Ch 14 Chemical Equilibrium

What is Chemical Equilibrium?
- At equilibrium, the reactant and product concentrations are no longer changing because:
  forward rate = reverse rate
- This process is called dynamic equilibrium because the forward and reverse reactions have not stopped occurring. They are both still occurring simultaneously at equilibrium.
- Equilibrium requires a reversible reaction system, such as catalytic methanation where the forward reaction produces methane from carbon monoxide.
  $$CO_{(g)} + 3H_{2(g)} \rightarrow CH_{4(g)} + H_2O_{(g)}$$
- The reverse reaction is called steam reforming, which produces H_2 and CO from methane and steam. The hydrogen and carbon monoxide products are typically used as manufacturing feedstocks or for fuel.
  $$CH_{4(g)} + H_2O_{(g)} \rightarrow CO_{(g)} + 3H_{2(g)}$$
- Symbolize both sides reacting simultaneously with a **reversible double arrow**.
  $$CO_{(g)} + 3H_{2(g)} \rightleftharpoons CH_{4(g)} + H_2O_{(g)}$$
- Conditions of the reaction can be changed to favor one side or the other.

Equilibrium Table
- If all initial concentrations are known, and at least one equilibrium concentration can be measured, then remaining concentrations can be determined from stoichiometry.
- The starting concentrations and the change in concentrations are combined algebraically to find the equilibrium concentrations for each reactant and product.

Example 14.01 Create an **Equilibrium Table** to Determine Concentrations at Equilibrium

	CO	+	$3H_2$	$\rightleftharpoons$	CH_4	+	H_2O
Initial (starting)	0.1500 M		0.2500 M		0		0
Change (with variable)	$-x$		$-3x$		$+x$		$+x$
Equilibrium (sum)	$0.1500 - x$		$0.2500 - 3x$		x		x

$[CH_4] = [H_2O] = x \qquad = \dfrac{0.402 \text{ moles}}{10.00 \text{ L}} \qquad = 0.0402 \text{ M}$

$[CO] \ = \ 0.1500 - x \ = \ 0.1500 - 0.0402 \qquad = 0.1098 \text{ M}$

$[H_2] \ = \ 0.2500 - 3x \ = \ 0.2500 - 3(0.0402) \qquad = 0.1294 \text{ M}$

Equilibrium Constant Expression
- If reversible reaction $aA + bB \rightleftharpoons cC + dD$ is at equilibrium, then the concentrations are no longer changing.
- So the relationship between concentrations can be defined by an expression, which is obtained by multiplying product concentrations, dividing reactant concentrations, and raising each concentration to its **stoichiometric coefficient** as its **exponent**.

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

Example 14.02 Write Equilibrium Constant Expressions

- For $CO + 3H_2 \rightleftharpoons CH_4 + H_2O$, the expression is

$$K_c = \frac{[CH_4][H_2O]}{[CO][H_2]^3}$$

- K_c for the reverse reaction, $CH_4 + H_2O \rightleftharpoons CO + 3H_2$, is the reciprocal: $K_c = \frac{[CO][H_2]^3}{[CH_4][H_2O]}$

- If we double the reaction coefficients, $2CO + 6H_2 \rightleftharpoons 2CH_4 + 2H_2O$,

  then we double the exponents:

$$K_c = \frac{[CH_4]^2[H_2O]^2}{[CO]^2[H_2]^6}$$

Law of Mass Action

- The numerical value of the equilibrium constant (K_c) is **constant**
  as long as temperature is held constant.
- The kinetics argument for this law is that K_c is constant because it is related to rate constants
  for elementary reactions, which have rate laws that are obtained from stoichiometry.
- For $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$ at equilibrium, the forward rate equals reverse rate.
  $$k_f[N_2O_4] = k_r[NO_2]^2 \quad \text{and} \quad K_c = k_f / k_r = [NO_2]^2/[N_2O_4]$$
  Since both rate constants (k_f and k_r) have constant values, K_c must as well.
- Since the rate-determining step for all reaction mechanisms is an elementary reaction,
  a constant K_c is found for all net chemical equations.

