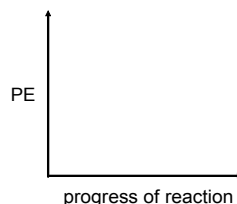


## Unit 2: Equilibrium

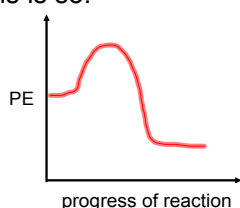
### 1) General Characteristics of Equilibrium

Theoretically, all chemical reactions can be reversible, meaning reactants can collide to make products, and products can collide to remake reactants. Using a typical PE curve, explain why this is so:



### 1) General Characteristics of Equilibrium

Theoretically, all chemical reactions can be reversible, meaning reactants can collide to make products, and products can collide to remake reactants. Using a typical PE curve, explain why this is so:



If reactant collisions can attain  $E_a$ , products will form. If products can attain the  $E_a$  for the reverse reaction, reactants can re-form.

Some chemical reactions are **spontaneously** reversible. What does this mean?

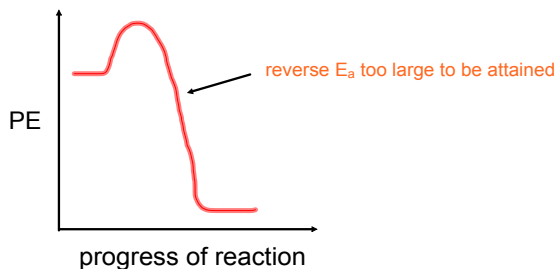
Some chemical reactions are **spontaneously** reversible. What does this mean?

Both the forward and reverse activation energies are attainable under the conditions of the reaction. Therefore, reactants are making products, and simultaneously products are making reactants. This would be the case if both the forward and reverse activation energies are somewhat low.

Though every reaction is theoretically reversible, some reactions cannot be reversed. Why is this the case?

Though every reaction is theoretically reversible, some reactions cannot be reversed. Why is this the case?

The forward activation energy is attainable, so reactants make products, but the reverse activation energy is much too high to be attained. For example, a combustion reaction is a one-way reaction.



Some reactions that are not spontaneously reversible can become reversible by manipulating conditions, such as raising the temperature, or supplying electricity. Thus, the reverse  $E_a$  becomes attainable due to the extra energy supplied to the system. For example, certain batteries can be recharged (the reverse of discharging) by plugging them in.

In this unit, we will study reversible reactions. An example of a spontaneously reversible reaction:



A 'double arrow' is used to show that the reaction is occurring in both directions.

Why would this reaction only occur in a 'closed' system?

<http://phet.colorado.edu/en/simulation/reversible-reactions>

In this unit, we will study reversible reactions. An example of a spontaneously reversible reaction:



A 'double arrow' is used to show that the reaction is occurring in both directions.

Why would this reaction only occur in a 'closed' system?

Because the substances are in the gas phase. In an 'open' system, the gases would escape.

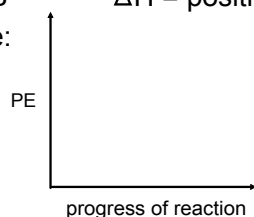
<http://phet.colorado.edu/en/simulation/reversible-reactions>

The following quantitative example will be used to show what inevitably occurs when a reversible reaction is left undisturbed.

Suppose our reaction is:



Sketch a PE curve:



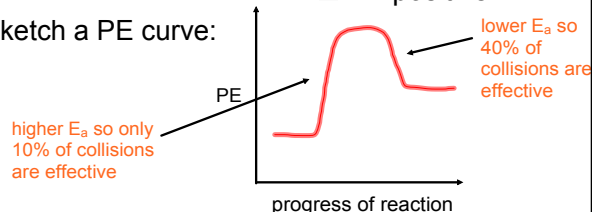
The reaction begins with 500 particles of A and 0 particles of B. 10% of the 'A' collisions are effective whereas 40% of the 'B' collisions are effective. How is this consistent with the PE curve?

The following quantitative example will be used to show what inevitably occurs when a reversible reaction is left undisturbed.

Suppose our reaction is:



Sketch a PE curve:



The reaction begins with 500 particles of A and 0 particles of B. 10% of the 'A' collisions are effective whereas 40% of the 'B' collisions are effective. How is this consistent with the PE curve? The fwd reaction has a higher  $E_a$ , so it will have a lower percentage of effective collisions.

Complete the table and think about what is developing.

Molecules of A	A moles reacting	A moles produced	Molecules of B	B moles reacting	B moles produced
500			0		

Molecules of A	A moles reacting	A moles produced	Molecules of B	B moles reacting	B moles produced
500	50	0	0	0	50
450	45	20	50	20	45
425	43	30	75	30	43
412	41	35	88	35	41
406	41	38	94	38	41
403	40	39	97	39	40
402	40	39	98	39	40
401	40	39	99	39	40
400	40	40	100	40	40
400	40	40	100	40	40
400	40	40	100	40	40
400	40	40	100	40	40
400			100		

**Things to Consider:**

1. The amount of 'A particles reacting' can be likened to the forward reaction rate, and the amount of 'B particles reacting' can be likened to the reverse reaction rate.
2. Think about how the forward and reverse rates are changing as the reaction proceeds and why this is the case. Also think about how the amount of 'Particles of A' are changing compared to the 'Particles of B', and how this is affecting the reaction rates.
3. What role does the % of effective collisions play in the system (10% for forward vs. 40% for reverse).
4. Can you explain the system at the end of the experiment?

Note any observations and thoughts from what has developed during the reaction:

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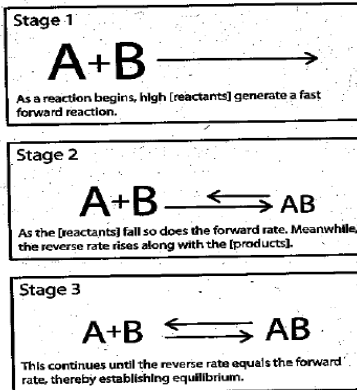
The forward reaction rate continually decreased due to the continual decrease in the amount of A particles available for collision.

The reverse reaction rate continually increased due to the continual increase in the amount of B particles being produced.

The forward reaction rate decreased, and the reverse reaction rate increased until they became equal (40 particles of A becoming B, and 40 particles of B becoming A. At this point, the amount of A and B particles remained constant.

The reaction rates became equal, but the amount of A and B particles are not equal at this point (400 A to 100 B). This is because only 10% of A collisions are effective (10% of 400 is 40) whereas 40% of B collisions are effective (40% of 100 is 40).

The reaction is now 'stuck' with equal rates and constant amounts of reactant and product.



[http://www.wnorton.com/college/chemistry/gilbert2/tutorials/interface.asp?chapter=chapter\\_15&folder=equilibrium](http://www.wnorton.com/college/chemistry/gilbert2/tutorials/interface.asp?chapter=chapter_15&folder=equilibrium)

**Conclusions:**

If a reversible system is left undisturbed, eventually the forward and reverse rates \_\_\_\_\_.

At this point, the reaction has attained \_\_\_\_\_.

The amount, or concentrations of both reactants and products have become \_\_\_\_\_ (but not \_\_\_\_\_ due to \_\_\_\_\_).

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<http://www.chm.davidson.edu/ronutt/che115/EquKin/EquKin.htm>

temp 380

Draw a graph that depicts the change in A particles and the change in B particles as the reversible reaction proceeds.

Draw a dashed vertical line to indicate where equilibrium was attained.

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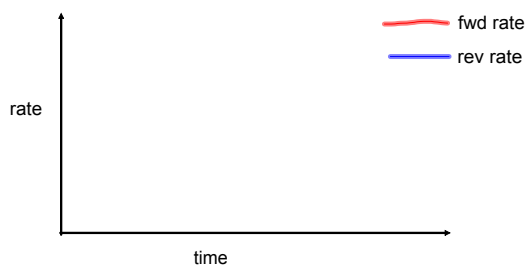
What if you start with 500 particles of B and 0 particles of A?

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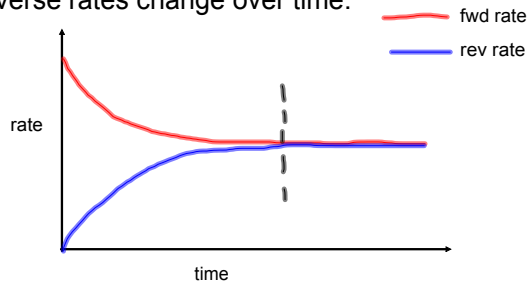
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Back to the original system we studied with a start of 500 particles of A and 0 particles of B. Draw a graph that shows how the forward and reverse rates change over time.



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Equilibria (plural for equilibrium) are **dynamic**. What does this mean?

<http://www.absorblearning.com/media/attachment.action?quick=w&att=2310>

What do you see when you look at an equilibrium system at the macroscopic level (with the naked eye)?

Equilibria (plural for equilibrium) are **dynamic**. What does this mean?

<http://www.absorblearning.com/media/attachment.action?quick=w&att=2310>

Even though reactant and product concentrations are constant, **both the forward and reverse reactions continue to occur**, albeit the rates are equal.

What do you see when you look at an equilibrium system at the macroscopic level (with the naked eye)?

The system looks static, meaning it looks like no change is happening. The forward and reverse reactions continue, but there is **no net change** to the system.

Here are some general characteristics of any equilibrium system:

- 1) Forward and reverse rates are \_\_\_\_\_.
- 2) Concentrations are \_\_\_\_\_.
- 3) Macroscopic properties are \_\_\_\_\_.
- 4) Equilibrium can be attained from either direction.
- 5) If gases are involved, the system must be \_\_\_\_\_.
- 6) Temperature must be constant.

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**Assignment 1:**

1) Explain the process of how equilibrium is attained. Use the reaction  $2\text{HI} \rightleftharpoons \text{H}_2 + \text{I}_2$  and suppose you start with only HI.  
 To get you started: *There are initially many HI collisions, causing an initial large forward rate. Since there are no H<sub>2</sub> and I<sub>2</sub> molecules, the initial reverse rate is zero. However, as HI molecules continue to collide, ....*

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2) Consider the following:

- I. forward and reverse rates are equal
- II. macroscopic properties are constant
- III. can be achieved from either direction
- IV. concentrations of reactants and products are equal

Which of the above are true for all equilibrium systems?

- A. I and II only
- B. I and IV only
- C. I, II, and III only
- D. I, II, III, and IV

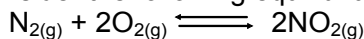
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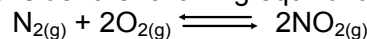
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Equal moles of N<sub>2</sub> and O<sub>2</sub> are added, under certain conditions, to a closed container. Which of the following describes the net change in the reverse reaction as the system proceeds toward equilibrium?

	Rate of Reverse Reaction	[NO <sub>2</sub> ]
A.	increases	increases
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4) In Hebden, read the bottom of page 38, the top of page 39, the first half of page 40, and the bottom of page 41. Then do (on p.40 and 41) # 6bcde and #7bcd.

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answers in the back of Hebden

### II) LeChatelier's Principle

What will happen if an equilibrium system is disturbed?

Possible disturbances include a change in concentration of one of the substances, a change in temperature, or a change in the pressure (essentially the concentration) of a gas, or the addition of a catalyst.

The French chemist LeChatelier developed a principle to help chemists predict the effect of a disturbance.

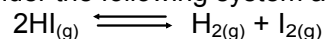
### **LeChatelier's Principle:**

### **LeChatelier's Principle:**

If an equilibrium system is subjected to a change, processes occur to **counteract** the change until a new equilibrium is established.

### **Concentration Change:**

Consider the following system at equilibrium:



Now, let's subject the equilibrium to a change: the addition of more  $\text{HI}_{(g)}$  to the system



What substance initially increases in concentration?  
How does this affect the amount of collisions?

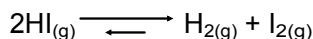
How does this affect the fwd and reverse reaction rates?

If one rate is temporarily greater than the other, we say a **shift** is taking place, as concentrations are no longer constant. In the case above, a shift to the **right** is taking place because the forward rate is temporarily \_\_\_\_\_ than the reverse rate



What substance initially increases in concentration? **HI**  
How does this affect the amount of collisions?  
*more collisions occurring between HI particles, therefore more effective collisions*  
How does this affect the fwd and reverse reaction rates? *Forward rate increases, reverse rate initially not affected. So now the fwd rate is greater than the reverse rate.*

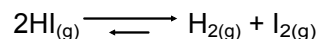
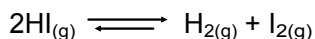
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Therefore, products are being produced faster than they are being used (resulting in a net increase), so during a shift right, we say that products are **favoured**. This is LeChatelier's 'counteraction' (we added more reactant, but now the product concentration is increasing).

Once products start increasing in concentration, what will happen to the reverse rate?

Concurrently, since the reactant is being used up faster than it is being produced, what starts to happen to the forward rate?

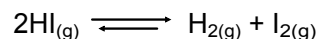


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Once products start increasing in concentration, what will happen to the reverse rate?

*it will start to increase due to increased collisions between products*

Concurrently, since the reactant is being used up faster than it is being produced, what starts to happen to the forward rate? *it will start to decrease*



The reverse rate continues to increase and the forward rate continues to decrease until...

The reverse rate continues to increase and the forward rate continues to decrease until...

*they become equal and a new equilibrium is established. At this point, reactant and product concentrations are once again constant.*



In summary:

[HI] initially \_\_\_\_\_, then due to the shift right it \_\_\_\_\_, but overall is slightly \_\_\_\_\_ (an initial change is always more drastic than a shift change).

[H<sub>2</sub>] \_\_\_\_\_ and [I<sub>2</sub>] \_\_\_\_\_ due to the shift right.

So how is it possible that all of [HI], [H<sub>2</sub>], and [I<sub>2</sub>] increased?

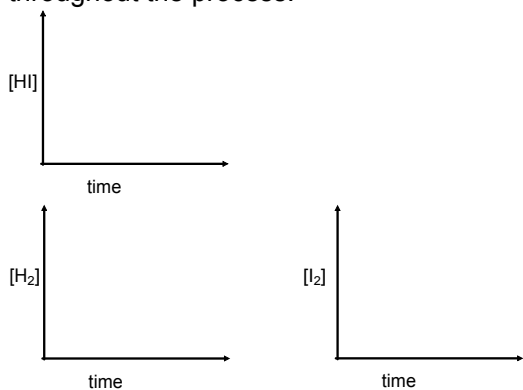
In summary:

[HI] initially increased, then due to the shift right it decreased, but overall is slightly increased (an initial change is always more drastic than a shift change).

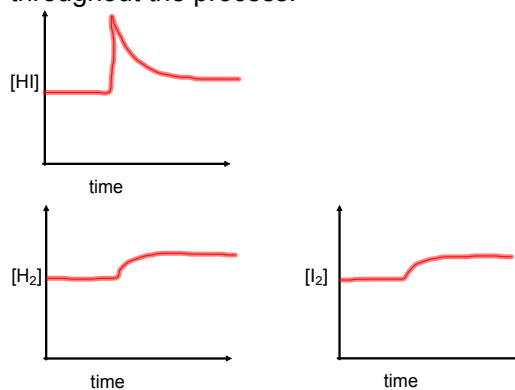
[H<sub>2</sub>] increased and [I<sub>2</sub>] increased due to the shift right.

