## Unit 7 - Equilibrium

Ch 15

## Dueling graduated cylinder activity

What do all the graphs on the board have in common? What does this tell you?

Chemical equilibrium, ch 15.1
What is a reversible reaction?

What happens to the forward rate as $C$ and $D$ are produced?

What is equilibrium? What MUST be equal? What does not have to be equal?


What is the concentration vs time graph showing?

What is the rate vs time graph showing?

Describe chemical and physical equilibrium

Describe homogeneous and heterogeneous equilibrium

What does it mean when the rate of the forward reaction is greater than the rate of the reverse reaction?

What does it mean when the rate of the reverse reaction is greater than the rate of the forward reaction?

What does it mean when the rate of the forward reaction is equal to the rate of the reverse reaction?

Equilibrium constants, ch 15.2
$a A+b B \leftrightarrow c C+d D$
Write the rate law for the forward reaction
Write the rate law for the reverse reaction
At equilibrium, what do you know about the rates?
Write the equilibrium-constant expression, $\mathrm{K}_{\mathrm{c}}$, for the generic reversible reaction above.

What is the difference between $K_{c}$ and $K_{p}$ ?

What species are not included when writing an equilibrium-constant expression?

What happens to the equilibrium constant when $T$ changes?

## Sample problem

- Write the equilibrium expression, $\mathrm{K}_{\mathrm{c}}$, for the following reaction:

$$
\mathrm{N}_{2}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{NH}_{3}(\mathrm{~g})
$$

- Write the equilibrium expression, $\mathrm{K}_{\mathrm{p}}$, for the same reaction:


## Practice 1

1. Write the equilibrium-constant expression $\mathrm{K}_{\mathrm{c}}$ for

$$
\mathrm{N}_{2} \mathrm{O}_{4}(g) \rightleftharpoons 2 \mathrm{NO}_{2}(g)
$$

2. Use the chart to calculate the value of $K_{c}$
3. Write the equilibrium-constant expression $K_{p}$ for

$$
2 \mathrm{~N}_{2} \mathrm{O}_{5}(g) \leftrightharpoons \mathrm{O}_{2}(g)+4 \mathrm{NO}_{2}(g)
$$

4. Use the data to calculate the value of $K_{p}$

Understanding K, ch 15.3

| If $K>1$ |  |  |
| :---: | :--- | :--- |
| If $K<1$ |  |  |

Describe the diagrams

(a) $K \gg 1$

(b) $K \ll 1$

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What does it mean if the value for $K$ is very large?

What does it mean if the value for K is very small?

Without doing any calculations, rank the three systems in order of increasing equilibrium constant, $K_{c}$


## Practice 2

1. Write the equilibrium-constant expression $\mathrm{K}_{\mathrm{c}}$. What does the value of $K_{c}$ indicate for this reaction?

$$
\begin{gathered}
\mathrm{CO}(g)+\mathrm{Cl}_{2}(g) \rightleftharpoons \mathrm{COCl}_{2}(g) \\
K_{c}=4.56 \times 10^{9}
\end{gathered}
$$

What is the difference between the equilibrium constant $K$ and the reaction quotient $Q$ ?
$a A+b B \leftrightarrow c C+d D$
Write the reaction quotient expression, Q , for the generic reversible reaction above.

What does it mean if $Q>K$ ?

What does it mean if $Q<K$ ?

What does it mean if $Q=K$ ?

## Sample problem

- For the reaction $\mathrm{N}_{2} \mathrm{O}_{4}(\mathrm{~g})<==>2 \mathrm{NO}_{2}(\mathrm{~g}), \mathrm{K}_{\mathrm{c}}=0.2$. At a particular time, the following concentrations are measured: $\left[\mathrm{N}_{2} \mathrm{O}_{4}\right]=2.0 \mathrm{M},\left[\mathrm{NO}_{2}\right]=0.2 \mathrm{M}$. Is this reaction at equilibrium? If not which direction will the reaction proceed?


## Practice 3

1. 2.00 M hydrogen, 1.00 M nitrogen, and 2.00 M ammonia is placed in a flask and allowed to react. How will the mixture react to reach equilibrium? $\mathrm{K}_{\mathrm{c}}=0.105$

$$
\mathrm{N}_{2}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{NH}_{3}(\mathrm{~g})
$$

What if instead of $a A+b B \leftrightarrow c C+d D$ we had $c C+d D \leftrightarrow a A+b B$ ?
What is the new equilibrium expression, $\mathrm{K}^{\prime}$ ?

