CHEM 116 Introducing Equilibrium

Today we will begin with the end of Lecture 14 notes that we didn't finish on Tuesday, about nuclear chemistry. If you have already printed Lecture 14, then bring it to lecture with you, and you can avoid re-printing those pages by not printing pages 2 to 6 of these Lecture 15 notes. Lecture 15 Prof. Sevian



Today's agenda

- Nuclear chemistry (the only parts we will cover in ch. 21)
 - Types of radiation
 - Nuclear decay equations
 - ---- End of material that is covered on Exam 2 ---
- Equilibrium (ch. 15, this material will be on Exam 3)
 - Measuring concentrations in the lab
 - Reaction quotient is a measure of the ratio of concentrations of chemicals that are changing in the reaction
 - Reaction quotient approaches a constant value as equilibrium is achieved
 - What is equilibrium?

Key points about rxn mechanisms

- A rxn mechanism is plausible if it satisfies two conditions
 - 1. The elementary steps must sum to the overall rxn
 - 2. The rate of the slowest elementary step has the same form as the experimentally determined rate law (may involve mathematical manipulation)
- You <u>cannot</u> write down a rate law by inspection of an overall reaction
- You CAN write down a rate law by inspection of an elementary step, because it contains information about the molecularity of the step
- Fast equilibrium/fast reversible reaction means forward rate equals reverse rate
- The chemicals that cancel out when you sum elementary steps are the intermediates in a rxn mechanism

A little bit about nuclear chemistry

- This is chapter 21
- Chemical bonding and chemical reactions are about what electrons do when one atom is near another atom – balance between energy changes and entropy changes
- Nuclear chemistry is about energy changes that occur when nuclear particles interact
- Practical uses of learning this
 - Medical applications (radiation therapy, diagnostic tools)
 - Archaeological dating
 - Nuclear power accounts for 20% of electricity generated in US
 - Nuclear weapons pose threats, are used in political bargaining...

Nuclear particles and processes

- Recall that protons determine identity and that different isotopes of an element result from differing quantities of neutrons
- Different isotopes of an element have different natural abundances
- Some isotopes are radioactive (unstable) and decay by specific processes to form more stable isotopes
- If a decay process results in a product with a different number of protons, then the identity of the product element is different than the original reactant
- Although conservation of mass does not apply (because mass and energy are inter-convertible), some conservation laws still apply in nuclear decays:
 - Conservation of mass number
 - Conservation of atomic number

Where does the mass go?



Positron is a positive electron (antielectron)

$${}^{11}_{6}\text{C} \rightarrow {}^{11}_{5}\text{B} + {}^{0}_{+1}\text{e}$$

More nuclear processes

- Gamma decay
 - Symbol is ${}^{0}_{0}\gamma$
 - Since no nuclear transmutations, no need to write equation
- Electrons and positrons can be captured ${}^{81}_{37}\text{Rb} + {}^{0}_{-1}\text{e} \rightarrow {}^{81}_{36}\text{Kr}$
- Larger nuclei can split (fission) into smaller nuclei (often by neutron bombardment)

$${}^{1}_{0}n + {}^{239}_{94}Pu \rightarrow {}^{95}_{40}Zr + {}^{142}_{54}Xe + 2 {}^{1}_{0}n$$

• Smaller nuclei can fuse into larger nuclei

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^{1}_{1}\text{H} + ^{2}_{1}\text{H} \rightarrow ^{3}_{2}\text{He}
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Why are some nuclei stable and others are not?

- Neutron to proton ratio
- If n/p is above belt of stability, need to make n smaller and/or p larger. How?
- Vice versa. How?



Key points about nuclear chemistry

- To write a nuclear equation, balance the protons (bottom number) and mass number (top number).
- There are many different kinds of nuclear processes.
- Most isotopes that exist are stable, some are unstable. Stability has to do with the n/p ratio.
- Protons and neutrons are held together in the nucleus by forces that are stronger than the + to + electrical repulsions. When the composition of the nucleus is changed, energy is released or must be absorbed.
- Energy and mass are related by E=mc².

What is equilibrium?

$2 \operatorname{NO}_2 \leftrightarrows \operatorname{NO}_2 \operatorname{O}_4$

http://www.chem.iastate.edu/group/Greenbowe/sections/projectfolder/animations/no2n2o 4equilV8.html

In this animation of the system at the particle level, what indication is there that the system is at equilibrium?

- Concentration of each chemical remains constant in time
- Both the forward and reverse reactions are occurring
- The rate of the forward reaction is EQUAL to the rate of the reverse reaction

At the macroscopic observable level: When a system is at equilibrium, it looks like nothing is happening!