So how is it possible that all of [HI], [H<sub>2</sub>], and [I<sub>2</sub>] increased? because more HI was added initially, there are more particles in the system, so all concentrations can and do increase

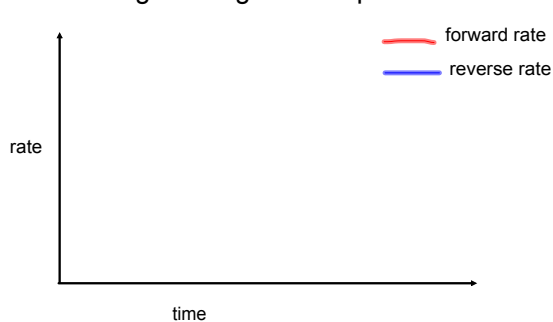
Graph the concentration changes that occur throughout the process:



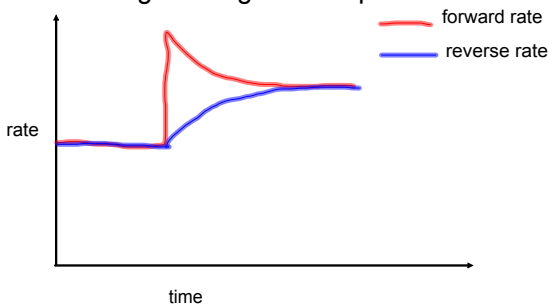
Graph the concentration changes that occur throughout the process:



Draw a graph to show how forward and reverse rates change throughout the process:



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How is it possible that both rates are now higher compared to the original equilibrium?

How is it possible that both rates are now higher compared to the original equilibrium?

Due to the addition of more HI, there are now more particles in the system, which means more collisions, more effective collisions, and higher reaction rates.

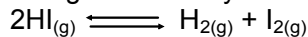
Summary using LeChatelier's Principle:

If an equilibrium is subjected to a change ( ), processes occur to counteract the change ( ) until a new equilibrium is established ( ).

Summary using LeChatelier's Principle:

If an equilibrium is subjected to a change (an increase in the # of HI molecules - an [HI] increase), processes occur to counteract the change (a shift right causing an [HI] decrease) until a new equilibrium is established (rates are now higher than they were originally and the concentrations are again constant but all higher than what they were originally).

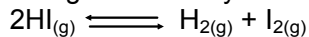
Considering the same system at equilibrium:



Explain what would occur if some  $\text{HI}_{(g)}$  is removed from the system.

-HI collisions would \_\_\_\_\_  
 -forward rate would \_\_\_\_\_  
 -thus, reverse rate will be temporarily \_\_\_\_\_ than the forward rate  
 -this will cause a shift \_\_\_\_\_, meaning \_\_\_\_\_ will be favoured  
 -so for a time, due to the shift, [HI] will \_\_\_\_\_ and  $[\text{H}_2]$  and  $[\text{I}_2]$  will \_\_\_\_\_  
 -eventually, the forward rate will start to \_\_\_\_\_ and the reverse rate will start to \_\_\_\_\_ until they \_\_\_\_\_.

Considering the same system at equilibrium:



Explain what would occur if some  $\text{HI}_{(g)}$  is removed from the system.

-HI collisions would decrease  
 -forward rate would decrease  
 -thus, reverse rate will be temporarily higher than the forward rate  
 -this will cause a shift left, meaning reactants will be favoured  
 -so for a time, due to the shift, [HI] will increase and  $[\text{H}_2]$  and  $[\text{I}_2]$  will both decrease  
 -eventually, the forward rate will start to increase and the reverse rate will start to decrease until they become equal.

-at this point, a new \_\_\_\_\_ has been established

In summary, [HI] initially \_\_\_\_\_, then \_\_\_\_\_, but overall slightly \_\_\_\_\_.

[H<sub>2</sub>] \_\_\_\_\_ and [I<sub>2</sub>] \_\_\_\_\_.

How is it that all concentrations decrease?

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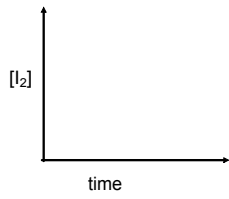
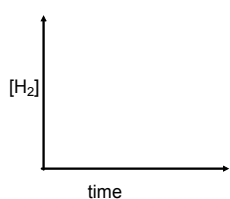
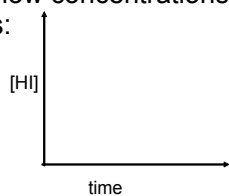
In summary, [HI] initially decreases, then increases, but overall slightly decreases.

[H<sub>2</sub>] decrease and [I<sub>2</sub>] decrease.

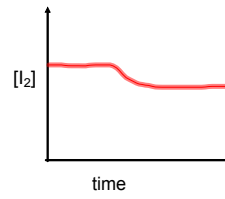
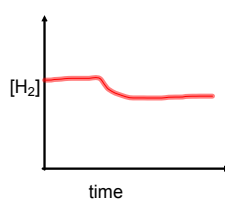
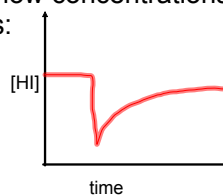
How is it that all concentrations decrease?

Particles were originally removed from the system so eventually all concentrations decrease.

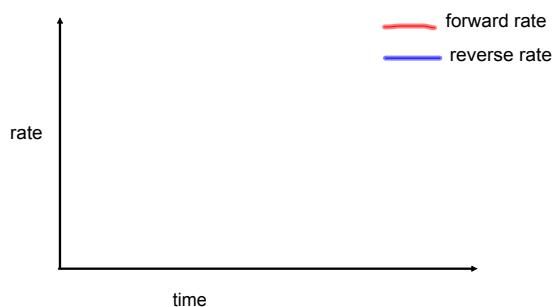
Graph how concentrations change during the process:



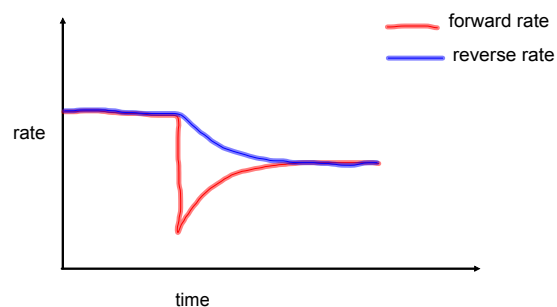
Graph how concentrations change during the process:



Graph how the rates change during the process:



Graph how the rates change during the process:



**LeChatelier's Principle:**

What was the initial change?

What was the 'counteraction'?

Why was it a 'new' equilibrium?

Note: The 'counteraction' is always the...

**LeChatelier's Principle:**

What was the initial change? the decrease in [HI]

What was the 'counteraction'? the shift left so that [HI] increased for a time

Why was it a 'new' equilibrium?

the rates are lower than originally, as are the concentrations

Note: The 'counteraction' is always the **shift that is the result of an initial disturbance.**

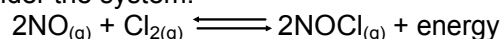
**Conclusion:**

**Increasing the concentration of a substance causes a shift to the opposite side.**

**Decreasing the concentration of a substance causes a shift to the same side.**

**Temperature Change:**

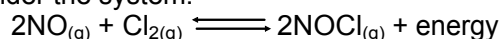
Consider the system:



We can disturb this equilibrium by decreasing the temperature (remove energy from the system). The forward reaction is \_\_\_\_\_ and the reverse reaction is \_\_\_\_\_. What will happen to both rates if you decrease temperature? \_\_\_\_\_ However, the endothermic reaction relies more on energy, so it will be affected to a greater extent.

**Temperature Change:**

Consider the system:



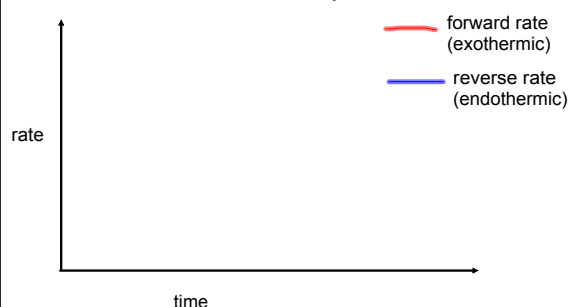
We can disturb this equilibrium by decreasing the temperature (remove energy from the system). The forward reaction is exothermic and the reverse reaction is endothermic.

What will happen to both rates if you decrease temperature? they will both decrease

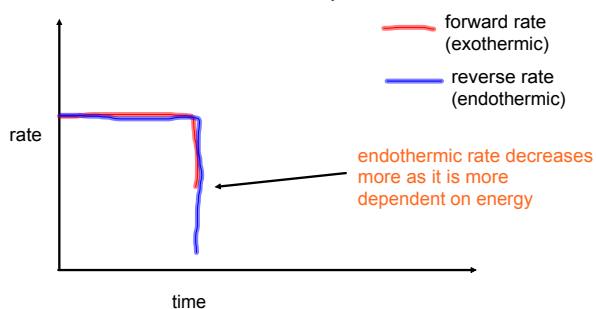
However, the endothermic reaction relies more on energy, so it will be affected to a greater extent.

the reverse reaction rate (endothermic in this example) will decrease to a greater extent than the forward reaction rate (exothermic)

Graph how the forward and reverse rates change due to the decrease in temperature.



Graph how the forward and reverse rates change due to the decrease in temperature.



Therefore, which rate is temporarily greater?

Therefore, there is a shift to the \_\_\_\_\_ and \_\_\_\_\_ are favoured.

This means, that for a time, products will be produced faster than they're being used (resulting in a net increase), and visa versa for reactants.

Eventually, the \_\_\_\_\_ rate will start to increase and the \_\_\_\_\_ rate will start to decrease until \_\_\_\_\_.

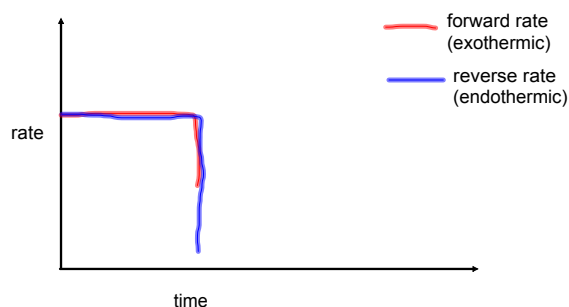
Therefore, which rate is temporarily greater?

Therefore, there is a shift to the right (exo side) and products are favoured.

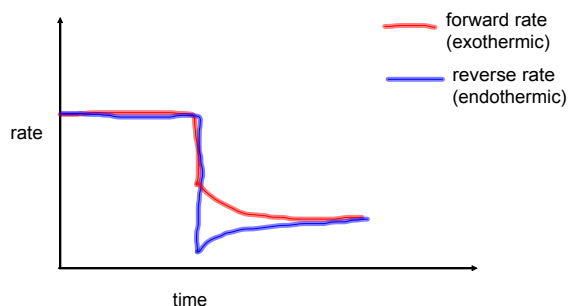
This means, that for a time, products will be produced faster than they're being used (resulting in a net increase), and visa versa for reactants.

Eventually, the reverse (endo) rate will start to increase and the forward (exo) rate will start to decrease until a new equilibrium is established.

Finish the rate graph:



Finish the rate graph:



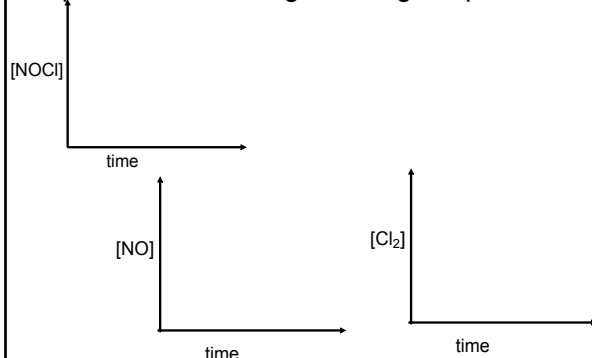
When equilibrium has been re-established, why are the rates lower than originally?

When equilibrium has been re-established, why are the rates lower than originally?

Temperature has been decreased, thus both rates are lower than before as there are less collisions, and the collisions aren't as hard.

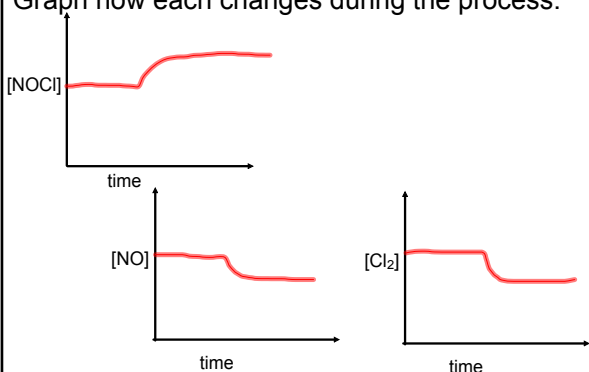
Due to the shift right (to the exothermic side), the [NOCl] \_\_\_\_\_, [NO] \_\_\_\_\_, and [Cl<sub>2</sub>] \_\_\_\_\_.

Graph how each changes during the process:

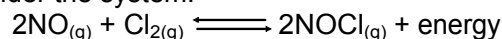


Due to the shift right (to the exothermic side), the [NOCl] \_\_\_\_\_ increases \_\_\_\_\_, [NO] \_\_\_\_\_ decreases \_\_\_\_\_, and [Cl<sub>2</sub>] \_\_\_\_\_ decreases \_\_\_\_\_.

Graph how each changes during the process:

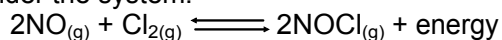


Consider the system:



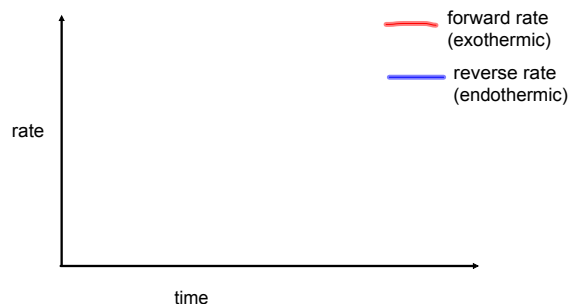
If the temperature was increased, both rates will \_\_\_\_\_, but since endothermic (reverse reaction in this example) relies more on energy, it will \_\_\_\_\_ more. Therefore, the \_\_\_\_\_ rate will temporarily be higher than the \_\_\_\_\_ rate, causing a shift to the \_\_\_\_\_ so that \_\_\_\_\_ are favoured.

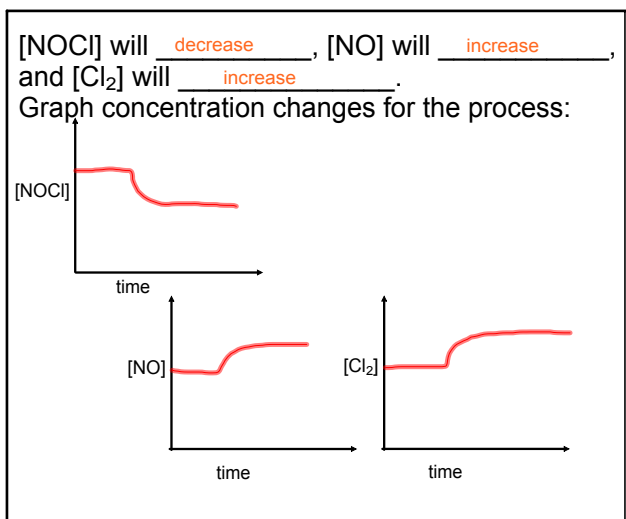
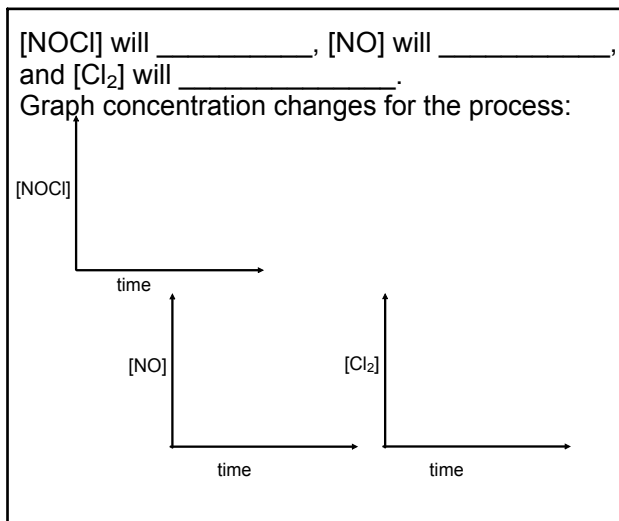
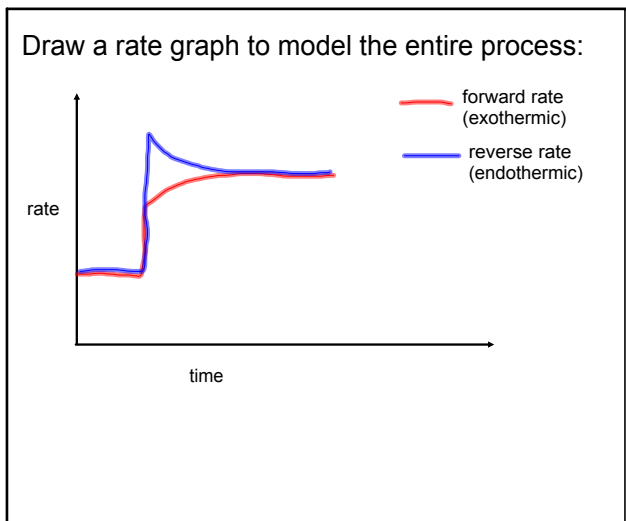
Consider the system:



If the temperature was increased, both rates will \_\_\_\_\_ increase \_\_\_\_\_, but since endothermic (reverse reaction in this example) relies more on energy, it will \_\_\_\_\_ increase \_\_\_\_\_ more. Therefore, the \_\_\_\_\_ reverse (endo) \_\_\_\_\_ rate will temporarily be higher than the \_\_\_\_\_ forward (exo) \_\_\_\_\_ rate, causing a shift to the \_\_\_\_\_ left \_\_\_\_\_ so that \_\_\_\_\_ reactants \_\_\_\_\_ are favoured.

