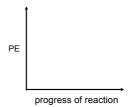
Unit 2: Equilibrium



"Scientists report that the Earth has reached equilibrium ... the state where half the scientists believe one thing and the other half the opposite."

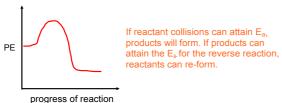
I) General Characterisitics of Equilibrium

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:



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

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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.

ex.
$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

reverse E_a too large to be attained progress of 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:

$$N_2O_{4(g)}$$
 + energy \Longrightarrow $2NO_{2(g)}$

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

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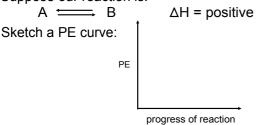
Why would this reaction only occur in a 'closed' system?

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.

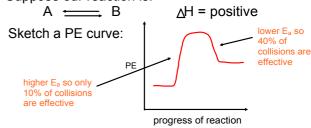
Suppose our reaction is:



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:



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

Molecu of A	les A molecs reacting	A molecs produced	Molecules of B	B molecs	B molecs produced
		produced		reacting	
500	50	P	0	0	50
450) 45	20	50	20	45
425	7 43	30	75	30	43
412	41	35	88	35	41
400	: 41	38	94	38	41
40.	3 40	39	97	39	40
407	2 40	39	98	39	40
401	40	39	99	39	40
400	9 40	40	100	40	40
400	140	40	100	40	40
400	1 4.	40	100	40	40
400	9 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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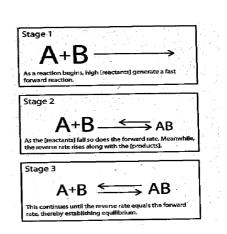
The forward reaction rate continually decreased due to the continual decrease in the amount of A particles available for collision.

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.



Conclusions:

http://www.wwnorton.com/college/chemistry/chemistry3/ch/16/chemtours.asp:

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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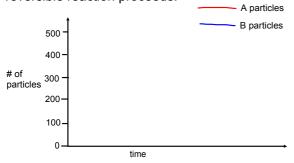
EQUILIBRIUM

The amount, or concentrations of both reactants and products have become <u>constant</u> (but not <u>equal</u> due to

the different %s of effective collisions for fwd and rev reactions

http://www.chm.davidson.edu/ronutt/che115/EquKin/EquKin.htm
temp 380

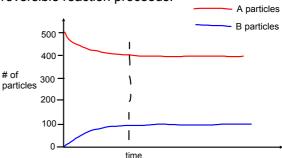
Draw a graph that depicts the change in A particles and the change in B particles as the reversible reaction proceeds.



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

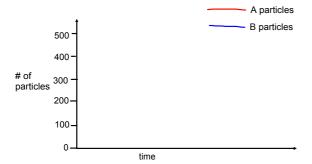
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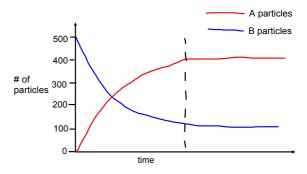
Draw a dashed vertical line to indicate where equilibrium was attained.

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



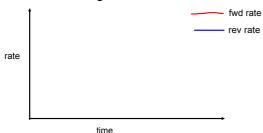
 $\label{eq:decomposition} \mbox{Draw a dashed vertical line to indicate where equilibrium was attained.}$

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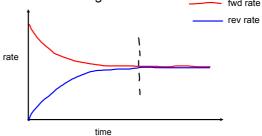
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Back to the original system we studied with a start of 500 particles of A and 0 particles of B. Draw a graph that shows how the forward and reverse rates change over time.



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

http://www.absorblearning.com/media/attachment.action?quick=w8&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=w8&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:

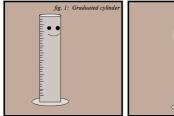
- 1) Forward and reverse rates are _
- 2) Concentrations are
- 3) Macroscopic properties are
- 4) Equilibrium can be attained from either direction.
- 5) If gases are involved, the system must be
- 6) Temperature must be constant.

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Assignment 1:

1) Explain the process of how equilibrium is attained. Use the reaction $2HI \longrightarrow H_2 + I_2$ 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_2 and I_2 molecules, the initial reverse rate is zero. However, as HI molecules continue to collide,

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1) Explain the process of how equilibrium is attained. Use the reaction $2HI \xrightarrow{} H_2 + I_2$ 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_2 and I_2 molecules, the initial reverse rate is zero. However, as HI molecules continue to collide, H_2 and I_2 molecules start to get produced and then start to collide to remake HI molecules. During this process, the forward rate starts to decrease (due to net loss of HI) and the reverse rate starts to increase (due to net increase in H_2 and I_2). This continues until the forward and reverse rates become equal, attaining equilibrium. At this point, the reactants and products are at constant concentrations.

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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3) Consider the following equilibrium:

 $N_{2(g)} + 2O_{2(g)} \Longrightarrow 2NO_{2(g)}$

Equal moles of N_2 and O_2 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 ₂]
A.	increases	increases
B.	decreases	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.

$2HI_{(g)} \longrightarrow H_{2(g)} + I_{2(g)}$

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

$$2HI_{(g)} \longrightarrow H_{2(g)} + I_{2(g)}$$

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?

$$2HI_{(g)} \longrightarrow H_{2(g)} + I_{2(g)}$$

Concentration Change:

Consider the following system at equilibrium: $2HI_{(g)} \longrightarrow H_{2(g)} + I_{2(g)}$

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

$$2HI_{(g)} \iff H_{2(g)} + I_{2(g)}$$

What substance initially increases in concentration?

How does this affect the amount of collisions? more collisions occuring 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.

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 greater than the reverse rate

$$2HI_{(g)} \xrightarrow{\qquad} H_{2(g)} + I_{2(g)}$$

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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

$$2HI_{(g)} \longrightarrow H_{2(g)} + I_{2(g)}$$

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 to the shift right it overall is slightly initial change is always change).	, then due , but (an more drastic than a shift
[H ₂]due to the shift right.	and [l ₂]

So how is it possible that all of [HI], [H₂], and

[l₂] increased?

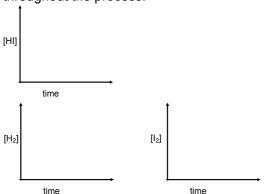
In summary:

[HI] initially	increased	, then due
to the shift right it	decreased	, but
overall is slightly _	increased	(ar
initial change is all	ways more dras	tic than a shift
change).	•	

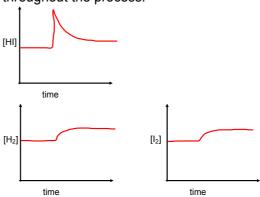
 $[H_2]$ <u>increased</u> and $[I_2]$ <u>increased</u> due to the shift right.

So how is it possible that all of [HI], [H₂], and [I₂] increased? because more HI was added initially, there are more particles in the system, so all concentrations can and do increase

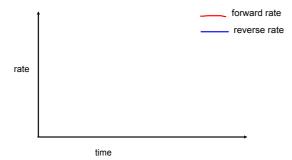
Graph the concentration changes that occur throughout the process:



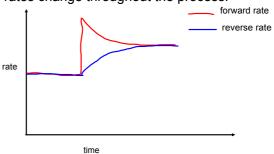
Graph the concentration changes that occur throughout the process:



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 (

).

Summary using LeChatelier's Principle:

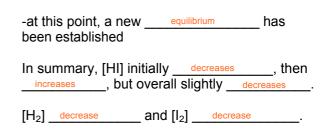
If an equilibrium is subjected to a change (an increase in the # of HI molecules - an [HI] increase), processes occur to counteract the change (a shift right causing an [HI] decrease) until a new equilibrium is established (rates are now higher than they were originally and the concentrations are again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

Considering the same system at equilibrium:	
$2HI_{(g)} \longleftrightarrow H_{2(g)} + I_{2(g)}$	
Explain what would occur if some HI(q) is remove)
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 [H ₂] and [I ₂] will	
-eventually, the forward rate will start to	
and the reverse rate will start to	
until they	

Considering the same $2HI_{(g)} \longleftrightarrow H_2$		brium:
Explain what would oc		is removed
from the system.	(3)	
-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 fa	avoured
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and [H ₂] and [I ₂] will _t	ooth decrease	_
-eventually, the forward		o increase
and the reverse rate w	ill start to decrea	ase
until thou hecome equal	l	

-at this point, a newbeen established	has
In summary, [HI] initially, but overall slightly	, then
[H ₂] and [I ₂]	

How is it that all concentrations decrease?



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

How is it that all concentrations decrease?

