CHEM 116

Introduction to Equilibrium: Rxn Quotients

October 24, 2006
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Agenda

- Equilibrium
  - 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?
  - Calculating equilibrium constants and/or concentrations at equilibrium

What is equilibrium?

$$2\ NO_2 \leftrightarrows N_2O_4$$

http://www.chem.iastate.edu/group/Greenbowe/sections/projectfolder/animations/no2n2o4equilV8.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?

$$2\ NO_2 \leftrightarrows N_2O_4$$

Is shorthand for saying:

Forward reaction: $2\ NO_2 \rightarrow N_2O_4$
happens simultaneously with
Reverse reaction: $N_2O_4 \rightarrow 2\ NO_2$

$\text{Rate}_{\text{forward}} = k_{\text{forward}}\ [NO_2]^2$
and
$\text{Rate}_{\text{reverse}} = k_{\text{reverse}}\ [N_2O_4]$

Remember that at (dynamic) equilibrium, the forward and reverse rates are equal

$\text{Rate}_{\text{forward}} = \text{Rate}_{\text{reverse}}$

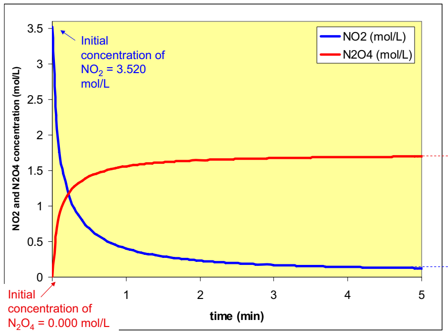
Therefore,

$k_{\text{forward}}\ [NO_2]^2 = k_{\text{reverse}}\ [N_2O_4]$

Concentrations: what we measure in lab

$2\,NO_2 \leftrightarrows N_2O_4$

Experiment performed at T = 25 ºC



Initial concentration of NO_2 = 3.520 mol/L

Initial concentration of N_2O_4 = 0.000 mol/L

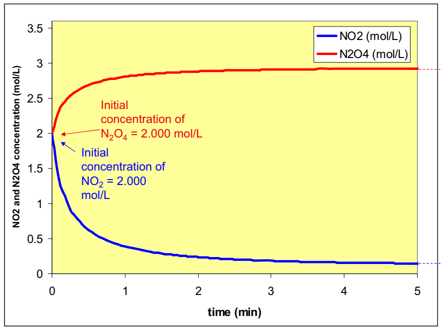
Equilibrium concentration of N_2O_4 = 1.710 mol/L

Equilibrium concentration of NO_2 = 0.1000 mol/L

Different initial conditions, same temperature

$2\,NO_2 \leftrightarrows N_2O_4$

Experiment performed at T = 25 ºC



Initial concentration of N_2O_4 = 2.000 mol/L

Initial concentration of NO_2 = 2.000 mol/L

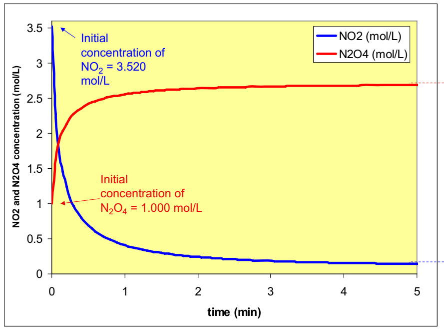
Equilibrium concentration of N_2O_4 = 2.934 mol/L

Equilibrium concentration of NO_2 = 0.1310 mol/L

Different initial conditions, same temperature

$2\,NO_2 \leftrightarrows N_2O_4$

Experiment performed at T = 25 ºC



Initial concentration of NO_2 = 3.520 mol/L

Initial concentration of N_2O_4 = 1.000 mol/L

Equilibrium concentration of N_2O_4 = 2.697 mol/L

Equilibrium concentration of NO_2 = 0.1256 mol/L

What does it mean?