How is this related to the old $\mathrm{K}_{\mathrm{c}}$ ?

What if instead of $\mathrm{aA}+\mathrm{bB} \leftrightarrow \mathrm{cC}+\mathrm{dD}$ we had $2 \mathrm{aA}+2 \mathrm{bB} \leftrightarrow 2 \mathrm{cC}+2 \mathrm{dD}$ ?
What is the new equilibrium expression, $\mathrm{K}^{\prime 2}$ ?

How is this related to the old $\mathrm{K}_{\mathrm{c}}$ ?

Solving equilibrium problems, ch 15.2, 15.5, 15.6
What does ICE stand for?

What units can be used in an ICE table?
What does $x$ indicate?
+/- x reactants (circle one) and +/-x products (circle one)
$-x$ or $+x$ *may be* negligible in which cases?

What do you do if -x or +x is NOT negligible?

Sample problems

| $\mathrm{M}^{2+}+2 \mathrm{~L} \leftrightarrows$ |  |  | $\mathrm{ML}_{2}{ }^{+}$ |
| :---: | :---: | :---: | :---: |
|  | $\left[\mathbf{M}^{2+}\right]$ | $[\mathbf{L}]$ | $\left[\mathbf{M L}_{\mathbf{4}}{ }^{+}\right]$ |
| I | 0.20 M | 0.40 M | 0 M |
| C | - |  |  |
| E | - |  |  |

- A mixture of 9.22 moles of $\mathbf{A}, 10.11$ moles $\mathbf{B}$, and 27.83 moles $\mathbf{C}$ is placed in a 1 L container. The reaction is allowed to reach equilibrium. At equilibrium the number of moles of $B$ is 18.32 . Calculate the equilibrium constant $\mathrm{K}_{\mathrm{c}}$ for the reaction:
A (g) +
2 B (g)
$\rightleftharpoons$
3 C (g


## Practice 4

1. When 4.00 mol of $A$ and 4.00 mole of $B$ are placed in a container and allowed to come to equilibrium, the mixture is found to contain 0.80 mol of $D$. What are the amounts of $A, B$, and $C$ at equilibrium?

$$
\mathrm{A}(\mathrm{~g})+3 \mathrm{~B}(\mathrm{~g}) \rightleftharpoons \mathrm{C}(\mathrm{~g})+\mathrm{D}(\mathrm{~g})
$$

## Sample problems

- What are the equilibrium concentrations of $A$ and $A_{2}$ if the initial $\left[A_{2}\right]$ is 0.60 M and initial $[A]=0$ M? (Small x approximation)

$$
\mathrm{A}_{2}(\mathrm{~g})=2 \mathrm{~A}(\mathrm{~g})
$$

$$
\mathrm{K}=4.2 \times 10^{-8}
$$

- The reaction of bromine gas with chlorine gas, shown here, has a Kc value of 7.20 at $200{ }^{\circ} \mathrm{C}$. If a closed vessel was charged with the two reactants, each at an initial concentration of 0.200 M , but with no initial concentration of BrCl , what would be the equilibrium concentration of $\mathrm{BrCl}(\mathrm{g})$ ? (Use quadratic)

$$
\mathrm{Br}_{2}(\mathrm{~g})+\mathrm{Cl}_{2}(\mathrm{~g}) \leftrightarrows 2 \mathrm{BrCl}(\mathrm{~g}) \quad \mathrm{K}=7.20
$$

## Practice 5

1. Given the initial concentrations shown below, find the equilibrium concentrations for $A, B$, and C. (Use small x approximation)

| $\mathrm{A}(\mathrm{g})+\mathrm{B}(\mathrm{g})$ |  |  |
| :--- | ---: | ---: |
| 0.500 M | 0.500 M | 0.000 M |$\quad \mathrm{K}=9.0 \times 10^{-8}$

