

## Equilibrium: Let's Get Balanced!

### Dynamic Equilibrium: A Quick Review

1. The concentrations of all reactants and products remain constant with time.
2. The reaction is proceeding in the forward and reverse direction simultaneously and at the same rate.
3. All macroscopic variables (such as concentration, partial pressure, and temperature) do NOT change over time, so nothing appears to be happening.
4. When equilibrium has been reached,  $Q = K$ .
5. **Equilibrium is temperature dependent!** Change the temperature, change ratio of products to reactants.

**The Equilibrium Constant,  $K$**  (the Law of Mass Action): relates the concentrations of reactants and products at equilibrium at a given temperature.

For the general reaction:  $aA + bB \rightleftharpoons cC + dD$

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} = \frac{[\text{Products}]^{\text{coefficient}}}{[\text{Reactants}]^{\text{coefficient}}}$$

- Each concentration is raised to the power of its stoichiometric coefficient in the balanced equation.
- **Note:** Only use gaseous and aqueous substances (**NO solids or pure liquids!**)
- There are NO units for the equilibrium constant,  $K$  (they cancel out).

### Let's Practice!

1. The decomposition of aqueous  $\text{Ca}(\text{HCO}_3)_2$  is allowed to come to equilibrium at 298 K. The measured equilibrium concentrations are  $[\text{Ca}(\text{HCO}_3)_2] = 0.025 \text{ M}$  and  $[\text{CO}_2] = 2.78 \text{ M}$ . What is the value of the equilibrium constant at this temperature?



$$K = \frac{[\text{CO}_2]}{[\text{Ca}(\text{HCO}_3)_2]} = \frac{2.78}{0.025} = \boxed{110}$$

2 s.f.

2. Consider the following reaction:



In an equilibrium mixture, the concentration of  $\text{COF}_2$  is 0.255 M and the concentration of  $\text{CH}_4$  is 0.118 M. What is the equilibrium concentration of  $\text{CO}_2$ ?

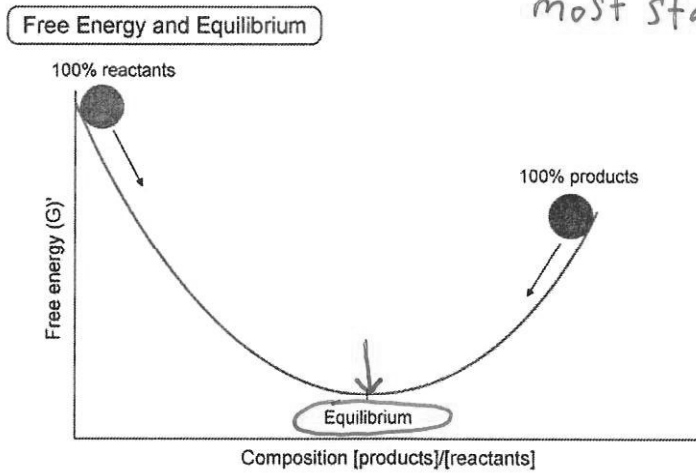
$$K = \frac{[\text{CO}_2][\text{CH}_4]}{[\text{COF}_2]^2} = \frac{[\text{CO}_2](0.118)}{(0.255)^2} = 2.00$$

$$[\text{CO}_2] = \frac{(2.00)(0.255)^2}{(0.118)} = \boxed{1.10 \text{ M}}$$

## What does $K$ mean?

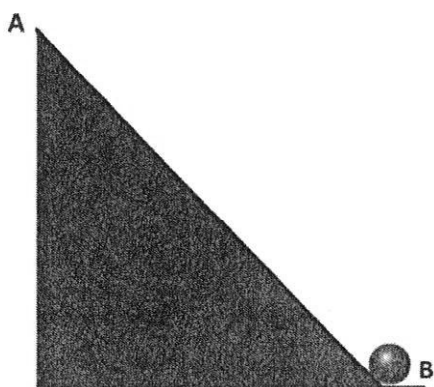
The equilibrium constant,  $K$ , tells you:

- the ratio of products to reactants when a given reaction reaches its lowest free energy state and "stops".

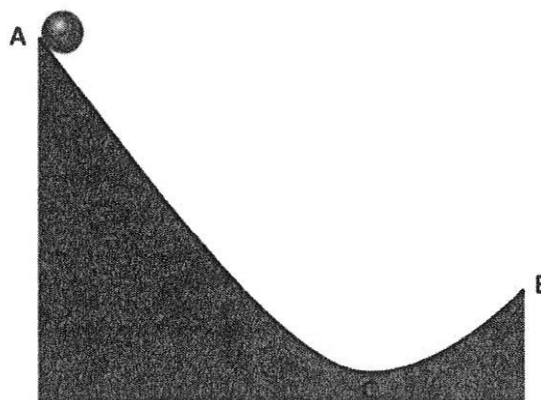
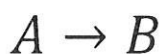