The Equilibrium Constant's Value

- The value of the equilibrium constant can be determined from concentration data.
- We can use the data from Example 14.01 on the previous page for catalytic methanation.
  $$K_c = \frac{[CH_4][H_2O]}{[CO][H_2]^3} = \frac{(0.0402 \text{ mol/L})(0.0402 \text{ mol/L})}{(0.1098 \text{ mol/L})(0.1294 \text{ mol/L})^3} = 6.80 \text{ L}^2/\text{mol}^2 \text{ at 1173 K}$$

Ex 14.03 Use an Equilibrium Table to Determine the Value of an Equilibrium Constant (300 K)

	$2HI_{(g)}$	$\rightleftharpoons$	$H_{2(g)}$	$+$	$I_{2(g)}$
Initial	0.994		0		0
Change	$-2x$		x		x
Equilibrium	$(0.994 - 2x)$		x		x

$[HI]_o = \frac{4.97 \text{ mol}}{5.00 \text{ L}} = 0.994$ M

$x = [I_2]_{eqm} = \frac{1.955 \text{ mol}}{5.00 \text{ L}} = 0.391$ M

$[HI]_{eqm} = (0.994 - 2x) = 0.212$ M

$K_c = \frac{[H_2][I_2]}{[HI]^2} = \frac{(0.391 \text{ M})^2}{(0.212 \text{ M})^2} = 3.40$

Equilibrium Constant of Gaseous Reactions using Partial Pressures (K_p)

- The ideal gas law, $PV = nRT$, can be rearranged to $P = (n/V) \times RT = [\text{mol/L}] \times RT$.
- So, equilibrium constants for gases can be expressed using the partial pressures
  of reactants and products, instead of their molarities.
- We can use partial pressures to get K_p at 1173 K for $CO + 3H_2 \rightleftharpoons CH_4 + H_2O$.
  $$K_p = \frac{P_{CH4}P_{H2O}}{P_{CO}P_{H2}^3} = \frac{([CH_4]RT)([H_2O]RT)}{([CO]RT)([H_2]RT)^3} = \frac{[CH_4][H_2O]}{[CO][H_2]^3} \times (RT)^{(1+1-1-3)} = K_c \times (RT)^{-2}$$
  $$K_p = (6.80 \tfrac{L^2}{mol^2}) \times (0.08206 \tfrac{L \cdot atm}{mol \cdot K} \times 1173 \text{ K})^{-2} = 7.34 \times 10^{-4} \text{ atm}^{-2}$$
- **$K_p = K_c(RT)^{\Delta n}$**, where **Δn** = (sum of product coefficients) − (sum of reactant coefficients).
  $\Delta n = (1+1) - (3+1) = -2$ for this reaction, which produces two moles from four moles.

Example 14.04 Find K_p for $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$ where $K_c = 2.11 \times 10^{-2}$ mol/L at 331 K

- $K_p = \frac{P_{PCl3}P_{Cl2}}{P_{PCl5}} = (K_c)(RT)^{(1+1-1)} = (2.11 \times 10^{-2} \text{ mol/L})(0.08206 \frac{\text{L·atm}}{\text{mol·K}} \times 331 \text{ K})^{(2-1)}$

- $K_p = (0.0211 \text{ mol/L})(27.2 \text{ L·atm/mol})^1 = 0.573$ atm

Sum of Chemical Equations
- If a net chemical equation is the **sum** of other net chemical equations, then the equilibrium constant for the sum reaction is the **product** of the component equilibrium constants.
- $CO_{(g)} + 3H_{2(g)} \rightleftharpoons CH_{4(g)} + H_2O_{(g)}$ $Kc_1 = 6.80 \text{ L}^2/\text{mol}^2$ at 1173 K

  $\underline{CH_{4(g)} + 2H_2S_{(g)} \rightleftharpoons CS_{2(g)} + 4H_{2(g)}}$ $Kc_2 = 3.6 \text{ mol}^2/\text{L}^2$ at 1173 K

  $CO_{(g)} + 2H_2S_{(g)} \rightleftharpoons CS_{2(g)} + H_2O_{(g)} + H_{2(g)}$ $Kc_3 = Kc_1 \times Kc_2 = (6.80 \text{ L}^2/\text{mol}^2)(3.6 \text{ mol}^2/\text{L}^2)$