Graph how concentrations change during the process:

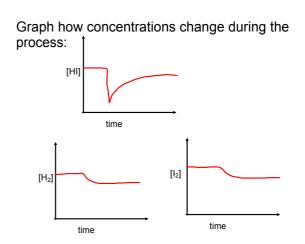
[HI]

time

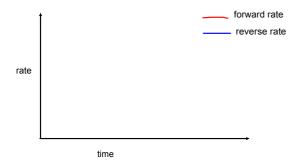
[I₂]

time

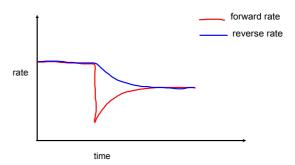
time



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:

$$2NO_{(g)} + Cl_{2(g)} \longrightarrow 2NOCl_{(g)} + energy$$

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:

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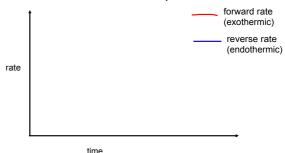
$$2NO_{(g)} + Cl_{2(g)} \longrightarrow 2NOCl_{(g)} + energy$$

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 .

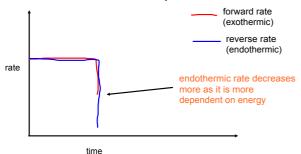
What will happen to both rates if you decrease temperature? ___they will both decrease However, the endothermic reaction relies more on energy, so it will be affected to a greater extent.

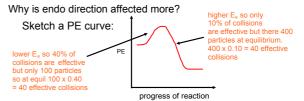
the reverse reaction rate (endothermic in this example) will decrease to a greater extent than the forward reaction rate (exothermic)

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.





If temperature decreased, it decreases for the entire system, so both sides are affected equally. Let's say % of effective collisions decreases by 5% due to the decrease. Reactant side only has 100 particles, now with 35% effective collisions. $100 \times 0.35 = 35$ effective collisions, so exo rate decreases by 5 effective collisions.

Product side has 400 particles, now with 5% effective collisions. 400 x 0.05 = 20 effective collisions, so endo rate decreases by 20 effective collisions. IT IS AFFECTED MORE BY THE TEMP CHANGE. Same, but opposite argument for a temperature increase.

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 _____.

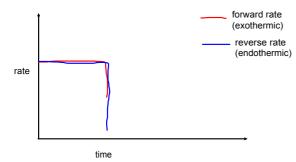
Therefore, which rate is temporarily greater?

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

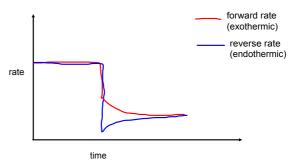
This means, that for a time, products will be produced faster than they're being used (resulting in a net increase), and visa versa for reactants.

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

Finish the rate graph:



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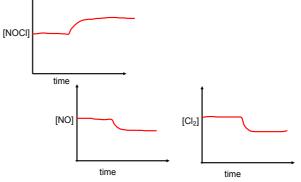
When equilibrium has been re-established, why are the rates lower than originally?

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.

time

Due to the shift right (to the exothermic side), the [NOCI] increases ___, [NO] ___decreases ___, and $[Cl_2]$ ___decreases ___. Graph how each changes during the process:



Consider the system:

favoured.

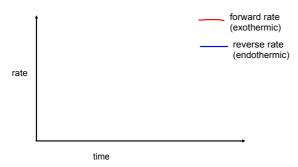
If the temperature was increased, both rates will _____, but since endothermic (reverse reaction in this example) relies more on energy, it will _____ more. Therefore, the _____ rate will temporarily be higher than the _____ rate, causing a shift to the _____ so that ____ are

Consider the system:

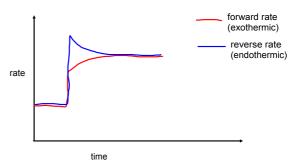
$$2NO_{(g)} + Cl_{2(g)} \longrightarrow 2NOCl_{(g)} + energy$$

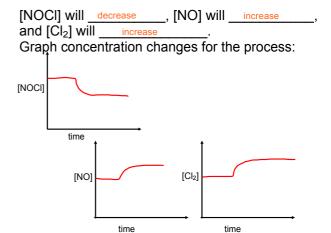
If the temperature was increased, both rates will lincrease, but since endothermic (reverse reaction in this example) relies more on energy, it will lincrease more. Therefore, the reverse (endo) rate will temporarily be higher than the forward (exo) rate, causing a shift to the left so that reactants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

Draw a rate graph to model the entire process:



Draw a rate graph to model the entire process:





Conclusion:

Decreasing temper	perature results in a shift direction.	
	ature results in a shift in direction.	

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CHEMISTRY JOKE CHEMISTRY JOKE (CH') | X LONG (CH') | X LONG

Conclusion:

Decre	asing tempera	ture results in a shift ir
the _	exothermic	direction.
Increa	asing temperat	ure results in a shift in
the _	endothermic	direction.

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

Assignment 2:

1)
$$2SO_{2(g)} + O_{2(g)} \longrightarrow 2SO_{3(g)}$$
 $\triangle H = -192kJ$

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 ₂]	[O ₂]	[SO ₃]
Increase temperature				
Decrease [O2]				
Inject more SO3				
Remove SO ₂				
Decrease temperature				
Decrease [SO3]				

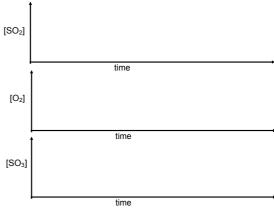
Assignment 2:

1)
$$2SO_{2(g)} + O_{2(g)} \longrightarrow 2SO_{3(g)} \Delta H = -192kJ$$

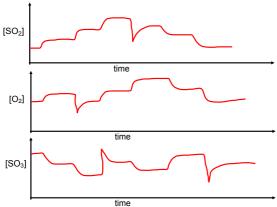
a) Indicate the shift that occurs using the words 'Right' or 'Left and use † or ↓ for concentration changes. Some boxes below may have three arrows: an initial change arrow, a shift change arrow, and a net (overall) change arrow.

Stress	Shift	[SO ₂]	[O ₂]	[SO ₃]
Increase temperature	left	1	1	↓
Decrease [O ₂]	left	1	[] = [ļ
Inject more SO₃	left	1	1	
Remove SO ₂	left		1	1
Decrease temperature	right	1	1	1
Decrease [SO3]	right	1	1	↓ ↑ = ↓

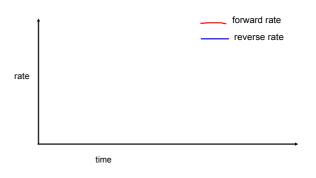
1b) Sketch a concentration vs. time graph for the entire table for each substance:



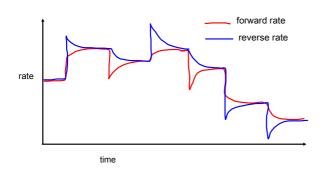
1b) Sketch a concentration vs. time graph for the entire table for each substance:



1c) Graph rate changes for the entire table:



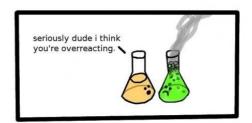
1c) Graph rate changes for the entire table:



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



N₂O₄ light yellow		NO ₂ dark amber
'energy' te		vrite the int.action?quick=wa&att=2314
http://www.mhhe.com/pi oc Pressure Chang	onc & temp review /	chemistry/flash/lechv17.swf pressure preview
The only state the every situation is or decreasing the only initially affect state substance.	pat fills its reads gas e volume of a ct the concent Then, an equatrations or ar	cting container in Thus, increasing reacting vessel will ration of anygas_ uilibrium shift may nounts of the non-
A decrease in vo pressure. An increase in vo pressure.		increase in decrease in
	ing that all ga	s an increase in as concentrations
An increase in variety mean immediately decrease	ing all gas co	es a decrease in oncentrations
http://www.absorblearning	.com/media/attachment.ac	tion?quick=vz&att=2292
Explain: If volume is decreased	I, you have the sam	e 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.

http://www.mhhe.com/physsci/chemistry/essentialchemistry/flash/lechv17.swf conc & temp review / pressure preview Pressure Change:	
The only state that fills its reacting container in every situation is Thus, increased the concentration of any	sing wil
state substance. Then, an equilibrium shift ma affect the concentrations or amounts of the no gaseous substances.	
A decrease in volume = an pressure.	_ in
An increase in volume = a pressure.	in

Explain:

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

If the pressure of a system is increased, gas particles are packed more 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?

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 $N_{2(g)} + 3H_{2(g)} \iff 2NH_{3(g)}$

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 $N_{2(g)} + 3H_{2(g)} \iff 2NH_{3(g)}$

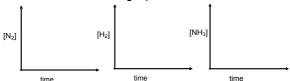
What happens to the pressure of the gases if the volume of the system is decreased? increase So what happens initially to all gas concentrations? all increase So what happens to the # of collisions? increase

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.

