

Equilibrium

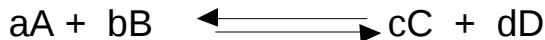
- Most chemical reactions are reversible: they can go in the forward or reverse direction.
- Equilibrium is the idea that reversible reactions will proceed to some point and then for every forward event there will be a reverse event. The reaction doesn't stop. It's just that the forward rate = reverse rate, and the concentration of all species becomes constant.
- The equilibrium constant is just a way of making a number that relates the concentrations of reactants and products at equilibrium.
- The formal way of writing out the equilibrium constant is pretty ugly, but I'm gonna write it out and try and learn ya somethin'...

$$K_C = \frac{\prod [\text{products}]^{\nu_i}}{\prod [\text{reactants}]^{\nu_j}}$$

This is the complicated way of writing the expression for the equilibrium constant. Mathematically, the Π symbol is like the Σ symbol only instead of meaning "the sum of" it means "the product of." So, this expression says that the equilibrium constant is equal to the product of the concentrations of the products raised to their stoichiometric coefficients divided by the product of the concentration of the reactants raised to their stoichiometric coefficients.

It's easier to see by example:

Let's look at any old generic reaction:



The equilibrium constant expression is:

$$K_C = \frac{[C]^c[D]^d}{[A]^a[B]^b} \quad (\text{remember, } [] \text{ means molarity})$$

Rules for writing K_C expressions:

1. K_C is a function of temperature even though it's not shown in the above expression.
2. It's not a function of original concentrations, volume, or pressure.
3. Don't put solids or pure liquids in the K_C expression (pay attention to s, g, l subscripts).
4. $K_C \text{ reverse} = \frac{1}{K_C \text{ forward}}$ <-- easy algebra.
5. Also if you multiply any chemical equation through by a factor it raises K_C to that power.
6. If you add chemical reactions to get a final rxn, multiply the K_C 's to get the final reaction's K_C .

Equilibrium Constant Problems

These are just little algebra problems that you have to be good at setting up. After that they are all kind of the same problem.

- Understand that starting, initial, or changes from equilibrium concentrations **are all nonequilibrium states** and that the system will react until equilibrium is established or re-established.
- If you are given some concentrations and you don't know which way a reaction will proceed, use Q_C , the reaction quotient, to figure out which way it will go. Q_C is algebraically the same expression as K_C . You are just plugging in nonequilibrium concentration values.

$Q_C = K_C$ means you are at equilibrium

$Q_C < K_C$ means not enough products, the rxn will go forward

$Q_C > K_C$ means too many products, the rxn will go reverse

- Now you do these problems by introducing one unknown, x , the concentration of a species, of your choice, reacted or formed and then set up an algebraic expression for K_C . (Remember to relate x to the other reactants and products with the stoichiometry of the chemical equation.)

Okay, here is an example of a problem in which you are given K_C and asked to find the equilibrium concentrations of all species from some given initial concentrations. (This example won't use numbers; it's kind of a template):

Always
Make this
kind of a
Table

	$A + B \rightleftharpoons 2 C$		
	<u>[A]</u>	<u>[B]</u>	<u>[C]</u>
initial	$[A]_0$	$[B]_0$	$[C]_0$
change	$-x$	$-x$	$2x$
final	$[A]_0 - x$	$[B]_0 - x$	$[C]_0 + 2x$

Obviously there are no numbers from which to determine the initial direction of the reaction so, I just assumed it to be forward--thus the $-x$.

This is a number given in the problem statement.

$$K_C = \frac{([C]_0 + 2x)^2}{([A]_0 - x)([B]_0 - x)}$$

Multiply everything out (remember the FOIL method) and you will get a quadratic in x :

$$ax^2 + bx + c = 0$$

Now, strictly speaking, you should use the quadratic equation to solve for x :

$$\frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

- In some problems, when you start with all reactants and no products, and when $K_C < 10^{-6}$, you can ignore the $-x$'s in the denominator terms because not much of the initial reactants gets used up. When you do this and multiply everything out, you end up just having to take a square root instead of using the quadratic equation.