Remember that at (dynamic) equilibrium

$\text{Rate}_{\text{forward}} = \text{Rate}_{\text{reverse}}$

Therefore, theoretically

$k_{\text{forward}}\,[NO_2]^2 = k_{\text{reverse}}\,[N_2O_4]$

Rearranging, at equilibrium: $\dfrac{k_{forward}}{k_{reverse}} = \dfrac{[N_2O_4]}{[NO_2]^2}$

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 NO_2 and N_2O_4 system we are examining,

$$Q = \frac{[N_2O_4]}{[NO_2]^2}$$

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 M, $[N_2O_4]$ = 0.000 M	0.1000	1.710	$Q=\frac{1.710}{(0.1000)^2}=171.0$
Initial conditions $[NO_2]$ = 3.520 M, $[N_2O_4]$ = 1.000 M	0.1256	2.697	$Q=\frac{2.697}{(0.1256)^2}=171.0$
Initial conditions $[NO_2]$ = 2.000 M, $[N_2O_4]$ = 2.000 M	0.1310	2.934	$Q=\frac{2.934}{(0.1310)^2}=171.0$

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

$$\text{General reaction:}\quad a\,\mathrm{A}+b\,\mathrm{B} \leftrightarrows c\,\mathrm{C}+d\,\mathrm{D}$$

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

- 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

Comparing Q to its value at equilibrium

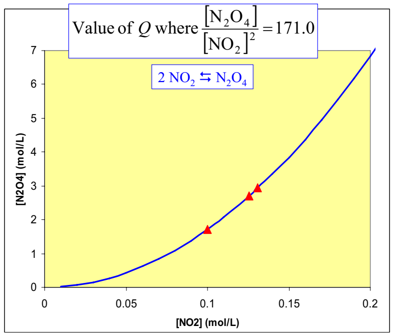
There are many sets of values for $[NO_2]$ and $[N_2O_4]$ where

$$\frac{[N_2O_4]}{[NO_2]^2}=171.0$$

If a system is not at equilibrium, the value of

$$Q=\frac{[N_2O_4]}{[NO_2]^2}$$

is not 171.0



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

Reaction Quotient vs. Equilibrium Constant

Reaction Quotient	Equilibrium Constant
Symbol: Q	Symbol: K_{eq} generally*
General reaction: $a\,\mathrm{A}+b\,\mathrm{B} \leftrightarrows c\,\mathrm{C}+d\,\mathrm{D}$ Reaction quotient: $Q=\frac{[\mathrm{C}]^c\,[\mathrm{D}]^d}{[\mathrm{A}]^a\,[\mathrm{B}]^b}$	General reaction: $a\,\mathrm{A}+b\,\mathrm{B} \leftrightarrows c\,\mathrm{C}+d\,\mathrm{D}$ Equilibrium constant: $K_c=\frac{[\mathrm{C}]^c\,[\mathrm{D}]^d}{[\mathrm{A}]^a\,[\mathrm{B}]^b}$
Situation: when the system is not at equilibrium	Situation: when the system is at equilibrium
The concentrations of the chemicals in the reaction continue to change as the reaction progresses toward 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.

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:

$$Q = \frac{(a_{NH_3})^2}{(a_{N_2})(a_{H_2})^3} = \frac{\left(\frac{[NH_3]}{[NH_3]_o}\right)^2}{\left(\frac{[N_2]}{[N_2]_o}\right)\left(\frac{[H_2]}{[H_2]_o}\right)^3} = \frac{\left(\frac{[NH_3]}{1\,M}\right)^2}{\left(\frac{[N_2]}{1\,M}\right)\left(\frac{[H_2]}{1\,M}\right)^3}$$

This is what we really mean

When we write reaction quotient

$$Q = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

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

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

$$H^+\,(aq) + OH^-\,(aq) \leftrightarrows H_2O\,(l)$$

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

By contrast, in one liter of water, moles of $H_2O\,(l)$ 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 $H_2O\,(l)$ 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)

$$K_p = \frac{(p_{N_2O_4})}{(p_{NO_2})^2} = \frac{\left(\frac{n_{N_2O_4}RT}{V}\right)}{\left(\frac{n_{NO_2}RT}{V}\right)^2} = \frac{\left(RT\left(\frac{n_{N_2O_4}}{V}\right)\right)}{\left(RT\left(\frac{n_{NO_2}}{V}\right)\right)^2} = (RT)^{-1}\cdot\frac{[N_2O_4]}{[NO_2]^2}$$

$$K_c = \frac{[N_2O_4]}{[NO_2]^2} = \frac{\left(\frac{n_{N_2O_4}}{V}\right)}{\left(\frac{n_{NO_2}}{V}\right)^2} = \frac{\left(\frac{p_{N_2O_4}}{RT}\right)}{\left(\frac{p_{NO_2}}{RT}\right)^2} = RT\,\frac{(p_{N_2O_4})}{(p_{NO_2})^2}$$