Draw a rate graph to model the entire process:





**Conclusion:**

Decreasing temperature results in a shift in the \_\_\_\_\_ direction.

Increasing temperature results in a shift in the \_\_\_\_\_ direction.

<http://www.absorblearning.com/media/attachment.action?quick=wa&att=2314>

**Conclusion:**

Decreasing temperature results in a shift in the exothermic direction.

Increasing temperature results in a shift in the endothermic direction.

<http://www.absorblearning.com/media/attachment.action?quick=wa&att=2314>

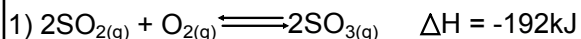
**Assignment 2:**

1)  $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g}) \quad \Delta H = -192\text{kJ}$

a) Indicate the shift that occurs using the words 'Right' or 'Left' and use ↑ or ↓ for concentration changes. Some boxes below may have three arrows: an initial change arrow, a shift change arrow, and a net (overall) change arrow.

Stress	Shift	[SO <sub>2</sub> ]	[O <sub>2</sub> ]	[SO <sub>3</sub> ]
Increase temperature				
Decrease [O <sub>2</sub> ]				
Inject more SO <sub>3</sub>				
Remove SO <sub>2</sub>				
Decrease temperature				
Decrease [SO <sub>3</sub> ]				

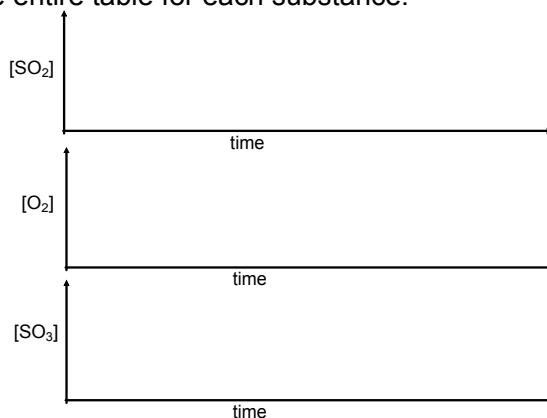
**Assignment 2:**



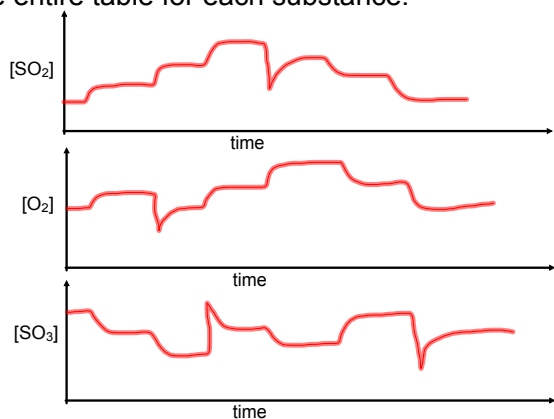
a) Indicate the shift that occurs using the words 'Right' or 'Left' and use  $\uparrow$  or  $\downarrow$  for concentration changes. Some boxes below may have three arrows: an initial change arrow, a shift change arrow, and a net (overall) change arrow.

Stress	Shift	[SO <sub>2</sub> ]	[O <sub>2</sub> ]	[SO <sub>3</sub> ]
Increase temperature	left	$\uparrow$	$\uparrow$	$\downarrow$
Decrease [O <sub>2</sub> ]	left	$\uparrow$	$\uparrow = \downarrow$	$\downarrow$
Inject more SO <sub>3</sub>	left	$\uparrow$	$\uparrow$	$\uparrow = \downarrow$
Remove SO <sub>2</sub>	left	$\downarrow = \uparrow$	$\uparrow$	$\downarrow$
Decrease temperature	right	$\downarrow$	$\downarrow$	$\uparrow$
Decrease [SO <sub>3</sub> ]	right	$\downarrow$	$\downarrow$	$\uparrow = \downarrow$

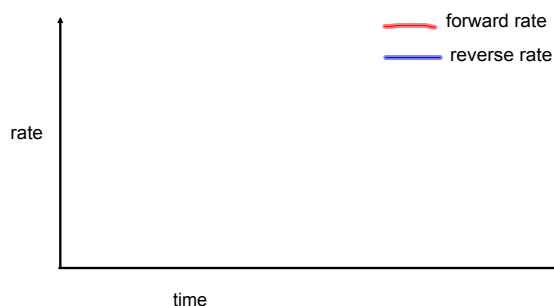
1b) Sketch a concentration vs. time graph for the entire table for each substance:



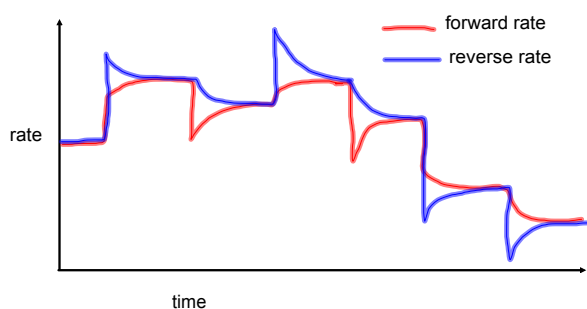
1b) Sketch a concentration vs. time graph for the entire table for each substance:



1c) Graph rate changes for the entire table:



1c) Graph rate changes for the entire table:



2) Hebden page 54, numbers 17-23: only answer concentration and temperature changes. Leave space in your work for the other changes, which you'll do as part of assignment 3.



2) Hebden page 54, numbers 17-23: only answer concentration and temperature changes. Leave space in your work for the other changes, which you'll do as part of assignment 3.

answers in the back of Hebden

<http://www.mhhe.com/physsci/chemistry/essentialchemistry/flash/lechl7.swf>  
 conc & temp review / pressure preview

**Pressure Change:**

The only state that fills its reacting container in every situation is \_\_\_\_\_. Thus, increasing or decreasing the volume of a reacting vessel will only initially affect the concentration of any \_\_\_\_\_ state substance. Then, an equilibrium shift may affect the concentrations or amounts of the non-gaseous substances.

A decrease in volume = an \_\_\_\_\_ in pressure.

An increase in volume = a \_\_\_\_\_ in pressure.

<http://www.mhhe.com/physsci/chemistry/essentialchemistry/flash/lechl7.swf>  
 conc & temp review / pressure preview

**Pressure Change:**

The only state that fills its reacting container in every situation is gas. Thus, increasing or decreasing the volume of a reacting vessel will only initially affect the concentration of any gas state substance. Then, an equilibrium shift may affect the concentrations or amounts of the non-gaseous substances.

A decrease in volume = an increase in pressure.

An increase in volume = a decrease in pressure.

A decrease in volume causes an increase in pressure, meaning that all gas concentrations \_\_\_\_\_.

An increase in volume causes a decrease in pressure, meaning all gas concentrations \_\_\_\_\_.

<http://www.absorblearning.com/media/attachment.action?quick=vz&att=2292>

Explain:

A decrease in volume causes an increase in pressure, meaning that all gas concentrations immediately increase.

An increase in volume causes a decrease in pressure, meaning all gas concentrations immediately decrease.

<http://www.absorblearning.com/media/attachment.action?quick=vz&att=2292>

Explain:

If volume is decreased, you have the same number of gas particles in a smaller volume of space, which means that there is more gas per unit space resulting in an increase in gas concentration (pressure). Visa versa for a volume increase.

A change in pressure **may** also cause a LeChatelier shift to occur.

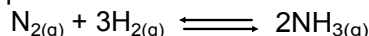
If the pressure of a system is increased, gas particles are packed for tightly together, so what can you say about collisions?

Therefore, what happens to both the forward and reverse rates?

However, one rate may increase more than the other. The side of the equation with more gas particles will experience a greater rate increase, causing a shift to the other side (the side with less gas particles). Soon the rates re-balance, and a new equilibrium is established.

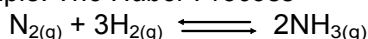
A change in pressure **may** also cause a LeChatelier shift to occur.  
 If the pressure of a system is increased, gas particles are packed tightly together, so what can you say about collisions? **more total collisions**  
 Therefore, what happens to both the forward and reverse rates? **they both increase**  
 However, one rate may increase more than the other. The side of the equation with more gas particles will experience a greater rate increase, causing a shift to the other side (the side with less gas particles). Soon the rates re-balance, and a new equilibrium is established.

Example: *The Haber Process*



What happens to the pressure of the gases if the volume of the system is decreased?  
 So what happens initially to all gas concentrations?  
 So what happens to the # of collisions?  
 What happens to the rates?  
 How many gas molecules on the reactant side?  
 How many gas molecules on the product side?  
 Thus, which rate will increase more?  
 Therefore, a shift has occurred to what side?  
 Then, the rates will eventually re-balance and a new equilibrium will be established.

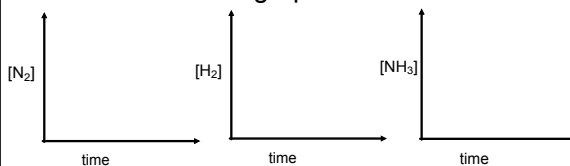
Example: *The Haber Process*



What happens to the pressure of the gases if the volume of the system is decreased? **increase**  
 So what happens initially to all gas concentrations? **all increase**  
 So what happens to the # of collisions? **increase**  
 What happens to the rates? **both increase**  
 How many gas molecules on the reactant side? **4**  
 How many gas molecules on the product side? **2**  
 Thus, which rate will increase more? **forward**  
 Therefore, a shift has occurred to what side? **right**  
 Then, the rates will eventually re-balance and a new equilibrium will be established.

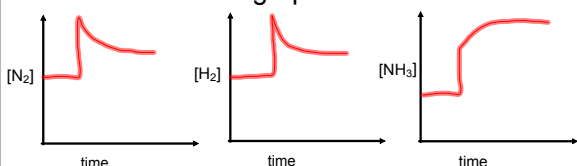
[N<sub>2</sub>] and [H<sub>2</sub>] will both initially \_\_\_\_\_, then due to the shift will \_\_\_\_\_, but overall will have a net \_\_\_\_\_.  
 [NH<sub>3</sub>] will initially \_\_\_\_\_, then due to the shift will \_\_\_\_\_.

Draw concentration graphs:

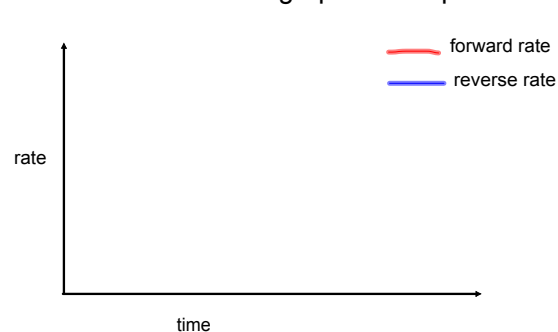


[N<sub>2</sub>] and [H<sub>2</sub>] will both initially **increase**, then due to the shift will **decrease**, but overall will have a net **increase**.  
 [NH<sub>3</sub>] will initially **increase**, then due to the shift will **increase more**.

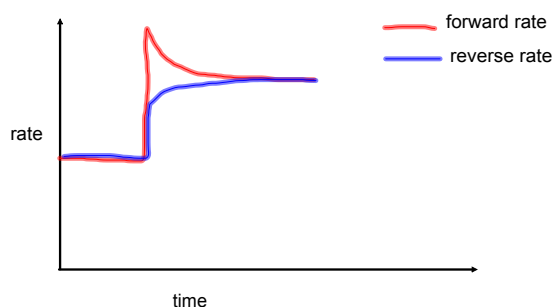
Draw concentration graphs:



Sketch a rate vs. time graph for the process:



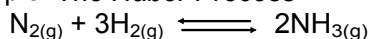
Sketch a rate vs. time graph for the process:



LeChatelier:

An increase in pressure (initial change) causes a shift to the side with less gas particles (counteraction) until a new equilibrium is established.

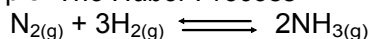
Example: *The Haber Process*



A increase in volume will cause a decrease in pressure (all gas concentrations immediately decrease). Both rates will decrease, but since the reactant side has more gas particles, the forward rate will be affected more, so it will decrease more than the reverse rate, causing a shift to the \_\_\_\_\_ (the side with more gas particles).

<http://www.absorblearning.com/media/attachment.action?quick=129&att=2743>

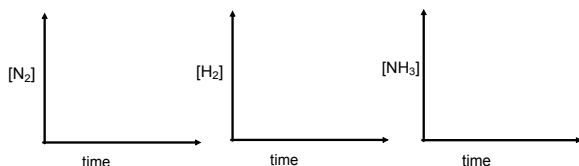
Example: *The Haber Process*



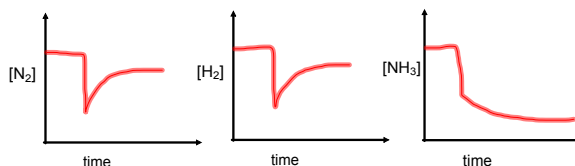
A increase in volume will cause a decrease in pressure (all gas concentrations immediately decrease). Both rates will decrease, but since the reactant side has more gas particles, the forward rate will be affected more, so it will decrease more than the reverse rate, causing a shift to the left side (the side with more gas particles).

<http://www.absorblearning.com/media/attachment.action?quick=129&att=2743>

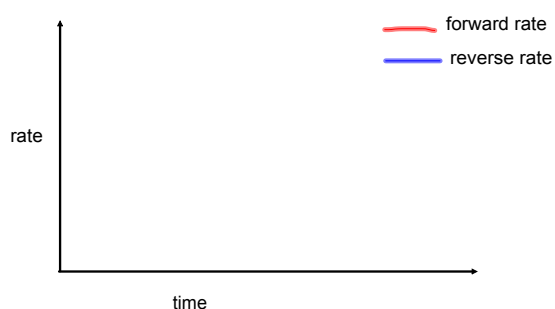
Draw concentration vs. time graphs for the process:



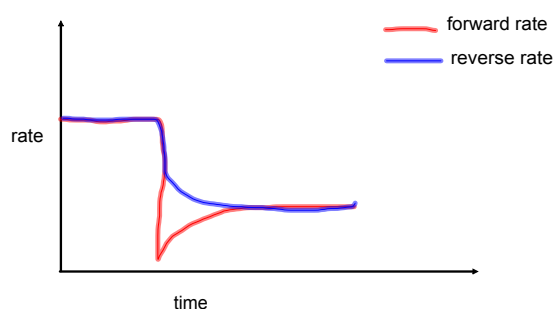
Draw concentration vs. time graphs for the process:



Sketch a rate vs. time graph for the process:



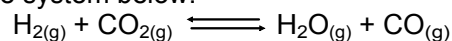
Sketch a rate vs. time graph for the process:



LeChatelier:

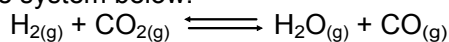
A decrease in pressure (initial change) causes a shift to the side with more gas particles (counteraction) until a new equilibrium is established.

