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}?

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 NOPE!!

8. The K_{eq} for the reaction: $2HI_{(g)} \leftrightarrows H_{2(g)} + I_{2(g)}$ is 85 at 25°C

Determine the value of K_{eq} for the reaction: $H_{2(g)} + I_{2(g)} \leftrightarrows 2HI_{(g)}$ at 25°C

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

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

Answer $= \frac{1}{85}$

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Chemistry 12: Lesson 7 – Equilibrium
Equilibrium Constants (Keq)

What is K_{eq}?

The "K" in K_{eq} stands for "Constant". The "eq" means that the reaction is at equilibrium.

Very roughly, K_{eq} tells you the ratio for a given reaction at *equilibrium* at a certain temperature. — can also be done for pressure $\frac{P}{R}$

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

The <u>only</u> thing that changes the *value* of K_{eq} for a given reaction is the *temperature*! — b/c temp can change [ ]'s

Writing K_{eq} Expressions

2 of these!

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

and the K_{eq} expression was:

$$K_{eq} = \frac{[I_2][H_2]}{[HI][HI]} \rightarrow K_{eq} = \frac{[I_2][H_2]}{[HI]^2}$$

notice coefficient became exponent

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

1. With this in mind, see if you can write the K_{eq} expression for the following reaction:

$$2NH_{3(g)} \rightleftharpoons N_{2(g)} + 3H_{2(g)} \qquad K_{eq} = \frac{[H_2]^3[N_2]}{[NH_3]^2}$$

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

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \qquad K_{eq} = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

The K_{eq} Expressions for Solids and Liquids

Consider the following reaction: $CaCO_{3(s)} \rightleftarrows CaO_{(s)} + CO_{2(g)}$
You might expect the Keq expression to be something like:

$$Keq = \frac{[CaO][CO_2]}{[CaCO_3]}$$

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 $CaCO_3$ are ~~constant~~ solids, we can assume that their **concentrations are** constant.

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

$$Keq = \frac{[constant][CO_2]}{[constant]}$$

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

$$K_{eq} = [CO_2]$$

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*** pure liquids.

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

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:

$$CaCO_{3(s)} + 2HF_{(g)} \rightleftarrows CaF_{2(s)} + H_2O_{(l)} + CO_{2(g)}$$

↖ Pure water (only liquid)

$$K_{eq} = \frac{[CO_2]}{[HF]^2}$$

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 → the *larger* the value of the fraction.
The *larger* the denominator → 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:

$N_{2(g)} + 3H_{2(g)} \rightleftarrows 2NH_{3(g)}$ is known to be **626.**

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

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:

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

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

The larger the value for K_{eq} the <u>closer to completion</u> 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 occured ***to a very great extent*** once equilibrium is reached.

Consider the following reaction: ***A + B ⇄ C + D*** K_{eq} = ***1.0***

The K_{eq} expression is:

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

∴ rxn has gone half way as the reactants and products are in 1:1 ratio

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

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

$1.6\times10^{-19} = [Cu^{2+}][OH^-]^2$

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

K_{eq} and Temperature

When the temperature changes, the value of K_{eq} also changes. — only with temp!!!

Consider the following **endothermic** reaction: **A + B + heat ⇄ 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:***

Shift to the Right

A + B + heat ⇄ C

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 K_{eq} 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 K_{eq} will*** decrease.

5. Given the equation for an ***exothermic*** reaction: **C + D ⇄ E + 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 ⇄ Z has a K_{eq} = 235 at 100°C.

When the temperature is raised to 200°C, the value for K_{eq} = 208

Is this reaction endothermic or exothermic? ___exothermic___

Explain your answer. ___if Keq ↓, reactants must have ↑ so eq. shifted ← so heat term must be on the right ∴ exo.___

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: $A + B \rightleftarrows C + D$ $K_{eq} = 4.0$

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)

Shift to the Left

$$\longleftarrow$$

$$A + B \leftrightarrow \mathbf{C} + D$$

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 Keq 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 Keq.

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: $N_{2(g)} + 3H_{2(g)} \rightleftarrows 2NH_{3(g)}$ $K_{eq} = 626$

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***:

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

4 moles of gas 2 moles of gas

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 Keq.. 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!)

   a) $A_{(s)} + B_{(g)} \rightleftarrows 2C_{(g)}$ $K_{eq} = \frac{[C]^2}{[B]}$

   b) $COCl_{2(g)} \rightleftarrows CO_{(g)} + Cl_{2(g)}$ $K_{eq} = \frac{[CO][Cl_2]}{[COCl_2]}$

   c) $Zn_{(s)} + 2HCl_{(aq)} \rightleftarrows H_{2(g)} + ZnCl_{2(aq)}$ $K_{eq} = \frac{[H_2][ZnCl_2]}{[HCl]^2}$

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:

$2NO_{2(g)} \leftrightarrows N_2O_{4(g)}$ + heat K_{eq} = 1.20 at 55°C

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

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

$K_{eq} \downarrow$

Explain why? ______

6. For the reaction: $PCl_{5(g)} \leftrightarrows PCl_{3(g)} + Cl_{2(g)}$ K_{eq} = 2.24 at 227°C

K_{eq} = 33.3 at 487°C

Is this reaction endothermic or exothermic? endothermic

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

Explain your answer ↑ temp = ↑ keq ∴ P↑ so shifted → so heat is on reactant side

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°C

Determine the value of K_{eq} for the reaction: $H_{2(g)} + I_{2(g)} \leftrightarrow 2HI_{(g)}$ at 25°C

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

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