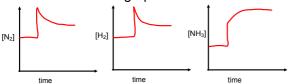
 $[N_2]$ and $[H_2]$ will both initially ______, then due to the shift will ______, but overall will have a net ______. [NH $_3$] will initially ______, then due to the shift will ______.

Draw concentration graphs:

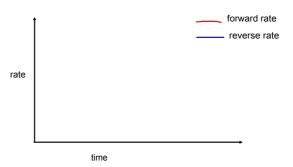


 $[N_2]$ and $[H_2]$ will both initially <u>increase</u>, then due to the shift will <u>decrease</u>, but overall will have a net <u>increase</u>. [NH $_3$] will initially <u>increase</u>, then due to the shift will <u>increase more</u>.

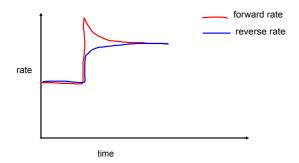
Draw concentration graphs:



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
$$N_{2(g)} + 3H_{2(g)} \iff 2NH_{3(g)}$$

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).

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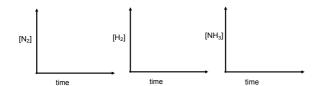
Example: The Haber Process
$$N_{2(g)} + 3H_{2(g)} \iff 2NH_{3(g)}$$

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

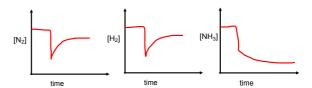
<u>left side</u> (the side with more gas particles).

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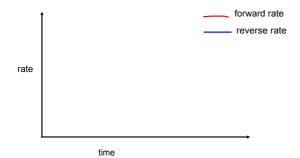
Draw concentration vs. time graphs for the process:



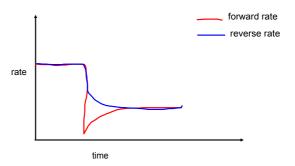
Draw concentration vs. time graphs for the process:



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:

$$H_{2(g)} + CO_{2(g)} \Longrightarrow H_2O_{(g)} + CO_{(g)}$$

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:

$$H_{2(q)} + CO_{2(q)} \rightleftharpoons H_2O_{(q)} + CO_{(q)}$$

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.dit.acum.chai/www.Clayurt if-Anthonium-2005/NSHA limit

Conclusion:

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

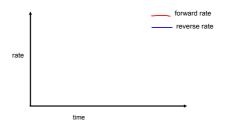
A decrease in pressure will cause all gas concentrations to initially <u>decrease</u>, and then a shift to the side with <u>more</u> gas particles will ensue.

Addition of an inert gas will not affect the equilibrium.

http://www.dlt.acsum.edu/cvet/Chapter14-Cas_Phase-Solubility-Complex_Los_Faquilbrias/Chapter14-Animationiz/NO3-N204 html

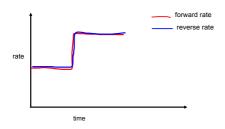
Addition of a Catalyst:

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 <u>increase</u> 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:

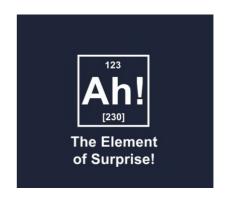


Important Concepts for Shifts:

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



Assignment 3

- 1) Finish Hebden page 54, numbers 17-23
- 2) Complete the table:

$$Ag_2CrO_{4(s)} \, + \, heat \, \Leftrightarrow \, 2Ag^{\scriptscriptstyle +}{}_{(aq)} \, + \, CrO_{4^{\scriptscriptstyle -}(aq)}$$

Stress	Shift	[Ag2CrO4]	[Ag+]	[CrO ₄ ² ·]
Add Ag ₂ CrO _{4(s)}				
Decrease temperature				
Increase pressure				
Decrease Ag+(aq)				
Increase CrO ₄ 2-(aq)				

Assignment 3

- 1) Finish Hebden page 54, numbers 17-23 answers in the back of Hebden
- 2) Complete the table:

$$Ag_2CrO_{4(s)} \, + \, heat \, \Leftrightarrow \, 2Ag^{\scriptscriptstyle +}{}_{(aq)} \, + \, CrO_{4^{\scriptscriptstyle -}(aq)}$$

Stress	Shift	[Ag ₂ CrO ₄]	[Ag+]	[CrO ₄ ² ·]
Add Ag ₂ CrO _{4(s)}	_		_	
Decrease temperature	L		1	1
Increase pressure			_	
Decrease Ag+(aq)	R		↓ † = ↓	1
Increase CrO ₄ ²⁻ (aq)	L		ļ	†1 = †

3) Complete the table:

$$BaCO_{3(s)} + heat \Leftrightarrow BaO_{(s)} + CO_{2(g)}$$

Stress	Shift	[BaCO ₃]	[BaO]	$[CO_2]$
Add BaCO _{3(s)}				
Increase temperature				
Decrease pressure				
Decrease volume				
Add CO _{2(g)}				
Remove CO _{2(g)}				

3) Complete the table:

$$BaCO_{3(s)} + heat \Leftrightarrow BaO_{(s)} + CO_{2(g)}$$

Stress	Shift	[BaCO ₃]	[BaO]	[CO ₂]
Add BaCO _{3(s)}	_	_		_
Increase temperature	R	_	_	1
Decrease pressure	R	_	_	↓ † = ↓
Decrease volume	L	_	_	1 = 1
Add CO _{2(g)}	L	_	_	
Remove CO _{2(g)}	R	_	_	[↑ = ↓

4) Complete the table:

$$CO_{(g)} \ + \ H_2O_{(g)} \iff CO_{2(g)} \ + \ H_{2(g)} \quad \ \Delta H = -41kJ$$

Stress	Shift	[CO]	[H ₂ O]	[CO ₂]	[H ₂]
Add CO _{2(g)}					
Increase temperature					
Remove H ₂ O _(g)					
Increase volume					
Add H _{2(g)}					
Increase pressure					
Inject Ar _(g)					

4) Complete the table:

$$CO_{(g)} \ + \ H_2O_{(g)} \iff CO_{2(g)} \ + \ H_{2(g)} \quad \ \Delta H = -41kJ$$

Stress	Shift	[CO]	[H ₂ O]	[CO ₂]	[H ₂]
Add CO _{2(g)}	L	1	1	↑ ↓ = ↑	↓
Increase temperature	L	1	1	1	ţ
Remove H ₂ O _(g)	L	1	$\dagger \downarrow = \uparrow$	↓ ↓	1
Increase volume	_	1	1	1	ļ
Add H _{2(g)}	L	1	1	1	1 1 = 1
Increase pressure	_	1	1	1	1
Inject Ar _(g)	_	_	_	—	_



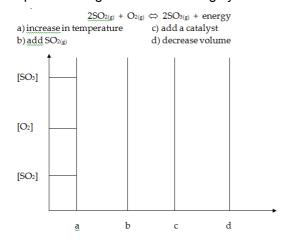
III) Equilibrium Graphs

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

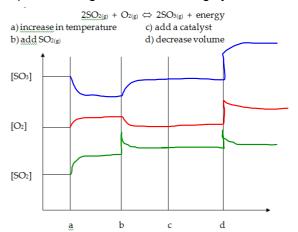
Things to remember:

- 1) Solid and liquid concentrations always remain
- 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.

Graph the changes for the following system:



Graph the changes for the following system:



Haber Process

The Haber Process for making ammonia (NH₃) 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 N₂. The ammonia could then be used as a precursor for TNT. Getting N₂ to react is very difficult due to its triple bond. However, Haber manipulated an equilibrium system to maximize the yield (amount) of NH₃.

$$N_{2(g)} + 3H_{2(g)} \iff 2NH_{3(g)} + 92.4kJ$$

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

http://www.absorblearning.com/media/attachment.action?quick=128&att=2741

The Haber Process:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} + 92.4kJ$$

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:

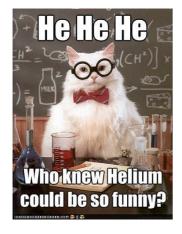
1) constant removal of NH_3 from the system to cause a permanent shift right

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:

) $2C_{(g)} + O_{2(g)} \Leftrightarrow 2CO_{(g)}$ $\Delta H = -97kJ$

stresses: a) decrease volume c) add CO

b) add O2 d) increase temperature

 $2) \hspace{0.5cm} SO_{3(g)} \hspace{0.1cm} + \hspace{0.1cm} NO_{(g)} \hspace{0.1cm} \Leftrightarrow \hspace{0.1cm} NO_{2(g)} \hspace{0.1cm} + \hspace{0.1cm} SO_{2(g)} \hspace{0.1cm} + \hspace{0.1cm} energy$

stresses: a) increase temperature

b) remove some NO_{2(g)}

c) decrease pressure

 $CH_{4(g)} + H_2O_{(g)} \Leftrightarrow CO_{(g)} + 3H_{2(g)}$ $\Delta H = +50kJ$

stresses: a) increase temperature d) decrease volume

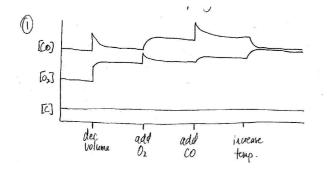
b) decrease temperature e) add something which reacts