Why would a pressure change not cause a shift for the system below:



Addition of an inert ( ) gas to an equilibrium will not affect the [reactants] or [products] enough to cause a significant change, and will not cause a shift of any kind.

Why would a pressure change not cause a shift for the system below:



There are equal numbers of gas particles on each side, so no shift will occur. However, any initial gas concentration changes due to a change in volume will occur.

Addition of an inert ( unreactive ) gas to an equilibrium will not affect the [reactants] or [products] enough to cause a significant change, and will not cause a shift of any kind.

**Conclusion:**

An increase in pressure will cause all gas concentrations to initially \_\_\_\_\_, and then a shift to the side with \_\_\_\_\_ gas particles will ensue.

A decrease in pressure will cause all gas concentrations to initially \_\_\_\_\_, and then a shift to the side with \_\_\_\_\_ gas particles will ensue.

Addition of an inert gas will not affect the equilibrium.

[http://www.dlt.ncssm.edu/core/Chapter14-Gas\\_Phase-Solubility-Complex\\_Ion\\_Equilibria/Chapter14-Animation2VOX-NDM.html](http://www.dlt.ncssm.edu/core/Chapter14-Gas_Phase-Solubility-Complex_Ion_Equilibria/Chapter14-Animation2VOX-NDM.html)

**Conclusion:**

An increase in pressure will cause all gas concentrations to initially increase, and then a shift to the side with less gas particles will ensue.

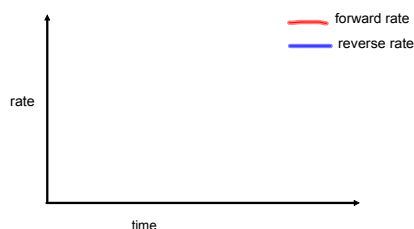
A decrease in pressure will cause all gas concentrations to initially decrease, and then a shift to the side with more gas particles will ensue.

Addition of an inert gas will not affect the equilibrium.

[http://www.dlt.ncssm.edu/core/Chapter14-Gas\\_Phase-Solubility-Complex\\_Ion\\_Equilibria/Chapter14-Animations/2NO2-N2O4.html](http://www.dlt.ncssm.edu/core/Chapter14-Gas_Phase-Solubility-Complex_Ion_Equilibria/Chapter14-Animations/2NO2-N2O4.html)

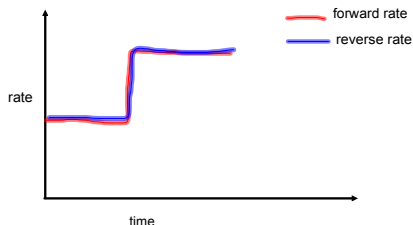
**Addition of a Catalyst:**

Catalysts \_\_\_\_\_ both forward and reverse reaction rates EQUALLY, therefore at no time do rates differ, so there is no shift. Keep in mind that both rates are higher than they were before. Graph the rate change below:



**Addition of a Catalyst:**

Catalysts increase both forward and reverse reaction rates EQUALLY, therefore at no time do rates differ, so there is no shift. Keep in mind that both rates are higher than they were before. Graph the rate change below:



**Important Concepts for Shifts:**

1) Equilibrium shifts will only affect the concentrations of gases and aqueous substances. The **amounts** of solid and liquid will be affected by shifts, but not their **concentrations**. In solids and liquids, concentrations are always constant because if you lose some mass, you also lose a proportional volume, so the concentration doesn't change. If you increase the mass, you increase volume proportionally.

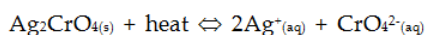
2) If more solid or liquid is added to an equilibrium mixture (or if some is removed), NO shift will occur and equilibrium will be maintained. Adding solid or liquid will cause a rate increase, but both the forward and reverse rates increase equally (they both decrease equally for a solid or liquid removal). The explanation behind why this is so is very advanced and difficult to conceptualize (it is beyond the scope of Chemistry 12).

[http://www.dlt.ncssm.edu/core/Chapter14-Gas\\_Phase-Solubility-Complex\\_Ion\\_Equilibria/Chapter14-Animations/CaO-CaCO3.html](http://www.dlt.ncssm.edu/core/Chapter14-Gas_Phase-Solubility-Complex_Ion_Equilibria/Chapter14-Animations/CaO-CaCO3.html)

**Assignment 3**

1) Finish Hebden page 54, numbers 17-23

2) Complete the table:

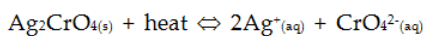


Stress	Shift	[Ag <sub>2</sub> CrO <sub>4</sub> ]	[Ag <sup>+</sup> ]	[CrO <sub>4</sub> <sup>2-</sup> ]
Add Ag <sub>2</sub> CrO <sub>4</sub> (s)				
Decrease temperature				
Increase pressure				
Decrease Ag <sup>+</sup> (aq)				
Increase CrO <sub>4</sub> <sup>2-</sup> (aq)				

**Assignment 3**

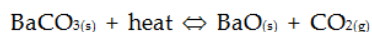
1) Finish Hebden page 54, numbers 17-23  
*answers in the back of Hebden*

2) Complete the table:



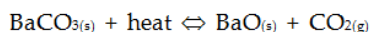
Stress	Shift	[Ag <sub>2</sub> CrO <sub>4</sub> ]	[Ag <sup>+</sup> ]	[CrO <sub>4</sub> <sup>2-</sup> ]
Add Ag <sub>2</sub> CrO <sub>4</sub> (s)	—	—	—	—
Increase temperature	L	—	↓	↓
Increase pressure	—	—	—	—
Decrease Ag <sup>+</sup> (aq)	R	—	↓↑ = ↓	↑
Increase CrO <sub>4</sub> <sup>2-</sup> (aq)	L	—	↓	↓↑ = ↑

3) Complete the table:



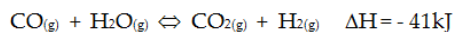
Stress	Shift	[BaCO <sub>3</sub> ]	[BaO]	[CO <sub>2</sub> ]
Add BaCO <sub>3</sub> (s)				
Increase temperature				
Decrease pressure				
Decrease volume				
Add CO <sub>2</sub> (g)				
Remove CO <sub>2</sub> (g)				

3) Complete the table:



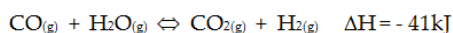
Stress	Shift	[BaCO <sub>3</sub> ]	[BaO]	[CO <sub>2</sub> ]
Add BaCO <sub>3</sub> (s)	—	—	—	—
Increase temperature	R	—	—	↑
Decrease pressure	R	—	—	↓↑ = ↓
Decrease volume	L	—	—	↓↑ = ↑
Add CO <sub>2</sub> (g)	L	—	—	↓↑ = ↑
Remove CO <sub>2</sub> (g)	R	—	—	↓↑ = ↓

4) Complete the table:



Stress	Shift	[CO]	[H <sub>2</sub> O]	[CO <sub>2</sub> ]	[H <sub>2</sub> ]
Add CO <sub>2</sub> (g)					
Increase temperature					
Remove H <sub>2</sub> O(g)					
Increase volume					
Add H <sub>2</sub> (g)					
Increase pressure					
Inject Ar(g)					

4) Complete the table:



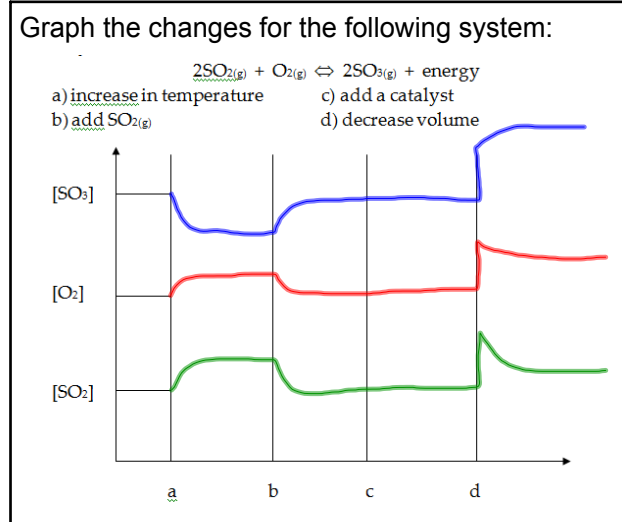
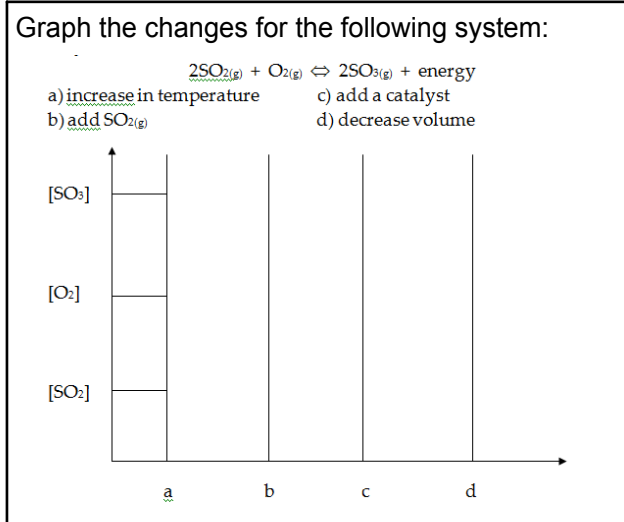
Stress	Shift	[CO]	[H <sub>2</sub> O]	[CO <sub>2</sub> ]	[H <sub>2</sub> ]
Add CO <sub>2</sub> (g)	L	↑	↑	↓↑ = ↑	↓
Increase temperature	L	↑	↑	↓	↓
Remove H <sub>2</sub> O(g)	L	↑	↓↑ = ↓	↓	↓
Increase volume	—	↓	↓	↓	↓
Add H <sub>2</sub> (g)	L	↑	↑	↓	↓↑ = ↑
Increase pressure	—	↑	↑	↓	↑
Inject Ar(g)	—	—	—	—	—

**III) Equilibrium Graphs**

Changes to an equilibrium system have been described in the last section. In this section, we will graphically represent concentration changes.

Things to remember:

- 1) Solid and liquid concentrations always remain constant.
- 2) When there is a temperature change, there are no immediate changes in concentration (spikes). The only changes are gradual (due to the shift) for (g) and (aq).
- 3) Changes in pressure result in immediate changes to gas concentrations, followed by a possible shift that will cause gradual changes in all (g) and (aq) substances.
- 4) A concentration change for a substance shows an immediate change for that substance, followed by gradual changes for the other (g) and (aq) substances.



**Haber Process**  
The Haber Process for making ammonia ( $\text{NH}_3$ ) was developed by German chemist Fritz Haber prior to WW1. In order for Germany to make TNT, which contains nitrogen, they needed a source of nitrates from soil, which they were purchasing from Chile. However, the British cut off the shipping lines from Chile once the war began. Haber had to develop a process to make ammonia from  $\text{N}_2$ . The ammonia could then be used as a precursor for TNT. Getting  $\text{N}_2$  to react is very difficult due to its triple bond. However, Haber manipulated an equilibrium system to maximize the yield (amount) of  $\text{NH}_3$ .

*The Haber Process:*  
$$\text{N}_{2(\text{g})} + 3\text{H}_{2(\text{g})} \rightleftharpoons 2\text{NH}_{3(\text{g})} + 92.4\text{kJ}$$

To maximize the yield of ammonia, the equilibrium must be shifted right as much as possible. What should temperature and pressure conditions (high or low) be to achieve this?  
\_\_\_\_\_ temperature & \_\_\_\_\_ pressure

What else did Haber do to maximize the yield of ammonia:

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$$\text{N}_{2(\text{g})} + 3\text{H}_{2(\text{g})} \rightleftharpoons 2\text{NH}_{3(\text{g})} + 92.4\text{kJ}$$

To maximize the yield of ammonia, the equilibrium must be shifted right as much as possible. What should temperature and pressure conditions (high or low) be to achieve this?  
low temperature & high pressure

What else did Haber do to maximize the yield of ammonia:

- 1) constant removal of  $\text{NH}_3$  from the system to cause a permanent shift right
- 2) added a catalyst (Fe) to make the rates go faster

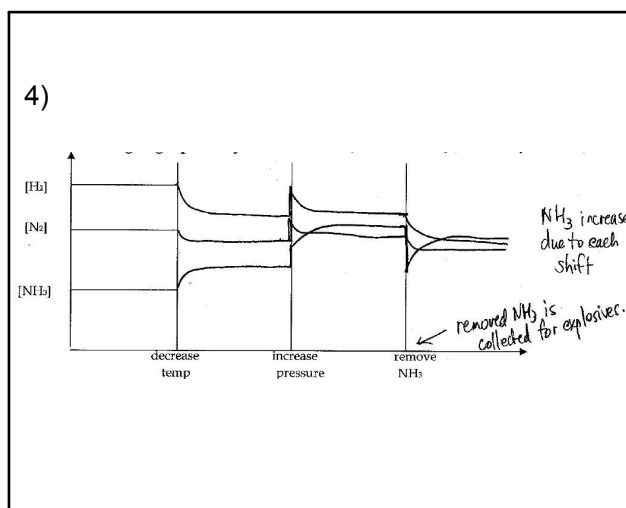
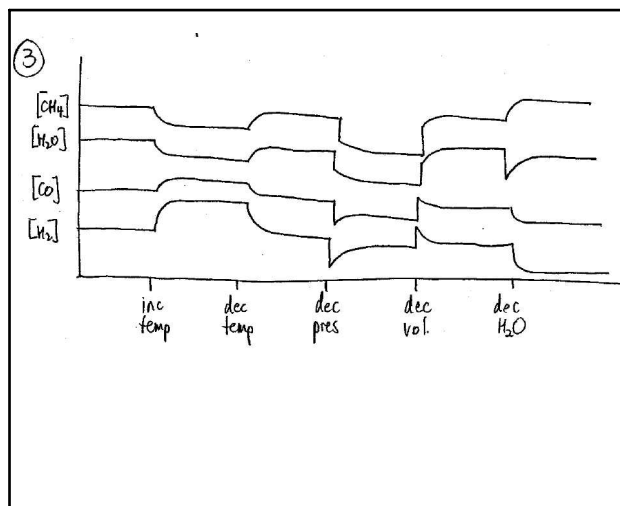
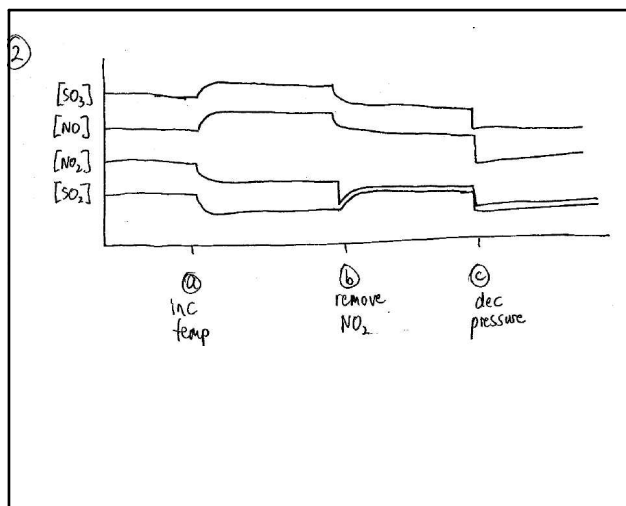
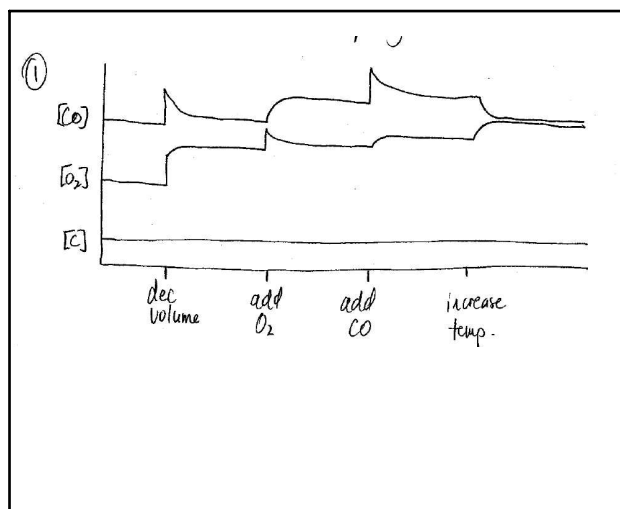
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Haber developed the process in 1910, and won the Nobel Prize for it in 1918.