Mathematically, what is equilibrium?

 $2 \text{ NO}_2 \leftrightarrows \text{N}_2\text{O}_4$

Remember from mechanisms that "\Gamma" is shorthand for saying:

Forward reaction: $2 \text{ NO}_2 \rightarrow \text{N}_2\text{O}_4$ happens simultaneously with Reverse reaction: $N_2O_4 \rightarrow 2 NO_2$ Rate_{forward} = $k_{forward} [NO_2]^2$ and

Remember that: $Rate_{reverse} = k_{reverse} [N_2O_4]$

Remember that at (dynamic) equilibrium, the forward and reverse rates reach the point of being equal

 $Rate_{forward} = Rate_{reverse}$

This equation can be rearranged to define a Therefore, $k_{\text{forward}} = k_{\text{reverse}} [N_2O_4]$ \downarrow $Q \equiv \frac{k_{\text{forward}}}{k_{\text{reverse}}} = \frac{[N_2O_4]}{[NO_2]^2}$ new variable called Q (the reaction quotient) which is a function of reaction progress (think "time") and can be measured at any time during the progress toward equilibrium, and which reaches (asymptote) a constant value K when the reaction reaches equilibrium: Q(t) approaches K as t approaches equilibrium



Concentrations: what we measure in lab

Different initial conditions, same temperature





Different initial conditions, same temperature

What does it mean?

Remember that at (dynamic) equilibrium

Rate_{forward} = Rate_{reverse} Therefore, theoretically $k_{\text{forward}} [\text{NO}_2]^2 = k_{\text{reverse}} [\text{N}_2\text{O}_4]$ Rearranging, at equilibrium: $\frac{k_{forward}}{k_{reverse}} = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2}$

Since the forward and reverse rate constants only depend on temperature, then their ratio also does. In particular, let's define something called the REACTION QUOTIENT, Q, which is what the ratio of $k_{forward}/k_{reverse}$ would be if you set the forward and reverse rates to be equal. In the case of the NO₂ and N₂O₄ system we are examining,

$$Q = \frac{\left[N_2 O_4\right]}{\left[NO_2\right]^2}$$

Reaction quotient always approaches the same constant as the reaction approaches equilbrium

• Experimentally, we find that that after enough time, no matter what the starting concentrations, the reaction quotient always approaches a constant that depends only on temperature (and not at all on the initial concentrations)

	Equilibrium value of [NO ₂] in mol/L	Equilibrium value of $[N_2O_4]$ in mol/L	Value of Q at equil.
Initial conditions $[NO_2] = 3.520 \text{ M},$ $[N_2O_4] = 0.000 \text{ M}$	0.1000	1.710	$Q = \frac{1.710}{\left(0.1000\right)^2} = 171.0$
Initial conditions $[NO_2] = 3.520 \text{ M},$ $[N_2O_4] = 1.000 \text{ M}$	0.1256	2.697	$Q = \frac{2.697}{(0.1256)^2} = 171.0$
Initial conditions $[NO_2] = 2.000 \text{ M},$ $[N_2O_4] = 2.000 \text{ M}$	0.1310	2.934	$Q = \frac{2.934}{(0.1310)^2} = 171.0$

Comparing Q to its value at equilibrium



What does it mean if Q > 171.0? What does it mean if Q < 171.0?

The value that the reaction quotient approaches is called the EQUILIBRIUM CONSTANT

 The reaction quotient is always a ratio of product concentrations over reactant concentrations

General reaction:
$$a \mathbf{A} + b \mathbf{B} \leftrightarrows c \mathbf{C} + d \mathbf{D}$$

Reaction quotient: $Q = \frac{[\mathbf{C}]^c [\mathbf{D}]^d}{[\mathbf{A}]^a [\mathbf{B}]^b}$

- There is information contained in the value of the reaction quotient before equilibrium is reached
- The reaction quotient approaches a constant value after enough time has passed and the system is at equilibrium
- The equilibrium constant, *K*, is the value of *Q* when all the chemicals in the reaction reach their equilibrium concentrations
- The equilibrium constant depends only on temperature

Reaction Quotient vs. Equilibrium Constant

Reaction Quotient

• Symbol: Q

General reaction: $a A + b B \leftrightarrows c C + d D$ Reaction quotient: $Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$

- Situation: when the system is not at equilibrium
- The concentrations of the chemicals in the reaction continue to change as the reaction progresses toward equilibrium

Equilibrium Constant

• Symbol: *K*_{eq} generally*

General reaction: $a \mathbf{A} + b \mathbf{B} \leftrightarrows c \mathbf{C} + d \mathbf{D}$ Equilibrium constant: $K_c = \frac{[\mathbf{C}]^c [\mathbf{D}]^d}{[\mathbf{A}]^a [\mathbf{B}]^b}$

- Situation: when the system is at equilibrium
- Once the system has reached equilibrium, the concentrations of chemicals involved in the reaction do not change

*The subscript on K usually gives some information. For example, "c" is concentration, "p" is pressure, "sp" means solubility product, and "a" means weak acid.

