**

Understanding Equilibrium

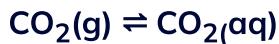
In the bottle below, CO_2 gas is leaving the dissolved state and entering the gas state



At the same time, CO_2 gas state is leaving the gas state and entering the liquid state



Since both the forward and backward reactions are occurring at the same time, we write:



- There are no visible changes while this is happening
- There are no (macroscopic/microscopic) _____ changes, but there are (macroscopic/microscopic) _____ changes

7.2

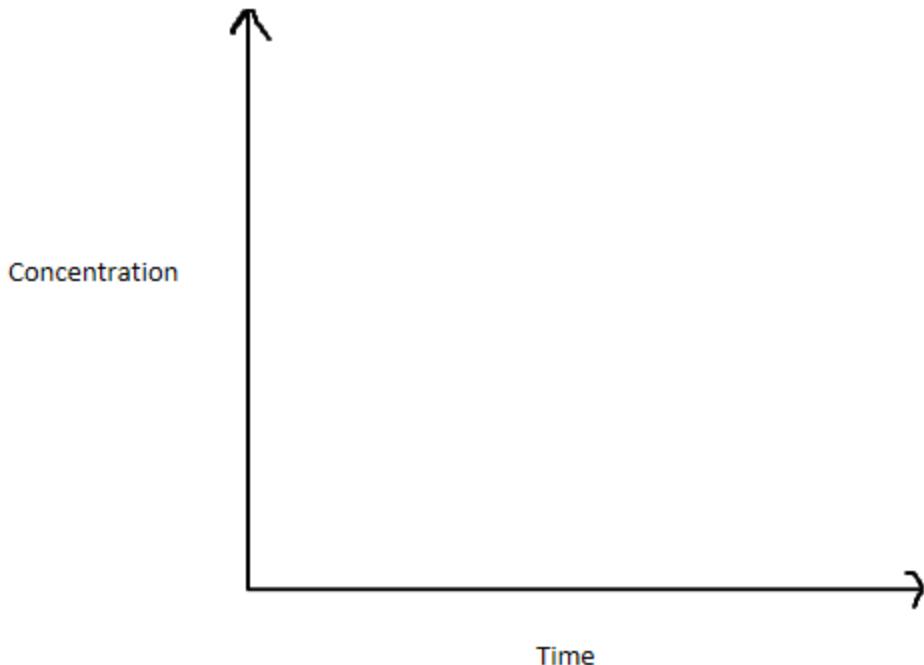
Concentration-Time Graphs

7.2.1

Concentration vs Time Graphs



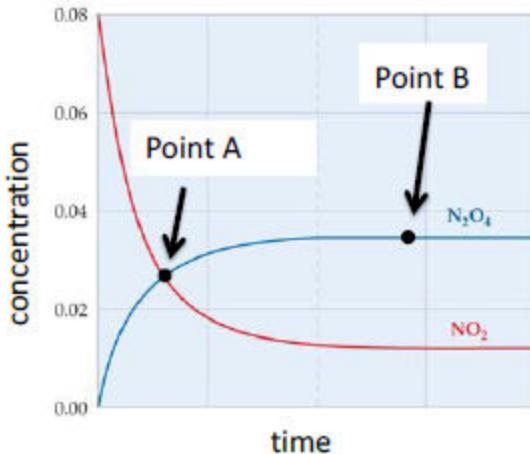
What would the concentration vs time graph look like if we started with our reactants?



We end up with **flat lines** because **at equilibrium**, the relative concentrations of reactants and products don't change!

Practice: Concentration vs Time Graph

Consider the following graph, which was obtained by monitoring the dimerization of NO_2 to N_2O_4 .