In 1931, the German chemist Carl Bosch won the Nobel Prize in Chemistry for transforming the process to an even larger scale.

**Assignment 4: Graph each system below:**

- 1)  $2C(s) + O_2(g) \rightleftharpoons 2CO(g)$   $\Delta H = -97kJ$   
 stresses: a) decrease volume c) add CO  
 b) add  $O_2$  d) increase temperature
- 2)  $SO_3(g) + NO(g) \rightleftharpoons NO_2(g) + SO_2(g) + \text{energy}$   
 stresses: a) increase temperature  
 b) remove some  $NO_2(g)$   
 c) decrease pressure
- 3)  $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$   $\Delta H = +50kJ$   
 stresses: a) increase temperature d) decrease volume  
 b) decrease temperature e) add something which reacts with  $H_2O$   
 c) decrease pressure
- 4) Make a graph for the Haber Process with each stress: (a) decrease temp (b) increase pressure (c) remove  $NH_3$
- 5) Hebden page 55, numbers 27 & 28



**IV) Predicting Whether a Reaction will go to Completion, to Equilibrium, or Not React**

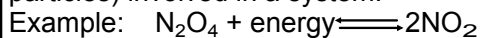
**Enthalpy**  
 Enthalpy is a term that describes the total potential energy content (the energy in the particles) involved in a system.  
 Example:  $N_2O_4 + \text{energy} \rightleftharpoons 2NO_2$   
 The forward reaction is \_\_\_\_\_.  
 The reverse reaction is \_\_\_\_\_.  
 For an endothermic reaction, is the enthalpy increasing or decreasing? Why?



**IV) Predicting Whether a Reaction will go to Completion, to Equilibrium, or Not React**

**Enthalpy**

Enthalpy is a term that describes the total potential energy content (the energy in the particles) involved in a system.



The forward reaction is endothermic.

The reverse reaction is exothermic.

For an endothermic reaction, is the enthalpy increasing or decreasing? Why?

Enthalpy is increasing because energy is being absorbed into the particles.

Endothermic reactions have increasing or \_\_\_\_\_ enthalpy because the particles are gaining energy.

Exothermic reactions have \_\_\_\_\_ or \_\_\_\_\_ enthalpy because the particles are \_\_\_\_\_ energy.

In nature, is it easier to gain or lose energy?

**Therefore, reactions naturally tend toward energy loss, meaning they tend toward the \_\_\_\_\_ direction. In other words they tend toward \_\_\_\_\_ or \_\_\_\_\_ enthalpy.**

Endothermic reactions have increasing or maximum enthalpy because the particles are gaining energy.

Exothermic reactions have decreasing or minimum enthalpy because the particles are releasing energy.

In nature, is it easier to gain or lose energy?  
lose energy

**Therefore, reactions naturally tend toward energy loss, meaning they tend toward the exothermic direction. In other words they tend toward decreasing or minimum enthalpy.**

**Entropy**

Entropy is the measure of disorder or randomness in a system.

Think of your bedroom. Is it easier for your bedroom to become messy or to keep it clean?

This comes down to probability. Out of all the possible states your room could be in (an infinite amount), many more of them are considered disordered states compared to ordered states.

So, nature tends toward disorder, or increasing entropy, for the simple reason that...

**Entropy**

Entropy is the measure of disorder or randomness in a system.

Think of your bedroom. Is it easier for your bedroom to become messy or to keep it clean?

let it become messy

This comes down to probability. Out of all the possible states your room could be in (an infinite amount), many more of them are considered disordered states compared to ordered states.

So, nature tends toward disorder, or increasing entropy, for the simple reason that...

there are many more disordered states compared to ordered states

Rank the states of matter [(aq) included] from most entropic to least entropic:

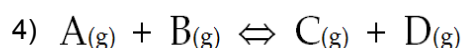
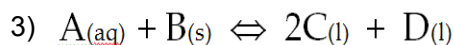
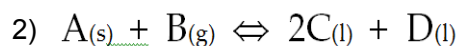
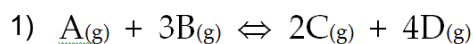
**Reactions tend toward increasing or maximum entropy (the side with the most gas particles).**

Rank the states of matter [(aq) included] from most entropic to least entropic:

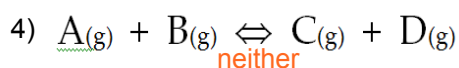
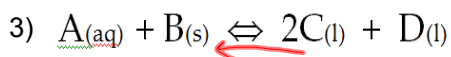
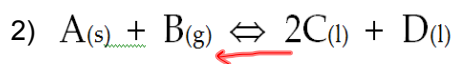
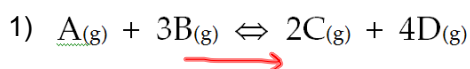
g, aq, l, s

Reactions tend toward increasing or maximum entropy (the side with the most gas particles).

Examples: Determine which direction entropy is increasing.



Examples: Determine which direction entropy is increasing.



**Summary:**

Reactions naturally tend towards \_\_\_\_\_ enthalpy and \_\_\_\_\_ entropy.

In other words, reactions tend toward the \_\_\_\_\_ direction and the side with \_\_\_\_\_ gas particles.

**Summary:**

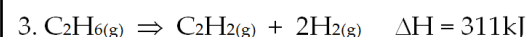
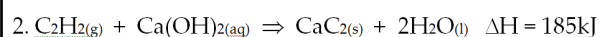
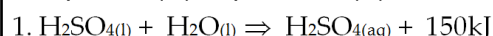
Reactions naturally tend towards \_\_\_\_\_ minimum \_\_\_\_\_ enthalpy and \_\_\_\_\_ maximum \_\_\_\_\_ entropy.

In other words, reactions tend toward the \_\_\_\_\_ exothermic \_\_\_\_\_ direction and the side with \_\_\_\_\_ more \_\_\_\_\_ gas particles.

So, we can use the summary to make predictions on whether reactions go to completion, form an equilibrium, or don't occur at all.

Examples:

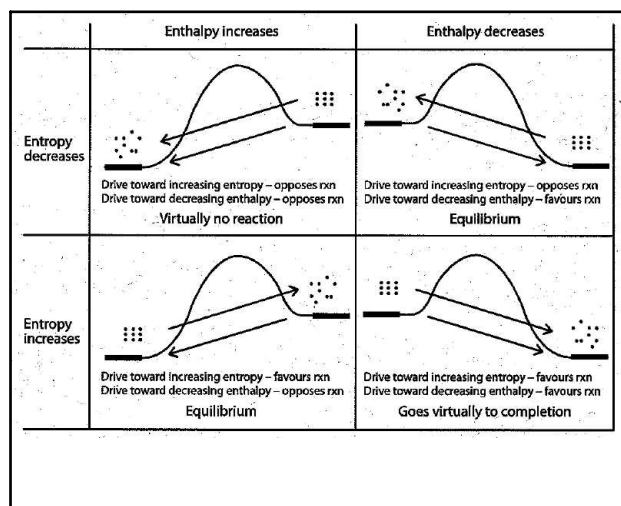
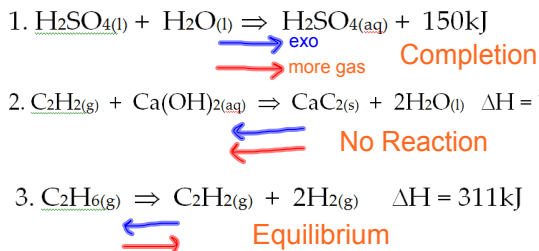
Predict whether each reaction will go to completion (C), equilibrium (E), or not react (NR)



So, we can use the summary to make predictions on whether reactions go to completion, form an equilibrium, or don't occur at all.

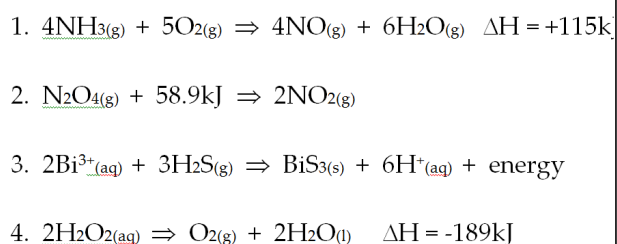
Examples:

Predict whether each reaction will go to completion (C), equilibrium (E), or not react (NR)



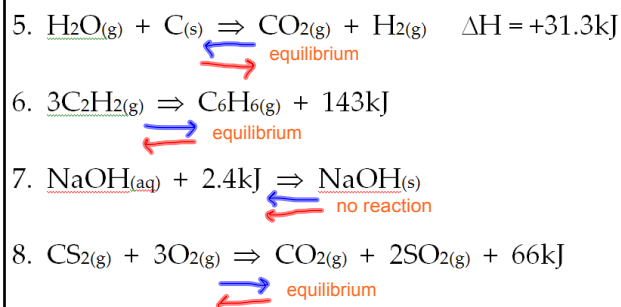
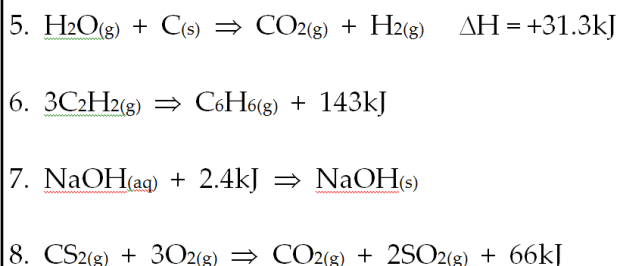
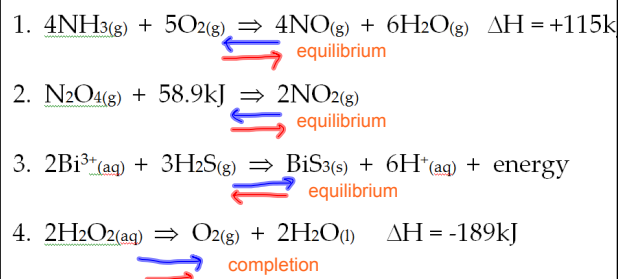
**Assignment 5:**

State whether each reaction will go to completion (C), equilibrium (E), or not react (NR)

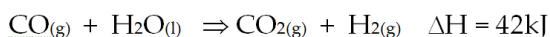


**Assignment 5:**

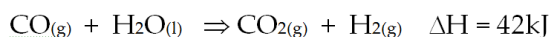
State whether each reaction will go to completion (C), equilibrium (E), or not react (NR)



9) A student predicts that the following reaction will go to completion. Do you agree or disagree? Support with an explanation.



9) A student predicts that the following reaction will go to completion. Do you agree or disagree? Support with an explanation.



Decreasing enthalpy is in the reverse direction and increasing entropy is in the forward direction. Therefore, this reaction will **NOT** go to completion. I **disagree** with the student.

10) For the following reaction, in which direction is enthalpy increasing? In which direction is entropy maximized? Will the reaction reach equilibrium?



10) For the following reaction, in which direction is enthalpy increasing? In which direction is entropy maximized? Will the reaction reach equilibrium?



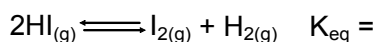
Enthalpy is increasing in the reverse direction, therefore it is decreasing in the forward direction. Entropy is increasing in the forward direction. Therefore, the reaction will not reach equilibrium. It will go to completion.

### V) The Equilibrium Constant

The equilibrium constant is called ' $K_{\text{eq}}$ ' and is found by multiplying product concentrations and dividing that by the result of multiplying reactant concentrations.

Do **not** include solids and liquids in  $K_{\text{eq}}$  expressions as the concentrations of these remain constant.

Example: Write the  $K_{\text{eq}}$  expression:

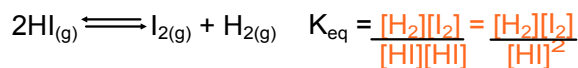


### V) The Equilibrium Constant

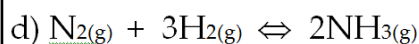
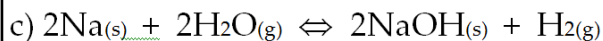
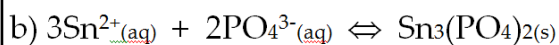
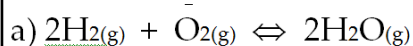
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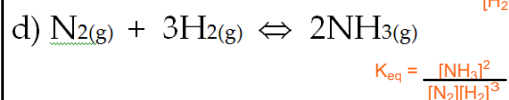
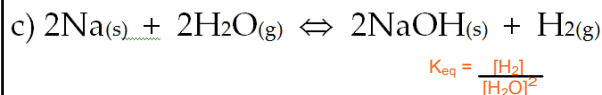
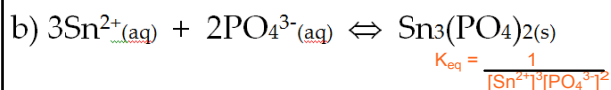
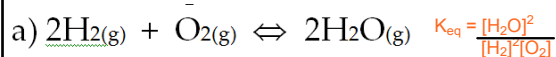
Example: Write the  $K_{\text{eq}}$  expression:



Examples: Write a  $K_{eq}$  for each of the following



Examples: Write a  $K_{eq}$  for each of the following



Go to page 40 & 41 in Hebden and look at the tables in #6 & #7 (you did these questions in Assignment 1). Calculate the  $K_{eq}$  constant for the equilibrium that was attained after 10 minutes (bottom of page 40).

Then, the equilibrium was disturbed by increasing [B] (see top of page 41). Calculate the  $K_{eq}$  after a new equilibrium was reached at 18 minutes.

Go to page 40 & 41 in Hebden and look at the tables in #6 & #7 (you did these questions in Assignment 1). Calculate the  $K_{eq}$  constant for the equilibrium that was attained after 10 minutes (bottom of page 40).

$$K_{eq} = \frac{1.000}{0.200} = 5.00$$

Then, the equilibrium was disturbed by increasing [B] (see top of page 41). Calculate the  $K_{eq}$  after a new equilibrium was reached at 18 minutes.

$$K_{eq} = \frac{1.500}{0.300} = 5.00$$

This is why it is a CONSTANT.

If equilibrium is disturbed due to a *concentration* or *pressure* change, it will shift and eventually return to a new equilibrium, and though the concentrations of each gas and aqueous substance may be different than they were originally, the equilibrium constant ( $K_{eq}$ ) - the ratio of products to reactants - will remain the same, hence why it is called a CONSTANT.

However, if equilibrium is disturbed due to a *temperature* change, the  $K_{eq}$  constant will change.

It is mathematically impossible for the  $K_{eq}$  to remain the same after a temperature change. Because there are no immediate changes in concentration due to a temperature change, when a shift occurs, one side increases and the other side decreases. When you apply this to a fraction (the  $K_{eq}$  expression), it cannot possibly stay constant.

It is mathematically impossible for the  $K_{eq}$  to remain the same after a temperature change. Because there are no immediate changes in concentration due to a temperature change, when a shift occurs, one side increases and the other side decreases. When you apply this to a fraction (the  $K_{eq}$  expression), it cannot possibly stay constant.

