Chemical Equilibrium

1.1 Reversible Reactions

Typically when we think of what happens during a chemical reaction we think of the reactants getting totally used up so that none are left ending up with only products.

Also, we generally consider chemical reactions as one-way events.

Here are some examples of reactions that can be reversed:

Nitrogen dioxide, NO_2, a reddish-brown gas, reacts to form colourless dinitrogen tetroxide, N_2O_4:

$$2\ NO_{2\ (g)} \rightarrow N_2O_{4\ (g)}$$

But the reaction can also go the other way

$$N_2O_{4\ (g)} \rightarrow 2\ NO_{2\ (g)}$$

We typically write a reaction that can go in both directions by using a double arrow

$$\boxed{2\ NO_{2\ (g)} \rightleftarrows N_2O_{4\ (g)}}$$

$Fe_3O_{4\,(s)} + 4\ H_{2\,(g)} \rightarrow 3\ Fe_{(s)} + 4\ H_2O_{(g)}$

The reverse reaction

$3\ Fe_{(s)} + 4\ H_2O_{(g)} \rightarrow Fe_3O_{4\,(s)} + 4\ H_{2\,(g)}$

$Fe_3O_{4\,(s)} + 4\ H_{2\,(g)} \rightleftarrows 3\ Fe_{(s)} + 4\ H_2O_{(g)}$

forward reaction

reverse reaction,

1.2 Equilibrium

Here's another example of a reversible reaction - dissolving salt in a beaker of water,

$$NaCl_{(s)} \rightleftharpoons NaCl_{(aq)}$$

If you keep adding more and more solid salt, eventually you'll reach the point where no more salt dissolves, and the excess sits at the bottom of the beaker. we have a saturated solution.

Has the dissolving reaction stopped? It would appear so, but that's not the case

What happens in our saturated solution, which has reached the point of **equilibrium**,

both the forward $NaCl_{(s)} \rightarrow NaCl_{(aq)}$

and reverse $NaCl_{(aq)} \rightarrow NaCl_{(s)}$

reactions are still going on, but at the same ***rate***.

This in effect cancels out any observable, or measurable, changes in our system.

At the same rate that solid NaCl produces aqueous NaCl (dissolved salt),

the dissolved salt is recrystallizing to form more solid NaCl.

Equilibrium is the state at which the rate of the forward reaction equals the rate of the reverse reaction.

At the point of equilibrium, no more measurable or observable changes in the system can be noted.

It is important for you to understand that equilibrium means the ***rates*** of the forward and reverse reactions are equal;

it does ***not*** mean that there are equal amount of reactants and products present at equilibrium.

Equilibrium is *dynamic* - both forward and reverse reactions continue,

even though the reaction appears to have stopped.

In order for a reversible reaction to reach the point of equilibrium,

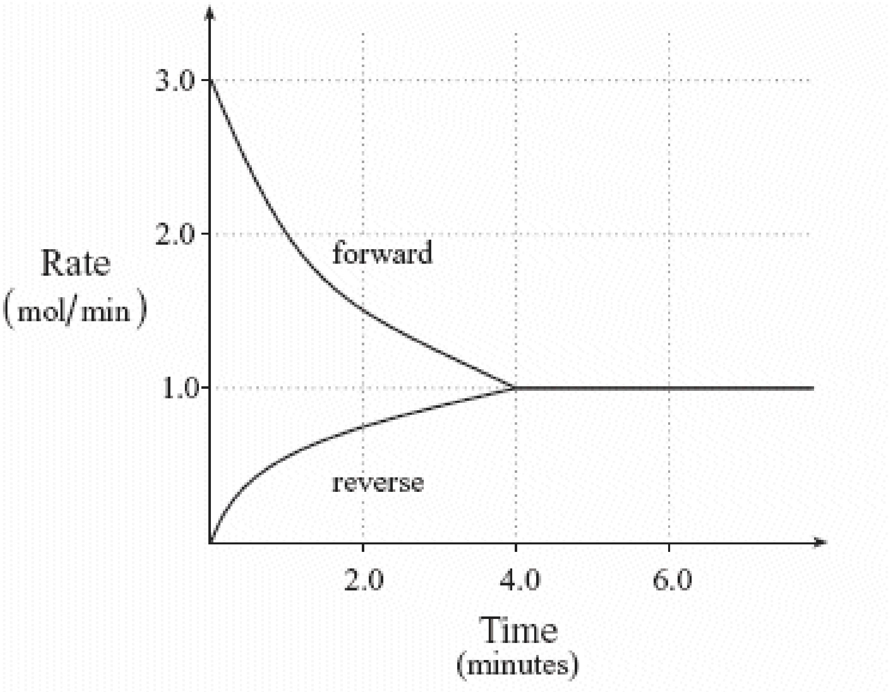
the reaction must be carried out in a **closed system**

