

Chemistry 132 NT

**I never let my
schooling get in the
way of my education.**

Mark Twain

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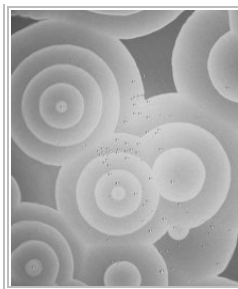
Chem 132 NT

Chemical Equilibrium

Module 1

Describing Chemical Equilibrium

- The Equilibrium Constant
- Equilibrium Constant for Sums of Reactions
- Heterogeneous Equilibria



Oscillating patterns
formed by a reaction
far from equilibrium

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Chemical Equilibrium

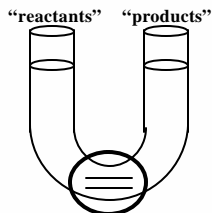
When compounds react, they eventually form a mixture of products and unreacted reactants, in a **dynamic equilibrium**.

- A **dynamic equilibrium** consists of a forward reaction, in which substances react to give products, and a reverse reaction, in which products react to give the original reactants.
- **Chemical equilibrium** is the state reached by a reaction mixture when the **rates of the forward and reverse reactions have become equal**.

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Chemical Equilibrium

Much like water in a U-shape tube, there is constant mixing back and forth through the lower portion of the tube.



It's as if the forward and reverse "reactions" were occurring at the same rate.

The system appears to static (stationary) when, in reality, it is **dynamic** (in constant motion).

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Chemical Equilibrium

Consider the gaseous reaction of carbon monoxide and hydrogen to produce methane and steam.



- Suppose you put 1.000 mol CO and 3.000 mol H₂ into a 10.00-L container at 1200 K.
- The rate of the forward reaction, which depends on reactant concentrations, is **large at first but steadily decreases**.

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Chemical Equilibrium

- Consider the gaseous reaction of carbon monoxide and hydrogen to produce methane and steam.



- Suppose you put 1.000 mol CO and 3.000 mol H₂ into a 10.00-L container at 1200 K.
- The rate of the reverse reaction **starts at zero but steadily increases.**

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Chemical Equilibrium

- Consider the gaseous reaction of carbon monoxide and hydrogen to produce methane and steam.

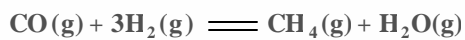


- Suppose you put 1.000 mol CO and 3.000 mol H₂ into a 10.00-L container at 1200 K.
- The **forward rate decreases** and the **reverse rate increases** until they eventually **become equal** and the reaction mixture has reached **equilibrium**.

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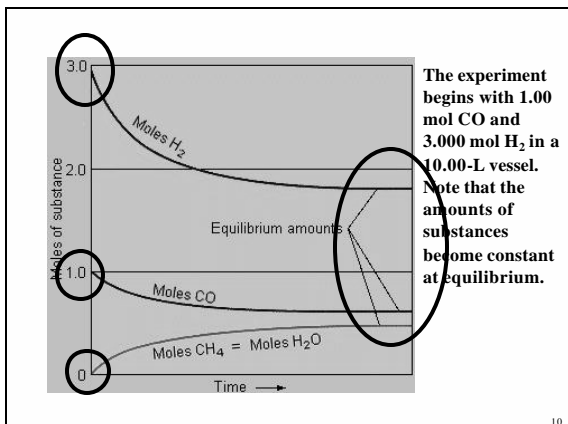
Chemical Equilibrium

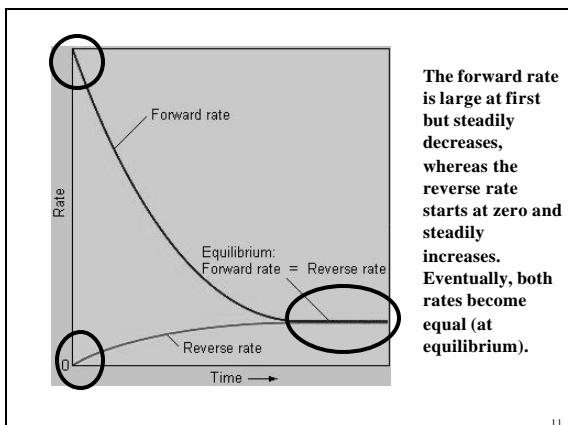
- Consider the gaseous reaction of carbon monoxide and hydrogen to produce methane and steam.