What are the units of reaction quotients and equilibrium constants?

- Equilibrium constant is unitless (i.e., has no dimensions) even when unequal dimensions of concentrations in numerator and denominator
 - This is due to thermodynamic definition of reaction quotient in terms of "activity" which is ratio of variable of interest to its reference value
 - Reference values of concentrations are 1-molar, so the units always cancel
 - Example: $N_2(g) + 3 H_2(g) \leftrightarrows 2 NH_3(g)$

Thermodynamic definition of reaction quotient is in terms of activities:

$$Q = \frac{\left(a_{\mathrm{NH}_3}\right)^2}{\left(a_{\mathrm{N}_2}\right)\left(a_{\mathrm{H}_2}\right)^3} = \frac{\left(\frac{\left[\mathrm{NH}_3\right]}{\left[\mathrm{NH}_3\right]_o}\right)^2}{\left(\frac{\left[\mathrm{N}_2\right]}{\left[\mathrm{N}_2\right]_o}\right)\left(\frac{\left[\mathrm{H}_2\right]}{\left[\mathrm{H}_2\right]_o}\right)^3} = \frac{\left(\frac{\left[\mathrm{NH}_3\right]}{1\,M}\right)^2}{\left(\frac{\left[\mathrm{N}_2\right]}{1\,M}\right)\left(\frac{1}{1\,M}\right)^3}$$

When we write reaction $Q = \frac{[NH_3]^2 \text{ quotient}}{[N_2][H_2]^3}$

This is what we really mean

Which chemicals are part of the expression for Q?

- Determine phase (liquid, gas, aqueous) the reaction takes place in
- Only chemicals that are in that phase are part of the reaction quotient, because chemicals in other phases remain in those phases
- In an aqueous reaction, spectator ion concentrations do not change, so spectator ions are not part of the reaction quotient either

• Examples:
1.
$$N_2(g) + 3 H_2(g) \leftrightarrows 2 NH_3(g)$$
 $Q_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$ $Q_p = \frac{(p_{NH_3})^2}{(p_{N_2})(p_{H_2})^3}$
2. $2 S(s) + 3 O_2(g) \leftrightarrows 2 SO_3(g)$ $Q_c = \frac{[SO_3]^2}{[O_2]^3}$ $Q_p = \frac{(p_{SO_3})^2}{(p_{O_2})^3}$
3. $Cu(NO_3)_2(aq) + Zn(s) \leftrightarrows Zn(NO_3)_2(aq) + Cu(s)$
net ionic reaction: $Cu^{2+}(aq) + Zn(s) \leftrightarrows Zn^{2+}(aq) + Cu(s)$ $Q = \frac{[Zn^{2+}]}{[Cu^{2+}]}$
4. $PbCl_2(s) \leftrightarrows Pb^{2+}(aq) + 2 Cl^{-}(aq)$ $Q = \frac{[Pb^{2+}][Cl^{-}]^2}{1} = [Pb^{2+}][Cl^{-}]^2$

An easy way to remember it: only the highest entropy phases appear in Q

Concentration (moles per unit volume) of a pure solid or liquid has a constant value

In a liquid-aqueous reaction

 $\mathrm{H}^{+}(aq) + \mathrm{OH}^{-}(aq) \leftrightarrows \mathrm{H}_{2}\mathrm{O}(l)$

 $[H^+] = \frac{moles \text{ of } H^+ \text{ ions}}{\text{liter of solution}}$ and $[OH^-] = \frac{moles \text{ of } OH^- \text{ ions}}{\text{liter of solution}}$ typically on order of 10⁻⁷ M

By contrast, in one liter of water, moles of $\mathrm{H_{2}O}\left(\mathit{l}\right)$ is approximately

 $1000 \ mL \times \frac{1.00 \ g}{mL} \times \frac{1 \ mol}{18.02 \ g} = 55.5 \ mol$ so when 10⁻⁷ moles of H₂O (*l*) react, the effect is negligible

In a reaction involving a pure solid or liquid

"Molarity" of a solid or liquid is moles of solid or liquid per volume taken up. If you double the amount of solid or liquid used in the reaction, then the "molarity" of the solid or liquid stays the same. Since the reaction quotient only involves quantities that change when the reaction occurs, then pure solids or liquids do not appear in *Q*.