no additional reactants can be added or

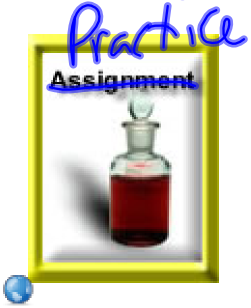
products removed.

steady state system.

Reactants being added and products being removed
(assembly line)


3.0
2.0
1.0
Rate
(mol/min)
forward
reverse
2.0
4.0
6.0
Time
(minutes)

Practice


~~Assignment~~

2.1 The Equilibrium Constant, K_{eq}

In the reaction:

$$aA + bB \rightleftharpoons cC + dD$$

$$K_{eq} = \frac{[C]^c \times [D]^d}{[A]^a \times [B]^b}$$

This mathematical relationship exists for all equilibrium systems,

and produces a constant ratio called the ***equilibrium constant, K_{eq}*** .

This equation is sometimes called the **mass-action expression.**

For the reaction between hydrogen and iodine gas to produce hydrogen iodide:

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

the equilibrium constant expression will be:

Pull

At equilibrium:	$[H_2] = 0.022$ M $[I_2] = 0.022$ M $[HI] = 0.156$ M

We substitute these values into our equilibrium expression and solve for K_{eq}:

Pull

K_{eq} relates the concentrations of products to reactants at equilibrium.

