

Key

7. If the temperature remains constant in an equilibrium:

a) Will changing the **concentration** of one of the substances change the value of  $K_{eq}$ ?

NO  
Answer \_\_\_\_\_

b) Will changing the **total pressure** of the system change the value of  $K_{eq}$ ?

NO  
Answer \_\_\_\_\_

c) Will changing the **total volume** of the system change the value of  $K_{eq}$ ?

NO  
Answer \_\_\_\_\_

d) Will adding a **catalyst** change the value of  $K_{eq}$ ?

NOPE!!  
Answer \_\_\_\_\_

8. The  $K_{eq}$  for the reaction:  $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$  is 85 at  $25^\circ C$

Determine the value of  $K_{eq}$  for the reaction:  $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$  at  $25^\circ C$

$$\frac{[H_2][I_2]}{[HI]^2} = \frac{85}{\text{Answer}} = \frac{1}{85}$$

$$\frac{[HI]^2}{[H_2][I_2]} = \frac{1}{85}$$

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## Chemistry 12: Lesson 7 – Equilibrium

### Equilibrium Constants (K<sub>eq</sub>)

#### What is K<sub>eq</sub>?

The "K" in K<sub>eq</sub> stands for "Constant". The "eq" means that the reaction is at equilibrium.

**Very roughly**, K<sub>eq</sub> tells you the ratio for a given reaction at equilibrium at a certain temperature.

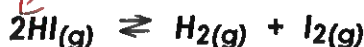
$$K_{eq} = \frac{[\text{Products}]}{[\text{Reactants}]}$$

can also be done for pressure  
 $\frac{P}{R}$

The only thing that changes the value of K<sub>eq</sub> for a given reaction is the temperature!

b/c temp can change [K] is

#### Writing K<sub>eq</sub> Expressions



and the K<sub>eq</sub> expression was:

$$K_{eq} = \frac{[\text{I}_2][\text{H}_2]}{[\text{HI}][\text{HI}]}$$

$$\rightarrow K_{eq} = \frac{[\text{I}_2][\text{H}_2]}{[\text{HI}]^2}$$

notice coefficient became exponent.

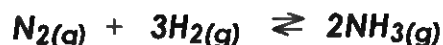
Also, notice that the **coefficient "2"** in the "**2**HI" in the **equation** ends up as an **exponent** for [HI] in the **K<sub>eq</sub> expression**.

1. With this in mind, see if you can write the K<sub>eq</sub> expression for the following reaction:



$$K_{eq} = \frac{[\text{N}_2]^3 [\text{H}_2]}{[\text{NH}_3]^2}$$

2. Write the K<sub>eq</sub> expression for the following reaction:



$$K_{eq} = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

### The $K_{eq}$ Expressions for Solids and Liquids

Consider the following reaction:  $\text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g)$   
 You might expect the  $K_{eq}$  expression to be something like:

$$K_{eq} = \frac{[\text{CaO}][\text{CO}_2]}{[\text{CaCO}_3]}$$

But when you consider a solid, the number of moles per litre or molecules in a certain volume is constant. The molecules everywhere in the solid are about the same distance apart and are the same size:

Since CaO and CaCO<sub>3</sub> are <sup>Solids</sup> ~~constant~~, we can assume that their **concentrations are constant**.

We can therefore rewrite the  $K_{eq}$  expression as follows:

$$K_{eq} = \frac{[\text{constant}][\text{CO}_2]}{[\text{constant}]}$$

In other words, the **concentrations of the solids** are incorporated into the value for  $K_{eq}$ .

$$K_{eq} = [\text{CO}_2]$$

Liquids also have a fairly constant concentration. They don't expand or contract that much even with changes in temperature.

When we write the  $K_{eq}$  expression for a reaction with solids or liquids, we simply leave out the solids and the liquids.

pure

→ liquids are pure if they are the only liquid in the system

Gases and aqueous solutions do undergo changes in concentration so they are always included in the  $K_{eq}$  expression.