  $Kc_3 = 2.4 \times 10^1$

Homogeneous Equilibrium (All substance are contained in a single phase.)
- All reactants and products are in the same phase, contained in a single liquid or gas solution.
- For example, in catalytic methanation, all of the substances are in the same gaseous mixture.
- Homogeneous reactions can also occur completely dissolved in a single aqueous solution, such as in the formation of a complex ion: $Cu^{2+}_{(aq)} + 4NH_{3(aq)} \rightleftharpoons Cu(NH_3)_4^{2+}_{(aq)}$

Heterogeneous Equilibrium (The reaction involves more than one phase.)
- Solids have surface concentrations that are small, difficult to measure, and are approximately constant.

- Pure liquids also have constant concentrations: $[H_2O_{(L)}] = \frac{1000 \frac{g}{L}}{18.02 \frac{g}{mol}} = 55.5$ M

- Equilibrium is not affected by the pure solids and liquids as long as they are simply present.
- **Omit solids and pure liquids from K_c** to simplify the expression by leaving out constants.

- For $3Fe_{(s)} + 4H_2O_{(g)} \rightleftharpoons Fe_3O_{4(s)} + 4H_{2(g)}$, the expression simplifies to $K_c = \frac{[H_{2(g)}]^4}{[H_2O_{(g)}]^4}$

- Similarly, $Ag_2CO_{3(s)} \rightleftharpoons 2Ag^{+1}_{(aq)} + CO_3^{-2}_{(aq)}$ has $K_c = [Ag^{+1}_{(aq)}]^2[CO_3^{-2}_{(aq)}]$

- Also, $HNO_{2(aq)} + H_2O_{(L)} \rightleftharpoons NO_2^{-1}_{(aq)} + H_3O^{+1}_{(aq)}$ has $K_c = \frac{[H_3O^{+1}_{(aq)}][NO_2^{-1}_{(aq)}]}{[HNO_{2(aq)}]}$

The equilibrium constant can be used to answer important questions about chemical reactions.
1) The magnitude of the constant's value tells us **whether reactants or products are favored.**
2) Kc can predict **direction of reaction** for a mixture that is not at equilibrium.
3) Kc can be used to **calculate equilibrium concentrations** using an equilibrium table.

Qualitatively Interpreting the **Magnitude** of the Equilibrium Constant
- **Large** value means **products** (in numerator) are favored ($K_c \gg 1$)
- **Small** value means **reactants** (in denominator) are favored ($K_c \ll 1$)
- If $Kc \approx 1$, then equilibrium mixture contains both reactants and products
- $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ has $K_c = 2.7 \times 10^8$ at 300 K, so $K_c \gg 1$ (large).
  If $[N_2] = [H_2] = 0.01$ M at equilibrium, then $[NH_3] = 1.6$ M (product is favored).
  The product's equilibrium concentration is much greater than that of the reactants.

Predicting the **Direction of Reaction** for a Mixture that is Not Necessarily at Equilibrium
- The direction can be predicted using the **reaction quotient (Q_c)**, which has exactly
  the same form as K_c, but uses **interim** (not necessarily equilibrium) concentrations.
- $Q_c = \frac{[C]_i^c [D]_i^d}{[A]_i^a [B]_i^b}$ where "**i**" stands for interim
- If $\mathbf{Q_c > K_c}$, the reaction will go to the **left**, towards the reactants.
  Shifting left decreases the numerator and increases the denominator, so that Q_c decreases.
- If $\mathbf{Q_c < K_c}$, the reaction will go to the **right**, towards the products.
  Shifting right increases the numerator and decreases the denominator, so that Q_c increases.
- If $\mathbf{Q_c = K_c}$, then the reaction is at **equilibrium**. No shift occurs.

Example 14.05 Determine Qc and Compare with Kc (4.1 at 600 K)
- $Q_c = \frac{[NH_3]_i^2}{[N_2]_i [H_2]_i^3} = \frac{(0.0100)^2}{(0.00800)(0.100)^3} = 12.5$
- $Q_c > K_c$ The reaction will go left (reverse) until $Q_c = K_c$.