Large $K$ $K \gg 1$	Intermediate $K$ $K \approx 1$	Small $K$ $K \ll 1$
Product-favored	Neither	Reactant-Favored
<p style="text-align: center;">Mostly products</p>	<p style="text-align: center;">Significant amounts of reactants and products</p>	<p style="text-align: center;">Mostly reactants</p>
<p>Forward reaction is thermodynamically favorable</p> <p style="text-align: center;">Pure reactants      Pure products</p>	<p>(b)</p> <p style="text-align: center;">Pure reactants      Pure products</p>	<p>Reverse reaction is thermodynamically favorable</p> <p style="text-align: center;">Pure reactants      Pure products</p>

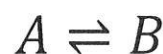
## Completion Reactions vs Equilibrium Reactions



**Complete Reaction:**  
Complete consumption of reactants.



**Equilibrium:** Reaction achieves equilibrium by reaching the lowest state of energy.



### Completion reactions:

- Non-reversible
- 100% of reactants convert to products
- Example: combustion

### Equilibrium reactions:

- Reversible
- Reaction will occur until lowest energy state is reached
- Example: weak acid dissolution

You can think of  $K$  as measuring how close a reaction will go towards 100% completion:

- High  $K$  = reaction came pretty close to completely turning reactants into products
- Low  $K$  = reaction did NOT come close to turning all reactants into products, mostly reactants just hung around

**Kinetic Control:** when a reaction is thermodynamically favorable ( $K > 1$ ), but products form soooooo slowly that it appears the reaction isn't happening (i.e., kinetically unfavorable)

$$-\Delta H, +\Delta S \Rightarrow \text{always } -\Delta G, (\text{always fav.})$$

Example Question: For a given reaction  $A \rightleftharpoons B$ ,  $\Delta H = -2.3 \text{ kJ/mol}$  and  $\Delta S = +25.9 \text{ J/mol K}$ . A student tries the reaction in lab, letting the reaction run over time. After two days, she measures the composition of her sample and discovers that it is primarily composed of reactants. Which of the following best explains why this might occur?

- This reaction is only thermodynamically favorable at low temperatures, and the student's lab must be too warm for the reaction to occur.
- This reaction has a small equilibrium constant,  $K$ , and thus the [reactants] will be much greater than [products] when the reaction system reaches its most stable state. *nope, b/c  $-\Delta G \Rightarrow K > 1$*
- This reaction has an extremely high activation energy, and thus the reaction rate is so slow no products will be observed despite its thermodynamic favorability.
- This reaction is only thermodynamically favorable at high temperatures, therefore the lab conditions are too cold for the reaction to occur in measurably quantities.

**Pesky Subscripts:** Different designations of K

In order to convey additional information, the equilibrium constant  $K$  may also have a Subscript to give information about the type of reaction being studied.

However, in ALL cases  $K$  is still defined as the ratio of products to reactants!

Type of Reaction		Reaction	Equilibrium Expression, $K$
General	$K_{eq}$	$aA + bB \rightleftharpoons cC + dD$	$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$
Concentration	$K_c$		
Pressure (only for gases!)	$K_p$	$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$	$K_p = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b}$
Dissolving a solid in water	$K_{sp}$	$AB(s) \rightleftharpoons A^+(aq) + B^-(aq)$	$K_{sp} = [A^+][B^-]$

 **$K_p$  = Ratio of Partial Pressures**

For the general reaction:  $aA + bB \rightleftharpoons cC + dD$

$$K_p = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b} = \frac{(P_{\text{products}})^{\text{coefficient}}}{(P_{\text{reactants}})^{\text{coefficient}}} \quad \text{where } P \text{ is the partial pressure of the gas}$$

\*Note:  $K_c$  can be converted into  $K_p$ , but that conversion is no longer AP tested! ;D

Let's Practice!

1. Given the following reaction, with  $K_p = 109$  at  $25^\circ\text{C}$ :  $2 \text{NO}(g) + \text{Br}_2(g) \rightleftharpoons 2 \text{NOBr}(g)$

If the equilibrium partial pressure of bromine gas is  $0.0159 \text{ atm}$  and the equilibrium partial pressure of  $\text{NOBr}$  is  $0.0768$ , calculate the equilibrium partial pressure of  $\text{NO}$ :

$$K_p = \frac{(P_{\text{NOBr}})^2}{(P_{\text{NO}})^2(P_{\text{Br}_2})} = \frac{(0.0768)^2}{(P_{\text{NO}})^2(0.0159)} = 109 \Rightarrow P_{\text{NO}} = \sqrt{\frac{(0.0768)^2}{(109)(0.0159)}} = \boxed{0.0583 \text{ atm}}$$

2. The reaction for the formation of nitrosyl chloride:  $2 \text{NO}(g) + \text{Cl}_2(g) \rightleftharpoons 2 \text{NOCl}(g)$  was studied at  $25^\circ\text{C}$ . The pressures at equilibrium were found to be  $P_{\text{NOCl}} = 1.2 \text{ atm}$ ,  $P_{\text{NO}} = 0.050 \text{ atm}$  and  $P_{\text{Cl}_2} = 0.30 \text{ atm}$ . Write the equilibrium expression,  $K_p$ , for this reaction and calculate its value at  $25^\circ\text{C}$ .

$$K_p = \frac{(P_{\text{NOCl}})^2}{(P_{\text{NO}})^2(P_{\text{Cl}_2})} = \frac{(1.2)^2}{(0.050)^2(0.30)} = \boxed{1900}$$