Let's say that originally  $K_{eq} = \frac{[p]}{[r]} = \frac{2}{5} = 0.40$

then after a temp shift left (prods dec and reacs inc)  $K_{eq} = \frac{1}{6} = 0.17$

The  $K_{eq}$  must change. Same idea if the shift is to the right.

So how is it possible that  $K_{eq}$  mathematically can, and actually will, stay the same after a concentration or pressure change?

Because there are immediate concentration changes before shift changes. For example, if you increase [HI] in this system:  $2HI_{(g)} \rightleftharpoons I_{2(g)} + H_{2(g)}$ , then all concentrations end up with a net increase, so the fraction can, and will, remain the same:

For example, originally,  $K_{eq} = \frac{(3.0)(3.0)}{(2.0)^2} = 2.25$

After [HI] inc,  $K_{eq} = \frac{(4.0)(4.0)}{(2.667)^2} = 2.25$

### The Size of the $K_{eq}$ Constant

Remember,  $K_{eq} = \frac{[\text{products}]}{[\text{reactants}]}$

If the  $K_{eq}$  is small (less than 1), does the equilibrium system contain a higher concentration of reactants or products (look at the fraction above)?

What about if the  $K_{eq}$  is large (greater than 1)?

### The Size of the $K_{eq}$ Constant

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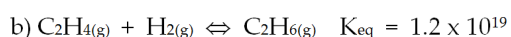
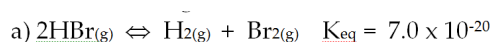
reactants, as the fraction above will be 'proper', meaning the denominator is larger than the numerator

What about if the  $K_{eq}$  is large (greater than 1)?

products, as the fraction above will be improper, meaning the numerator will be larger than the denominator

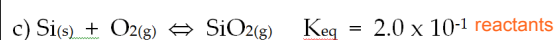
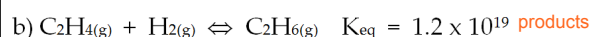
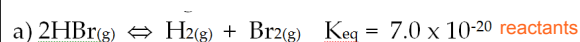
Examples:

Do the following equilibria favour reactants or products?



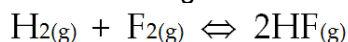
Examples:

Do the following equilibria favour reactants or products?



**Writing the equation the other way around**

For the following reaction:



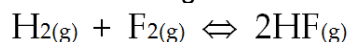
a) Write the  $K_{\text{eq}}$  equation. The  $K_{\text{eq}} = 0.25$

b) Now, write the  $K_{\text{eq}}$  expression for the this reaction, and find the  $K_{\text{eq}}$  constant value:



**Writing the equation the other way around**

For the following reaction:



a) Write the  $K_{\text{eq}}$  equation. The  $K_{\text{eq}} = 0.25$

$$K_{\text{eq}} = \frac{[\text{HF}]^2}{[\text{H}_2][\text{F}_2]} = 0.25$$

b) Now, write the  $K_{\text{eq}}$  expression for the this reaction, and find the  $K_{\text{eq}}$  constant value:



$K_{\text{eq}} = \frac{[\text{H}_2][\text{F}_2]}{[\text{HF}]^2}$  It is the reciprocal of the equation above, so the  $K_{\text{eq}}$  constant is the reciprocal of 0.25. The  $K_{\text{eq}}$  is  $\frac{1}{0.25} = 4.0$

**VI) Temperature and the  $K_{\text{eq}}$  Constant**

If temperature is increased for an equilibrium system, in what direction does the system shift?

What if temperature is decreased?

If a shift right results due to a temperature change, will the  $K_{\text{eq}}$  increase or decrease?

If a shift left results due to a temperature change, will the  $K_{\text{eq}}$  increase or decrease?

**VI) Temperature and the  $K_{\text{eq}}$  Constant**

If temperature is increased for an equilibrium system, in what direction does the system shift?

endothermic

What if temperature is decreased?

exothermic

If a shift right results due to a temperature change, will the  $K_{\text{eq}}$  increase or decrease?

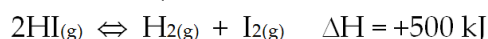
increase

If a shift left results due to a temperature change, will the  $K_{\text{eq}}$  increase or decrease?

decrease

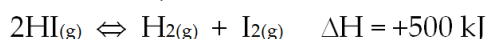
Example:

If the temperature is decreased in the following system, will  $K_{\text{eq}}$  increase or decrease? Explain.



Example:

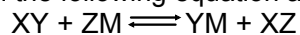
If the temperature is decreased in the following system, will  $K_{\text{eq}}$  increase or decrease? Explain.



- forward reaction is endo and reverse is exo
- a temp decrease causes a shift exo
- so in this case, a temp decrease causes a shift to the left
- a shift left causes a  $K_{\text{eq}}$  decrease

Example:

Given the following equation and data:



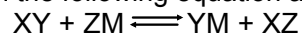
$$K_{eq} = 60.0 \text{ at } 300 \text{ degrees C}$$

$$K_{eq} = 45.0 \text{ at } 500 \text{ degrees C}$$

Is the forward reaction endothermic or exothermic? Explain.

Example:

Given the following equation and data:



$$K_{eq} = 60.0 \text{ at } 300 \text{ degrees C}$$

$$K_{eq} = 45.0 \text{ at } 500 \text{ degrees C}$$

Is the forward reaction endothermic or exothermic? Explain.

- as temperature increases (300 to 500),  $K_{eq}$  decreases (60.0 to 45.0)
- a temp increase causes a shift endo
- a  $K_{eq}$  decrease is a shift left
- therefore, endo must be left
- so, the forward reaction must be exothermic

### Assignment 6

1) Hebden page 60, #31acegj, 32, 35abcd, and page 62, #36, 40, 41, 44-46

2) Given the following equation and data:



$$K_{eq} = 12.0 \text{ at } 200 \text{ degrees C}$$

$$K_{eq} = 20.0 \text{ at } 300 \text{ degrees C}$$

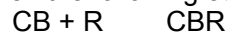
Is the forward reaction exothermic or endothermic? Support your answer with explanations.

### Assignment 6

1) Hebden page 60, #31acegj, 32, 35abcd, and page 62, #36, 40, 41, 44-46

answers in the back of Hebden

2) Given the following equation and data:



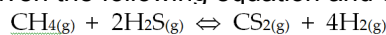
$$K_{eq} = 12.0 \text{ at } 200 \text{ degrees C}$$

$$K_{eq} = 20.0 \text{ at } 300 \text{ degrees C}$$

Is the forward reaction exothermic or endothermic? Support your answer with explanations.

- as temperature increases (200 to 300),  $K_{eq}$  also increases (12.0 to 20.0)
- a temperature increase causes a shift endo
- a  $K_{eq}$  increase means a shift right
- therefore the forward reaction is endothermic

3) Given the following equation and data:

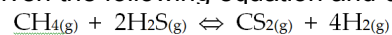


$$K_{eq} = 1.0 \times 10^{-2} \text{ at } 500^\circ\text{C}$$

$$K_{eq} = 2.4 \times 10^{-3} \text{ at } 800^\circ\text{C}$$

- a) Is the forward reaction endothermic or exothermic? Explain.
- b) What effect will increasing  $[H_2S]$  have on the value of  $K_{eq}$ ?

3) Given the following equation and data:



$$K_{eq} = 1.0 \times 10^{-2} \text{ at } 500^\circ\text{C}$$

$$K_{eq} = 2.4 \times 10^{-3} \text{ at } 800^\circ\text{C}$$

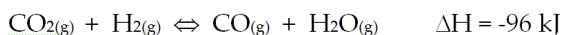
- a) Is the forward reaction endothermic or exothermic? Explain.
- b) What effect will increasing  $[H_2S]$  have on the value of  $K_{eq}$ ?

- a) -as temp increases (500 to 800),  $K_{eq}$  decreases (0.010 to 0.0024)
- a temp increase shifts endo
- a  $K_{eq}$  decrease is a shift left
- therefore the reverse reaction is endothermic
- thus, the forward reaction is exothermic

b) a change in concentration causes a shift but does not change the value of  $K_{eq}$ . Only a temperature change can.

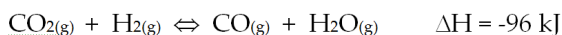


4) For the following reaction:



What effect will decreasing temperature have on the value of  $K_{\text{eq}}$ ? Support your answer with explanations.

4) For the following reaction:



What effect will decreasing temperature have on the value of  $K_{\text{eq}}$ ? Support your answer with explanations.

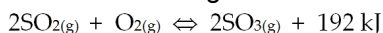
- a decrease in temp causes a shift exo
- exo in this reaction is forward
- thus, a decrease in temp causes a shift in the forward direction
- this will cause the  $K_{\text{eq}}$  to increase

### VII) Type 1 $K_{\text{eq}}$ Problems

For Type 1  $K_{\text{eq}}$  problems, the data provided in the question is exclusively equilibrium data.

Example:

1. For the following reaction:



Equilibrium concentrations were found to be as follows:

$$[\text{SO}_2] = 2.0\text{M}, [\text{O}_2] = 0.50\text{M}, [\text{SO}_3] = 1.6\text{M}$$

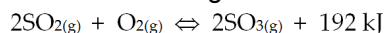
Calculate the value of  $K_{\text{eq}}$ .

### VII) Type 1 $K_{\text{eq}}$ Problems

For Type 1  $K_{\text{eq}}$  problems, the data provided in the question is exclusively equilibrium data.

Example:

1. For the following reaction:



Equilibrium concentrations were found to be as follows:

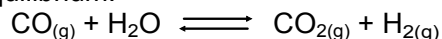
$$[\text{SO}_2] = 2.0\text{M}, [\text{O}_2] = 0.50\text{M}, [\text{SO}_3] = 1.6\text{M}$$

Calculate the value of  $K_{\text{eq}}$ .

$$K_{\text{eq}} = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]} = \frac{(1.6)^2}{(2.0)^2(0.50)} = 1.3$$

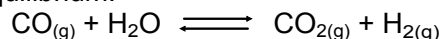
Example:

2) At equilibrium, a 2.00L vessel contained 0.750mol CO, 0.276mol  $\text{H}_2\text{O}$ , 0.600mol  $\text{CO}_2$  and a  $K_{\text{eq}} = 0.986$ . Calculate the moles of  $\text{H}_2$  at equilibrium.



Example:

2) At equilibrium, a 2.00L vessel contained 0.750mol CO, 0.276mol  $\text{H}_2\text{O}$ , 0.600mol  $\text{CO}_2$  and a  $K_{\text{eq}} = 0.986$ . Calculate the moles of  $\text{H}_2$  at equilibrium.



$$[\text{CO}] = \frac{0.750\text{mol}}{2.00\text{L}} = 0.375\text{M} \quad [\text{H}_2\text{O}] = \frac{0.276\text{mol}}{2.00\text{L}} = 0.138\text{M}$$

$$[\text{CO}_2] = \frac{0.600\text{mol}}{2.00\text{L}} = 0.300\text{M} \quad K_{\text{eq}} = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]}$$

$$0.986 = \frac{(0.300)[\text{H}_2]}{(0.375)(0.138)} \quad [\text{H}_2] = 0.170\text{M}$$

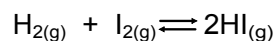
$$\text{moles H}_2 = (0.170\text{M})(2.00\text{L}) = 0.340 \text{ moles}$$

**VIII) Type 2  $K_{eq}$  Problems**

Type 2  $K_{eq}$  problems provide some initial data and some equilibrium data for certain substances, which you are to use to calculate the  $K_{eq}$  constant. Use an 'ICE' table for assistance.

Example:

1) A mixture of  $H_2$  and  $I_2$  was prepared by placing 0.100mol of  $H_2$  and 0.100mol of  $I_2$  into a 1.00L flask. At equilibrium, the  $[I_2]$  dropped to 0.020M. Calculate the  $K_{eq}$ .



**I**nitial  
**C**hange  
**E**quilibrium

Example:

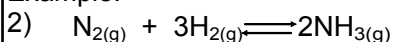
1) A mixture of  $H_2$  and  $I_2$  was prepared by placing 0.100mol of  $H_2$  and 0.100mol of  $I_2$  into a 1.00L flask. At equilibrium, the  $[I_2]$  dropped to 0.020M. Calculate the  $K_{eq}$ .

\*In a 1.00L flask, the moles = molarity

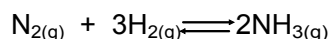
	$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$		
<b>I</b> nitial	0.100M	0.100M	0
<b>C</b> hange	-0.080M	-0.080M	+0.16M
<b>E</b> quilibrium	0.020M	0.020M	0.16M

$$K_{eq} = \frac{[HI]^2}{[H_2][I_2]} = \frac{(0.16)^2}{(0.020)^2} = 64$$

Example:

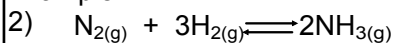


Given:  $[N_2]_i = 0.32M$ ,  $[H_2]_i = 0.66M$ ,  $[H_2]_{eq} = 0.30M$   
Calculate  $K_{eq}$ .



**I**nitial  
**C**hange  
**E**quilibrium

Example:



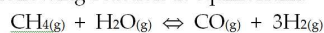
Given:  $[N_2]_i = 0.32M$ ,  $[H_2]_i = 0.66M$ ,  $[H_2]_{eq} = 0.30M$   
Calculate  $K_{eq}$ .

	$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$		
<b>I</b> nitial	0.32M	0.66M	0.00M
<b>C</b> hange	-0.12M	-0.36M	+0.24M
<b>E</b> quilibrium	0.20M	0.30M	0.24M

$$K_{eq} = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(0.24)^2}{(0.20)(0.30)^3} = 11$$

**Assignment 7**

1. For the following reaction at equilibrium:



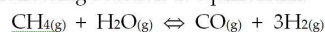
$$[CH_4] = 0.600M \quad [H_2O] = 0.060M$$

$$[CO] = 0.200M \quad [H_2] = 0.700M$$

Calculate the  $K_{eq}$  for this reaction. Are the reactants or products favoured?

### Assignment 7

1. For the following reaction at equilibrium:



$$[\text{CH}_4] = 0.600\text{M} \quad [\text{H}_2\text{O}] = 0.060\text{M}$$

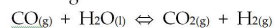
$$[\text{CO}] = 0.200\text{M} \quad [\text{H}_2] = 0.700\text{M}$$

Calculate the  $K_{\text{eq}}$  for this reaction. Are the reactants or products favoured?

$$K_{\text{eq}} = \frac{[\text{CO}][\text{H}_2]^3}{[\text{CH}_4][\text{H}_2\text{O}]} = \frac{(0.200)(0.700)^3}{(0.600)(0.060)} = 1.9$$

products are favoured  
because  $K_{\text{eq}} > 1$

2. For the following reaction:



At equilibrium in a 1.0L container, 0.020mol of CO, 0.010mol H<sub>2</sub>O, 0.030 mol CO<sub>2</sub>, and 0.010mol of H<sub>2</sub> are present.

- Calculate the  $K_{\text{eq}}$
- State whether reactants or products are favoured
- If H<sub>2</sub> is removed from the system and equilibrium is re-established, how does the value of  $K_{\text{eq}}$  change?

2. For the following reaction:



At equilibrium in a 1.0L container, 0.020mol of CO, 0.010mol H<sub>2</sub>O, 0.030 mol CO<sub>2</sub>, and 0.010mol of H<sub>2</sub> are present.

- Calculate the  $K_{\text{eq}}$
- State whether reactants or products are favoured
- If H<sub>2</sub> is removed from the system and equilibrium is re-established, how does the value of  $K_{\text{eq}}$  change?

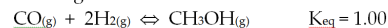
1.0L container, so moles = molarity

$$\text{a) } K_{\text{eq}} = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}]} = \frac{(0.030)(0.010)}{(0.020)} = 0.015$$

b) products favoured because the  $K_{\text{eq}} > 1$

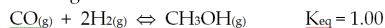
c) the  $K_{\text{eq}}$  will not change. Only a temperature change can cause a change in  $K_{\text{eq}}$

3. For the following reaction:



At equilibrium in a 2.0L container, 0.420mol CO and 0.100mol H<sub>2</sub> are present. Calculate the number of moles of CH<sub>3</sub>OH present.