- i. $[\text{NO}_2] = [\text{N}_2\text{O}_4]$ at point A;
- ii. $[\text{NO}_2] = [\text{N}_2\text{O}_4]$ at point B;
- iii. Point A is at equilibrium;
- iv. Point B is at equilibrium;

Part 1

Which of the following statements are true?

i only

i, iv

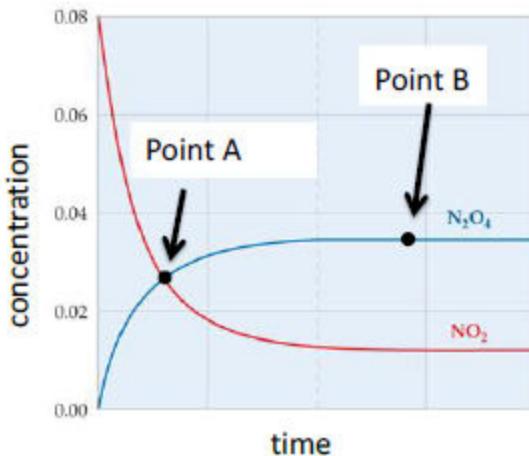
ii, iv

i, ii, iii

All of the statements

Practice: Concentration vs Time Graph

Consider the following graph, which was obtained by monitoring the dimerization of NO_2 to N_2O_4 .



i. $[\text{NO}_2] = [\text{N}_2\text{O}_4]$ at point A;

ii. $[\text{NO}_2] = [\text{N}_2\text{O}_4]$ at point B;

iii. Point A is at equilibrium;

iv. Point B is at equilibrium;

Part 2

What is the equilibrium concentration of N_2O_4 ? (in M)

0

0.018

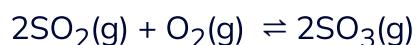
0.022

0.038

0.06

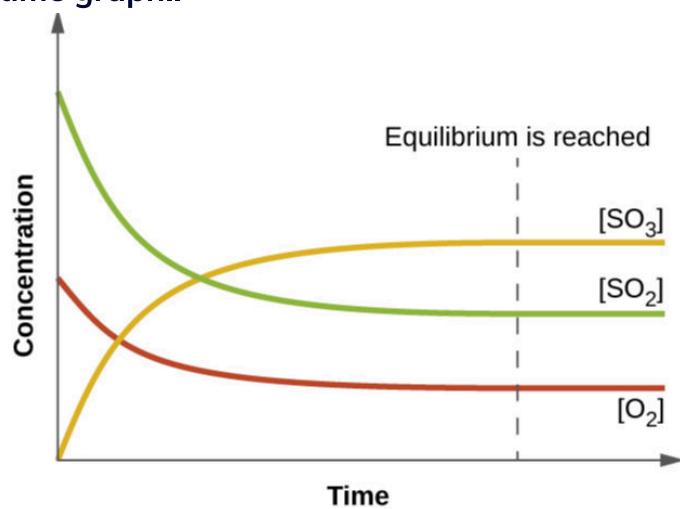
Practice: Concentration Vs Time Graphs

Use the following reaction to answer the following questions:



Part 1

Below is a concentration-time graph..



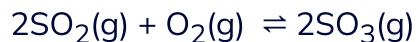
The concentration-time graph is not showing the above reaction correctly.

The concentration-time graph is correct and is showing the forward reaction.

The concentration-time graph is correct and is showing the reverse reaction.

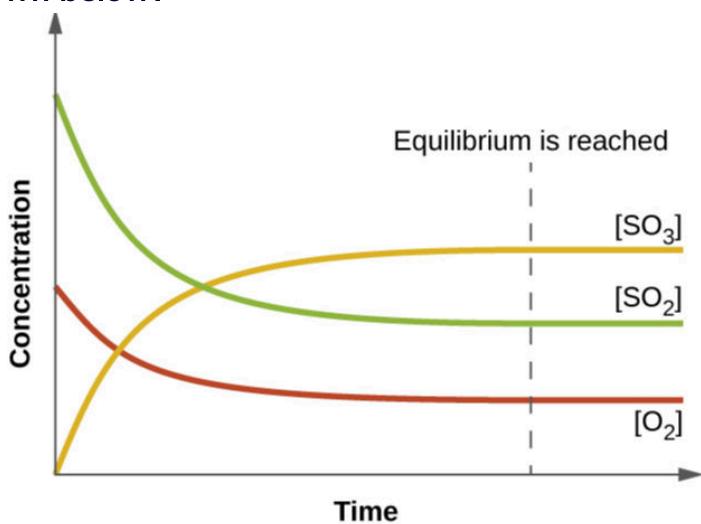
Practice: Concentration Vs Time Graphs

Use the following reaction to answer the following questions:



Part 2

Using the concentration-time graph from part 2, draw out the concentration-time graph for the reaction in the opposite direction. If the environment, system, and total mass remain the same, should the equilibrium concentrations of our reactants and products in the opposite direction be the same as the ones shown below?