Equilibrium Concentrations can be determined by the following steps.
1) Set up an equilibrium table with the three lines to represent the concentrations:
   initial, **change** (including the variable), and **equilibrium** (as their sum).
2) Substitute the equilibrium line (including the variable) into the **Kc expression**.
3) Use the value for Kc to **solve** for the variable, and then find the concentrations.

Example 14.07 Solve for Equilibrium Concentrations with a Perfect Square
- For the reaction $CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$, we have $[CO_{(g)}]_o = [H_2O_{(g)}]_o = 0.0250$ M
- The equilibrium table is similar to Example 14.01.

  The result here gives us: $K_c = \frac{[CO_{2(g)}][H_{2(g)}]}{[CO_{(g)}][H_2O_{(g)}]} = \frac{(x)(x)}{(0.0250 - x)(0.0250 - x)} = \frac{x^2}{(0.0250 - x)^2}$

- Solve for x by taking the square root of the equation: $\frac{x}{(0.0250 - x)} = \pm \sqrt{K_c}$

- The square root of the equation can then be rearranged: $1x = (0.0250 - x)(\pm\sqrt{K_c})$

- Then, place the terms with x on the same side: $[1 + (\pm\sqrt{K_c})](x) = (0.0250)(\pm\sqrt{K_c})$

- Finally, solve for x: $x = \frac{(0.0250)(\pm\sqrt{K_c})}{1 + (\pm\sqrt{K_c})}$

- $K_C = 0.625$ at 990 °C gives us: $[CO_{2(g)}] = [H_{2(g)}] = x = 0.0110$ M
  $[CO_{(g)}] = [H_2O_{(g)}] = 0.0250 - x = 0.0140$ M

Solving Equilibrium Tables that do Not have Perfect Squares
- If the reactant concentrations in Example 14.07 were not equal,
  then the K_c expression would not be a perfect square.
- Examples 13.9 and 13.10 in Open Stax also have expressions that are not perfect squares.
- In those cases, the expressions can be rearranged to create a binomial: $ax^2 + bx + c = 0$
- The binomial can be solved with the quadratic formula: $x = \dfrac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

Effect of Changing Conditions on Equilibrium Concentrations
- The equilibrium concentrations can be changed by:
  o adding or removing either reactants or products
  o changing partial pressures (P_A) of reactants and products by changing the volume
  o changing the temperature
- The effect can be predicted from LeChatelier's principle of dynamic equilibrium.
  **When a system at chemical eqm is disturbed by a change in [concentration], P_A , or T,
  then the equilibrium concentrations shift to counteract that change.**

Adding and Removing Substances Involved in a Reaction
- If you remove or add a substance involved in the reaction,
  the equilibrium constant will not change, but Q_c does.
- The reaction will proceed to restore the balance, until $Q_c = K_c$ again.
- If reactant is added or product is removed, then **$Q_c < K_c$** and the eqm shifts right (forward).
- If a reactant is removed or a product is added, then **$Q_c > K_c$** and the eqm shifts left (reverse).

Example 14.09 Shifting Equilibrium by Changing Concentrations
- $H_{2(g)} + Br_{2(g)} \rightleftharpoons 2HBr_{(g)}$ is initially at equilibrium, and then $H_{2(g)}$ reactant is removed.
- Removing a reactant will increase the value of Q_c, so that $Q_c > K_c$.
- The equilibrium shifts left, the reaction goes in reverse, and more $H_{2(g)}$ is created.

Changing Partial Pressures Affects Equilibrium Concentrations
- Reactions involving gases can shift their equilibrium as a result of changes to pressure
  and volume. Suppose the partial pressures of the gases are all increased proportionally
  by **decreasing the volume**. The reaction will counteract the change by shifting the
  equilibrium **towards fewer moles of gas**. This occurs because, as moles (n) decrease,
  the pressure does also, which counteracts the change.
- Also, **increasing the volume** will shift the equilibrium **towards more moles of gas**.
- Reducing partial pressures shifts the equilibrium to the right for $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$.