2. A flask contains 1.000 M hydrogen and 2.000 M iodine. $\mathrm{Kc}=50.5$. What are the equilibrium concentrations of hydrogen, iodine, and hydrogen iodide in moles/L? (Use quadratic)
$\mathrm{H}_{2}(g)+\mathrm{I}_{2}(g) \rightleftharpoons 2 \mathrm{HI}(g)$
3. If 0.820 mole of NO and 0.223 mole each of $\mathrm{N}_{2}$ and $\mathrm{O}_{2}$ are mixed in a 1.00 L container at 1100 C , what are the concentrations of $\mathrm{NO}, \mathrm{N}_{2}$, and $\mathrm{O}_{2}$ at equilibrium?
$2 \mathrm{NO}(\mathrm{g}) \rightleftharpoons \mathrm{N}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g})$

$$
\mathrm{K}_{\mathrm{c}}=2.60 \times 10^{-7}
$$

FOLLOW-UP PROBLEM 17.9 In a study of halogen bond strengths, 0.50 mol of $\mathrm{I}_{2}$ was heated in a 2.5 -L vessel, and the following reaction occurred: $\mathrm{I}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{I}(\mathrm{g})$. (a) Calculate $\left[\mathrm{I}_{2}\right]$ and $[\mathrm{I}]$ at equilibrium at $600 \mathrm{~K} ; K_{\mathrm{c}}=2.94 \times 10^{-10}$.
(b) Calculate $\left[\mathrm{I}_{2}\right]$ and [I] at equilibrium at $2000 \mathrm{~K} ; K_{\mathrm{c}}=0.209$.

## Le Châtelier's Principle, ch 15.7

What can you change to shift the balance in a system at equilibrium?

What is Le Châtelier's Principle?

What effect does adding or removing a component in a reaction system at equilibrium have (increasing or decreasing concentration)? Why?

Did $k_{f}$ or $k_{r}$ change? Did Q? Did $K_{c}$ ?

What effect does adding or removing a component in a gaseous reaction system at equilibrium have (increasing or decreasing partial pressure)? Why?

Did $k_{f}$ or $k_{r}$ change? Did Q? Did $K_{c}$ ?

What effect does adding an inert gas to a reaction system at equilibrium have? Why?

What effect does changing the volume of a gaseous reaction system at equilibrium have (increasing or decreasing volume)? Why?

Did $k_{f}$ or $k_{r}$ change? Did Q? Did $K_{c}$ ?

## Sample problem

$$
\mathrm{N}_{2}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{NH}_{3}(\mathrm{~g})
$$

- The system is at equilibrium. What happens to the concentrations of nitrogen and ammonia after additional hydrogen is added?
- What happens to the concentrations of nitrogen and hydrogen after ammonia is removed from the system?
- What happens to the position of equilibrium when the partial pressure of nitrogen is increased?
- What happens to the system when the volume of the container is decreased?
- What happens when the pressure inside the container is increased by the addition of helium gas?

Changes in concentration and pressure will change the $\qquad$ of equilibrium but will NOT change the $\qquad$ .

Why does changing $T$ change the value of $K$ ?

For endothermic reactions, $\Delta \mathrm{H}$ is $+/$ - (circle one)
$556 \mathrm{~kJ}+\mathrm{CaCO}_{3(\mathrm{~s})} \leftrightarrows \mathrm{CaO}_{(\mathrm{s})}+\mathrm{CO}_{2(\mathrm{~g})}$
Adding heat will cause the reaction to shift $\qquad$ Removing heat will cause the reaction to shift $\qquad$
The value of $K$ will $\qquad$ .

For exothermic reactions, $\Delta \mathrm{H}$ is + / - (circle one)
$\mathrm{N}_{2(\mathrm{~g})}+3 \mathrm{H}_{2(\mathrm{~g})} \leftrightarrows 2 \mathrm{NH}_{3(\mathrm{~g})}+92 \mathrm{~kJ}$
Adding heat will cause the reaction to shift $\qquad$ Removing heat will cause the reaction to shift $\qquad$

The value of $K$ will $\qquad$

## Sample problem

$$
2 \mathrm{POCl}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{PCl}_{3}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g})
$$

$$
\Delta \mathrm{H}=508.3 \mathrm{~kJ}
$$

- Rewrite the equation with heat as a reactant or product.
- If heat is added to the equilibrium system, in which direction would the equilibrium shift?
- How would equilibrium shift if the system is cooled?

What effect will adding a catalyst have to a system at equilibrium? Why?