7.3 The Equilibrium Constant (K)

7.3.1

Equilibrium Constant (K)

To define the extent to which equilibrium favors one side of the reaction over the other, we can use the **Equilibrium Constant**.

Given the model reaction:



A & B are reactants and C & D are products.
a,b,c,d are their stoichiometric coefficients

The **Equilibrium Expression** (in terms of concentration) can be written as:

$$K_c = \frac{[\text{Products}]}{[\text{Reactants}]} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

The **equilibrium constant (K)** is a ratio used to describe the relative concentrations of products and reactants **at equilibrium!**

You may also see it called the **Law of Mass Action**.

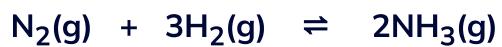
Examples:

K_{eq} (at equilibrium), K_a (for acids), K_b (for bases), K_w (for water), K_{sp} (solubility product constant)

WIZE CONCEPT

K can have different subscripts, but **all K's follow the same rules!**

Example: What is the K expression for the reaction below?



i WIZE TIP

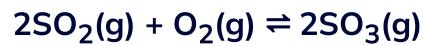
Since coefficients become exponents in the K expression, we need to **make sure that our equation is balanced!**

Additional Notes About K:

1) Above we wrote **Kc**. The **c** stands for **concentration** because we are considering the concentrations of the species in **mol/L**.

2) If instead we were considering **gases** and their **pressures** in atm, then we would write **Kp**!

Example: What is the Kp expression for the following reaction?



3) If any species in the reaction are **solids (s)** or **liquids (l)**, their concentrations do not affect equilibrium and therefore they **do not appear in the equilibrium expression!**

Example: What is the equilibrium expression for the following reaction?



4) We will see that changes in volume, pressure, temperature, and concentration can shift the equilibrium (according to Le Chatelier's Principle)

But the **only factor that will change K is temperature!**

The Magnitude of the Equilibrium Constant, K

K tells us which side of the reaction (**products or reactants**) are favored and to what extent.

Example:

If we had the K value 1.8×10^{10} would products or reactants be favored at equilibrium?

Since there is an exponent of 10, then (products/reactants) _____ are favored to a (small/great) _____ extent!

Example:

If K was 1.2×10^{-8} then are products or reactants favored at equilibrium? And to a great or small extent?

_____ are favored to a _____ extent!

Example: Are products or reactants favored at equilibrium according to the following reaction and concentration time graph?

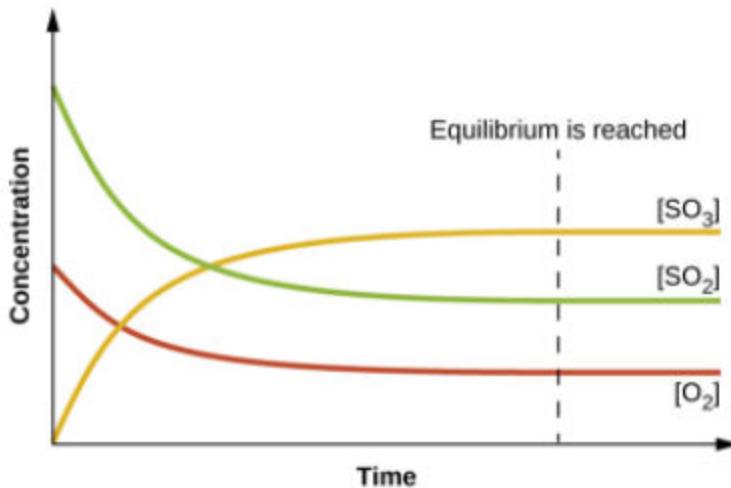
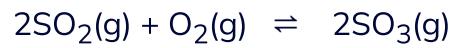