- Suppose you put 1.000 mol CO and 3.000 mol H₂ into a 10.00-L container at 1200 K.
- The next figure illustrates this approach to equilibrium.

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Chemical Equilibrium

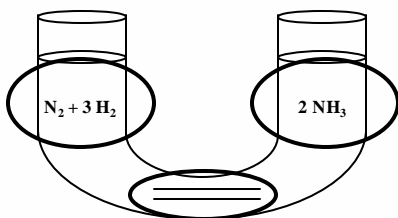
- ◆ Another example is the Haber process for producing ammonia from N₂ and H₂ which does not go to completion.

$$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$$

- ◆ It establishes an equilibrium state where all three species are present.

Chemical Equilibrium

- ◆ Another example is the Haber process for producing ammonia from N_2 and H_2 which does not go to completion.

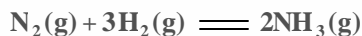


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A Problem To Consider

- ◆ Applying Stoichiometry to an Equilibrium Mixture.

- ◆ Suppose we place 1.000 mol N_2 and 3.000 mol H_2 in a reaction vessel at $450^\circ C$ and 10.0 atmospheres of pressure. The reaction is:



- ◆ What is the composition of the equilibrium mixture if it contains 0.080 mol NH_3 ?

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A Problem To Consider

- ◆ Using the information given, set up the following table.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

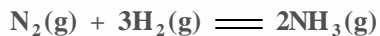
Starting	1.000	3.000	0
Change	-x	-3x	+2x
Equilibrium	1.000-x	3.000-3x	2x = 0.080 mol

- ◆ The equilibrium amount of NH_3 was given as 0.080 mol. Therefore, $2x = 0.080 \text{ mol } NH_3$ ($x = 0.040 \text{ mol}$).

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A Problem to Consider

• Using the information given, set up the following table.



Starting	1.000	3.000	0
Change	-x	-3x	+2x
Equilibrium	1.000-x	3.000-3x	2x = 0.080 mol

$$\begin{aligned}\text{Equilibrium amount of N}_2 &= 1.000 - 0.040 \\ &= 0.960 \text{ mol N}_2\end{aligned}$$

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A Problem to Consider

• Using the information given, set up the following table.



Starting	1.000	3.000	0
Change	-x	3x	+2x
Equilibrium	1.000-x	3.000-3x	2x = 0.080 mol

$$\begin{aligned}\text{Equilibrium amount of H}_2 &= 3.000 - (3 \times 0.040) \\ &= 2.880 \text{ mol H}_2\end{aligned}$$

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A Problem to Consider

• Using the information given, set up the following table.



Starting	1.000	3.000	0
Change	-x	-3x	+2x
Equilibrium	1.000-x	3.000-3x	2x = 0.080 mol

$$\begin{aligned}\text{Equilibrium amount of NH}_3 &= 2x \\ &= 0.080 \text{ mol NH}_3\end{aligned}$$

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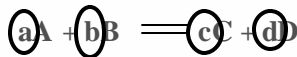
The Equilibrium Constant

- Every reversible system has its own “position of equilibrium” under any given set of conditions.
- The **ratio of products produced to unreacted reactants** for any given reversible reaction remains constant under constant conditions of pressure and temperature.
- The numerical value of this ratio is called the **equilibrium constant** for the given reaction.

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The Equilibrium Constant

- The **equilibrium-constant expression** for a reaction is obtained by multiplying the concentrations of products, dividing by the concentrations of reactants, and raising each concentration to a power equal to its coefficient in the balanced chemical equation.



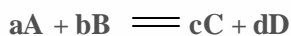
- For the general equation above, the equilibrium-constant expression would be:

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

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The Equilibrium Constant

- The **equilibrium-constant expression** for a reaction is obtained by multiplying the concentrations of products, dividing by the concentrations of reactants, and raising each concentration to a power equal to its coefficient in the balanced chemical equation.