3. For the following reaction:



At equilibrium in a 2.0L container, 0.420mol CO and 0.100mol H<sub>2</sub> are present. Calculate the number of moles of CH<sub>3</sub>OH present.

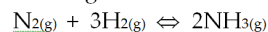
$$[\text{CO}] = \frac{0.420\text{mol}}{2.0\text{L}} = 0.21\text{M} \quad [\text{H}_2] = \frac{0.100\text{mol}}{2.0\text{L}} = 0.050\text{M}$$

$$K_{\text{eq}} = \frac{[\text{CH}_3\text{OH}]}{[\text{CO}][\text{H}_2]^2} \quad 1.00 = \frac{[\text{CH}_3\text{OH}]}{(0.21)(0.050)^2}$$

$$[\text{CH}_3\text{OH}] = 1.00(0.21)(0.050)^2 = 0.000525$$

$$\text{moles CH}_3\text{OH} = (0.000525)(2.0\text{L}) = 1.1 \times 10^{-3}$$

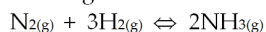
4. For the following reaction and data:



	[N <sub>2</sub> ] (M)	[H <sub>2</sub> ] (M)	[NH <sub>3</sub> ] (M)
Trial 1	0.200	0.400	0.500
Trial 2	?	0.300	0.600

Find [N<sub>2</sub>] in Trial 2.

4. For the following reaction and data:



	[N <sub>2</sub> ] (M)	[H <sub>2</sub> ] (M)	[NH <sub>3</sub> ] (M)
Trial 1	0.200	0.400	0.500
Trial 2	?	0.300	0.600

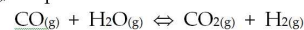
Find [N<sub>2</sub>] in Trial 2.

$$\text{Trial 1: } K_{\text{eq}} = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(0.500)^2}{(0.200)(0.400)^3} = 19.531$$

$$\text{Trial 2: } 19.531 = \frac{(0.600)^2}{[\text{N}_2](0.300)^3} \quad [\text{N}_2] = \frac{(0.600)^2}{19.531(0.300)^3} = 0.683\text{M}$$

**Type II Exercises (ICE diagrams)**

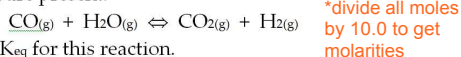
5. A mixture consisting of 1.00mol CO<sub>(g)</sub> and 1.00mol H<sub>2</sub>O<sub>(g)</sub> is placed in a 10.00L container. At equilibrium, 0.665mol CO<sub>2(g)</sub> and 0.665mol H<sub>2(g)</sub> are present.



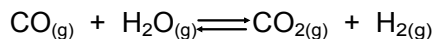
Calculate the K<sub>eq</sub> for this reaction.

**Type II Exercises (ICE diagrams)**

5. A mixture consisting of 1.00mol CO<sub>(g)</sub> and 1.00mol H<sub>2</sub>O<sub>(g)</sub> is placed in a 10.00L container. At equilibrium, 0.665mol CO<sub>2(g)</sub> and 0.665mol H<sub>2(g)</sub> are present.



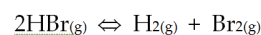
Calculate the K<sub>eq</sub> for this reaction.



I	0.100M	0.100M	0.00M	0.00M
C	-0.0665M	-0.0665M	+0.0665M	+0.0665M
E	0.0335M	0.0335M	0.0665M	0.0665M

$$K_{\text{eq}} = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]} = \frac{(0.0665)^2}{(0.0335)^2} = 3.9$$

6. When 1.00M HBr is placed into a flask, the following equilibrium is achieved:

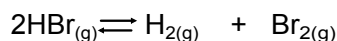


At equilibrium, 0.140M H<sub>2</sub> is present. Calculate the K<sub>eq</sub>.

6. When 1.00M HBr is placed into a flask, the following equilibrium is achieved:



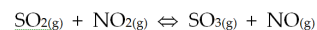
At equilibrium, 0.140M H<sub>2</sub> is present. Calculate the K<sub>eq</sub>.



I	1.00M	0.00M	0.00M
C	-0.280M	+0.140M	+0.140M
E	0.72M	0.140M	0.140M

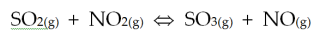
$$K_{\text{eq}} = \frac{[\text{H}_2][\text{Br}_2]}{[\text{HBr}]^2} = \frac{(0.140)^2}{(0.72)^2} = 0.038$$

7. A 5.00L vessel was initially filled with 6.00mol SO<sub>2</sub>, 2.50mol NO<sub>2</sub>, and 1.00mol SO<sub>3</sub>.



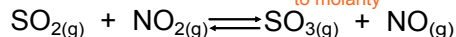
At equilibrium, the vessel was found to contain 3.00mol SO<sub>3</sub>. What is the K<sub>eq</sub> for the reaction?

7. A 5.00L vessel was initially filled with 6.00mol SO<sub>2</sub>, 2.50mol NO<sub>2</sub>, and 1.00mol SO<sub>3</sub>.



At equilibrium, the vessel was found to contain 3.00mol SO<sub>3</sub>.

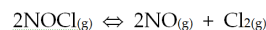
What is the K<sub>eq</sub> for the reaction? *\*divide by 5.00 to get moles to molarity*



I	1.20M	0.500M	0.200M	0.00M
C	-0.400M	-0.400M	+0.400M	+0.400M
E	0.80M	0.100M	0.600M	0.400M

$$K_{eq} = \frac{[\text{SO}_3][\text{NO}]}{[\text{SO}_2][\text{NO}_2]} = \frac{(0.600)(0.400)}{(0.80)(0.100)} = 3.0$$

8. 0.50mol of NOCl was introduced into a 1.0L flask and allowed to come to equilibrium:

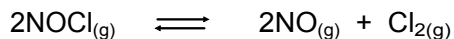


At equilibrium, there was 0.10mol of Cl<sub>2</sub>. What is the K<sub>eq</sub>?

8. 0.50mol of NOCl was introduced into a 1.0L flask and allowed to come to equilibrium:



At equilibrium, there was 0.10mol of Cl<sub>2</sub>. What is the K<sub>eq</sub>? *\*moles = molarity because 1.0L flask*



I	0.50M	0.00M	0.00M
C	-0.20M	+0.20M	+0.10M
E	0.30M	0.20M	0.10M

$$K_{eq} = \frac{[\text{NO}]^2[\text{Cl}_2]}{[\text{NOCl}]^2} = \frac{(0.20)^2(0.10)}{(0.30)^2} = 4.4 \times 10^{-2}$$

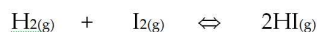
### IX) Type 3 K<sub>eq</sub> Problems

Type 3 K<sub>eq</sub> problems give some initial data and a K<sub>eq</sub> constant. You must find equilibrium concentrations. OR You will be provided with some equilibrium data and a K<sub>eq</sub> constant. You must find an initial concentration.

1.  $\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g)$  K<sub>eq</sub> = 55.6

[H<sub>2</sub>]<sub>i</sub> = 0.200M, [I<sub>2</sub>]<sub>i</sub> = 0.200M

What is the equilibrium [HI]?



I  
C  
E

1.  $\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g)$  K<sub>eq</sub> = 55.6

[H<sub>2</sub>]<sub>i</sub> = 0.200M, [I<sub>2</sub>]<sub>i</sub> = 0.200M

What is the equilibrium [HI]?



I	0.200M	0.200M	0.00M	$7.45654(0.200 - x) = 2x$
C	-x	-x	+2x	$1.4913 - 7.45654x = 2x$
E	0.200 - x	0.200 - x	2x	$1.4913 = 9.45654x$

$x = 0.1577$   
[H]<sub>eq</sub> = 2x = 2(0.1577)  
[HI]<sub>eq</sub> = 0.315M

Let  $x = \Delta[\text{H}_2]$   $55.6 = \frac{(2x)^2}{(0.200 - x)^2}$

$$K_{eq} = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{7.45654}{0.200 - x} = \frac{2x}{0.200 - x}$$

$$55.6 = \frac{(2x)^2}{(0.200 - x)^2}$$

2.  $\text{CO}_{(g)} + \text{H}_2\text{O}_{(g)} \rightleftharpoons \text{CO}_{2(g)} + \text{H}_2_{(g)}$   $K_{\text{eq}} = 4.06$   
 $[\text{CO}]_i = 0.10\text{M}$ ,  $[\text{H}_2\text{O}]_i = 0.10\text{M}$   
 What are the equilibrium concentrations of all species?

I  
C  
E

$$\text{CO}_{(g)} + \text{H}_2\text{O}_{(g)} \rightleftharpoons \text{CO}_{2(g)} + \text{H}_2_{(g)}$$

2.  $\text{CO}_{(g)} + \text{H}_2\text{O}_{(g)} \rightleftharpoons \text{CO}_{2(g)} + \text{H}_2_{(g)}$   $K_{\text{eq}} = 4.06$   
 $[\text{CO}]_i = 0.10\text{M}$ ,  $[\text{H}_2\text{O}]_i = 0.10\text{M}$   
 What are the equilibrium concentrations of all species?

I  
C  
E

	$\text{CO}_{(g)}$	$+$	$\text{H}_2\text{O}_{(g)}$	$\rightleftharpoons$	$\text{CO}_{2(g)}$	$+$	$\text{H}_2_{(g)}$	
I	0.10M		0.10M		0		0	
C	-x		-x		+x		+x	
E	0.10 - x		0.10 - x		x		x	

Let  $x = \Delta[\text{CO}]$   $\sqrt{4.06} = \frac{(x)^2}{(0.10 - x)^2}$   $2.015(0.10 - x) = x$   
 $0.2015 - 2.015x = x$   
 $0.2015 = 3.015x$   
 $x = 0.06683$

$K_{\text{eq}} = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]}$   $4.06 = \frac{(x)^2}{(0.10 - x)^2}$   $2.015 = \frac{x}{0.10 - x}$   $[\text{CO}]_{\text{eq}} \& [\text{H}_2\text{O}]_{\text{eq}} = 0.10 - x = 0.10 - 0.06683 = 0.03\text{M}$   
 $[\text{CO}_2]_{\text{eq}} \& [\text{H}_2]_{\text{eq}} = 0.067\text{M}$

3. A certain amount of  $\text{H}_2\text{O}$  was placed in a 2.00L closed flask. When equilibrium was reached, the  $[\text{H}_2]$  was 0.500M. If  $K_{\text{eq}} = 16.0$  at this temperature, how many moles of  $\text{H}_2\text{O}$  were originally placed in the flask?

I  
C  
E

$$2\text{H}_2\text{O}_{(g)} \rightleftharpoons 2\text{H}_{2(g)} + \text{O}_{2(g)}$$

3. A certain amount of  $\text{H}_2\text{O}$  was placed in a 2.00L closed flask. When equilibrium was reached, the  $[\text{H}_2]$  was 0.500M. If  $K_{\text{eq}} = 16.0$  at this temperature, how many moles of  $\text{H}_2\text{O}$  were originally placed in the flask?

I  
C  
E

	$2\text{H}_2\text{O}_{(g)}$	$\rightleftharpoons$	$2\text{H}_{2(g)}$	$+$	$\text{O}_{2(g)}$	
I	x		0		0	$x - 0.500 = 0.0625$
C	-0.500M		+0.500M		+0.250M	$x = 0.5625$
E	x - 0.500		0.500M		0.250M	$[\text{H}_2\text{O}]_i = 0.5625\text{M}$

Let  $x = [\text{H}_2\text{O}]_i$   $16.0(x - 0.500)^2 = (0.500)^2(0.250)$   
 $K_{\text{eq}} = \frac{[\text{H}_2]^2[\text{O}_2]}{[\text{H}_2\text{O}]^2}$   $(x - 0.500)^2 = \frac{(0.500)^2(0.250)}{16.0}$   
 $16.0 = \frac{(0.500)^2(0.250)}{(x - 0.500)^2}$   $(x - 0.500)^2 = 3.906 \times 10^{-3}$   $\sqrt{(x - 0.500)^2} = \sqrt{3.906 \times 10^{-3}}$   $\text{mol H}_2\text{O} = (0.5625)(2.00) = 1.13 \text{ moles}$

**Assignment 8**

1. For the following reaction:  
 $\text{H}_2_{(g)} + \text{CO}_{2(g)} \rightleftharpoons \text{H}_2\text{O}_{(g)} + \text{CO}_{(g)}$   $K_{\text{eq}} = 0.771$   
 If 0.0100mol of  $\text{H}_2$  and 0.0100mol of  $\text{CO}_2$  are mixed in a 1.00L container, what are the concentrations of all substances at equilibrium?

**Assignment 8**

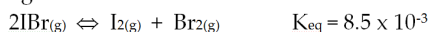
1. For the following reaction:  
 $\text{H}_2_{(g)} + \text{CO}_{2(g)} \rightleftharpoons \text{H}_2\text{O}_{(g)} + \text{CO}_{(g)}$   $K_{\text{eq}} = 0.771$   
 If 0.0100mol of  $\text{H}_2$  and 0.0100mol of  $\text{CO}_2$  are mixed in a 1.00L container, what are the concentrations of all substances at equilibrium?

I  
C  
E

	$\text{H}_2_{(g)}$	$+$	$\text{CO}_{2(g)}$	$\rightleftharpoons$	$\text{H}_2\text{O}_{(g)}$	$+$	$\text{CO}_{(g)}$
I	0.0100M		0.0100M		0.00M		0.00M
C	-x		-x		+x		+x
E	0.0100 - x		0.0100 - x		x		x

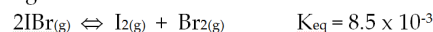
Let  $x = \Delta[\text{H}_2]$   $\sqrt{0.771} = \frac{(x)^2}{(0.0100 - x)^2}$   $x = 0.004674$   
 $K_{\text{eq}} = \frac{[\text{H}_2][\text{CO}_2]}{[\text{H}_2\text{O}][\text{CO}]}$   $0.771 = \frac{(x)^2}{(0.0100 - x)^2}$   $0.878066 = \frac{x}{0.0100 - x}$   $[\text{H}_2]_{\text{eq}} \& [\text{CO}]_{\text{eq}} = 0.0100 - x = 0.0053\text{M}$   
 $[\text{H}_2\text{O}]_{\text{eq}} \& [\text{CO}_2]_{\text{eq}} = 0.00468\text{M}$

2. For the following reaction:



If 0.0600 mol of IBr is placed in a 1.0L container, what are the concentrations of all three substances at equilibrium?

2. For the following reaction:



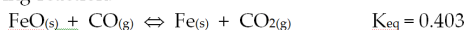
If 0.0600 mol of IBr is placed in a 1.0L container, what are the concentrations of all three substances at equilibrium?

	$2\text{IBr(g)}$	$\rightleftharpoons$	$\text{I}_2\text{(g)}$	$+$	$\text{Br}_2\text{(g)}$	
I	0.0600M		0.00M		0.00M	
C	-2x		+x		+x	
E	0.0600 - 2x		x		x	

Let  $x = \Delta[\text{I}_2]$   
 $K_{\text{eq}} = \frac{[\text{I}_2][\text{Br}_2]}{[\text{IBr}]^2} = 0.0085 = \frac{(x)^2}{(0.0600 - 2x)^2}$   
 $\sqrt{0.0085} = \frac{x}{(0.0600 - 2x)}$   
 $x = 0.004671$   
 $[\text{Br}_2]_{\text{eq}} \text{ \& } [\text{I}_2]_{\text{eq}} = 0.0047\text{M}$

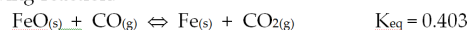
$0.0085 = \frac{(x)^2}{(0.0600 - 2x)^2}$   
 $0.092195 = \frac{x}{0.0600 - 2x}$   
 $[\text{H}_2]_{\text{eq}} \text{ \& } [\text{CO}_2]_{\text{eq}} = 0.0600 - 2x = 0.051\text{M}$

3. For the following reaction:



If 0.0500 mol of CO and excess solid FeO are placed in a 1.00L container, what are the concentrations of CO and CO<sub>2</sub> when equilibrium has been attained?