## Practice 6

$$
\mathrm{H}_{2}(g) \quad+\mathrm{Br}_{2}(g) \leftrightarrows 2 \mathrm{HBr}(g)
$$

$$
\Delta \mathrm{H}^{\circ}=-103.7 \mathrm{~kJ}
$$

| Change | $\left[\mathrm{H}_{2}\right]$ | $\left[\mathrm{Br}_{2}\right]$ | $[\mathrm{HBr}]$ | K value |
| :--- | :--- | :--- | :--- | :--- |
| 1. Some $\mathrm{H}_{2}$ added |  |  |  |  |
| 2. Some HBr added |  |  |  |  |
| 3. Some $\mathrm{H}_{2}$ removed |  |  |  |  |
| 4. Some HBr removed |  |  |  |  |
| 5. The temperature is increased |  |  |  |  |
| 6. The temperature is decreased |  |  |  |  |
| 7. Pressure is increased and the <br> container volume decreased |  |  |  |  |

Solubility equilibria, ch 17.4
Take notes on solubility

## Sample problem

- Write the solubility-product expression ( $\mathrm{K}_{\text {sp }}$ ) for barium sulfate, which is only slightly soluble in water.

What is the difference between solubility and solubility product $\left(\mathrm{K}_{\text {sp }}\right)$ ?

## Sample problem

- Write the solubility-product expression for $\mathrm{K}_{\mathrm{sp}}$ for calcium fluoride. Calculate the solubility of calcium fluoride in $\mathrm{mol} / \mathrm{L}$ and $\mathrm{g} / \mathrm{L}$. $\mathrm{K}_{\text {sp }}=3.9 \times 10^{-11}$
- Silver chromate is added to water. At equilibrium some solid is left undissolved. $0.022 \mathrm{~g} / \mathrm{L}$ of silver chromate is dissolved. Calculate the $\mathrm{K}_{\text {sp }}$ and write the solubility-product expression.


## Practice 7

1. The $\mathrm{K}_{\text {sp }}$ for $\mathrm{LaF}_{3}$ is $2 \times 10^{-19}$. Write the expression for $\mathrm{K}_{\text {sp }}$. What is the solubility of $\mathrm{LaF}_{3}$ in $\mathrm{mol} / \mathrm{L}$ and $\mathrm{g} / \mathrm{L}$ ?
2. Calculate the $\mathrm{K}_{\mathrm{sp}}$ for magnesium hydroxide. Write the expression for $\mathrm{K}_{\mathrm{sp}}$. The concentration of hydroxide in solution is $1.5 \times 10^{-4} \mathrm{M}$.

When can you compare $K_{\text {sp }}$ values for different compounds? What does a larger $K_{\text {sp }}$ indicate? Smaller $K_{\text {sp }}$ ?

Common ion effect, ch 17.5
Describe the common ion effect in your own words.

Sample problem

- Calculate the molar solubility of calcium fluoride in a solution that is 0.0010 M in calcium nitrate.


## Practice 8

1. Calculate the solubility of $\mathrm{SrSO}_{4}$, $\left(\mathrm{K}_{\text {sp }}\right.$ of $\left.3.2 \times 10^{-7}\right)$ in M and $\mathrm{g} / \mathrm{L}$ in a solution of $0.010 \mathrm{M} \mathrm{Na}_{2} \mathrm{SO}_{4}$.
2. Calculate the solubility of $\mathrm{SrSO}_{4}$, $\left(\mathrm{K}_{\text {sp }}\right.$ of $\left.3.2 \times 10^{-7}\right)$ in M and $\mathrm{g} / \mathrm{L}$ in a solution of $0.010 \mathrm{M} \mathrm{SrNO}_{3}$.

How does the pH of a solution affect the solubility of a salt?

Precipitation, ch 17.6
Using the generic equation $Q=\left[\mathrm{M}^{+}\right]^{\mathrm{a}}\left[\mathrm{Nm}^{-}\right]^{b}$, what do the following indicate?
$\mathrm{Q}=\mathrm{K}_{\text {sp }}$
$\mathrm{Q}>\mathrm{K}_{\text {sp }}$
$Q<K_{\text {sp }}$
Sample problem

- A solution of 750.0 mL of $4.00 \times 10^{-3} \mathrm{M} \mathrm{Ce}\left(\mathrm{NO}_{3}\right)_{3}$ is added to 300.0 mL of $2.00 \times 10^{-2} \mathrm{M} \mathrm{KIO}_{3}$. Will $\mathrm{Ce}\left(\mathrm{IO}_{3}\right)_{3}\left(\mathrm{~K}_{\text {sp }}=1.9 \times 10^{-10} \mathrm{M}\right)$ precipitate and if so, what is the concentration of the ions?

What is a complex ion?

Why is this in the equilibrium unit?