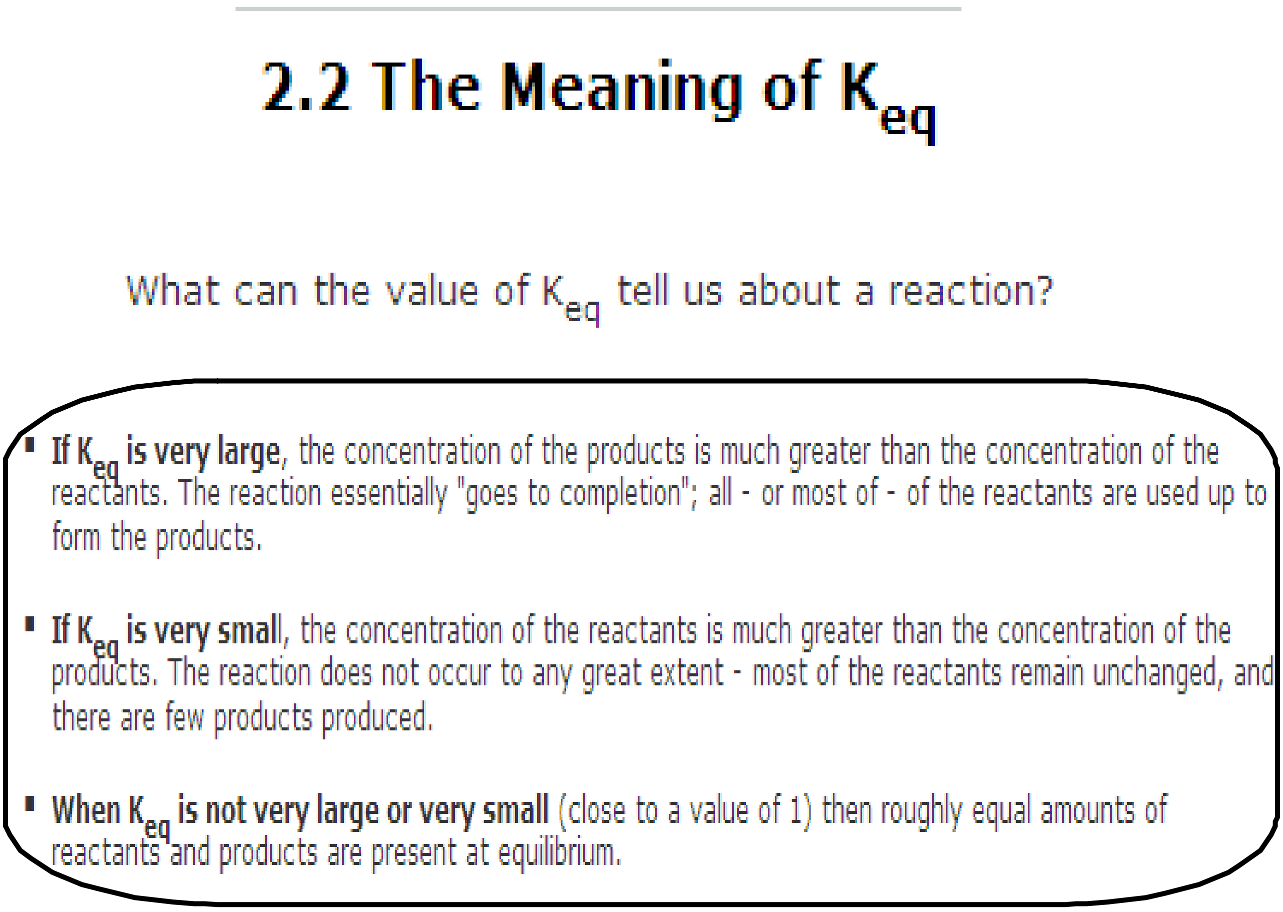
Be on the lookout for (aq) or (g) participants

$$CaO_{(s)} + CO_{2\,(g)} \rightleftharpoons CaCO_{3\,(s)}$$

The equilibrium constant for this reaction is

Pull

Pull



2.2 The Meaning of K_{eq}

What can the value of K_{eq} tell us about a reaction?

- **If K_{eq} is very large**, the concentration of the products is much greater than the concentration of the reactants. The reaction essentially "goes to completion"; all - or most of - of the reactants are used up to form the products.
- **If K_{eq} is very small**, the concentration of the reactants is much greater than the concentration of the products. The reaction does not occur to any great extent - most of the reactants remain unchanged, and there are few products produced.
- **When K_{eq} is not very large or very small** (close to a value of 1) then roughly equal amounts of reactants and products are present at equilibrium.

Here are some examples to consider:

the decomposition of ozone, O_3

$2\ O_{3\ (g)} \rightleftarrows 3\ O_{2\ (g)}$ $K_{eq} = 2.0 \times 10^{57}$

K_{eq} is very large, indicating that mostly O_2 is present in an equilibrium system, with very little O_3

production of nitrogen monoxide

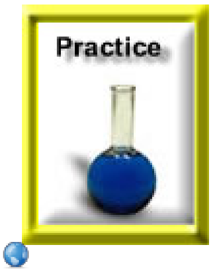
$N_{2\ (g)} + O_{2\ (g)} \rightleftarrows 2\ NO_{(g)}$ $K_{eq} = 1.0 \times 10^{-25}$

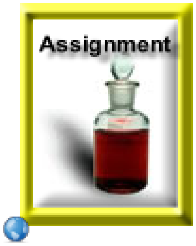
Very little NO is produced by this reaction; N_2 and O_2 do not react readily to produce NO (lucky for us - otherwise we would have little oxygen to breath in our atmosphere!)