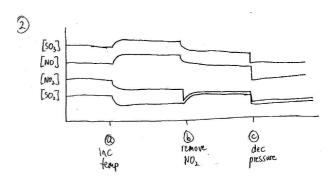
c) <u>decrease</u> pressure with H₂O

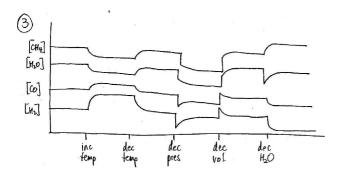
4) Make a graph for the Haber Process with each stress: (a) decrease temp (b) increase pressure

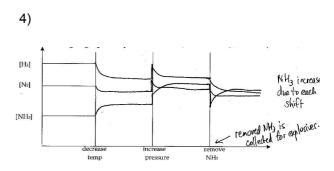
(c) remove NH₃

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 + ene	ergy====2NO ₂	
The forward	d reaction is		
The reverse	e 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 is a term that describes the total potential energy content (the energy in the particles) involved in a system.

Example: N_2O_4 + energy \Longrightarrow 2NO₂

The forward reaction is ____endothermic The reverse reaction is

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

Enthalpy is increasing because energy is being absorbed into

tend toward enthalpy.	or
energy loss, mea	ons naturally tend toward aning they tend toward the ction. In other words they
In nature, is it easi	er to gain or lose energy?
are	energy.
Exothermic reaction	ons have or enthalpy because the particle
are gaining energy	
	tions have increasing or thalpy because the particles

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

Exothermic reactions have _____ecreasing _____or ____minimum ____enthalpy because the particles are _____releasing ____energy.

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

In refore, reactions naturally tend toward energy loss, meaning they tend toward the ____exothermic ____direction. In other words they tend toward _____decreasing ____or ____minimum _____

Entropy

Entropy is the measure of disorder or randomness in a system.
Think of your bedroom. If 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

enthalpy.

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

Think of your bedroom. If 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:

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

Examples: Determine which direction entropy is increasing.

1)
$$A_{(g)} + 3B_{(g)} \Leftrightarrow 2C_{(g)} + 4D_{(g)}$$

2)
$$A_{(s)} + B_{(g)} \Leftrightarrow 2C_{(l)} + D_{(l)}$$

3)
$$A_{(aq)} + B_{(s)} \Leftrightarrow 2C_{(l)} + D_{(l)}$$

4)
$$A(g) + B(g) \Leftrightarrow C(g) + D(g)$$

Examples: Determine which direction entropy is increasing.

1)
$$\underline{A}_{(g)} + 3\underline{B}_{(g)} \Leftrightarrow 2C_{(g)} + 4\underline{D}_{(g)}$$

$$\textbf{2)} \quad A(\textbf{s}) + B(\textbf{g}) \iff 2C(\textbf{l}) + D(\textbf{l})$$

3)
$$A_{(aq)} + B_{(s)} \Leftrightarrow 2C_{(l)} + D_{(l)}$$

4)
$$\underline{\underline{A}}_{(g)} + \underline{B}_{(g)} \Leftrightarrow \underline{C}_{(g)} + \underline{D}_{(g)}$$

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 <u>minimum</u> enthalpy and <u>maximum</u> 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)

1.
$$H_2SO_{4(1)} + H_2O_{(1)} \Rightarrow H_2SO_{4(ag)} + 150kJ$$

2.
$$C_2H_{2(g)} + C_4(OH)_{2(ag)} \Rightarrow C_4C_{2(s)} + 2H_2O_{(1)} \Delta H = 185kJ$$

3.
$$C_2H_{6(g)} \Rightarrow C_2H_{2(g)} + 2H_{2(g)} \quad \Delta H = 311kJ$$

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:

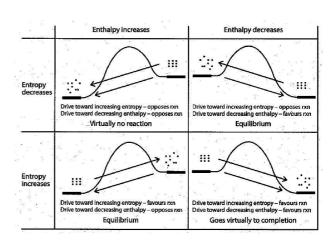
Predict whether each reaction will go to completion (C), equilibrium (E), or not react (NR)

$$1. \begin{tabular}{lll} $H_2SO_{4(l)} +$ $H_2O_{(l)} \Rightarrow $H_2SO_{4(\underline{aq})} +$ $150kJ$ \\ \hline & & exo \\ \hline & more gas \end{tabular}$$

2.
$$\underline{\text{C2H2}}_{(g)} + \text{Ca}(\text{OH})_{2(aq)} \Rightarrow \text{CaC}_{2(s)} + 2\text{H2O}_{(l)} \quad \Delta H = 185\text{kJ}$$
No Reaction

3.
$$C_2H_{6(g)} \Rightarrow C_2H_{2(g)} + 2H_{2(g)} \quad \Delta H = 311kJ$$

Equilibrium





and the natural order."

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Assignment 5:

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

1.
$$4NH_{3(g)} + 5O_{2(g)} \Rightarrow 4NO_{(g)} + 6H_2O_{(g)} \Delta H = +115k$$

$$2. \ \underline{N_2O_{4(g)}} + 58.9kJ \ \Rightarrow \ 2NO_{2(g)}$$

3.
$$2Bi_{(aq)}^{3+} + 3H_2S_{(g)} \Rightarrow BiS_{3(s)} + 6H_{(aq)}^{+} + energy$$

4.
$$2H_2O_{2(ag)} \Rightarrow O_{2(g)} + 2H_2O_{(l)} \quad \Delta H = -189kJ$$

Assignment 5:

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

1.
$$4NH_{3(g)} + 5O_{2(g)} \Rightarrow 4NO_{(g)} + 6H_2O_{(g)} \Delta H = +115k_g$$

$$2. \ \, \underline{N_2O_{4(g)}} \, + \, 58.9kJ \underset{\qquad \qquad \text{equilibrium}}{\Longrightarrow} \, 2NO_{2(g)}$$

3.
$$2Bi_{(aq)}^{3+} + 3H_2S_{(g)} \Rightarrow BiS_{3(s)} + 6H_{(aq)}^{+} + energy$$
 equilibrium

4.
$$2\text{H}_2\text{O}_{2(aq)} \Rightarrow \text{O}_{2(g)} + 2\text{H}_2\text{O}_{(1)} \quad \Delta H = -189\text{kJ}$$

completion

5.
$$H_2O_{(g)} + C_{(s)} \Rightarrow CO_{2(g)} + H_{2(g)} \quad \Delta H = +31.3kJ$$

6.
$$3C_2H_{2(g)} \Rightarrow C_6H_{6(g)} + 143kJ$$

7.
$$NaOH_{(aq)} + 2.4kJ \Rightarrow NaOH_{(s)}$$

8.
$$CS_{2(g)} + 3O_{2(g)} \Rightarrow CO_{2(g)} + 2SO_{2(g)} + 66kJ$$

5.
$$\underline{H_2O_{(g)}} + C_{(s)} \Rightarrow CO_{2(g)} + H_{2(g)} \quad \Delta H = +31.3kJ$$

$$6. \ \ \underline{3C_2H_{2(g)}} \Longrightarrow C_6H_{6(g)} + \ 143kJ$$
 equilibrium

7.
$$\underbrace{NaOH_{(aq)}} + 2.4kJ \Rightarrow \underbrace{NaOH_{(s)}}_{\text{no reaction}}$$

$$8. \ CS_{2(g)} + 3O_{2(g)} \Rightarrow CO_{2(g)} + 2SO_{2(g)} + 66kJ$$
 equilibrium

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

$$CO_{(g)} + H_2O_{(l)} \Rightarrow CO_{2(g)} + H_{2(g)} \Delta H = 42kJ$$

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

$$CO_{(g)} + H_2O_{(1)} \Longrightarrow CO_{2(g)} + H_{2(g)} \quad \Delta H = 42kJ$$

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?

$$2C_4H_{10(g)} + 13O_{2(g)} \Rightarrow 8CO_{2(g)} + 10H_2O_{(g)} + 128kJ$$

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

$$\underbrace{2C_4H_{10(g)} + 13O_{2(g)} \Rightarrow 8CO_{2(g)} + 10H_2O_{(g)} + 128kJ}_{\text{decreasing enthalpy (exo)}}$$

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.



"One misplaced decimal point and here you are?"