Photo by OpenStax / CC BY

Summary of What K Tells Us

$$K_c = \frac{[Products]}{[Reactants]}$$

K_{eq} > 1

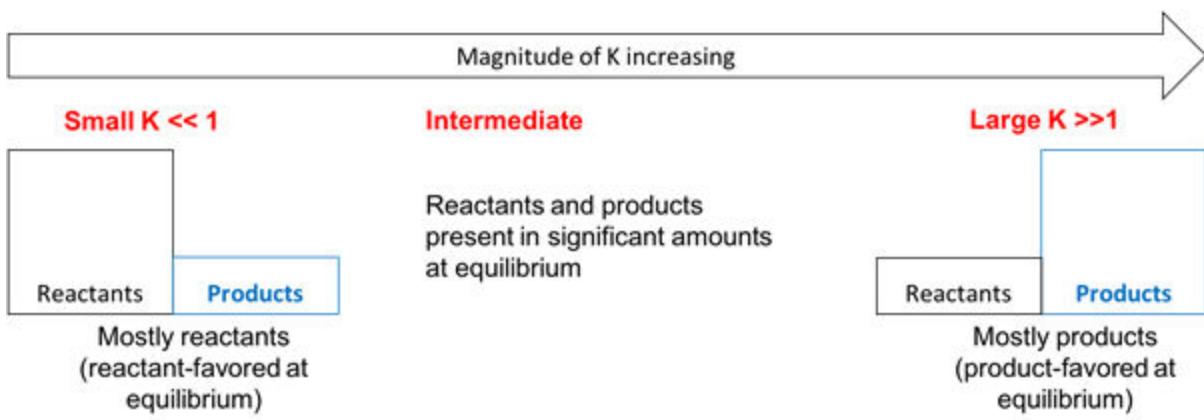
- At equilibrium, products/reactants are favored: _____
- This is because products/reactants are more stable: _____
- As a result, at equilibrium there will be more reactants, more products, or equal amounts of products and reactants: _____

K_{eq} = 1

- At equilibrium, products/reactants are favored: _____
- This is because products/reactants are more stable: _____
- As a result, at equilibrium there will be more reactants, more products, or equal amounts of products and reactants: _____

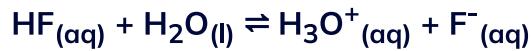
K_{eq} < 1

- At equilibrium, products/reactants are favoured: _____
- This is because products/reactants are more stable: _____
- As a result, at equilibrium there will be more reactants, more products, or equal amounts of products and reactants: _____



Practice: Writing Equilibrium Constants

Which of the following expression is the correct equilibrium-constant expression for the reaction below?



1.

$$K_c = \frac{[\text{HF}][\text{H}_2\text{O}]}{[\text{H}_3\text{O}^+][\text{F}^-]}$$

2.

$$K_c = \frac{1}{[\text{HF}]}$$

3.

$$K_c = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}][\text{H}_2\text{O}]}$$

4.

$$K_c = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]}$$

5.

$$K_c = \frac{[\text{F}^-]}{[\text{HF}]}$$

2



3



4



5



Practice: Calculating the Equilibrium Constant

For the process:



Determine the value of K_c when an equilibrium mixture contains 0.0420 mol N_2 , 0.516 mol H_2 , and 0.0357 mol NH_3 in a 1.00 liter container at 400°C .

0.221

6.19

16.4

4.43

0.0588

7.4

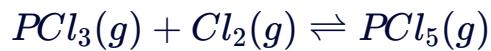
Solving for K in Different Scenarios

7.4.1

Manipulating Equilibrium Constants

Now we are going to take a look at how the value for K changes in different scenarios (when we reverse the reaction, multiply a reaction by a coefficient, and add two reactions together).

First, let's write the K expression for the reaction below:



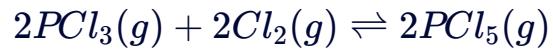
What happens to K when we reverse the reaction?



 **WIZE TIP**

If you reverse a reaction, take the inverse of K to find K_{new} !

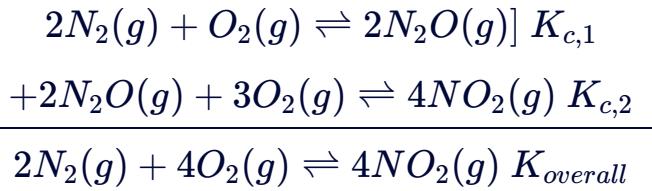
What happens to K when we multiply the reaction by a factor?



 **WIZE TIP**

When you multiply a reaction by a coefficient, take K to the power of that factor to solve for K_{new}!

How do we solve for K_{overall} given K for reactions that are being added together?

