

Equilibrium Reference Materials

Equilibrium

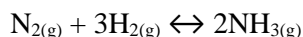
Equilibrium is a condition that occurs when a chemical reaction is reversible, and the forward and reverse reactions occur simultaneously, at the same rate. Chemical reactions can be classified into one of two broad categories: those reactions that “go to completion” and those reactions that establish equilibrium”.

Burning methane in oxygen to form carbon dioxide and water is a “goes to completion” reaction, and is indicated using a single-headed reaction arrow: $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$

Equilibrium reactions do not go to completion; instead, the two reactions (arbitrarily labeled “forward” and “reverse”) occur simultaneously. The forward and reverse reactions are opposite; the reverse reaction is the forward reaction written backwards. For example, nitrogen gas and hydrogen gas react to form ammonia: $\text{N}_{2(\text{g})} + 3\text{H}_{2(\text{g})} \rightarrow 2\text{NH}_{3(\text{g})}$

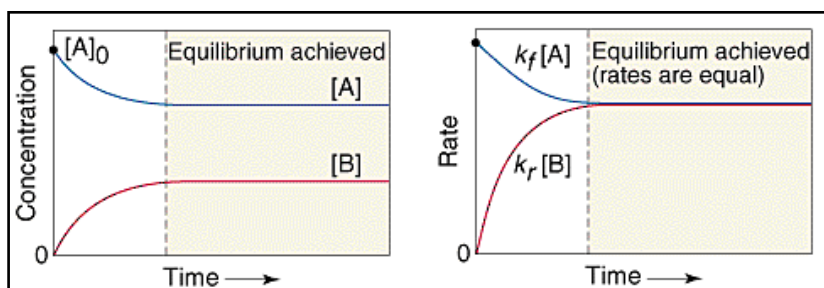
This reaction requires pressures between 2100 and 3600 psi and temperatures between 300 and 550 °C. At these pressures and temperatures ammonia spontaneously decomposes into nitrogen and hydrogen gas: $2\text{NH}_{3(\text{g})} \rightarrow \text{N}_{2(\text{g})} + 3\text{H}_{2(\text{g})}$

Eventually, these two reactions occur at the same rate. When this happens, the concentrations of nitrogen, hydrogen, and ammonia become constant, and the system is said to be “at equilibrium”. Typically, we represent chemical equilibrium using a double-headed reaction arrow:



Chemical Equilibrium, the Equilibrium Constant (K_{eq}), and the Reaction Quotient (Q)

As a reaction proceeds in a closed system, the concentrations of reactants and products change until, at **equilibrium**, the *rate* of the forward reaction is equal to the *rate* of the reverse reaction. At that point there is **no net change** in the concentrations of reactants or products. For example, for the simple reaction: $\text{A} = \text{B}$:



Regardless of the initial concentrations, the concentrations of reactants and products present at **equilibrium** are related through the equilibrium constant (K_{eq}).

If all reactants and products are in solution for the reaction: $a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$

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

**The subscript “eq” indicates “equilibrium” concentration. The subscript “c” stands for “concentration”.
The exponents are the coefficients from the balanced equation.**

If all reactants and products are ideal gases then **either** partial pressures or concentrations can be used in the equilibrium constant expression. You can convert back and forth from K_{c} to K_{p} . In terms of partial pressures:

$$K_{\text{eq}} = K_{\text{p}} = \frac{(P_{\text{C}})_{\text{eq}}^c (P_{\text{D}})_{\text{eq}}^d}{(P_{\text{A}})_{\text{eq}}^a (P_{\text{B}})_{\text{eq}}^b}$$

The subscript “p” stands for “pressure”

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Important points about equilibrium constants

1. **Every reaction has a characteristic equilibrium constant that depends only on temperature.** The value of the equilibrium constant is independent of the initial concentrations of reactants and products.
2. **Equilibrium constants have no units.** This is because each concentration or pressure is actually a ratio of the concentration or pressure to their standard values. Standard concentration for a substance in solution is 1 M and standard pressure for a gas is 1 atm. This portion of the equation that we don't see in our level of chemistry allows the units to cancel out.
3. **The concentrations of pure solids or pure liquids do not appear explicitly in the equilibrium constant expression.** The concentrations of pure solids and liquids are constant (density divided by molar mass). These constant concentrations are simply incorporated into the equilibrium constant. Their concentrations do not change so they do not mathematically affect the equilibrium expression.
4. **All reactants and products must be present at equilibrium.** Even though pure solids and liquids do not appear in an equilibrium constant expression, if they participate in a reaction they must be present to establish equilibrium. You still need them for the reaction to occur, they just are not going to affect the position of equilibrium.
5. **The numerical value of the equilibrium constant expresses the tendency for reactants to be converted to products.** If $K_{eq} \gg 1$ we say that "products are favored". If $K_{eq} \ll 1$ we say that "reactants are favored". A very large equilibrium constant (>1000) means that the reaction will nearly go to completion. A very small equilibrium constant (<0.001) means very little product will be present at equilibrium (or that the reverse reaction goes to completion).
6. **Changing the initial concentrations of reactants or products does NOT change the equilibrium constant.** The equilibrium concentrations of reactants and products will change but K_{eq} will not change. The value of K_{eq} depends only on the identity of the reactants and products and on temperature. Every reaction has a unique K_{eq} at a fixed temperature.
7. **A catalyst does NOT change the equilibrium constant.** A catalyst increases the rates of the forward and reverse reactions by the same factor.
8. **Changing the temperature DOES change the equilibrium constant.** Increasing the temperature increases the equilibrium constant for an endothermic reaction and decreases the equilibrium constant for an exothermic reaction. **Increasing the temperature shifts equilibrium in the endothermic direction.**
9. **The equilibrium constant for a reaction in the reverse direction is the reciprocal of the equilibrium constant in the forward direction.** $K' = 1/K$, when K is for the forward direction and K' is for the backwards direction.
10. **Equilibrium constants are independent of mechanism! (Unlike rate laws!)** At equilibrium every step is at equilibrium. We are concerned about the place we end up – equilibrium, we don't care how the reaction gets to that point. In kinetics the rate is determined by the way we get to our end point.