- The molar concentration of a substance is denoted by writing its formula in square brackets.

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

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The Equilibrium Constant

✎ The **equilibrium constant K_c** is the value obtained for the equilibrium-constant expression when equilibrium concentrations are substituted.

$$\text{Since } K_c \propto \frac{\text{products}}{\text{reactants}}$$

• A **large K_c** indicates high concentrations of product at equilibrium.

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The Equilibrium Constant

✎ The **equilibrium constant K_c** is the value obtained for the equilibrium-constant expression when equilibrium concentrations are substituted.

$$\text{Since } K_c \propto \frac{\text{products}}{\text{reactants}}$$

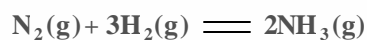
• A **small K_c** indicates a large concentration of unreacted reactants at equilibrium.

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The Equilibrium Constant

✎ The **law of mass action** states that the value of the equilibrium constant expression K_c is constant for a particular reaction **at a given temperature, whatever** equilibrium concentrations are substituted.

• Consider the equilibrium established in the Haber process.



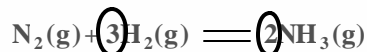
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The Equilibrium Constant

- The equilibrium-constant expression would be:

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

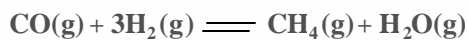
- Note that the stoichiometric coefficients in the balanced equation have become the powers to which each concentration is raised.



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A Problem To Consider

- Write the equilibrium-constant expression K_c for catalytic methanation.

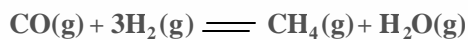


- Write the concentrations of products in the top (numerator) of the equilibrium constant expression, and write the concentrations of reactants in the bottom (denominator).

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A Problem To Consider

- Write the equilibrium-constant expression K_c for catalytic methanation.

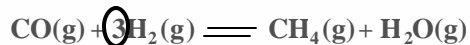


- Raise each concentration term to the power equal to the coefficient of the substance in the chemical equation.

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A Problem To Consider

- Write the equilibrium-constant expression K_c for catalytic methanation.

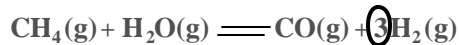


$$K_c = \frac{[\text{CH}_4][\text{H}_2\text{O}]}{[\text{CO}][\text{H}_2]^3}$$

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A Problem To Consider

- Write the equilibrium-constant expression K_c for the reverse of the previous reaction.

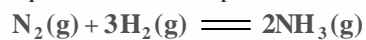


$$K_c = \frac{[\text{CO}][\text{H}_2]^3}{[\text{CH}_4][\text{H}_2\text{O}]}$$

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A Problem To Consider

- Our previous look at the Haber process led us to the equilibrium-constant expression below.

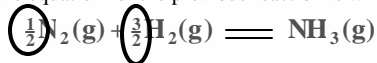


$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

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A Problem To Consider

- Write the equilibrium-constant expression K_c when the equation for the previous reaction is written.



- Whether coefficients are fractional or not, they still become exponents in the equilibrium-constant expression.

$$K_c = \frac{[\text{NH}_3]}{[\text{N}_2]^{\left(\frac{1}{2}\right)}[\text{H}_2]^{\left(\frac{3}{2}\right)}}$$

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Equilibrium: A Kinetics Argument

- If the forward and reverse reaction rates in a system at equilibrium are equal, then it follows **that their rate laws would be equal.**

- Consider the decomposition of N_2O_4 , dinitrogen tetroxide.



- If we start with some dinitrogen tetroxide and heat it, it begins to decompose to produce NO_2 .

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Equilibrium: A Kinetics Argument

- If the forward and reverse reaction rates in a system at equilibrium are equal, then it follows that their rate laws would be equal.

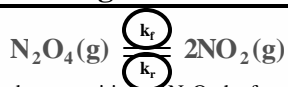
- Consider the decomposition of N_2O_4 , dinitrogen tetroxide.



- However, once some NO_2 is produced it can recombine to form N_2O_4 .