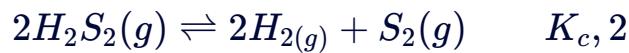
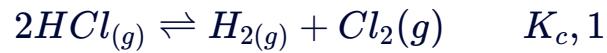


 **WIZE TIP**

When adding two reactions together, multiply their K values together to solve for K_{overall} !

Practice: Solving For K

Consider the following equilibria:



The equilibrium constant for the reaction is:



a) $K_c3 = \frac{K_{c,1}}{K_{c,2}}$

b) $K_c3 = \frac{K_{c,2}}{K_{c,1}}$

c) $K_c3 = \frac{2K_{c,1}}{K_{c,2}}$

d) $K_c3 = \frac{K_{c,1}}{K_{c,2^{\frac{1}{2}}}}$

e) $K_c3 = \frac{K_{c,2^2}}{K_{c,1}}$

a)

b)

c)

d)

e)

7.5 Q (Reaction Quotient)

7.5.1

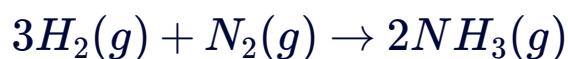
Predicting Equilibria: The Reaction Quotient (Q)

When reactants and products are mixed, there are two questions we ask ourselves:

1. Are we at equilibrium?
2. If not, which direction will the reaction shift (right or left) to get to equilibrium?

We use the **Reaction Quotient (Q)** to determine how close we are to equilibrium conditions (at time, t) and which direction the reaction will shift.

During **non-equilibrium conditions**, we use **Q** instead of **K**:

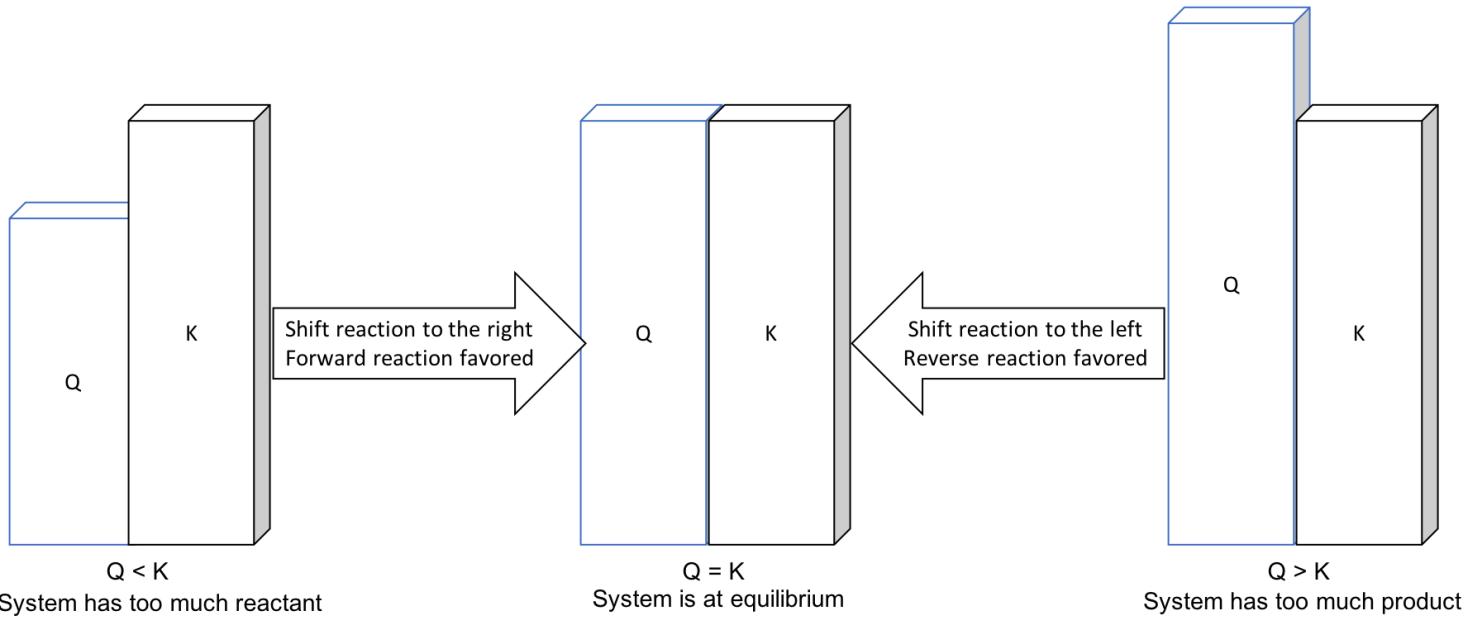


$$Q = \frac{[NH_3]_t^2}{[H_2]_t^3[N_2]_t} \quad K = \frac{[NH_3]_{eq}^2}{[H_2]_{eq}^3[N_2]_{eq}}$$