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Reaction quotient (Q)

At any point during a reaction, if we know the concentrations of reactants and products, we can calculate the **reaction quotient (Q)**.

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

notice that the concentrations are **NOT** necessarily equilibrium concentrations

Make sure you understand the difference between Q and K_{eq} :

Q tells you how far a reaction is from equilibrium.

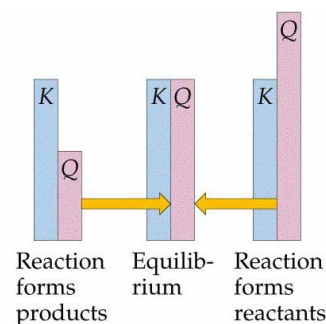
K_{eq} tells you where the reaction is trying to go.

By comparing the values of Q and K_{eq} , you can determine whether or not the reaction is at equilibrium. If the reaction is not at equilibrium, you can decide whether the (net) reaction is going in the forward or reverse direction.

If $Q = K_{eq}$, then $rate_{forward} = rate_{reverse}$, the **reaction is at equilibrium** and no net change

If $Q < K_{eq}$ then $rate_{forward} > rate_{reverse}$, reaction will **proceed to the right** (→ more products)

If $Q > K_{eq}$, then $rate_{forward} < rate_{reverse}$, reaction will **proceed to the left** (← more reactants)

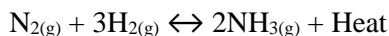


Le Chatelier's Principle

Arguably, the single most important rule governing chemical equilibrium is Le Chatelier's Principle, promulgated by French chemist Henry Louis Le Chatelier (1850 – 1936):

“If a chemical system at equilibrium experiences a change in concentration, temperature or total pressure, the equilibrium will shift in order to minimize that change.”

Consider the following equilibrium:



Any change in concentration, temperature, or total pressure can affect this equilibrium by increasing or decreasing the relative amounts of “reactants” and “products”. When the equilibrium is disturbed, it re-establishes a new equilibrium. Since equilibrium point is simply a ratio of products to reactants where the rate forward equals the rate backwards, there are infinite ratios that can reach an equilibrium point. You will never quite get back to where you started, but it will find a new equilibrium point. The easiest way to think about which way a reaction will shift is:

If you add something, use it up – move away from it.

If you take something away, make more of it – move towards it.

You can treat heat the same way you would one of the chemicals – if you raise the temperature you have added more heat and you need to use it up. If you lower the temperature you have taken away some heat and you need to make more of it.

A couple examples for the equation above. See your notes for more detailed explanations as always! ☺

Add N_2	Shift Right	$[N_2]$ slight ↑	$[H_2]$ ↓	$[NH_3]$ ↑	Temp. ↑	<i>Remember – solids, liquids, inert gases, and catalysts do not shift equilibrium!</i>
Take away H_2	Shift Left	$[N_2]$ ↑	$[H_2]$ slight ↓	$[NH_3]$ ↓	Temp. ↓	
Take away NH_3	Shift Right	$[N_2]$ ↓	$[H_2]$ ↓	$[NH_3]$ slight ↓	Temp. ↑	
Raise the Temp	Shift Left	$[N_2]$ ↑	$[H_2]$ ↑	$[NH_3]$ ↓	Temp. slight ↑	
Lower Pressure	Shift Left	$[N_2]$ ↑	$[H_2]$ ↑	$[NH_3]$ ↓	Temp. ↓	
Add Argon gas	No change	No change	No change	No change	No change	

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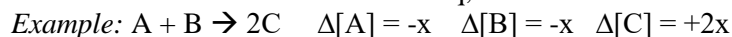
ICE Tables

If you know information about the balanced equation, K_{eq} , and initial concentrations of the chemicals before equilibrium is reached, you can determine the concentrations of each chemical once the reaction has reached equilibrium. Due to the fact that there are so many numbers involved, an ICE Table can be very useful. ICE stands for –

Initial – Write down the initial [] of each chemical

Change – Use a variable (x) to represent the change each chemical will undergo.

Take into account the coefficients in the balanced eq, and if the chemical is being used up or made.