reaction of carbon monoxide and water

$CO_{(g)} + H_2O_{(g)} \rightleftarrows CO_{2\ (g)} + H_{2\ (g)}$ $K_{eq} = 5.09$ (at 700 K)

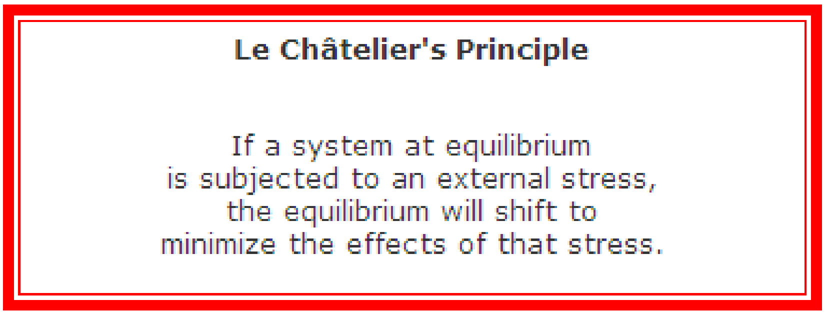
The concentrations of the reactants are very close to the concentrations of the products at equilibrium





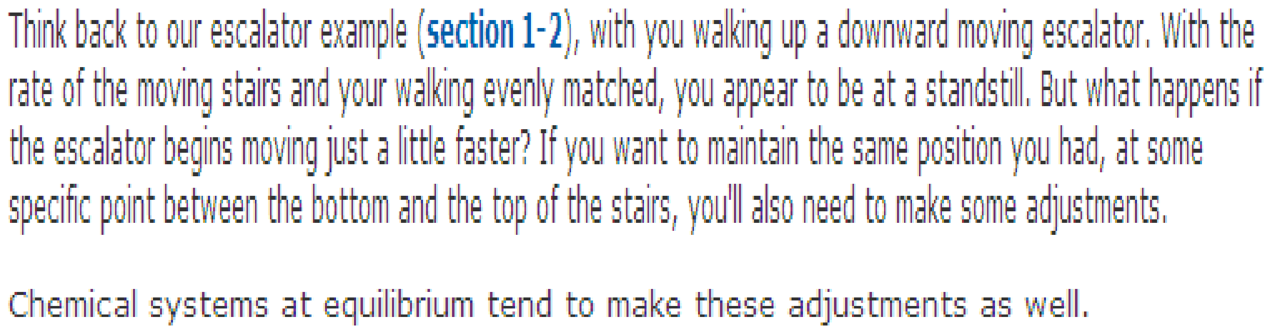
3.1 Le Châtelier's Principle

A French Chemist,Henri Louis Le Chatelier, was the first to describe the following:



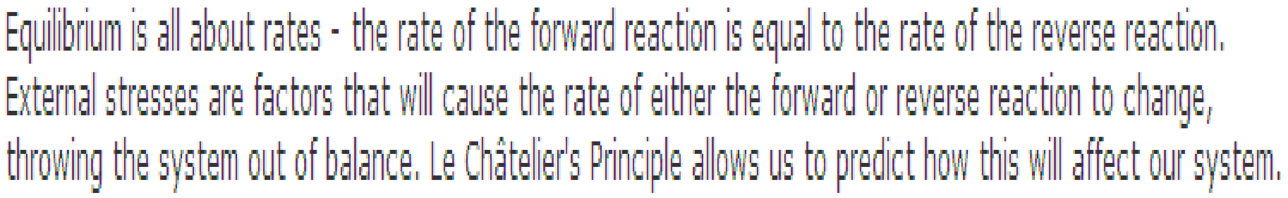
Le Châtelier's Principle

If a system at equilibrium
is subjected to an external stress,
the equilibrium will shift to
minimize the effects of that stress.



Think back to our escalator example (section 1-2), with you walking up a downward moving escalator. With the rate of the moving stairs and your walking evenly matched, you appear to be at a standstill. But what happens if the escalator begins moving just a little faster? If you want to maintain the same position you had, at some specific point between the bottom and the top of the stairs, you'll also need to make some adjustments.