V) The Equilibrium Constant

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

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

Example: Write the K_{eq} expression:

$$2HI_{(g)} \longrightarrow I_{2(g)} + H_{2(g)}$$
 $K_{eq} =$

V) The Equilibrium Constant

The equilibrium constant is called ${}^tK_{eq}{}^t$ and is found by multiplying product concentrations and dividing that by the result of multiplying reactant concentrations.

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

Example: Write the K_{eq} expression:

$$2HI_{(g)} \stackrel{\longleftarrow}{\longleftarrow} I_{2(g)} + H_{2(g)} \quad K_{eq} = \underbrace{[H_2][I_2]}_{[HI][HI]} = \underbrace{[H_2][I_2]}_{[HI]^2}$$

Examples: Write a Keq for each of the following

a)
$$2H_{2(g)} + O_{2(g)} \Leftrightarrow 2H_2O_{(g)}$$

b)
$$3Sn^{2+}(aq) + 2PO_4^{3-}(aq) \iff Sn_3(PO_4)_{2(s)}$$

c)
$$2Na(s) + 2H_2O(g) \Leftrightarrow 2NaOH(s) + H_2(g)$$

d)
$$N_{2(g)} + 3H_{2(g)} \Leftrightarrow 2NH_{3(g)}$$

Examples: Write a Keq for each of the following

a)
$$2H_{2(g)} + O_{2(g)} \Leftrightarrow 2H_{2}O_{(g)} \xrightarrow{K_{eq} = \frac{[H_{2}O]^{2}}{[H_{2}]^{2}[O_{2}]}}$$

b)
$$3Sn^{2+}(aq) + 2PO4^{3-}(aq) \Leftrightarrow Sn_3(PO_4)_{2(s)} \atop K_{eq} = \frac{1}{[Sn^{2+}]^3[PO_4]^{3+}}$$

c)
$$2Na(s)$$
 + $2H_2O(g)$ \Leftrightarrow $2NaOH(s)$ + $H_2(g)$ $K_{eq} = \frac{[H_2]}{[H_2O]^2}$

d)
$$N_{2(g)} + 3H_{2(g)} \Leftrightarrow 2NH_{3(g)}$$

$$K_{eq} = \frac{[NH_3]^2}{[N_3][H_3]^3}$$

Go to page 40 & 41 in Hebden and look at the tables in #6 & #7 (you did these questions in Assignment 1). Calculate the $K_{\rm eq}$ 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 $K_{\rm eq}$ 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 $K_{\rm eq}$ after a new equilibrium was reached at 18 minutes.

$$K_{eq} = \underbrace{1.500}_{0.300} = 5.00$$
 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 $K_{\rm eq}$ 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 $K_{\rm eq}$ 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: $2HI_{(g)} \longrightarrow I_{2(g)} + H_{2(g)}$, 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, $K_{eq} = [products]$ [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 Keq Constant

Remember, $K_{eq} = [products]$ [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)?

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?

a)
$$2HBr(g) \Leftrightarrow H_{2(g)} + Br_{2(g)} \quad \underline{K}_{eq} = 7.0 \times 10^{-20}$$

b)
$$C_2H_{4(g)} + H_{2(g)} \Leftrightarrow C_2H_{6(g)}$$
 $K_{eq} = 1.2 \times 10^{19}$

c)
$$Si_{(s)} + O_{2(g)} \Leftrightarrow SiO_{2(g)} \quad \underline{K}_{eq} = 2.0 \times 10^{-1}$$

Examples:

Do the following equilibria favour reactants or products?

a)
$$2HBr(g) \Leftrightarrow H_{2(g)} + Br_{2(g)} \quad \underline{K_{eq}} = 7.0 \times 10^{-20}$$
 reactants

b)
$$C_2H_{4(g)} + H_{2(g)} \Leftrightarrow C_2H_{6(g)} \quad \underline{K_{eq}} = 1.2 \times 10^{19} \text{ products}$$

c)
$$Si_{(s)} + O_{2(g)} \Leftrightarrow SiO_{2(g)}$$
 $K_{eq} = 2.0 \times 10^{-1}$ reactants

Writing the equation the other way around

For the following reaction:

$$H_{2(g)} + F_{2(g)} \Leftrightarrow 2HF_{(g)}$$

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

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

$$2HF_{(g)} \Leftrightarrow H_{2(g)} + F_{2(g)}$$

Writing the equation the other way around

For the following reaction:

$$H_{2(g)} + F_{2(g)} \Leftrightarrow 2HF_{(g)}$$

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

$$K_{eq} = \frac{[HF]^2}{[H_2][F_2]} = 0.25$$

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

$$2HF_{(g)} \Leftrightarrow H_{2(g)} + F_{2(g)}$$

$$K_{\text{eq}} = \underbrace{[H_2][F_2]}_{\text{[HF]}} \quad \text{It is the reciprocal of} \\ \text{the equation above,} \\ \text{so the } K_{\text{eq}} \text{ constant is} \\ \text{the reciprocal of 0.25}.$$

The
$$K_{eq}$$
 is $\frac{1}{0.25} = 4.0$

VI) Temperature and the Keg 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_{eq} increase or decrease?

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

VI) Temperature and the Keg 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_{eq} increase or decrease?

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

decrease

Example:

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

$$2HI_{(g)} \Leftrightarrow H_{2(g)} + I_{2(g)} \quad \Delta H = +500 \text{ kJ}$$

Example:

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

$$2HI_{(g)} \Leftrightarrow H_{2(g)} + I_{2(g)} \quad \Delta H = +500 \text{ kJ}$$

-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_{eq} decrease

Example:

Given the following equation and data:

 $XY + ZM \longrightarrow YM + XZ$

 K_{eq} = 60.0 at 300 degrees C

 K_{eq} = 45.0 at 500 degrees C

Is the forward reaction endothermic or exothermic? Explain.

Example:

Given the following equation and data:

 $XY + ZM \longrightarrow YM + XZ$

 K_{eq} = 60.0 at 300 degrees C

 K_{eq} = 45.0 at 500 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



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Assignment 6

- 1) Hebden page 60, #31acegj, 32, 35abcd, and page 62, #36, 40, 41, 44-46
- 2) Given the following equation and data:

CB + R CBR

K_{eq} = 12.0 at 200 degrees C

K_{eq} = 20.0 at 300 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:

CB + R CBR

K_{eq} = 12.0 at 200 degrees C

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

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

- -as temperature increases (200 to 300), $\ensuremath{\mbox{K}_{\mbox{\scriptsize eq}}}$ 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:

 $\underline{CH_{4(g)} \ + \ 2H_2S_{(g)}} \iff CS_{2(g)} \ + \ 4H_{2(g)}$

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

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

- 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:

$$\begin{array}{l} \underline{CH_{4(g)}} \ + \ 2H_{2}S_{(g)} \ \Leftrightarrow \ CS_{2(g)} \ + \ 4H_{2(g)} \\ \underline{K_{eq}} = 1.0 \ x \ 10^{-2} \ at \ 500 ^{\circ}C \\ K_{eq} = 2.4 \ x \ 10^{-3} \ at \ 800 ^{\circ}C \end{array}$$

- 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 $K_{\rm eq}.$ Only a temperature change can.

4) For the following reaction:

$$CO_{2(g)} + H_{2(g)} \Leftrightarrow CO_{(g)} + H_2O_{(g)}$$
 $\Delta H = -96 \text{ kJ}$

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

4) For the following reaction:

$$CO_{2(g)} + H_{2(g)} \Leftrightarrow CO_{(g)} + H_2O_{(g)}$$
 $\Delta H = -96 \text{ kJ}$

What effect will decreasing temperature have on the value of $K_{\rm eq}$? 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 Keq to increase



The undocumented first use of this well-known phrase.

VII) Type 1 Keg Problems

For Type 1 K_{eq} problems, the data provided in the question is exclusively equilibrium data. Example:

1. For the following reaction:

$$2SO_{2(g)} + O_{2(g)} \Leftrightarrow 2SO_{3(g)} + 192 \text{ kJ}$$

Equilibrium concentrations were found to be as follows: $[SO_2] = 2.0M$, $[O_2] = 0.50M$, $[SO_3] = 1.6M$ Calculate the value of K_{eq} .