3. For the following reaction:



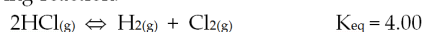
If 0.0500 mol of CO and excess solid FeO are placed in a 1.00L container, what are the concentrations of CO and CO<sub>2</sub> when equilibrium has been attained?

	$\text{FeO(s)} + \text{CO(g)}$	$\rightleftharpoons$	$\text{Fe(s)} + \text{CO}_2\text{(g)}$
I	0.0500M		0.00M
C	-x		+x
E	0.0500 - x		x

Let  $x = \Delta[\text{CO}_2]$   
 $K_{\text{eq}} = \frac{[\text{CO}_2]}{[\text{CO}]} = 0.403$   
 $x = 0.01436$   
 $[\text{CO}_2]_{\text{eq}} = 0.0144\text{M}$

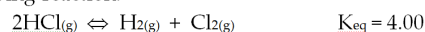
$0.403 = \frac{x}{0.0500 - x}$   
 $[\text{CO}]_{\text{eq}} = 0.0500 - x = 0.0356\text{M}$

4. For the following reaction:



An unknown [HCl] was added to a 2.00L flask and allowed to reach equilibrium. At equilibrium, [H<sub>2</sub>] = 0.200M. How many moles of HCl was originally placed in the flask?

4. For the following reaction:



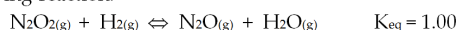
An unknown [HCl] was added to a 2.00L flask and allowed to reach equilibrium. At equilibrium, [H<sub>2</sub>] = 0.200M. How many moles of HCl was originally placed in the flask?

	$2\text{HCl(g)}$	$\rightleftharpoons$	$\text{H}_2\text{(g)} + \text{Cl}_2\text{(g)}$	
I	x		0	0
C	-0.400M		+0.200M	+0.200M
E	x - 0.400		0.200M	0.200M

Let  $x = [\text{HCl}]$   
 $K_{\text{eq}} = \frac{[\text{H}_2][\text{Cl}_2]}{[\text{HCl}]^2} = 4.00$   
 $4.00(x - 0.400)^2 = (0.200)^2$   
 $(x - 0.400)^2 = \frac{(0.200)^2}{4.00}$   
 $(x - 0.400)^2 = 0.0100$   
 $\sqrt{(x - 0.400)^2} = \sqrt{0.0100}$   
 $x - 0.400 = 0.100$   
 $x = 0.500$   
 $[\text{HCl}] = 0.500$

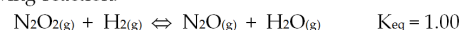
mol HCl =  $(0.500)(2.00) = 1.00$  mole

5. For the following reaction:

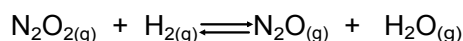


If 0.150mol each of N<sub>2</sub>O and H<sub>2</sub>O are introduced into a 1.00L flask and allowed to come to equilibrium, what concentration of N<sub>2</sub>O<sub>2</sub> will be present at equilibrium?

5. For the following reaction:



If 0.150mol each of N<sub>2</sub>O and H<sub>2</sub>O are introduced into a 1.00L flask and allowed to come to equilibrium, what concentration of N<sub>2</sub>O<sub>2</sub> will be present at equilibrium?



I	0.00M	0.00M	0.150M	0.150M
C	+x	+x	-x	-x
E	x	x	0.150 - x	0.150 - x

$$K_{\text{eq}} = \frac{[\text{H}_2\text{O}][\text{N}_2\text{O}]}{[\text{N}_2\text{O}_2][\text{H}_2]} = 1.00 = \frac{(0.150 - x)^2}{(x)^2} \quad x = 0.0750$$

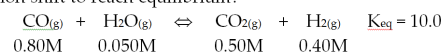
$$1.00 = \frac{(0.150 - x)^2}{(x)^2} \quad 1.00 = \frac{0.150 - x}{x} \quad [\text{N}_2\text{O}_2]_{\text{eq}} = 0.0750\text{M}$$

### X) Type 4 K<sub>eq</sub> Problems

Type 4 problems use a TRIAL K<sub>eq</sub> (called 'Q' in Hebden), which can be used to predict whether or not a system is at equilibrium. If the system is not at equilibrium, the trial K<sub>eq</sub> value compared to the actual K<sub>eq</sub> can be used to predict in what direction the system is shifting to attain equilibrium.

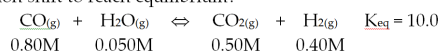
### Example:

1. Is the following reaction at equilibrium? If not, in which direction must the reaction shift to reach equilibrium?



### Example:

1. Is the following reaction at equilibrium? If not, in which direction must the reaction shift to reach equilibrium?



$$\text{Trial } K_{\text{eq}} = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]} = \frac{(0.50)(0.40)}{(0.80)(0.050)} = 5.0$$

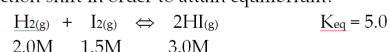
The trial K<sub>eq</sub> does not equal the actual K<sub>eq</sub> so currently not at equilibrium.

Trial K<sub>eq</sub> of 5.0 < Actual K<sub>eq</sub> of 10.0

Therefore, the system must shift RIGHT to attain equilibrium.

### Example:

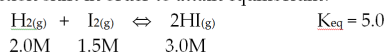
2. Is the following reaction at equilibrium? If not, in which direction must the reaction shift in order to attain equilibrium?





**Example:**

2. Is the following reaction at equilibrium? If not, in which direction must the reaction shift in order to attain equilibrium?



$$\text{Trial } K_{\text{eq}} = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(3.0)^2}{(2.0)(1.5)} = 3.0$$

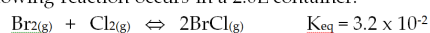
The trial  $K_{\text{eq}}$  does not equal the actual  $K_{\text{eq}}$  so currently not at equilibrium.

Trial  $K_{\text{eq}}$  of 3.0 < Actual  $K_{\text{eq}}$  of 5.0

Therefore, the system must shift **RIGHT** to attain equilibrium.

**Example:**

3. The following reaction occurs in a 2.0L container:



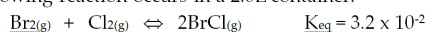
Quantities of gases were found to be as follows:

$\text{Br}_2 = 0.60 \text{ mol}$ ,  $\text{Cl}_2 = 0.80 \text{ mol}$ ,  $\text{BrCl} = 2.20 \text{ mol}$

What will happen to the  $[\text{Br}_2]$  as the system approaches equilibrium?

**Example:**

3. The following reaction occurs in a 2.0L container:



Quantities of gases were found to be as follows:

$\text{Br}_2 = 0.60 \text{ mol}$ ,  $\text{Cl}_2 = 0.80 \text{ mol}$ ,  $\text{BrCl} = 2.20 \text{ mol}$

What will happen to the  $[\text{Br}_2]$  as the system approaches equilibrium?

\*divide moles by 2 to get molarity

$$\text{Trial } K_{\text{eq}} = \frac{[\text{BrCl}]^2}{[\text{Br}_2][\text{Cl}_2]} = \frac{(1.1)^2}{(0.30)(0.40)} = 1.0 \times 10^1$$

The trial  $K_{\text{eq}}$  does not equal the actual  $K_{\text{eq}}$  so currently not at equilibrium.

Trial  $K_{\text{eq}}$  of  $1.0 \times 10^1 >$  Actual  $K_{\text{eq}}$  of  $3.2 \times 10^{-2}$

Therefore, the system must shift **LEFT** to attain equilibrium, so  $[\text{Br}_2]$  will increase.

**Assignment 9**

1. For the following reaction:  $2\text{O}_3(\text{g}) \rightleftharpoons 3\text{O}_2(\text{g})$   $K_{\text{eq}} = 75$

Predict the direction in which the equilibrium will shift, if any, when the following substances are introduced into a 10.0L container? 0.60mol  $\text{O}_3$  and 3.0mol  $\text{O}_2$

**Assignment 9** \*divide moles by 10.0 to get molarities

1. For the following reaction:  $2\text{O}_3(\text{g}) \rightleftharpoons 3\text{O}_2(\text{g})$   $K_{\text{eq}} = 75$

Predict the direction in which the equilibrium will shift, if any, when the following substances are introduced into a 10.0L container? 0.60mol  $\text{O}_3$  and 3.0mol  $\text{O}_2$

$$\text{Trial } K_{\text{eq}} = \frac{[\text{O}_2]^3}{[\text{O}_3]^2} = \frac{(0.30)^3}{(0.060)^2} = 7.5$$

The trial  $K_{\text{eq}}$  does not equal the actual  $K_{\text{eq}}$  so currently not at equilibrium.

Trial  $K_{\text{eq}}$  of 7.5 < Actual  $K_{\text{eq}}$  of 75

Therefore, the system must shift **RIGHT** to attain equilibrium.

2. Consider the following reaction:  $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$   $K_{\text{eq}} = 75$

A student places 0.50moles  $\text{SO}_2$ , 0.080mol  $\text{O}_2$ , and 1.0mol  $\text{SO}_3$  into a 1.0L flask. The student predicts that the  $[\text{SO}_2]$  will decrease as equilibrium is established. Do you agree with the student's prediction? Explain using appropriate calculations.

2. Consider the following reaction:  $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$   $K_{\text{eq}} = 75$   
 A student places 0.50 moles  $\text{SO}_2$ , 0.080 mol  $\text{O}_2$ , and 1.0 mol  $\text{SO}_3$  into a 1.0L flask. The student predicts that the  $[\text{SO}_2]$  will decrease as equilibrium is established. Do you agree with the student's prediction? Explain using appropriate calculations.

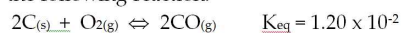
$$\text{Trial } K_{\text{eq}} = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]} = \frac{(1.0)^2}{(0.50)^2(0.080)} = 5.0 \times 10^1$$

The trial  $K_{\text{eq}}$  does not equal the actual  $K_{\text{eq}}$  so currently not at equilibrium.

Trial  $K_{\text{eq}}$  of  $5.0 \times 10^1 <$  Actual  $K_{\text{eq}}$  of 75

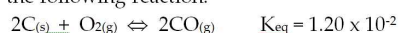
Therefore, the system must shift RIGHT to attain equilibrium, so  $[\text{SO}_2]$  will decrease. I agree with the student.

3. Consider the following reaction:



If 2.0 mol C, 0.800 mol  $\text{O}_2$ , and 0.600 mol CO are placed into a 1.0L flask, in which direction will the equilibrium shift in order to achieve equilibrium? What will happen to the [C]? Show all calculations.

3. Consider the following reaction:



If 2.0 mol C, 0.800 mol  $\text{O}_2$ , and 0.600 mol CO are placed into a 1.0L flask, in which direction will the equilibrium shift in order to achieve equilibrium? What will happen to the [C]? Show all calculations.

$$\text{Trial } K_{\text{eq}} = \frac{[\text{CO}]^2}{[\text{O}_2]} = \frac{(0.600)^2}{(0.800)} = 0.45$$

The trial  $K_{\text{eq}}$  does not equal the actual  $K_{\text{eq}}$  so currently not at equilibrium.

Trial  $K_{\text{eq}}$  of 0.45  $>$  Actual  $K_{\text{eq}}$  of  $1.20 \times 10^{-2}$

Therefore, the system must shift LEFT to attain equilibrium. The [C] will remain constant, as it's a solid.

4. For the following reaction:  $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{HCl}(\text{g})$   $K_{\text{eq}} = 0.15$

Equal moles of each of the three gases are in a 1.0L vessel. What direction will the reaction shift in order to reach equilibrium?

4. For the following reaction:  $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{HCl}(\text{g})$   $K_{\text{eq}} = 0.15$

Equal moles of each of the three gases are in a 1.0L vessel. What direction will the reaction shift in order to reach equilibrium?

$$\text{Trial } K_{\text{eq}} = \frac{[\text{HCl}]^2}{[\text{H}_2][\text{Cl}_2]} = \frac{(x)^2}{(x)(x)} = \frac{x^2}{x^2} = 1$$

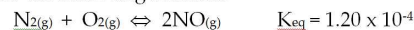
The trial  $K_{\text{eq}}$  does not equal the actual  $K_{\text{eq}}$  so currently not at equilibrium.

Trial  $K_{\text{eq}}$  of 1  $>$  Actual  $K_{\text{eq}}$  of 0.15

Therefore, the system must shift LEFT to attain equilibrium.

5. \*Type III & Type IV hybrid question ©

Consider the following reaction:



If 0.060 mol  $\text{N}_2$ , 0.060 mol  $\text{O}_2$ , and 0.00025 mol NO are mixed in a 1.0L container, in which direction will the reaction proceed in order to achieve equilibrium? What will be the equilibrium  $[\text{N}_2]$ ,  $[\text{O}_2]$ , and  $[\text{NO}]$ ?

5. \*Type III & Type IV hybrid question ☺

Consider the following reaction:

$$\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g}) \quad K_{\text{eq}} = 1.20 \times 10^{-4}$$

If 0.060mol N<sub>2</sub>, 0.060mol O<sub>2</sub>, and 0.00025mol NO are mixed in a 1.0L container, in which direction will the reaction proceed in order to achieve equilibrium? What will be the equilibrium [N<sub>2</sub>], [O<sub>2</sub>], and [NO]?

<p>Trial <math>K_{\text{eq}} = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} = \frac{(0.00025)^2}{(0.060)^2} = 1.7 \times 10^{-5}</math></p> <p>The trial <math>K_{\text{eq}}</math> does not equal the actual <math>K_{\text{eq}}</math> so currently not at equilibrium.                  Trial <math>K_{\text{eq}}</math> of <math>1.7 \times 10^{-5} &lt;</math> Actual <math>K_{\text{eq}}</math> of <math>1.20 \times 10^{-4}</math></p> <p>Therefore, the system must shift RIGHT to attain equilibrium.</p>	<table border="0" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 10%;"></td> <td style="width: 10%; text-align: center;">N<sub>2(g)</sub></td> <td style="width: 10%; text-align: center;">+ O<sub>2(g)</sub></td> <td style="width: 10%; text-align: center;">2NO<sub>(g)</sub></td> </tr> <tr> <td>I</td> <td style="text-align: center;">0.060</td> <td style="text-align: center;">0.060</td> <td style="text-align: center;">0.00025</td> </tr> <tr> <td>C</td> <td style="text-align: center;">-x</td> <td style="text-align: center;">-x</td> <td style="text-align: center;">+2x</td> </tr> <tr> <td>E</td> <td style="text-align: center;">0.060 - x</td> <td style="text-align: center;">0.060 - x</td> <td style="text-align: center;">0.00025 + 2x</td> </tr> </table>		N <sub>2(g)</sub>	+ O <sub>2(g)</sub>	2NO <sub>(g)</sub>	I	0.060	0.060	0.00025	C	-x	-x	+2x	E	0.060 - x	0.060 - x	0.00025 + 2x	
	N <sub>2(g)</sub>	+ O <sub>2(g)</sub>	2NO <sub>(g)</sub>															
I	0.060	0.060	0.00025															
C	-x	-x	+2x															
E	0.060 - x	0.060 - x	0.00025 + 2x															
<p><math>K_{\text{eq}} = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]}</math></p> <p><math>1.20 \times 10^{-4} = \frac{(0.00025 + 2x)^2}{(0.060 - x)^2}</math></p> <p>square root each side</p>	<p><math>0.0109545 = \frac{0.00025 + 2x}{0.060 - x}</math></p> <p><math>x = 2.025 \times 10^{-4}</math></p> <p>[N<sub>2</sub>]<sub>eq</sub> &amp; [O<sub>2</sub>]<sub>eq</sub> = 0.060 - x = 0.060M</p> <p>[NO]<sub>eq</sub> = 6.6 × 10<sup>-4</sup>M</p>																	