Example 14.10 Determine Shift Direction when Partial Pressures of All Gases are Increased
- $CO_{(g)} + 2H_{2(g)} \rightleftharpoons CH_3OH_{(g)}$ Fewer moles of gas is towards the right (forward).
- $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$ Fewer moles of gas is towards the left (reverse).
- $S_{(s)} + O_{2(g)} \rightleftharpoons SO_{2(g)}$ No shift at all because each side has one mole of gas.

Changing Partial Pressures Affects the Reaction Quotient (Q_c)
- If volume (V) is reduced by half, then each concentration (n/V) doubles.
  If we double concentrations for $CO_{(g)} + 3H_{2(g)} \rightleftharpoons CH_{4(g)} + H_2O_{(g)}$, the result is:
  $$Q_c = \frac{(2[CH_4]_0)(2[H_2O]_0)}{(2[CO]_0)(2[H_2]_0)^3} = \frac{4}{16} \times \frac{[CH_4]_0[H_2O]_0}{[CO]_0[H_2]_0^3} = \frac{1}{4} \times K_c$$
  So, $Q_c < K_c$ and the reaction goes to the right, where there are fewer moles of gas.
- Adding a nonparticipant (like He), though, only changes the total moles and total pressure.
  The nonparticipant does not change any other substance's partial pressure or concentration.
  So, the Q_c and the equilibrium concentrations will not change as a result.

Temperature affects Equilibrium Concentrations by **Changing K_c**
- For an endothermic reaction ($\Delta H > 0$), more heat favors products.
  Increasing T will increase Kc and make $Q_c < K_c$, so that equilibrium shifts right (forward).
  $\qquad$ Reactant + Heat $\rightleftharpoons$ Product
  Adding heat (by increasing T) to an endothermic reaction is like adding a reactant.
- For an exothermic reaction ($\Delta H < 0$), less heat favors products.
  Decreasing T will increase Kc and make $Q_c < K_c$, so that equilibrium shifts right (forward).
  $\qquad$ Reactant $\rightleftharpoons$ Product + Heat
  Removing heat (by decreasing T) from an exothermic reaction is like removing product.
- Increasing T, by comparison, shifts the exothermic reaction to the left (reverse).
  Kc **decreases** as T increases.

Optimizing an Exothermic Reaction
- For $CO_{(g)} + 3H_{2(g)} \rightleftharpoons CH_{4(g)} + H_2O_{(g)}$, we have $\Delta H = -206 \frac{kJ}{mol\ CO}$.
- Increase T just enough to increase rate constant and the reaction rate,
  but not enough to reduce Kc significantly for the exothermic reaction.
  Somewhere between 230 ^{o}C and 450 ^{o}C is ideal.
- Also, increase the partial pressures of reactants (P_{CO} and P_{H2}) moderately
  in order to shift the equilibrium to the right, towards fewer moles of gas.

Catalysts
- Catalysts are **not** part of the K_c expression.
- Catalysts do **not** affect equilibrium compositions.
- However, they **decrease the time** needed to reach equilibrium.
- For $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$, we have $K_c = 7.9 \times 10^4$ L/mol at 527 ^oC.
  The reaction has a very large K_c and is used industrially to produce H_2SO_4 from sulfur.
  However, the uncatalyzed combustion of sulfur produces mostly $SO_{2(g)}$ and very little $SO_{3(g)}$.
  The uncatalyzed conversion into $SO_{3(g)}$ is very slow, and it doesn't reach equilibrium.
  $Pt_{(s)}$ and $V_2O_{5(s)}$ increase the rate for creating SO_3 so that **the equilibrium can be reached**.
- For $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$, we have $K_c = 2.0 \times 10^{-25}$ at 100 ^oC
  This reaction has a very small K_c at 100 ^oC.
  Catalysts will not help at low temperatures in this reaction
  because catalysts do not change equilibrium concentrations.
  K_c increases with T, and higher temperatures have higher product concentrations at eqm.
  So, air can be used with a catalyst at 2000 ^oC to form 0.4 % $NO_{(g)}$ in the air mixture.