Converting between K_c and K_p

- Use gas law, pV = nRT
- Or partial pressure of a component gas in a mixture:

$$p_{component}V = n_{component}RT$$

Concentration is moles per liter (n/V)

$$K_{p} = \frac{\left(p_{N_{2}O_{4}}\right)}{\left(p_{NO_{2}}\right)^{2}} = \frac{\left(\frac{n_{N_{2}O_{4}}RT}{V}\right)}{\left(\frac{n_{NO_{2}}RT}{V}\right)^{2}}$$
$$= \frac{\left(RT\left(\frac{n_{N_{2}O_{4}}}{V}\right)\right)}{\left(RT\left(\frac{n_{NO_{2}}}{V}\right)^{2}} = \left(RT\right)^{-1} \cdot \frac{\left[N_{2}O_{4}\right]}{\left[NO_{2}\right]^{2}}$$
$$= \frac{\left(\frac{p_{N_{2}O_{4}}}{RT}\right)}{\left(\frac{p_{NO_{2}}}{RT}\right)^{2}} = RT\frac{\left(p_{N_{2}O_{4}}\right)}{\left(p_{NO_{2}}\right)^{2}}$$

Another example of converting between K_c and K_p

Remember, this is valid only for gas phase reactions

$$N_{2}(g) + 3 H_{2}(g) \leftrightarrows 2 NH_{3}(g)$$

$$K_{p} = \frac{(p_{NH_{3}})^{2}}{(p_{N_{2}})(p_{H_{2}})^{3}} \text{ and } pV = nRT \text{ and } [X] = \frac{\text{moles of } X}{\text{volume in liters}}$$
For any gas, $p_{X} = \frac{n_{X}RT}{V} = \left(\frac{n_{X}}{V}\right)RT = [X](RT)$
Therefore,
$$K_{p} = \frac{(p_{NH_{3}})^{2}}{(p_{N_{2}})(p_{H_{2}})^{3}} = \frac{([NH_{3}](RT))^{2}}{([N_{2}](RT))([H_{2}](RT))^{3}}$$

$$= \frac{[NH_{3}]^{2}}{[N_{2}][H_{2}]^{3}} \left(\frac{(RT)^{2}}{(RT)(RT)^{3}}\right)$$

$$= \frac{[NH_{3}]^{2}}{[N_{2}][H_{2}]^{3}} \left(\frac{1}{(RT)^{2}}\right) = K_{c}(RT)^{-2}$$
Generally speaking,
$$K_{p} = K_{c}(RT)^{\Delta n}$$
where
$$\Delta n = \sum_{products} n - \sum_{reactant.} n + \frac{1}{2} \sum_{reac$$

K_c vs. K_p: Different equilibrium constants?

- For an aqueous system, it only makes sense to use molarities $Cu^{2+} (aq) + Zn (s) \leftrightarrows Zn^{2+} (aq) + Cu (s)$ $K_c = \begin{bmatrix} Zn^{2+} \\ Cu^{2+} \end{bmatrix}$
- For a gas system, you could use either molarities or partial pressures N₂ (g) + 3 H₂ (g) ≒ 2 NH₃ (g) at 25 °C

$$K_{c} = \frac{\left[\mathrm{NH}_{3}\right]^{2}}{\left[\mathrm{N}_{2}\right]\left[\mathrm{H}_{2}\right]^{3}} = 3.8 \times 10^{8} \qquad K_{p} = \frac{\left(p_{\mathrm{NH}_{3}}\right)^{2}}{\left(p_{\mathrm{N}_{2}}\right)\left(p_{\mathrm{H}_{2}}\right)^{3}} = 1.08 \times 10^{5} \text{ when pressures in atm}$$

- Sometimes it is easier to work with partial pressures (e.g., if there are inert gases also in the mixture)
- If you're working with a gas phase equilibrium, you need to know which value of K is given, and you need to know how to convert between them
- Remember that in a gas system, you can use the ideal gas law
- Remember that molarity = moles of the chemical per unit volume

Values of K_{eq} have been measured for many reactions

$$2 \operatorname{NO}_2(g) \leftrightarrows \operatorname{N}_2\operatorname{O}_4(g)$$
 at 25 °C $K_c = \frac{[\operatorname{N}_2\operatorname{O}_4]}{[\operatorname{NO}_2]^2} = 171.0$