K_p, Gas Phase Equilibrium Problems

- Very similar to K_C problems except you are using partial pressures instead of concentrations.
- Again leave out solids and pure liquids.

For example: $aA_{(g)} + bB_{(g)} \rightleftharpoons cC_{(g)} + dD_{(g)}$

$$K_p = \frac{P_A^a \cdot P_B^b}{P_C^c \cdot P_D^d}$$

The relationship between K_C and K_p is an easy derivation from the ideal gas law: $PV = nRT$

for the partial pressure of gas i: $P_i = n_i \frac{RT}{V}$ and $\frac{n_i}{V} = [\text{gas } i]$ ← just the molar concentration

so, $K_p = K_C \cdot (RT)^{\Delta n}$ "Δn" just equals the sum of the stoichiometric coefficients of the products minus the sum of the stoichiometric coefficients of the reactants (like, $c + d - a - b$).

So you can relate K_p to K_C as a function of temperature and change in number of moles between products and reactants.

- To do these problems, just algebraically proceed in the same way as K_C. Set up the table and the expression for K_p. Then solve for x.

Le Chatelier's Principle

Le Chat's principle is great chemistry. The people who write the AP do a good job of testing students on their "chemistry intuition." Along with shielding, sublevel stability, and like-dissolves-like, Le Chat's is one of the intuitive rules to know.

Le Chatelier's Principle is just: **A chemical reaction will try to counter, if it can, any change imposed on it. It tries to do the opposite of what is done to it.**

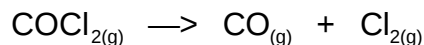
- If you add a product or reactant, the reaction shifts in the direction to use it up.
- If you increase temperature, the reaction will shift in the endothermic direction to try to decrease temperature.
- If you decrease temperature, the reaction will shift in the exothermic direction to try to increase temperature.
- If you increase pressure the rxn will try to decrease pressure by shifting in the direction which makes fewer molecules and vice-versa. (If both sides have the same # of molecules it can't do anything.)
(Also, remember that volume changes are like pressure changes. Increasing volume decreases the pressure and decreasing the volume increases the pressure.)
- Adding species that don't take part in the reaction does nothing.

Student Packet: 5.1: Liquid and Gas Phases: AssessMe questions

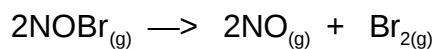
- 1) Atom X has 12 protons, 12 electrons, and 13 neutrons. Atom Y has 10 protons, 10 electrons, and 15 neutrons. It can therefore be concluded that:
- A) atoms X and Y are isotopes.
B) atom X is more massive than atom Y.
C) atoms X and Y have the same mass number.
D) atoms X and Y have the same atomic number.
E) I'm clueless
- 2) What is the maximum number of electrons that can have a principal quantum number of 3 within one atom?
- A) 3 B) 8 C) 18 D) 32 E) I'm clueless
- 3) Which of the following is a polar molecular compound?
- A) CH₄ B) SO₂ C) SiO₂ D) hydrogen E) I'm clueless
- 4) Which of the following processes would require the most energy?
- A) melting iodine B) boiling SiH₄
C) dissolving Br₂ in CCl₄ D) decomposing H₂O₂ E) I'm clueless
- 5) If $K_{eq} = 0.01$, then at equilibrium which species will be found in higher concentrations?
- A) Reactants
B) Products
C) The answer to this question depends on the exact mathematical form of the equilibrium equation.
D) None of the above.
E) I'm clueless
- 6) Consider the equilibrium reaction: $\text{CaCO}_{3(s)} + \text{H}_2\text{O} \rightarrow \text{CO}_{2(g)} + \text{Ca(OH)}_{2(aq)}$
Which is the accepted equilibrium expression for this reaction?
- A) $K_{eq} = P_{\text{CO}_2}[\text{Ca(OH)}_2]/[\text{CaCO}_3]$ B) $K_{eq} = P_{\text{CO}_2}[\text{Ca(OH)}_2]/([\text{CaCO}_3][\text{H}_2\text{O}])$
C) $K_{eq} = P_{\text{CO}_2}[\text{Ca(OH)}_2]$ D) $K_{eq} = [\text{Ca(OH)}_2]/([\text{CaCO}_3][\text{H}_2\text{O}])$
E) I'm clueless

Student Packet: 5.1: Liquid and Gas Phases: ShowMe questions

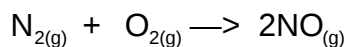
- 1) If the equilibrium constant for this reaction is 8×10^{-1} and the starting concentration of COCl_2 is 1 M, what is the equilibrium concentration of $\text{CO}_{(g)}$?