VII) Type 1 Keg Problems

For Type 1 K_{eq} problems, the data provided in the question is exclusively equilibrium data. Example:

1. For the following reaction:

$$2SO_{2(g)} + O_{2(g)} \Leftrightarrow 2SO_{3(g)} + 192 \text{ kJ}$$

Equilibrium concentrations were found to be as follows: $[SO_2] = 2.0M$, $[O_2] = 0.50M$, $[SO_3] = 1.6M$ Calculate the value of K_{eq} .

$$K_{eq} = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{(1.6)^2}{(2.0)^2(0.50)} = 1.3$$

Example:

2) At equilibrium, a 2.00L vessel contained 0.750mol CO, 0.276mol H₂O, 0.600mol CO₂ and a K_{eq} = 0.986. Calculate the moles of H_2 at equilibrium.

$$CO_{(g)} + H_2O \implies CO_{2(g)} + H_{2(g)}$$

Example:

2) At equilibrium, a 2.00L vessel contained 0.750mol CO, 0.276mol H₂O, 0.600mol CO₂ and a K_{eq} = 0.986. Calculate the moles of H_2 at equilibrium.

$$CO_{(g)} + H_2O \longrightarrow CO_{2(g)} + H_{2(g)}$$

$$[CO] = \underbrace{0.750\text{mol}}_{2.00L} = 0.375\text{M} \qquad [H_2O] = \underbrace{0.276\text{mol}}_{2.00L} = 0.138\text{M}$$

$$[CO_2] = \underbrace{0.600\text{mol}}_{2.00L} = 0.300\text{M} \qquad K_{eq} = \underbrace{[CO_2][H_2]}_{[CO][H_2O]}$$

$$0.986 = \underbrace{(0.300)[H_2]}_{(0.375)(0.138)} \qquad [H_2] = 0.170\text{M}$$

moles $H_2 = (0.170M)(2.00L) = 0.340$ 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 H₂ and I₂ was prepared by placing 0.100mol of H_2 and 0.100mol of I_2 into a 1.00L flask. At equilibrium, the [I₂] dropped to 0.020M. Calculate the Keq.

$$H_{2(g)} + I_{2(g)} \Longrightarrow 2HI_{(g)}$$

Change **E**quilibrium

<u>I</u>nitial

Example:

1) A mixture of H₂ and I₂ was prepared by placing 0.100mol of H_2 and 0.100mol of I_2 into a 1.00L flask. At equilibrium, the [I₂] dropped to 0.020M. Calculate the K_{eq}. *In a 1.00L flask, the

$$H_{2(g)} + I_{2(g)} \Longrightarrow 2HI_{(g)}$$
Initial 0.100M 0.100M 0
Change -0.080M -0.080M +0.16M
Equilibrium 0.020M 0.020M 0.16M

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

Example:

Example:
$$N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$$
 Given:
$$[N_2]_i = 0.32M, [H_2]_i = 0.66M, [H_2]_{eq} = 0.30M$$
 Calculate K_{eq} .
$$N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$$
 I
$$C$$
 E

Example:

2)
$$N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$$

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

$$N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$$

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



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Assignment 7

1. For the following reaction at equilibrium:

$$CH_{4(g)} + H_2O_{(g)} \Leftrightarrow CO_{(g)} + 3H_{2(g)}$$

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

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

Calculate the \underline{Keq} for this reaction. Are the reactants or products favoured?

Assignment 7

1. For the following reaction at equilibrium:

$$CH_{4(g)} + H_2O_{(g)} \Leftrightarrow CO_{(g)} + 3H_{2(g)}$$

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

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

Calculate the \underline{Keq} for this reaction. Are the reactants or products favoured?

$$K_{eq} = \frac{[CO][H_2]^3}{[CH_4][H_2O]} = \frac{(0.200)(0.700)^3}{(0.600)(0.060)} = 1.9$$

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

2. For the following reaction:

 $CO(g) + H_2O(l) \Leftrightarrow CO_2(g) + H_2(g)$

At equilibrium in a 1.0L container, 0.020mol of CO, 0.010mol H_2O , $\underline{0.030}$ $\underline{mol\ CO_2}$, and 0.010mol of H_2 are present.

- a) Calculate the Keq
- b) State whether reactants or products are favoured
- c) If H_2 is removed from the system and equilibrium is re-established, how does the value of \underline{K}_{eq} change?

2. For the following reaction:

 $CO_{(g)} + H_2O_{(l)} \Leftrightarrow CO_{2(g)} + H_{2(g)}$

At equilibrium in a 1.0L container, 0.020mol of CO, 0.010mol H₂O, $\underline{0.030}$ mol CO₂, and 0.010mol of H₂ are present.

- a) Calculate the Keq
- b) State whether reactants or products are favoured
- c) If H_2 is removed from the system and equilibrium is re-established, how does the value of \underline{K}_{eq} change?
- 1.0L container, so moles = molarity

a)
$$K_{eq} = \frac{[CO_2][H_2]}{[CO]} = \frac{(0.030)(0.010)}{(0.020)} = 0.015$$

- b) reactants favoured because the K_{eq} < 1
- c) the $K_{\rm eq}$ will not change. Only a temperature change can cause a change in $K_{\rm eq}$

3. For the following reaction:

 $CO_{(g)} + 2H_{2(g)} \Leftrightarrow CH_3OH_{(g)}$ $K_{eq} = 1.00$ At equilibrium in a 2.0L container, 0.420mol CO and 0.100mol H2 are present. Calculate the number of moles of CH3OH present.

3. For the following reaction:

 $CO(g) + 2H_{2}(g) \Leftrightarrow CH_{3}OH(g)$ $K_{eq} = 1.00$ At equilibrium in a 2.0L container, 0.420mol CO and 0.100mol H2 are present. Calculate the number of moles of CH3OH present.

[CO] =
$$0.420$$
mol = 0.21M [H₂] = 0.100 mol = 0.050M 0.0 = 0.050M

$$K_{eq} = \frac{[CH_3OH]}{[CO][H_2]^2}$$
 1.00 = $\frac{[CH_3OH]}{(0.21)(0.050)}$

$$[CH_3OH] = 1.00(0.21)(0.050)^2 = 0.000525$$

moles
$$CH_3OH = (0.000525)(2.0L) = 1.1 \times 10^{-3}$$

4. For the following reaction and data: $N_{2(g)} + 3H_{2(g)} \Leftrightarrow 2NH_{3(g)}$

	$[N_2](M)$	[H ₂] (M)	[NH ₃] (M)
Trial 1	0.200	0.400	0.500
Trial 2	?	0.300	0.600

Find [N₂] in Trial 2.

4. For the following reaction and data:

$$N_{2(g)} + 3H_{2(g)} \Leftrightarrow 2NH_{3(g)}$$

	$[N_2](M)$	[H ₂] (M)	[NH ₃] (M)
Trial 1	0.200	0.400	0.500
Trial 2	?	0.300	0.600

Find $[N_2]$ in Trial 2.

Trial 1:
$$K_{eq} = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(0.500)^2}{(0.200)(0.400)^3} = \frac{19.5}{31}$$

Trial 2:
$$\frac{19.5}{[N_2](0.300)^3} = \frac{(0.600)^2}{[N_2](0.300)^3} = \frac{(0.600)^2}{19.531(0.300)^3} = 0.683M$$

Type II Exercises (ICE diagrams)

5. A mixture consisting of 1.00mol $\underline{CO_{(g)}}$ and 1.00mol $H_2O_{(g)}$ is placed \underline{in} a 10.00L container. At equilibrium, 0.665mol $\underline{CO_{2(g)}}$ and 0.665mol $H_{2(g)}$ are present.

 $\underline{CO_{(g)}} \ + \ H_2O_{(g)} \ \Leftrightarrow \ CO_{2(g)} \ + \ H_{2(g)}$ Calculate the $\underline{K_{\text{eq}}}$ for this reaction.

Type II Exercises (ICE diagrams)

5. A mixture consisting of $1.00 \text{mol} \ \underline{CO}_{(g)}$ and $1.00 \text{mol} \ H_2O_{(g)}$ is placed \underline{in} a 10.00L container. At equilibrium, 0.665mol $\underline{CO_{2(g)}}$ and 0.665mol $H_{2(g)}$ are present.

 $\underline{CO}_{(g)} + H_2O_{(g)} \Leftrightarrow \underline{CO}_{2(g)} + H_{2(g)}$ by 10.0 to get Calculate the \underline{K}_{eq} for this reaction.

*divide all moles

$$CO_{(g)} + H_2O_{(g)} \longrightarrow CO_{2(g)} + H_{2(g)}$$

$$K_{eq} = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{(0.0665)^2}{(0.0335)^2} = 3.9$$

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

$$\underline{2HBr}_{(g)} \iff H_{2(g)} + Br_{2(g)}$$

At equilibrium, 0.140M H₂ is present. Calculate the Keq.

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

$$2HBr(g) \Leftrightarrow H_{2(g)} + Br_{2(g)}$$

At equilibrium, 0.140M H₂ is present. Calculate the K_{eq}.

$$K_{eq} = \frac{[H_2][Br_2]}{[HBr]^2} = \frac{(0.140)^2}{(0.72)^2} = 0.038$$

7. A 5.00L vessel was initially filled with 6.00mol SO_2 , 2.50mol NO_2 , and 1.00mol SO₃.

$$\underline{SO_{2(g)}} \ + \ NO_{2(g)} \ \Leftrightarrow \ SO_{3(g)} \ + \ NO_{(g)}$$

At equilibrium, the vessel was found to contain 3.00mol SO₃. What is the \underline{K}_{eq} for the reaction?