CH₃COOH (*aq*) + H₂O (*l*) ≒ H₃O⁺ (*aq*) + CH₃COO⁻ (*aq*) at 25 °C $K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = 1.8 \times 10^{-5}$

 $N_2H_4(aq) + H_2O(l) \leftrightarrows N_2H_5^+(aq) + OH^-(aq)$ at 25 °C

$$K_{b} = \frac{\left[N_{2}H_{5}^{+}\right]\left[OH^{-}\right]}{\left[N_{2}H_{4}\right]} = 8.5 \times 10^{-7}$$

 $PbBr_2(s) \leftrightarrows Pb^{2+}(aq) + 2 Br^{-}(aq)$ at 25 °C

$$K_{sp} = \left[\text{Pb}^{2+} \right] \left[\text{Br}^{-} \right]^2 = 6.6 \times 10^{-6}$$

ICE tables make it easy to keep track of the stoichiometry

ICE = initial, change, at equilibrium

- Initial: the non-equilibrium conditions initially present (i.e., initial concentrations or partial pressures – must use one of these, not moles)
- **Change**: as reaction proceeds in one direction or the other, if *x* moles/volume (or *x* atm of partial pressure) of one chemical react, stoichiometry dictates how much of the other chemicals will react or form
- Equilibrium: what was initially present, plus the change, equals the equilibrium values

Using the **equilibrium expression**, K=..., will often result in an equation in which you have to solve for *x*. Once you solve for *x*, you can calculate everything else.

A simple example of using ICE

Practice Exercise on p. 645

Sulfur trioxide decomposes at high temperature in a sealed container:

 $2 \operatorname{SO}_3(g) \leftrightarrows 2 \operatorname{SO}_2(g) + \operatorname{O}_2(g)$

Initially, the vessel is charged at 1000 K with SO₃ (*g*) at a partial pressure of 0.500 atm. At equilibrium, the SO₃ partial pressure is 0.200 atm. Calculate the value of K_p at 1000 K.

partial pressures	2 $SO_3(g)$	\Rightarrow 2 SO ₂ (g)	+ $O_2(g)$
Initial	0.500 atm	0 atm	0 atm
Change	- 2 <i>x</i>	+ 2x	+ <i>x</i>
Equilibrium	0.200 = 0.500 - 2x	x 2x	x

If you know the value of K_c and the initial conditions you can figure out the final concentrations – Use an ICE table

To complement Practice Exercises on pp. 644-645 At some temperature, $K_c = 33$ for the reaction

$$H_{2}(g) + I_{2}(g) \leftrightarrows 2 \operatorname{HI}(g)$$

If the initial concentrations of both $\rm H_2$ and $\rm I_2$ are 6.00 \times 10 3 mol/L, find the concentration of each reactant and product at equilibrium.

Molarity	$\mathrm{H}_{2}\left(g\right) +$	$\mathbf{I}_{2}\left(g ight)$	ţ	$2 \operatorname{HI}(g)$
Initial	$6.00 imes 10^{-3} \text{ M}$	$6.00 imes 10^{-3} \text{ M}$		0 M
Change	- <i>x</i>	- <i>x</i>		+ 2 <i>x</i>
Equilibrium	$(6.00 \times 10^{-3}) - x$	$(6.00 \times 10^{-3}) - x$		2x

Many variations on the theme

Graphite and carbon dioxide are kept at 1000 K until the reaction

 $C(s, graphite) + CO_2(g) \leftrightarrows 2 CO(g)$

has come to equilibrium. At this temperature, K = 0.021. The initial concentration of CO₂ is 0.012 M. Calculate the equilibrium concentration of CO.

Molarity	C (s, graphite)	+ $\operatorname{CO}_2(g)$	⇆	2 CO (g)
Initial		0.012 M		0 M
Change		- <i>x</i>		+ 2 <i>x</i>
Equilibrium		0.012 <i>- x</i>		2x

Key points about equilibrium constants

- Reaction quotient (Q) and equilibrium constant (K) have the same form (expression).
- Q and K both depend on temperature. Q and K have no units.
- K is the value of Q at equilibrium conditions. There are many nonequilibrium conditions, so Q can have many values. There is only one value for K at a given temperature.
- Comparing Q (at some conditions) to K (a constant) will tell you which direction a reaction must proceed in order to move toward equilibrium.
- K (or Q) can be expressed in terms of concentrations (for any situation) or partial pressures (only for gases). You can convert between K_p and K_c for a gas phase equilibrium, using the ideal gas law.
- Initial-change-equilibrium tables help to keep track of the stoichiometry. The key is to figure out what to set *x* equal to. After that, solving equilibrium problems is algebra.