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Equilibrium: A Kinetics Argument

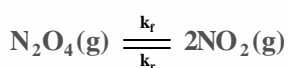


- Call the decomposition of N_2O_4 the forward reaction and the formation of N_2O_4 the reverse reaction.
- These are elementary reactions, and you can immediately write the rate law for each.

$\text{Rate}_{(\text{forward})} = k_f [\text{N}_2\text{O}_4]$ Here k_f and k_r represent the forward and reverse rate constants.
 $\text{Rate}_{(\text{reverse})} = k_r [\text{NO}_2]^2$

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Equilibrium: A Kinetics Argument

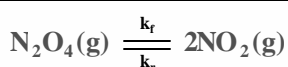


- Ultimately, this reaction reaches an equilibrium state where the rate of the forward and reverse reactions are equal, therefore:

$$\underbrace{k_f [\text{N}_2\text{O}_4]}_{\text{rate forward}} = \underbrace{k_r [\text{NO}_2]^2}_{\text{rate reverse}}$$

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Equilibrium: A Kinetics Argument



- Combining the constants you can identify the equilibrium constant K_c , as the ratio of the forward and reverse rate constants.

$$K_c = \frac{k_f}{k_r} = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$$

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Obtaining Equilibrium Constants for Reactions

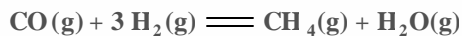
⚠ Equilibrium concentrations for a reaction must be obtained **experimentally** and then **substituted** into the equilibrium-constant expression in order to calculate K_c .

◆ This K_c can then be used to define any equilibrium composition for that particular reaction.

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Obtaining Equilibrium Constants for Reactions

⚠ Consider the reaction below.

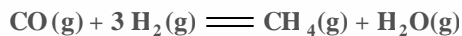


◆ Suppose we started with initial concentrations of CO and H₂ of 0.100 M and 0.300 M, respectively.

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Obtaining Equilibrium Constants for Reactions

⚠ Consider the reaction below.



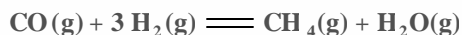
◆ When the system finally settled into equilibrium we determined the equilibrium concentrations to be as follows.

Reactants	Products
[CO] = 0.0613 M	[CH ₄] = 0.0387 M
[H ₂] = 0.1893 M	[H ₂ O] = 0.0387 M

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Obtaining Equilibrium Constants for Reactions

⚡ Consider the reaction below.



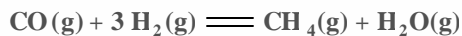
• The equilibrium-constant expression for this reaction is:

$$K_c = \frac{[\text{CH}_4][\text{H}_2\text{O}]}{[\text{CO}][\text{H}_2]^3}$$

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Obtaining Equilibrium Constants for Reactions

⚡ Consider the reaction below.



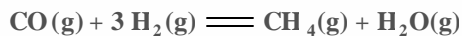
• If we substitute the equilibrium concentrations, we obtain:

$$K_c = \frac{(0.0387\text{M})(0.0387\text{M})}{(0.0613\text{M})(0.1839\text{M})^3} = 3.93$$

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Obtaining Equilibrium Constants for Reactions

⚡ Consider the reaction below.

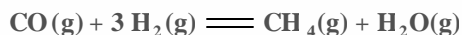


• Note that regardless of initial concentrations (whether they be reactants or products) the law of mass action dictates that the reaction will always settle into an equilibrium **where the equilibrium-constant expression equals K_c** .

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Obtaining Equilibrium Constants for Reactions

⚡ Consider the reaction below.



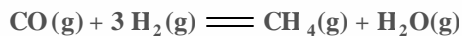
- For example, if we repeat the previous experiment, only this time, starting with initial concentrations of products:

$$[\text{CH}_4]_{\text{initial}} = 0.1000 \text{ M} \text{ and } [\text{H}_2\text{O}]_{\text{initial}} = 0.1000 \text{ M}$$

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Obtaining Equilibrium Constants for Reactions

⚡ Consider the reaction below.



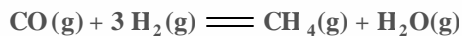
- We find that these initial concentrations result in the following equilibrium concentrations.