3. Write the  $K_{eq}$  expression for the following reaction:



$$K_{eq} = \frac{[\text{CO}_2]}{[\text{HF}]^2}$$

→ pure water (only liquid)

## Value of $K_{eq}$ and the Extent of Reaction

Remember that  $K_{eq}$  is a **fraction** (or ratio). The products are on the top and the reactants are on the bottom.

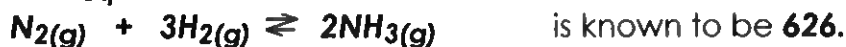
The larger the numerator  $\rightarrow$  the larger the value of the fraction.

The larger the denominator  $\rightarrow$  the smaller the value of the fraction.

$$\frac{P \uparrow}{R} = \uparrow K_{eq}$$

$$\frac{P}{R \uparrow} = \downarrow K_{eq}$$

At 200 °C, the  $K_{eq}$  for the reaction:



$K_{eq}$  is equal to the ratio =  $\frac{[NH_3]^2}{[N_2][H_2]^3}$

Since this ratio is very large (626) at 200°C, we can say that  $[NH_3]^2$  (the numerator) must be quite large and  $[N_2][H_2]^3$  (the denominator) must be small:



In other words, a large value for  $K_{eq}$  means that at equilibrium, there is lots of product and very little reactant left.

**The larger the value for  $K_{eq}$  the closer to completion the reaction is at equilibrium.**

(NOTE: "Completion" means reactants have been completely converted to products.)

A very small value for  $K_{eq}$  means that there is **very little product** and **lots of reactant** at equilibrium.

In other words, a very small  $K_{eq}$  means that the reaction has not occurred to a very great extent once equilibrium is reached.

Consider the following reaction:  $A + B \rightleftharpoons C + D$        $K_{eq} = 1.0$

The  $K_{eq}$  expression is:

$$K_{eq} = \frac{[C][D]}{[A][B]} = 1.0$$

$\therefore$  rxn has gone half way as the reactants and products are in 1:1 ratio

4. For the reaction:  $Cu(OH)_2(s) \rightleftharpoons Cu^{2+}(aq) + 2OH^-(aq)$        $K_{eq} = 1.6 \times 10^{-19}$

Describe the extent of the reaction and the relative amounts of reactant and product at equilibrium.

$$1.6 \times 10^{-19} = [Cu^{2+}][OH^-]^2$$

A small  $K_{eq}$  means more reactants than products  
The rxn has not occurred.  
(very little  $Cu^{2+}$  &  $OH^-$ )

Keq and Temperature

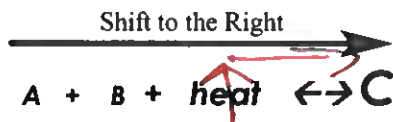
When the temperature changes, the value of Keq also changes.

— only with temp!!!

Consider the following **endothermic** reaction:  $A + B + \text{heat} \rightleftharpoons C$   
 The  $K_{eq}$  expression for this is:

$$K_{eq} = \frac{[C]}{[A][B]}$$

Now, let's say that we **increase the temperature** of this system. By LCP, adding heat to an endothermic reaction will make it **shift to the right**:



Because it **shifts to the right**, a new equilibrium is established which has a **higher [C]** and a **lower [A] and [B]**.

Therefore the  $K_{eq}$  will have a large **numerator** and a small **denominator**:

$$K_{eq} = \frac{[C]}{[A][B]}$$

This will make the value of  $K_{eq}$  larger than it was before.

So we can summarize by saying:

When the **temperature is increased** in an **endothermic** reaction, the equilibrium will **shift to the right** and the **value of Keq will increase**.

So we can say:

When the **temperature is decreased** in an **endothermic** reaction, the equilibrium will **shift to the left** and the **value of Keq will decrease**.