There are three possible situations:

1. **Q = K:** The system is **at equilibrium**.
2. **Q > K:** The **[products]** is too (high/low) _____ compared to [reactants]. The **equilibrium will shift** _____
3. **Q < K:** The **[products]** is too (high/low) _____ compared to [reactants]. The **equilibrium will shift** _____

Visual Representation



Example: Is the Reaction at Equilibrium?

If the current concentrations of H₂O, H₂, and O₂ were 1.2M, 0.7M, and 3.2M, respectively, is this reaction at equilibrium? If not, which direction must the reaction shift to reach equilibrium? K=1.2x10⁻².



7.5.3

Practice: Understanding Q vs K

Which of the following statements regarding the reaction quotient Q_c and the equilibrium constant K_c is true?

Q_c is always larger than K_c

Q_c is always less than K_c

When $Q_c > K_c$ the reaction proceeds toward the products to achieve equilibrium

When $Q_c < K_c$ the reaction proceeds toward the products to achieve equilibrium

When $Q_c = K_c$ the reaction proceeds toward the products to achieve equilibrium

Practice: Predicting and Interpreting Equilibrium

Silver chloride will react with acetic acid to form the complex ion silver acetate. A reaction mixture is prepared by adding 0.25 g of AgCl to a 1.25 L solution that already contains 4.6×10^{-6} M Ag(CH₃COO)⁻, 2.3×10^{-3} M Cl⁻, 1.1×10^{-8} M H⁺, and 0.010 M CH₃COOH. Based on this information, which of the statements below is true?



After allowing this solution to rest for some time:

Nearly all of the AgCl added will be consumed by the reaction.

More products will be present than initially because a reactant was added.

The concentration of Cl⁻ will be lower than the initial value.

There will be no change in the concentrations, since solids do not affect equilibrium.

7.6 Le Chatelier's Principle

7.6.1

Le Chatelier's Principle

When any system at equilibrium is subjected to change in **concentration, temperature, volume, or pressure**, then the system readjusts itself to counteract the effect of the applied change in order to establish a new equilibrium.



Which direction will the equilibrium shift in the following scenarios?

1) If we add $\text{N}_2(\text{g})$, equilibrium will shift to the _____

2) If we take away $\text{H}_2(\text{g})$, equilibrium will shift to the _____

3) If we increase the volume of the container:

• Does the **pressure** inside the container increase or decrease? _____

◦ If pressure is decreased, the equilibrium will want to shift to the side with _____ moles of gas

◦ If pressure is increased, the equilibrium will want to shift to the side with _____ moles of gas

• In our example, the equilibrium will shift to the _____ side since it has _____ moles

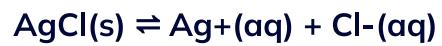


4) If we add heat:

- We want to treat temperature as a reagent
- To do this, we need to figure out what side of the reaction temperature is on for this particular reaction
- We are given an enthalpy value that is negative, does this mean that our reaction is endothermic or exothermic?

- Based on this, does our reaction require energy or is it releasing energy?
 - It _____ energy
- So would we expect to see temperature on the left or right side of the equation? (write it above)
_____ side
- Now this question is asking what direction the equilibrium will shift, so treat temperature as any other reagent on the _____ side
 - Equilibrium will shift to the _____!

5) For the following reaction what direction would the equilibrium shift if we **added more AgCl(s)**:





6) If we added a catalyst what direction would the equilibrium shift in?



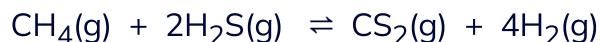
7) If we add an inert gas to the mixture, what direction would the reaction shift:

a) If the container keeps a **constant volume**

b) **Low yield:** If the container was a **constant pressure** container

Practice: Le Chatelier's Principle (Direction of Equilibrium Shift)

Given the following exothermic reaction, decide which direction the equilibrium will shift (if any) in each scenario.