Reactants	Products
$[\text{CO}] = 0.0613 \text{ M}$	$[\text{CH}_4] = 0.0387 \text{ M}$
$[\text{H}_2] = 0.1893 \text{ M}$	$[\text{H}_2\text{O}] = 0.0387 \text{ M}$

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Obtaining Equilibrium Constants for Reactions

⚡ Consider the reaction below.



- Substituting these values into the equilibrium-constant expression, we obtain the same result.

$$K_c = \frac{(0.0387\text{M})(0.0387\text{M})}{(0.0613\text{M})(0.1839\text{M})^3} = 3.93$$

- Whether we start with reactants initially or products, the system establishes the same ratio.

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The Equilibrium Constant K_p

✎ In discussing **gas-phase equilibria**, it is often more convenient to express concentrations in terms of partial pressures rather than molarities.

- It can be seen from the ideal gas equation that partial pressure of a gas is proportional to its molarity.

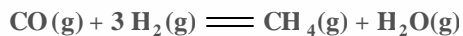
$$P = \left(\frac{n}{V}\right)RT = MRT$$

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The Equilibrium Constant K_p

✎ If we express a gas-phase equilibria in terms of partial pressures, we obtain K_p .

- Consider the reaction below.



- The equilibrium-constant expression in terms of partial pressures becomes:

$$K_p = \frac{P_{\text{CH}_4} P_{\text{H}_2\text{O}}}{P_{\text{CO}} P_{\text{H}_2}^3}$$

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The Equilibrium Constant K_p

✎ In general, the numerical value of K_p is different than that of K_c .

- From the relationship $n/V = P/RT$, one can show

$$K_p = K_c (RT)^{\Delta n}$$

where Δn is the sum of the moles of gaseous products in a reaction minus the sum of the moles of gaseous reactants.

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A Problem To Consider

Consider the reaction



The K_c for the reaction is 2.8×10^2 at 1000 K.
Calculate the K_p for the reaction at this temperature.

Therefore, $\Delta n = -1$

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A Problem To Consider

Consider the reaction



Since

$$K_p = K_c (RT)^{\Delta n}$$

and from the equation we see that $\Delta n = -1$, we can simply substitute the given reaction temperature and the value of R ($0.08206 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K}$) to obtain K_p .

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A Problem To Consider

Consider the reaction



Since

$$K_p = K_c (RT)^{\Delta n}$$

$$K_p = 2.8 \times 10^2 \left(0.08206 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}} \times 1000 \text{ K}\right)^{-1}$$

$$K_p = 3.4$$

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Equilibrium Constant for the Sum of Reactions

Similar to the method of combining reactions we saw using Hess' law in chapter 6, we can combine equilibrium reactions whose K_c 's are known to obtain the K_c for the overall reaction.

- Just as with Hess' law, when we reversed reactions or took multiples of them prior to adding them together, we had to manipulate the ΔH 's to reflect what we had done.
- The rules are a bit different for manipulating K_c 's.

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Equilibrium Constant for the Sum of Reactions

1. If you **reverse** a reaction, **invert** the value of K_c .

For example, $aA + bB \rightleftharpoons cC + dD$

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

If we reverse : $cC + dD \rightleftharpoons aA + bB$

$$K_{\text{reverse}} = \frac{1}{K_{\text{forward}}} = \frac{[A]^a [B]^b}{[C]^c [D]^d}$$

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Equilibrium Constant for the Sum of Reactions

2. If you **multiply** each of the coefficients in an equation by the same factor (2, 3, ...), **raise the K_c to the same power** (2, 3, ...).

For example, $A + B \rightleftharpoons C + D$

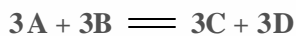
$$K_{\text{initial}} = \frac{[C][D]}{[A][B]}$$

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Equilibrium Constant for the Sum of Reactions

2. If you **multiply** each of the coefficients in an equation by the same factor (2, 3, ...), **raise the K_c to the same power** (2, 3, ...).

If we triple the reaction:



$$K_{\text{triple}} = \frac{[C]^3[D]^3}{[A]^3[B]^3} = (K_{\text{initial}})^3$$

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Equilibrium Constant for the Sum of Reactions

3. If you **divide** each of the coefficients in an equation by the same factor (2, 3, ...) **take the corresponding root of the K_c** (i.e., square root, cube root, ...).