Chemical systems at equilibrium tend to make these adjustments as well.



Equilibrium is all about rates - the rate of the forward reaction is equal to the rate of the reverse reaction. External stresses are factors that will cause the rate of either the forward or reverse reaction to change, throwing the system out of balance. Le Châtelier's Principle allows us to predict how this will affect our system.

In our unit on Kinetics we examined factors that influenced reaction rates. Recall these factors:

1. concentration
2. pressure and volume
3. temperature, and
4. catalysts

We'll see how changing these factors affects a system at equilibrium.

3.2 Changes in Concentration

Consider the following equilibrium system:

A + B <-----> C

If we add more A to the system, that is increase [A] (concentration of A), what will happen? According Le Chatelier, the system will **shift** to minimize this stressor.

Since A is on the reactant side, the rate of the forward reaction will increase to "use up" the additional reactant. This will cause the equilibrium system to **shift right** producing more C. There are a few ways we can say what happens when we add more A, that is increase [A]. They all mean the same thing.

- equilibrium shifts right
    - equilibrium shifts to the product side
    - the forward reaction is favored

How does the addition of one reactant cause other participants to behave/change?

A since this is what we added to cause the stress, the concentration of A ([A]) will increase

[A] goes up

B equilibrium will shift right which will use up the reactants. The concentration of B ([B]) will decrease as the forward rate continues

[B] goes down

C with the forward rate increasing, more products are formed and the concentration of C ([C]) will increase

[C] goes up

Now, what about K_{eq}?

The value of K_{eq} **does not change** when changes in concentration causes shifts in equilibrium

Now, what about if we stressed the product side? What if we add more C? What if we increase [C]? Again, equilibrium will shift to minimize this stress. It will shift to use up added substance, in this case, C. In this case the equilibrium will shift to favor the reverse reaction since the reverse reaction will have to use up the additional C.

Again, the addition of C ([C] increasing) can be expressed in different ways all meaning the same thing.

-equilibrium shifts left
-equilibrium shifts to the reactant side
-the reverse reaction is favored.

Now, how the concentrations of the other participants change?

A [A] goes up as the reverse reaction is favored

B [B] goes up as the reverse reaction is favored

C [C] goes up as this is what we initially added.

Concentration can also act as a stressor by **removing**a substance from the reaction instead of adding it. This is often accomplished by adding a new substance that reacts with something already in the reaction.

Let's remove B from the system (perhaps by adding "D" causing B to leave the system). What will happen now? The system's equilibrium will shift to replace the missing B. The reverse reaction will be favored because that is the direction that produces B. The equilibrium will:

- shift left
-shift to the reactant side
-shift to favor the reverse reaction

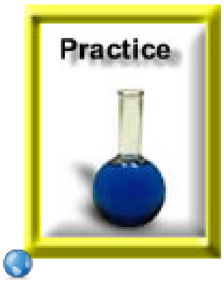
How does the concentration of the other participants change to minimize the loss of B ([B] goes down)?

A [A] goes up as reverse reaction is favored

B [B] goes down as it was initially removed, however [B] will go up
as the reverse reaction is favored

C [C] will go down as the reverse reaction is favored

Let's try these together



3.3 Changes in Volume & Pressure

Changing the pressure or volume of a container enclosing an equilibrium system will only affect the reaction if gases are present.

How does changing pressure and volume affect equilibrium systems?

- If you increase the pressure of a system at equilibrium (typically by reducing the volume of the container), the stress will best be reduced by reaction favouring the side with the ***fewest*** moles of gas, since fewer moles will occupy the smallest volume.

- Conversely, if you decrease the pressure (by increasing the volume of the container), equilibrium will shift to favour the side with the ***most*** moles of gas, since more moles will occupy a greater volume.