Equilibrium – The initial plus any change that took place.

Example:

A container has a mixture of 1 M carbon monoxide gas, 2 M water vapor, and 1 M carbon dioxide gas. The following reversible reaction takes place $CO + H_2O \leftrightarrow CO_2 + H_2$. This reaction has an equilibrium constant of 0.64. What is the concentration of each chemical once equilibrium is obtained?

Since there is initially no water vapor in the vessel the reaction must begin going from the left to the right. So let the right side be the reactants and the left the product. So now consider the rows of the ICE table.

	CO	+	H ₂ O	↔	CO ₂	+	H ₂
Initial	1		2		1		0
Change	- x		- x		+ x		+ x
Equilibrium	1 - x		2 - x		1 + x		0 + x

Once you have your ice table values, plug them into the equilibrium expression and solve for x.

Note – Sometimes solving for x is straightforward, sometimes you have to use the quadratic formula, and sometimes you can use the “5% Rule” as a shortcut to not have to use the quadratic formula. To use the 5% rule, $K < 1$ (and a better rule of thumb is K must be 1000x smaller than your initial concentrations, that is more likely to follow the 5% rule)

You must always check to see if $\frac{x}{[initial]} \times 100 < 5\%$ in order to use the rule! If not, then solve with quadratic.

Example using 5% rule

	CO	+	H ₂ O	↔	CO ₂	+	H ₂
Initial	1		2		1		0
Change	- x		- x		+ x		+ x
Equilibrium	1 - x		2 - x		1 + x		0 + x
5% Rule	~ 1		~ 2		~ 1		x

$$K_{eq} = \frac{[CO_2][H_2]}{[CO][H_2O]} \quad \text{plug numbers/variables in} \rightarrow 0.64 = \frac{[1][x]}{[1][2]} \quad \text{solve for x} \rightarrow 1.28 = x$$

Check 5% Rule $\rightarrow \frac{1.28}{1} \neq 5\%$ so you cannot use the rule...have to do it the long way unfortunately ☹

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Example finished NOT Using 5% Rule

	CO	+	H ₂ O	↔	CO ₂	+	H ₂
Initial	1		2		1		0
Change	- x		- x		+ x		+ x
Equilibrium	1 - x		2 - x		1 + x		0 + x

$$K_{eq} = \frac{[CO_2][H_2]}{[CO][H_2O]} \quad \text{plug numbers/variables in} \rightarrow 0.64 = \frac{[1+x][x]}{[1-x][2-x]} \quad \text{move denominator to the other side by multiplying}$$

$$\rightarrow 0.64(1-x)(2-x) = (1+x)(x) \quad \text{start simplifying by distributing} \rightarrow (0.64 - 0.64x)(2-x) = x + x^2 \quad \text{use "F.O.I.L"} \rightarrow$$

$$1.28 - 0.64x - 1.28x + 0.64x^2 = x + x^2 \quad \text{simplify and move everything to one side} \rightarrow 0 = 0.36x^2 + 2.92x - 1.28 \rightarrow$$

$$\text{Now you can use the quadratic formula to solve for } x \quad \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \quad \text{when } (ax^2 + bx + c)$$

$$\frac{-2.92 \pm \sqrt{2.92^2 - 4(0.36)(-1.28)}}{2(0.36)}$$

$$\text{Our two solutions are } x = -8.5, 0.42$$

The first solution cannot be physically realistic as it would mean that hydrogen would end up with a negative concentration. So 0.42 must be the desired answer for x.

Now that you have x you can finish your ICE Table!

If the question asks for moles make sure to change your M into moles by using $M = \text{mol/L}$

	CO	+	H ₂ O	↔	CO ₂	+	H ₂
Initial	1		2		1		0
Change	- x		- x		+ x		+ x
Equilibrium	1 - x = 1 - 0.42 = 0.58 M		2 - x = 2 - 0.42 = 1.58 M		1 + x = 1 + 0.42 = 1.42 M		0 + x = 0 + 0.42 = 0.42 M

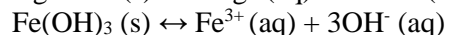
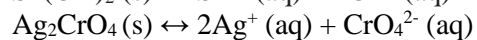
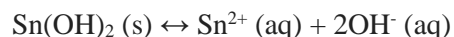
K_{sp} – Solubility Product Constant

The solubility product constant, K_{sp}, is the equilibrium constant for a solid substance dissolving in an aqueous solution. It represents the level at which a solute dissolves in solution. The more soluble a substance is, the higher the K_{sp} value it has.

In order to determine the K_{sp} of a substance you need to write the dissociation reaction first. You write the K_{sp} equation the same way as a normal K_{eq} - products over reactants, and solids do not factor into the equations.

Do not forget to balance your dissociation reactions! The coefficients are the exponents in your K_{sp} equations so the balancing matters!

Examples:



$$K_{sp} = [\text{Sn}^{2+}][\text{OH}^-]^2$$

$$K_{sp} = [\text{Ag}^+]^2 [\text{CrO}_4^{2-}]$$

$$K_{sp} = [\text{Fe}^{3+}] [\text{OH}^-]^3$$