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

$$\Delta n = \sum_{products} n - \sum_{reactants} n$$

K_c vs. K_p: Different equilibrium constants?

- For an aqueous system, it only makes sense to use molarities

  $Cu^{2+}\ (aq) + Zn\ (s) \leftrightarrows Zn^{2+}\ (aq) + Cu\ (s)$

  $$K_c = \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

- For a gas system, you could use either molarities or partial pressures

  $N_2\ (g) + 3\ H_2\ (g) \leftrightarrows 2\ NH_3\ (g)$ at 25 °C

  $$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = 3.8\times10^8 \quad K_p = \frac{(p_{NH_3})^2}{(p_{N_2})(p_{H_2})^3} = 1.08\times10^5 \text{ when pressures in atm}$$

- 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

$2\ NO_2\ (g) \leftrightarrows N_2O_4\ (g)$ at 25 °C

$$K_c = \frac{[N_2O_4]}{[NO_2]^2} = 171.0$$

$CH_3COOH\ (aq) + H_2O\ (l) \leftrightarrows H_3O^+\ (aq) + CH_3COO^-\ (aq)$ at 25 °C

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = 1.8\times10^{-5}$$

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

$$K_b = \frac{[N_2H_5^+][OH^-]}{[N_2H_4]} = 8.5\times10^{-7}$$

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

$$K_{sp} = [Pb^{2+}][Br^-]^2 = 6.6\times10^{-6}$$

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:

$$2\ \mathrm{SO_3}\ (g) \rightleftarrows 2\ \mathrm{SO_2}\ (g) + \mathrm{O_2}\ (g)$$

Initially, the vessel is charged at 1000 K with SO_3 (*g*) at a partial pressure of 0.500 atm. At equilibrium, the SO_3 partial pressure is 0.200 atm. Calculate the value of K_p at 1000 K.

partial pressures	$2\ \mathrm{SO_3}\ (g)$	$\rightleftarrows$	$2\ \mathrm{SO_2}\ (g)$	+	$\mathrm{O_2}\ (g)$
Initial	0.500 atm		0 atm		0 atm
Change	$-2x$		$+2x$		$+x$
Equilibrium	0.200 = 0.500 – $2x$		$2x$		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

$$\mathrm{H_2}\ (g) + \mathrm{I_2}\ (g) \rightleftarrows 2\ \mathrm{HI}\ (g)$$

If the initial concentrations of both H_2 and I_2 are 6.00 × 10^{-3} mol/L, find the concentration of each reactant and product at equilibrium.

Molarity	$\mathrm{H_2}\ (g)$	+	$\mathrm{I_2}\ (g)$	$\rightleftarrows$	$2\ \mathrm{HI}\ (g)$
Initial	6.00 × 10^{-3} M		6.00 × 10^{-3} M		0 M
Change	$-x$		$-x$		$+2x$
Equilibrium	(6.00 × 10^{-3}) – x		(6.00 × 10^{-3}) – x		$2x$

Many variations on the theme

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

$$\mathrm{C}\ (s,\ graphite) + \mathrm{CO_2}\ (g) \rightleftarrows 2\ \mathrm{CO}\ (g)$$

has come to equilibrium. At this temperature, K = 0.021. The initial concentration of CO_2 is 0.012 M. Calculate the equilibrium concentration of CO.

Molarity	$\mathrm{C}\ (s,\ graphite)$	+	$\mathrm{CO_2}\ (g)$	$\rightleftarrows$	$2\ \mathrm{CO}\ (g)$
Initial			0.012 M		0 M
Change			$-x$		$+2x$
Equilibrium			0.012 – x		$2x$

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 non-equilibrium 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.