- If both sides of the equation have the same number of moles of gas, then there will be no change in the position of equilibrium.

consider the following equilibrium system:

A(g) <-----> 2B(g)

If we increase pressure (decrease volume), what will happen?

Which side has the fewest moles of gas?

The reactant side has only 1 mole of gas while the product side has 2 moles of gas.

Increasing pressure will favor the side with the fewest moles of gas. Therefore, the equilibrium will shift to the left (reactant side or reverse reaction is favored)

Now, how about this equilibrium system:

2A(g) + B(g) <-----> 4C(g)

If we decrease the pressure (increase the volume), what will happen?

Which side has the most moles of gas?

The reactant side has 3 moles of gas while the product side has 4 moles of gas.

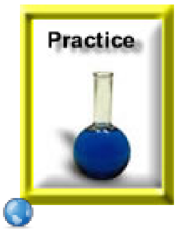
Decreasing the pressure will favor the side with the most moles of gas. Therefore equilibrium will shift right (forward reaction is favored or reaction shifts to the product side)

Finally, consider the following equilibrium system:

$3A(g) + 2B(g) \longleftrightarrow C(g) + 4D(g)$

If there is an increase in pressure, what will happen?

Notice both sides have 5 moles of gas. Since these quantities are equal, there will be no shift in equilibrium.



3.4 Changes in Temperature

exo $\Delta t \uparrow$
endo $\Delta t \downarrow$

When temperature is the stress that affects a system at equilibrium, there are two important consequences:

- an increase in temperature will favour that reaction direction that ***absorbs*** heat (i.e. the endothermic reaction)
- the value of K_{eq} will change

Consider the following equilibrium system:

endo - forward
exo - reverse

$A_{(g)} \longleftrightarrow 2B_{(g)}$ $\Delta H = 58kJ$

recall this means:

$A_{(g)} + 58kJ \longleftrightarrow 2B_{(g)}$

-positive values for H are endothermic and the term goes on the reactant side
-negative values for H are exothermic and the term goes on the product side

Now, if we increase temperature (adding heat), equilibrium will shift to use up the heat. Which way will our system shift?

Consider the following equilibrium system:

$A_{(g)} \longleftrightarrow 2B_{(g)}\ \Delta H = 58kJ$

$$\overrightarrow{A(g) + 58KJ} \longleftrightarrow 2B(g)$$

Which direction is endothermic? forward

This system will shift in the forward direction (favor the reactant side or shift right)

Also, the value of K_{eq} will change. Why? Because forward direction is endo

endo $\Delta H+$

Keq will increase

Mathematically, here's the reason:

$$K_{eq} = \frac{[products]\uparrow}{[reactants]\downarrow}$$

If the forward reaction is favored (add heat), then more products are formed with fewer reactants. As a result:

$$K_{eq} = \frac{[\text{products}]}{[\text{reactants}]} \qquad \frac{\text{big \#}}{\text{small \#}}$$

creates a larger # overall

If the reverse reaction is favored (remove heat), then more reactants are made with fewer products. As a result:

$$K_{eq} = \frac{[\text{products}]}{[\text{reactants}]} \qquad \frac{\text{small \#}}{\text{big \#}}$$

creates a smaller # overall

So, for our reaction:

$$A(g) + 58KJ \text{ <-----> } 2B(g)$$

increasing temperature will favor the forward direction (endo direction), and the value of K_{eq} will increase.

Decreasing temperature (removing heat) will favor the exothermic direction. For example:

exo - for
endo - rev.