Part 1

The concentration of dihydrogen sulfide is decreased.

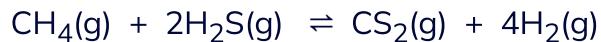
Equilibrium will shift to the left.

Equilibrium will shift to the right.

Equilibrium will not shift.

Practice: Le Chatelier's Principle (Direction of Equilibrium Shift)

Given the following exothermic reaction, decide which direction the equilibrium will shift (if any) in each scenario.



Part 2

When the concentration of dihydrogen sulfide is increased, which of the following statements is true as a result of the equilibrium shift?

$[\text{CH}_4]$ decreases, while $[\text{CS}_2]$ and $[\text{H}_2]$ increases.

$[\text{CH}_4]$ increases, while $[\text{CS}_2]$ and $[\text{H}_2]$ decreases.

The concentrations of reactants and products would remain the same.

Practice: Le Chatelier's Principle (Direction of Equilibrium Shift)

Given the following exothermic reaction, decide which direction the equilibrium will shift (if any) in each scenario.



Part 3

The pressure of the system is increased.

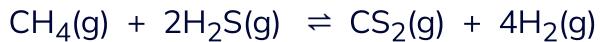
Equilibrium will shift to the left.

Equilibrium will shift to the right.

Equilibrium will not shift.

Practice: Le Chatelier's Principle (Direction of Equilibrium Shift)

Given the following exothermic reaction, decide which direction the equilibrium will shift (if any) in each scenario.



Part 4

The temperature is increased.

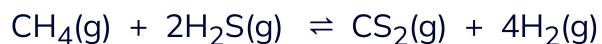
Equilibrium will shift to the left.

Equilibrium will shift to the right.

Equilibrium will not shift.

Practice: Le Chatelier's Principle (Direction of Equilibrium Shift)

Given the following exothermic reaction, decide which direction the equilibrium will shift (if any) in each scenario.



Part 5

The concentration of carbon disulfide is decreased.

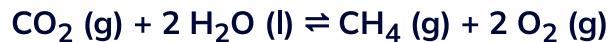
Equilibrium will shift to the left.

Equilibrium will shift to the right.

Equilibrium will not shift.

Practice: Le Chatelier's Principle

The reaction below is at equilibrium. You want to apply Le Chatelier's principle to produce a higher quantity of product gases. Which change will accomplish this effect?



Increase the pressure on the system

Add a catalyst to the reaction.

Adding some water

Increase the volume of the system

Add an inert gas to the reaction.

7.7 ICE Tables

7.7.1

ICE Tables

In equilibrium problems we will have to use something called an **ICE table**:

I= initial concentration of reactants and products before the reaction

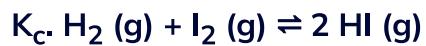
C=change in concentration of reactants and products

E=concentration of reactants and products **at equilibrium**

7.7.2

Example: ICE Tables (Solve for K_{eq})

H₂ and I₂ are placed in a closed flask such that the concentrations of H₂ and I₂ are both 0.10 M respectively. The mixture is heated to 400°C and equilibrium is reached. Analysis of the equilibrium mixture finds HI to have a concentration of 0.050 M. Calculate the value of the equilibrium constant,



Write out an ICE Table:

From $[HI]$ at equilibrium, solve for x :

Solve for $[I_2]$ and $[H_2]$ at equilibrium using x :

Plug equilibrium concentrations into K expression to solve for K:

Example: ICE Tables (Solve for Equilibrium Concentrations)

At 150°C, K for the reaction is $I_2(g) + Br_2(g) \rightleftharpoons 2IBr(g)$ $K=1.20\times10^2$. Starting with 4 mol of each of iodine and bromine in a 2L flask, calculate the equilibrium concentrations of all reactant components.

What info are we given?

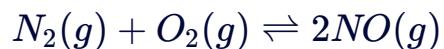
Now let's fill out the ICE table:

Now plug in the equilibrium concentrations into the K expression to solve for x:

Now since we solved for x we can plug that into the equilibrium concentrations from our E part of the ICE table to solve for the equilibrium concentrations

Example: Calculating a Missing Equilibrium Concentration

Nitrogen oxides are air pollutants produced by the reaction of nitrogen and oxygen at high temperatures. At 2000 °C, the value of the equilibrium constant for the reaction is 4.1×10^{-4} . Find the concentration of NO(g) in an equilibrium mixture with air at 1 atm pressure at this temperature. In air, $[N_2] = 0.036\text{ M}$ and $[O_2] = 0.0089\text{ M}$.