5. Given the equation for an **exothermic** reaction:  $C + D \rightleftharpoons E + \text{heat}$

a) Write the  $K_{eq}$  expression for this reaction:

$$K_{eq} = \frac{[E]}{[C][D]}$$

b) If the **temperature** of this exothermic reaction is **increased**, the equilibrium will shift

left

- c) The shift will make [E] smaller er, and [C] and [D] larger er than they were before.
- d) Since the numerator is small er and the denominator is bigg er, the value of the  $K_{eq}$  will be small er than it was before.
- e) If the temperature of this system is **decreased**, the equilibrium will shift to the right, and the value of  $K_{eq}$  will increase.
- f). Fill in the following blanks:

When the **temperature is increased** in an **exothermic** reaction, the equilibrium will

shift to the left and the value of  $K_{eq}$  will decrease.

**and**

When the **temperature is decreased** in an **exothermic** reaction, the equilibrium will

shift to the right and the value  $K_{eq}$  will increase.

6. The reaction:  $X + Y \rightleftharpoons Z$  has a  $K_{eq} = 235$  at  $100^{\circ}\text{C}$ .

When the temperature is raised to  $200^{\circ}\text{C}$ , the value for  $K_{eq} = 208$

Is this reaction endothermic or exothermic? Exothermic

Explain your answer. if  $K_{eq} \downarrow$ , reactants must have  $\uparrow$  so eq. shifted  $\leftarrow$  so heat term must be on the right.  $\therefore$  exo.

$K_{eq} \downarrow$   $\frac{P_{prod}}{R_{prod}} \downarrow$   
 $\uparrow$   $\uparrow$

## Changes in Concentration and $K_{eq}$

Now, as you know, changing the concentration of one of the reactants or products will cause the reaction to shift right or left. **But this does not change the value for  $K_{eq}$  as long as the temperature remains constant.**

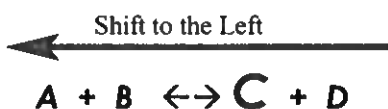
Consider the reaction:  $A + B \rightleftharpoons C + D$        $K_{eq} = 4.0$

The  $K_{eq}$  expression is:

$$K_{eq} = \frac{[C][D]}{[A][B]} = 4.0$$

Let's say we quickly add some C to the system at equilibrium. Of course [C] would increase, and temporarily equilibrium would be destroyed.

But, of course, things don't stay like this. When [C] has been increased, the equilibrium will shift to the **left** (by LeChatelier's Principle)



In the shift to the left [A] and [B] will get a little larger and the big [C] will get smaller and [D] will get smaller. – **the ratio will go back to the original value**

If no temp change, the eq. will shift just enough to keep ratios equal and  $K_{eq}$  constant.

## Effect of Catalysts on the Value of $K_{eq}$

As we saw in the lesson on LeChatelier's Principle: Addition of a **catalyst** speeds up the forward reaction and the reverse reaction by *the same amount*. Therefore, it does not cause any shift of the equilibrium. Because there is no shift, the value of the  $K_{eq}$  will also remain unchanged.

Addition of a catalyst does not change  $K_{eq}$ .



Effect of Pressure or Volume on the Value of  $K_{eq}$ 

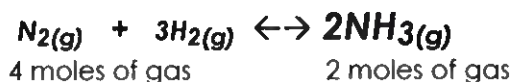
Like changes in concentration, changes in the total pressure or volume can cause an equilibrium to shift left or right. (If there is a different number of moles of gas on each side.)

For example: Given the reaction:  $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$   $K_{eq} = 626$

Let's say the **volume** of the container is **decreased**. This **increases** the **total pressure** of the system. Increasing the pressure will increase the concentrations of all three species the same amount.