A(g) <-----> 3B(g) $\Delta H = -110$ kJ

A(g) <-----> 3B(g) + 110 kJ

If we decrease the temperature of this system, which direction will be favored? forward

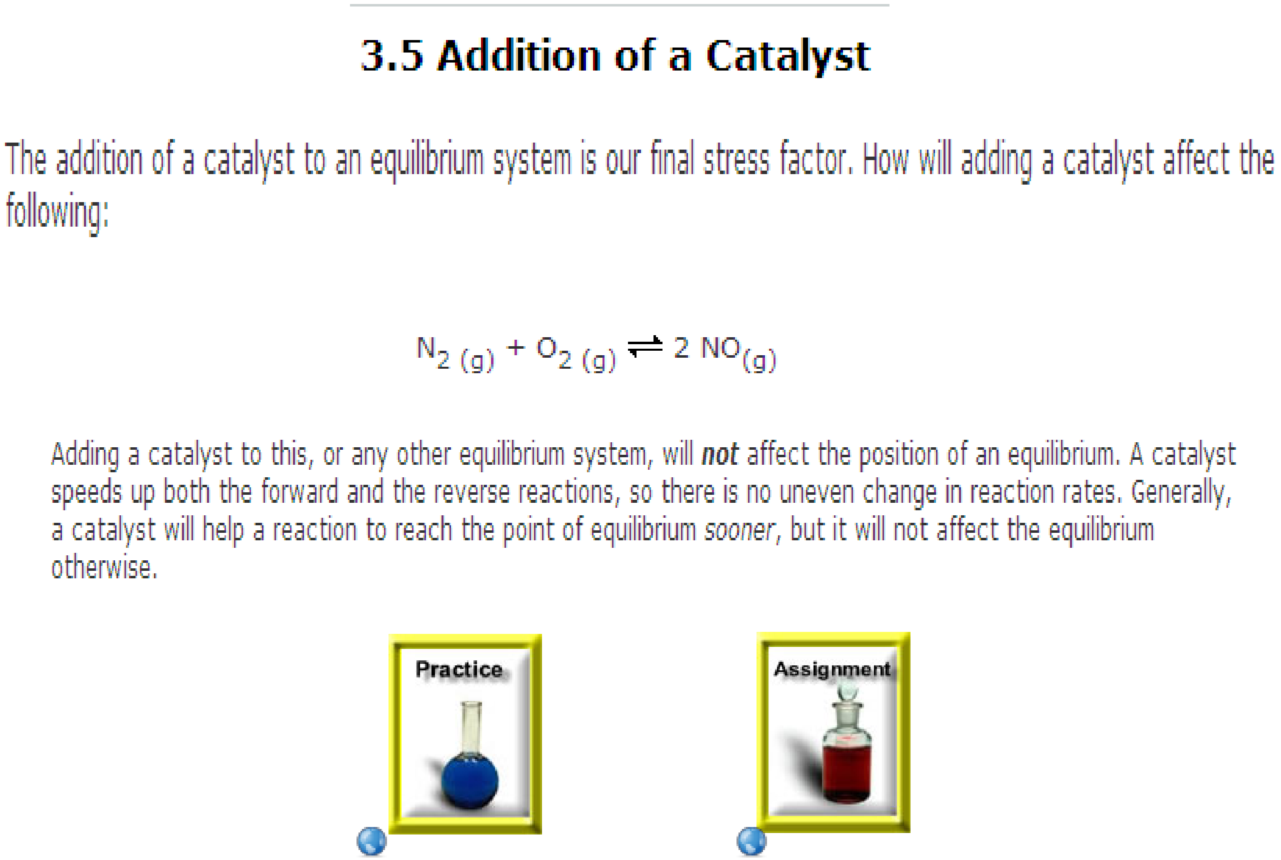
Which direction is exothermic? forward

This system will shift right.

What happens to Keq? Why?

$$K_{eq} = \frac{[B]^3}{[A]} \quad \frac{\text{big \#}}{\text{small \#}}$$

$\therefore$ overall, K_{eq} will increase!



3.5 Addition of a Catalyst

The addition of a catalyst to an equilibrium system is our final stress factor. How will adding a catalyst affect the following:

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

Adding a catalyst to this, or any other equilibrium system, will ***not*** affect the position of an equilibrium. A catalyst speeds up both the forward and the reverse reactions, so there is no uneven change in reaction rates. Generally, a catalyst will help a reaction to reach the point of equilibrium *sooner*, but it will not affect the equilibrium otherwise.