7. A 5.00L vessel was initially filled with 6.00mol SO₂, 2.50mol NO₂, and 1.00mol SO₃.

$$SO_{2(g)} + NO_{2(g)} \Leftrightarrow SO_{3(g)} + NO_{(g)}$$

At equilibrium, the vessel was found to contain 3.00mol SO₃. *divide by 5.00 to get moles What is the K_{eq} for the reaction? to molarity

$$K_{eq} = \frac{[SO_3][NO]}{[SO_2][NO_2]} = \frac{(0.600)(0.400)}{(0.80)(0.100)} = 3.0$$

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

$$2NOCl_{(g)} \Leftrightarrow 2NO_{(g)} + Cl_{2(g)}$$

At equilibrium, there was 0.10mol of Cl₂. What is the $\underline{K_{eq}}$?

8. 0.50mol of \underline{NOCl} was introduced into a 1.0L flask and allowed to come to equilibrium: *moles = molarity

$$2NOCl_{(g)} \Leftrightarrow 2NO_{(g)} + Cl_{2(g)}$$
 because 1.0L flask

At equilibrium, there was 0.10mol of Cl2. What is the Keq?

$$K_{eq} = \frac{[NO]^2[Cl_2]}{[NOCI]^2} = \frac{(0.20)^2(0.10)}{(0.30)^2} = 4.4 \times 10^{-2}$$



IX) Type 3 K_{eq} Problems

Type 3 $K_{\rm eq}$ problems give some initial data and a $K_{\rm eq}$ constant. You must find equilibrium concentrations. OR You will be provided with some equilibrium data and a $K_{\rm eq}$ constant. You must find an initial concentration.

$$\underline{H_{2(g)}} \quad + \qquad I_{2(g)} \quad \iff \quad 2HI_{(g)}$$

I C

E

1. $\underline{H_{2(g)}} + I_{2(g)} \Leftrightarrow 2HI_{(g)} \qquad \underline{K_{eq}} = 55.6$ $[H_2]_{\underline{i}} = 0.200M$, $[I_2]_{\underline{i}} = 0.200M$ What is the equilibrium [HI]? 7.45654(0.200 - x) = 2x2HI(g) 1.4913 - 7.45654x = 2x $H_{2(g)}$ + $I_{2(g)}$ 0.200M 0.200M <u>1.49</u>13 = <u>9.45</u>654x x = 0.1577C $[HI]_{eq} = 2x = 2(0.1577)$ E 0.200 - x 0.200 - x $[HI]_{eq} = 0.315M$ Let $x = \Delta[H_2]$ $\frac{7.45}{0.200 - x}$

$$\begin{split} 2. & \underline{CO_{(g)}} \ + \ H_2O_{(g)} \Leftrightarrow CO_{2(g)} \ + \ H_{2(g)} & \underline{K_{eq}} = 4.06 \\ & [CO]_i = 0.10M, [H_2O]_i = 0.10M \end{split}$$
 What are the equilibrium concentrations of all species?

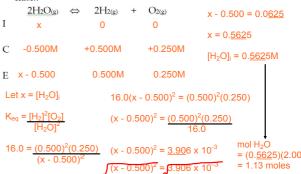
$$\begin{split} 2. \quad & \underline{CO}_{(g)} \, + \, H_2O_{(g)} \Leftrightarrow CO_{2(g)} \, + \, H_{2(g)} \quad \underline{K_{eq}} = 4.06 \\ & [CO]_{\underline{i}} = 0.10M, \, [H_2O]_{\underline{i}} = 0.10M \end{split}$$
 What are the equilibrium concentrations of all species?

3. A certain amount of H₂O was placed in a 2.00L closed flask. When equilibrium was reached, the [H₂] was 0.500M. If $\underline{K_{eq}}$ = 16.0 at this temperature, how many moles of H₂O were originally placed in the flask?

$$\frac{2H_2O_{(g)}}{2H_2O_{(g)}} \Leftrightarrow 2H_{2(g)} + O_{2(g)}$$
 I

E

3. A certain amount of H₂O was placed in a 2.00L closed flask. When equilibrium was reached, the [H₂] was 0.500M. If \underline{K}_{eq} = 16.0 at this temperature, how many moles of H₂O were originally placed in the flask?





"Rats! I thought lanthanoids and actanoids were gonna be giant robots or something."

Assignment 8

1. For the following reaction:

 $\underline{H_{2(g)}} + CO_{2(g)} \Leftrightarrow H_{2}O_{(g)} + CO_{(g)} \qquad \underline{K_{eq}} = 0.771$ If 0.0100mol of H2 and 0.0100mol of CO2 are mixed in a 1.00L container, what are the concentrations of all substances at equilibrium?

Assignment 8

1. For the following reaction:

H_{2(g)} + CO_{2(g)} \Leftrightarrow H₂O_(g) + CO_(g) $\underset{\leftarrow}{\text{Keq}} = 0.771$ If 0.0100mol of H₂ and 0.0100mol of CO₂ are mixed in a 1.00L container, what are the concentrations of all substances at equilibrium?

2. For the following reaction:

 $\frac{2IBr_{(g)} \Leftrightarrow I_{2(g)} + Br_{2(g)}}{\text{If } 0.0600 \text{mol of } \underline{IBr} \text{ is placed in a } 1.0L \text{ container, what are the } \\ \underline{\text{concentrations}} \text{ of all three substances at equilibrium?}$

2. For the following reaction:

 $\frac{2IBr_{(g)}}{2IBr_{(g)}} \Leftrightarrow I_{2(g)} + Br_{2(g)} \qquad \underline{K_{eq}} = 8.5 \times 10^{-3}$ If 0.0600mol of \underline{IBr} is placed in a 1.0L container, what are the concentrations of all three substances at equilibrium?

3. For the following reaction:

3. For the following reaction:

 $\label{eq:FeO} \frac{FeO_{(s)} + CO_{(g)} \Leftrightarrow Fe_{(s)} + CO_{2(g)}}{K_{eq} = 0.403}$ If 0.0500mol of CO and excess solid FeO are placed in a 1.00L container, what are the concentrations of CO and CO2 when equilibrium has been attained?

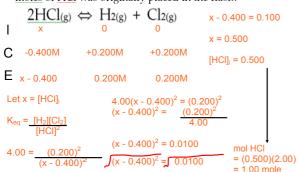
$FeO_{(s)}$	+ CO _{(g} Fe	$e_{(s)} + CO_{2(g)}$
1	0.0500M	0.00M
С	-X	+x
E	0.0500 - x	x
Let $x = \Delta[CO]$ $K_{eq} = \underline{[CO_2]}$	x = 0.014	<u>43</u> 6
[CO]	[CO ₂] _{eq} =	= 0.0144M
0.403 = x 0.050		0.0500 - x 356M

4. For the following reaction:

 $\frac{2HCl_{(g)}}{An \text{ unknown } [HCl]} \Leftrightarrow H_{2(g)} + Cl_{2(g)} \qquad \underline{K_{eq}} = 4.00$ An unknown [HCl] was added to a 2.00L flask and allowed to reach equilibrium. At equilibrium, $[H_2] = 0.200M$. How many moles of HCl was originally placed in the flask?

4. For the following reaction:

 $\begin{array}{ccc} 2HCl_{(g)} \Leftrightarrow H_{2(g)} + Cl_{2(g)} & \underline{K_{eq}} = 4.00 \\ \text{An unknown [HCl] was added to a 2.00L flask and allowed to} \\ \underline{reach} \ equilibrium. & \text{At equilibrium, [H2]} = 0.200M. & \text{How many} \\ \underline{moles} \ of \ \underline{HCl} \ was \ originally \ placed \ in the flask?} \end{array}$



5. For the following reaction:

 $\frac{N_2O_{2(g)} + H_{2(g)} \Leftrightarrow N_2O_{(g)} + H_2O_{(g)}}{N_2O_{2(g)} + H_2O_{(g)}} \qquad \underbrace{K_{eq}}_{eq} = 1.00$ If 0.150mol each of N₂O and H₂O are introduced into a 1.00L $\underbrace{flask}_{eq} \text{ and allowed to come to equilibrium, what concentration of N₂O₂ will be present at equilibrium?}$

5. For the following reaction:

 $\frac{N_2O_{2(g)} + H_{2(g)} \Leftrightarrow N_2O_{(g)} + H_2O_{(g)}}{\text{If } 0.150 \text{mol each of } N_2O \text{ and } H_2O \text{ are introduced into a } 1.00L \\ \frac{flask}{2} \text{ and allowed to come to equilibrium, what concentration of } N_2O_2 \text{ will be present at equilibrium?}$



"I was close to a loreal/through when the grant money ran out,"