Example: ICE Tables (Solve for Equilibrium Concentrations + Simplifying x)

Carbon monoxide can decompose at high temperatures to CO₂ and graphite as follows:



1.5 mol of CO (g) is placed in an empty 0.50 L flask and allowed to come to equilibrium. What is the concentration of CO₂ (g) in the flask when equilibrium is reached at 1500 K?

$$K_C = \frac{[CO_2]}{[CO]^2} = \frac{x}{(3.0 - 2x)^2}$$

 **WIZE TIP**

There are a few different ways to check if we can simplify this:

"Small x" Approximation rule:

- If $1000 \times K_c < [A]_0$, then $[A]_0 - x \approx [A]_0$
- In other words, this means that the change in the initial concentration is small and it can be ignored. It won't cause a significant change in the initial concentration.

Another rule we can use to simplify is:

- $K=x^2/(y-x)$
- $y/K > 400$ then the assumption $y - x \sim y$ can be made and we can ignore the " $-x$ "

Justification:

- As long as the error is less than 5%, the approximate solution is considered valid. To see if the approximation is valid take:

$$\frac{x}{[A]_0} \times 100\% < 5\%$$

Applying the small x approximation, means that $3.0 - 2x \approx 3.0$, then:

$$K_C = \frac{x}{(3.0)^2} = 6.8 \times 10^{-4}$$

$$x = 6.1 \times 10^{-3} M = [CO_2]$$

Example: ICE Tables (with Quadratic Equation)

We have 0.280 moles of $SbCl_3$ and 0.160 moles of Cl_2 in a 2.5L container. What are the concentrations for $SbCl_5$, $SbCl_3$ and Cl_2 at equilibrium? $K_c=0.025$.

Step 1: Balanced equation:



Step 2: Equilibrium expression

$$K = \frac{[SbCl_3][Cl_2]}{[SbCl_5]}$$

Step 3: We are given initial amounts in moles and a volume, so we can calculate concentration.



Recall: $n=cv$, so $c=n/v$ (solve for initial concentrations and plug into table)

	$SbCl_5(g) \rightleftharpoons$	$SbCl_3(g) +$	$Cl_2(g)$
I (M)	0	0.112M	0.064M
C (M)	+x	-x	-x
E(M)	x	0.112-x	0.064-x

**Here we start with 0 reactants so the reaction will proceed to the left.

This is why there is a + sign for reactants

And a - sign for products!

Step 4: The relative change is found from stoichiometry. Make sure the coefficients in the 'change' line match the equation stoichiometry. Forgetting these coefficients is a common mistake on exams.

Step 5: Substitute the equilibrium line into the equilibrium expression and solve for x:

$$K = \frac{[SbCl_3][Cl_2]}{[SbCl_5]} = \frac{(0.11 - x)(0.064 - x)}{(x)} = 0.025$$

- Here you can **check the assumption** for: $y_1=0.11$ and $y_2=0.064$
 - If we take y/K and we get >400 for both y_1 and y_2 , then we don't have to use the quadratic equation and can ignore the " - x" parts!
 - $0.11/0.025=4.4 < 400$ so we must use the " - x" part

$$(0.11 \times 0.064 - 0.11x - 0.064x + x^2) = 0.025x$$

$$0.00704 - 0.174x + x^2 - 0.025x = 0$$

$$x^2 - 0.199x + 0.00704 = 0$$

Here we will use the **quadratic equation**:

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

$$x = [0.16, 0.046]$$

One of these x values does not make sense...why?

Solve for the Equilibrium Concentrations Using x

$$[SbCl_5]_e = x = 0.046M$$

$$[SbCl_3]_e = 0.11M - 0.046M = 0.066M$$

$$[Cl_2]_e = 0.064M - 0.046M = 0.018M$$

Step 6: Can double check by substituting in these equilibrium concentrations into the equilibrium equation.

$$K = \frac{[SbCl_3][Cl_2]}{[SbCl_5]} = \frac{(0.0657M)(0.0177M)}{(0.0463M)} = 2.5 \times 10^{-2}$$