For example, $A + B \rightleftharpoons C + D$

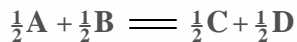
$$K_{\text{initial}} = \frac{[C][D]}{[A][B]}$$

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Equilibrium Constant for the Sum of Reactions

3. If you **divide** each of the coefficients in an equation by the same factor (2, 3, ...) **take the corresponding root of the K_c** (i.e., square root, cube root, ...).

If we halve the reaction:

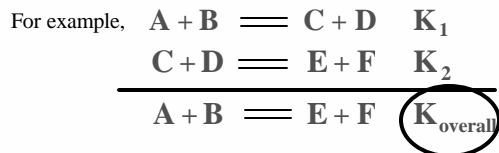


$$K_{\text{halved}} = \frac{[C]^{\frac{1}{2}}[D]^{\frac{1}{2}}}{[A]^{\frac{1}{2}}[B]^{\frac{1}{2}}} = (K_{\text{initial}})^{\frac{1}{2}} = \sqrt{K_{\text{initial}}}$$

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Equilibrium Constant for the Sum of Reactions

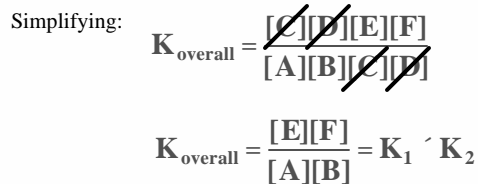
4. When you finally combine (that is, add) the individual equations together, take the **product** of the equilibrium constants to obtain the **overall K_c** .



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Equilibrium Constant for the Sum of Reactions

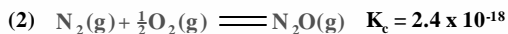
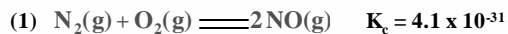
4. When you finally combine (that is, add) the individual equations together, take the **product** of the equilibrium constants to obtain the **overall K_c** .



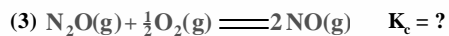
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Equilibrium Constant for the Sum of Reactions

- For example, nitrogen and oxygen can combine to form either NO(g) or N₂O(g) according to the following equilibria.



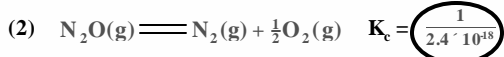
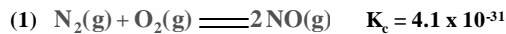
*Using these two equations, we can obtain the K_c for the formation of NO(g) from N₂O(g)



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Equilibrium Constant for the Sum of Reactions

◆ To combine equations (1) and (2) to obtain equation (3), we must first reverse equation (2). When we do we must also take the reciprocal of its K_c value.



$$K_c(\text{overall}) = (4.1 \times 10^{-31}) \cdot \left(\frac{1}{2.4 \times 10^{18}} \right) = 1.7 \times 10^{-13}$$

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Heterogeneous Equilibria

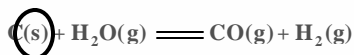
◆ A **heterogeneous equilibrium** is an equilibrium that involves reactants and products in more than one phase.

- ◆ The equilibrium of a heterogeneous system is unaffected by the amounts of pure solids or liquids present, as long as some of each is present.
- ◆ The concentrations of pure solids and liquids is considered to be "1" and therefore, do not appear in the equilibrium expression.

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Heterogeneous Equilibria

◆ Consider the reaction below.



- ◆ The equilibrium-constant expression contains terms for only those species in the homogeneous gas phase... H_2O , CO , and H_2 .

$$K_c = \frac{[\text{CO}][\text{H}_2]}{[\text{H}_2\text{O}]}$$

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Operational Skills

- ✎ Applying stoichiometry to an equilibrium mixture
- ✎ Writing equilibrium-constant expressions
- ✎ Obtaining the equilibrium constant from reaction composition
- ✎ Determining equilibrium constants for sums of reactions

Time for a few review questions.

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