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X) Type 4 K_{eq} Problems

Type 4 problems use a TRIAL K_{eq} (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_{eq} value compared to the actual K_{eq} 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?

$$\begin{array}{ccccc} \underline{CO}_{(g)} & + & H_2O_{(g)} & \Leftrightarrow & CO_{2(g)} & + & H_{2(g)} & \underline{Keq} = 10.0 \\ 0.80M & 0.050M & 0.50M & 0.40M & \end{array}$$

Example:

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

$$\underline{CO_{(g)}}$$
 + $H_2O_{(g)}$ \Leftrightarrow $CO_{2(g)}$ + $H_{2(g)}$ $\underline{K_{eq}} = 10.0$
0.80M 0.050M 0.50M 0.40M

Trial
$$K_{eq} = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{(0.50)(0.40)}{(0.80)(0.050)} = 5.0$$

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

Trial K_{eq} of 5.0 < Actual K_{eq} 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?

$$\underline{\text{H2}}_{(g)} + \text{I2}_{(g)} \Leftrightarrow 2\text{HI}_{(g)}$$
 $\underline{\text{Keq}} = 5.0$
 $2.0\text{M} \quad 1.5\text{M} \quad 3.0\text{M}$

Example:

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

$$\underline{\underline{H}_{2(g)}}$$
 + $\underline{I}_{2(g)}$ \Leftrightarrow $2H\underline{I}_{(g)}$ $\underline{\underline{K}_{eq}}$ = 5.0 $\underline{\underline{N}_{eq}}$ = 5.0

Trial
$$K_{eq} = \frac{[HI]^2}{[H_2][I_2]} = \frac{(3.0)^2}{(2.0)(1.5)} = 3.0$$

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

Trial K_{eq} of 3.0 < Actual K_{eq} of 5.0

Therefore, the system must shift RIGHT to attain equilibrium.

Example:

What will happen to the [Br2] as the system approaches equilibrium?

Example:

3. The following reaction occurs in a 2.0L container: $\frac{Br_{2(g)} + Cl_{2(g)}}{Br_{2(g)} + Cl_{2(g)}} \Leftrightarrow 2BrCl_{(g)} \qquad \frac{K_{eq}}{K_{eq}} = 3.2 \times 10^{-2} \text{ by 2 to}$ Quantities of gases were found to be as follows: $Br_{2} = 0.60 \text{ mol}, Cl_{2} = 0.80 \text{ mol}, BrCl_{2} = 2.20 \text{ mol}$ What will happen to the [Br₂] as the system approaches equilibrium?

Trial
$$K_{eq} = \frac{[BrCl]^2}{[Br_2][Cl_2]} = \frac{(1.1)^2}{(0.30)(0.40)} = 1.0 \times 10^1$$

The trial K_{eq} does not equal the actual K_{eq} so currently not at equilibrium. Trial K_{eq} of 1.0 x 10¹ > Actual K_{eq} of 3.2 x 10⁻²

Therefore, the system must shift LEFT to attain equilibrium, so [Br₂] will increase.



Assignment 9

For the following reaction: 2O₃(g) ⇔ 3O₂(g) Keq = 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 O₃ and 3.0mol O₂

Assignment 9 *divide moles by 10.0 to get molarities

For the following reaction: 2O₃(g) ⇔ 3O₂(g) Keq = 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 O₃ and 3.0mol O₂

Trial
$$K_{eq} = \frac{[O_2]^3}{[O_3]^2} = \frac{(0.30)^3}{(0.060)^2} = 7.5$$

The trial K_{eq} does not equal the actual K_{eq} so currenot at equilibrium.

Trial K_{eq} of 7.5 < Actual K_{eq} of 75

Therefore, the system must shift RIGHT to attain equilibrium.

- 2. Consider the following reaction: $\underline{2SO_{2(g)}} + O_{2(g)} \Leftrightarrow 2SO_{3(g)} \ \underline{K_{eq}} = 75$ A student places 0.50moles SO₂, 0.080mol O₂, and 1.0mol SO₃ into a 1.0L flask. The student predicts that the [SO₂] will decrease as equilibrium is established. Do you agree with the student's prediction? Explain using appropriate calculations.
- 2. Consider the following reaction: $\underline{2SO_{2(g)}} + O_{2(g)} \Leftrightarrow 2SO_{3(g)}$ $\underline{Keq} = 75$ A student places 0.50moles SO₂, 0.080mol O₂, and 1.0mol SO₃ into \underline{a} 1.0L flask. The student predicts that the [SO₂] will decrease as $\underline{equilibrium}$ is established. Do you agree with the $\underline{student's}$ $\underline{prediction}$? Explain using appropriate calculations.

Trial
$$K_{eq} = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{(1.0)^2}{(0.50)^2(0.080)} = 5.0 \times 10^1$$

The trial K_{eq} does not equal the actual K_{eq} so currentl not at equilibrium.

Trial
$$K_{eq}$$
 of 5.0 x 10^1 < Actual K_{eq} of 75

Therefore, the system must shift RIGHT to attain equilibrium, so $[SO_2]$ will decrease. I agree with the student.

3. Consider the following reaction:

 $\begin{array}{ccc} 2C_{(s)}\pm O_{2(g)} & \Leftrightarrow 2CO_{(g)} & \underline{K_{eq}} = 1.20\times 10^{-2}\\ \text{If 2.0mol C, 0.800mol O2, and 0.600mol CO are placed into a 1.0L}\\ \underline{flask}\text{, in which direction will the equilibrium shift in order to}\\ \underline{achieve}\text{ equilibrium? What will happen to the [C]? Show all calculations.} \end{array}$

3. Consider the following reaction:

 $\begin{array}{ccc} 2C_{(s)} \pm O_{2(g)} & \Leftrightarrow 2CO_{(g)} & \underline{K_{eq}} = 1.20 \times 10^{-2} \\ \text{If 2.0mol C, 0.800mol O2, and 0.600mol CO are placed into a 1.0L} \\ \underline{flask}\text{, in which direction will the equilibrium shift in order to} \\ \underline{achieve}\text{ equilibrium? What will happen to the [C]? Show all} \\ \underline{calculations}. \end{array}$

Trial
$$K_{eq} = \frac{[CO]^2}{[O_2]} = \frac{(0.600)^2}{(0.800)} = 0.45$$

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

Trial K_{eq} of 0.45 > Actual K_{eq} of 1.20 x 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: $\underline{H_{2(g)}} + Cl_{2(g)} \Leftrightarrow 2HCl_{(g)} \underline{K_{eq}} = 0.15$ Equal moles of each of the three gases are in a 1.0L vessel. What <u>direction</u> will the reaction shift in order to reach equilibrium?
- 4. For the following reaction: $\underline{H_{2(g)}} + Cl_{2(g)} \Leftrightarrow 2HCl_{(g)} \underline{K_{eq}} = 0.15$ Equal moles of each of the three gases are in a 1.0L vessel. What <u>direction</u> will the reaction shift in order to reach equilibrium?

Trial
$$K_{eq} = \frac{[HCI]^2}{[H_2][CI_2]} = \frac{(x)^2}{(x)(x)} = \frac{x^2}{x^2} = 1$$

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

Trial K_{eq} of 1 > Actual K_{eq} of 0.15

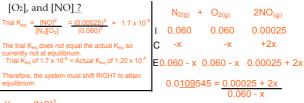
Therefore, the system must shift LEFT to attain equilibrium.

5. *Type III & Type IV hybrid question © Consider the following reaction:

 $\frac{N_{2(g)} + O_{2(g)}}{N_{2(g)}} \Leftrightarrow 2NO_{(g)} \qquad \underline{K_{eq}} = 1.20 \times 10^{-4}$ If 0.060mol N_2 , 0.060mol O_2 , and 0.00025mol N_2 0 are mixed in a 1.0L container, in which direction will the reaction proceed in $\underline{\text{order}}$ to achieve equilibrium? What will be the equilibrium [N₂], [O₂], and [NO]?

5. *Type III & Type IV hybrid question © Consider the following reaction:

 $N_{2(g)} + O_{2(g)} \Leftrightarrow 2NO_{(g)}$ $N_{eq} = 1.20 \times 10^{-4}$ If 0.060mol N₂, 0.060mol O₂, 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 [N₂], [O₂] and [NO₁]?



$$\begin{split} K_{eq} &= \underbrace{[NO]^2}_{[N_2][O_2]} & x = \underbrace{2.02}_{2.025} \times 10^{-4} \\ 1.20 \times 10^{-4} &= \underbrace{(0.00025 + 2x)^2}_{(0.060 - x)^2} & [N_2]_{eq} \& [O_2]_{eq} = 0.060 - x = 0.060M \\ &= [NO]_{eq} = 6.6 \times 10^{-4}M \end{split}$$