Since there are more moles of gas ( $N_2(g) + 3H_2(g)$ ) on the left side, there is more "stuff" increased in the denominator of the ratio, so the value of the ratio will temporarily go down:

But, by LCP, **increased pressure** will cause the equilibrium to shift to the **right**:

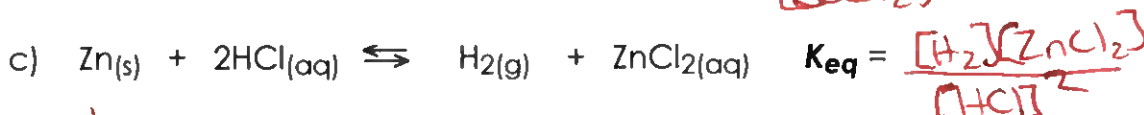
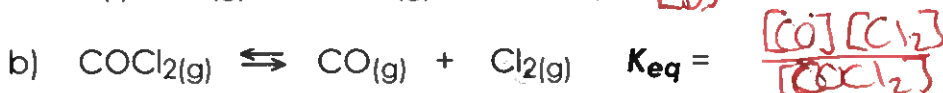
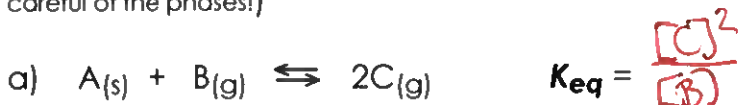


This will bring  $[NH_3]$  up, so the numerator of the ratio ( $[NH_3]^2$ ) will increase. Thus, the value of the ratio increases again. And guess what? It increases until it just reaches 626 again. The ratio is now equal to  $K_{eq}$  and equilibrium has again been achieved!

A change in total volume or total pressure will ~~not~~ not change  $K_{eq}$ . The eq. will always shift to keep it constant.

More Questions:

1. Write the **Equilibrium Constant Expression** for each of the following reactions. (Be careful of the phases!)



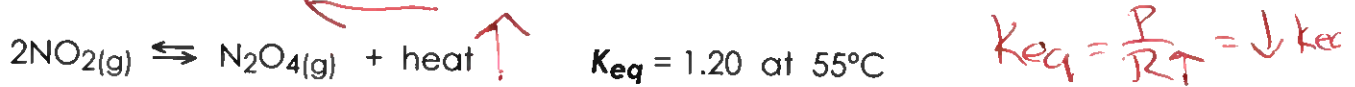
2. A large value for  $K_{eq}$  means that a reaction has gone close to completion.



3. A Small value for  $K_{eq}$  means that a reaction has not occurred to much of an extent.

4. A value of around 1.0 for  $K_{eq}$  means rxn is half way  $[P] = [R]$

5. Given the equilibrium equation:



What will happen to the value of  $K_{eq}$  if the temperature is increased?

$K_{eq} \downarrow$

Explain why? \_\_\_\_\_

6. For the reaction:  $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$   $K_{eq} = 2.24$  at  $227^\circ C$

$K_{eq} = 33.3$  at  $487^\circ C$

Is this reaction endothermic or exothermic?

endothermic

Explain your answer

$\uparrow \text{temp} = \uparrow K_{eq} \therefore P \uparrow$  so shifted  $\rightarrow$   
so heat is on reactant side  $T K_{eq} = \frac{P \uparrow}{R}$

7. If the temperature remains constant in an equilibrium:

a) Will changing the **concentration** of one of the substances change the value of  $K_{eq}$ ?

Answer NO

b) Will changing the **total pressure** of the system change the value of  $K_{eq}$ ?

Answer NO

c) Will changing the **total volume** of the system change the value of  $K_{eq}$ ?

Answer NO

d) Will adding a **catalyst** change the value of  $K_{eq}$ ?

Answer NO

8. The  $K_{eq}$  for the reaction:  $2HI(g) \leftrightarrow H_2(g) + I_2(g)$  is 85 at  $25^\circ C$

Determine the value of  $K_{eq}$  for the reaction:  $H_2(g) + I_2(g) \leftrightarrow 2HI(g)$  at  $25^\circ C$

Answer  $\frac{1}{85}$   
 $\uparrow$  reverse!

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