- 2) The equilibrium constant for this reaction is 3.07×10^{-4} at 24°C . What is K_p ?

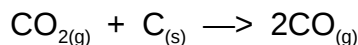


- 3) Consider the following reaction:



$K_c = 2.5 \times 10^{-3}$. If the concentrations are as follows, does the reaction go to the right or to the left? $[\text{N}_2] = 1.3 \text{ M}$, $[\text{O}_2] = 2.7 \text{ M}$ and $[\text{NO}] = 1.5 \text{ M}$.

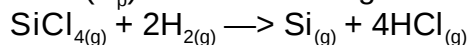
- 4) The equilibrium constant K_c is 1.17 at 1000°C for the following reaction:



What is the equilibrium concentration of CO if the concentration of CO_2 is 1 M and there are 5 g of solid carbon?

Student Packet: 5.1: Liquid and Gas Phases: TestMe questions

- 1) What is the equilibrium constant (
- K_p
-) for the following reaction?



$$\text{A) } K_p = \frac{(P_{\text{Si}})(P_{\text{HCl}})^4}{(P_{\text{H}_2})^2 (P_{\text{SiCl}_4})} \quad \text{B) } K_p = \frac{(P_{\text{HCl}})}{(P_{\text{SiCl}_4})(P_{\text{SiCl}_4})}$$

$$\text{C) } K_p = \frac{(P_{\text{HCl}})^2 (P_{\text{Si}})}{(P_{\text{SiCl}_4})^4 (P_{\text{H}_2})} \quad \text{D) } K_p = \frac{(P_{\text{HCl}})^4}{(P_{\text{SiCl}_4})(P_{\text{H}_2})}$$

$$\text{E) } K_p = (P_{\text{Si}})$$

- 2) Phosphorus pentachloride dissociates according to the following reaction:



K_c for the reaction is 3.26×10^{-2} . The starting concentration of PCl_5 is 7 M. What is the equilibrium concentration of Cl_2 gas?

- A) 2.7 M B) .462 M C) 0.23 M D) 0.055 M E) 0.48 M

- 3)
- $$2\text{HI}_{(g)} \longrightarrow \text{H}_{2(g)} + \text{I}_{2(g)}$$

If K_c for this reaction is 0.0201 at 458°C , what is K_p ?

- A) 0.0201 B) 1.270 C) 0.527 D) 2.103 E) None of the above

- 4)
- $$\text{COCl}_{2(g)} \longrightarrow \text{CO}_{(g)} + \text{Cl}_{2(g)}$$

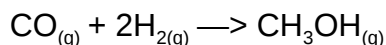
At 400°C the equilibrium constant $K_c = 8.05 \times 10^{-4}$.

Which of the following are true based on the data given above?

- I. At equilibrium the mixture is mostly reactants
 II. At equilibrium the mixture is mostly products
 III. At equilibrium there is no COCl_2
 IV. At equilibrium there are 5 moles of CO and Cl_2 for every one mole of COCl_2

- A) I B) II C) III, IV D) I, IV E) None of the above

- 5) At
- 255°C
- ,
- K_p
- for the following reaction is
- 6.3×10^{-3}
- .



If the flask containing these gases in equilibrium has a partial pressure of $\text{H}_2 = 0.4 \text{ atm}$ and $\text{CH}_3\text{OH} = 0.7 \text{ atm}$, what is the partial pressure of CO ?

- A) 6.9 atm B) 0.4 atm C) 135 atm D) 690 atm E) None of the above