CHEM 116
Equilibrium: Working with the Equations

October 31, 2006
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Agenda

- Equilibrium
  - ICE tables
    - Different problems result when different values are given
  - What happens to K_{eq} when you change around the reaction (relating chemical equations and equilibrium constants)
  - Le Chatelier's principle

- Group problem #4 (if time, otherwise on Thursday)

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:

$$2\ SO_3\ (g) \leftrightarrows 2\ SO_2\ (g) + O_2\ (g)$$

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	$2\ SO_3\ (g)$	$\leftrightarrows$	$2\ SO_2\ (g)$	+	$O_2\ (g)$
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

$$H_2\ (g) + I_2\ (g) \leftrightarrows 2\ HI\ (g)$$

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	$H_2\ (g)$	+	$I_2\ (g)$	$\leftrightarrows$	$2\ HI\ (g)$
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

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

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

Some relationships among K values

- Multiplying a reaction by a number
- Adding up reactions to total an overall reaction

Multiplying Rxns by a Number

(1) Compare to this reaction

$2\ NOBr\ (g) + Cl_2\ (g) \leftrightarrows 2\ NO\ (g) + 2\ BrCl\ (g)$

$$K_1 = \frac{[NOBr]^2[Cl_2]}{[NO]^2[BrCl]^2}$$

(2) What if you double the reaction?

x 2

$4\ NOBr\ (g) + 2\ Cl_2\ (g) \leftrightarrows 4\ NO\ (g) + 4\ BrCl\ (g)$

$$K_2 = \frac{[NOBr]^4[Cl_2]^2}{[NO]^4[BrCl]^4} = (K_1)^2$$

(3) What if you reverse the reaction?

x (-1)

$2\ NO\ (g) + 2\ BrCl\ (g) \leftrightarrows 2\ NOBr\ (g) + Cl_2\ (g)$

$$K_3 = \frac{[NO]^2[BrCl]^2}{[NOBr]^2[Cl_2]} = (K_1)^{-1}$$

Summing reactions to an overall rxn

Overall reaction

$O_3\ (g) + 2\ NO_2\ (g) \leftrightarrows N_2O_5\ (g) + O_2\ (g)$

$$K_{overall} = \frac{[N_2O_5]\,[O_2]}{[O_3]\,[NO_2]^2}$$

Reaction mechanism

1) $O_3\ (g) + NO_2\ (g) \leftrightarrows NO_3\ (g) + O_2\ (g)$

$$K_1 = \frac{[NO_3]\,[O_2]}{[O_3]\,[NO_2]}$$

2) $NO_3\ (g) + NO_2\ (g) \leftrightarrows N_2O_5\ (g)$

$$K_2 = \frac{[N_2O_5]}{[NO_3]\,[NO_2]}$$

$$(K_1)\cdot(K_2) = \left(\frac{[NO_3]\,[O_2]}{[O_3]\,[NO_2]}\right)\cdot\left(\frac{[N_2O_5]}{[NO_3]\,[NO_2]}\right) = \frac{[N_2O_5]\,[O_2]}{[O_3]\,[NO_2]^2} = K_{overall}$$

Relating equilibrium constants and reactions

- If you multiply a reaction by a number (e.g., x(-1) or x2), you do that to the exponent of the equilibrium constant
- If you add two reactions together to get an overall reaction, then the product of the two equilibrium constants is the overall K_{eq}

Disturbing a chemical equilibrium

When a system is at equilibrium, it remains at equilibrium, unless an outside force disturbs it (Newton? No, le Chatelier)

The system reacts by opposing the outside force to partially un-do its effects

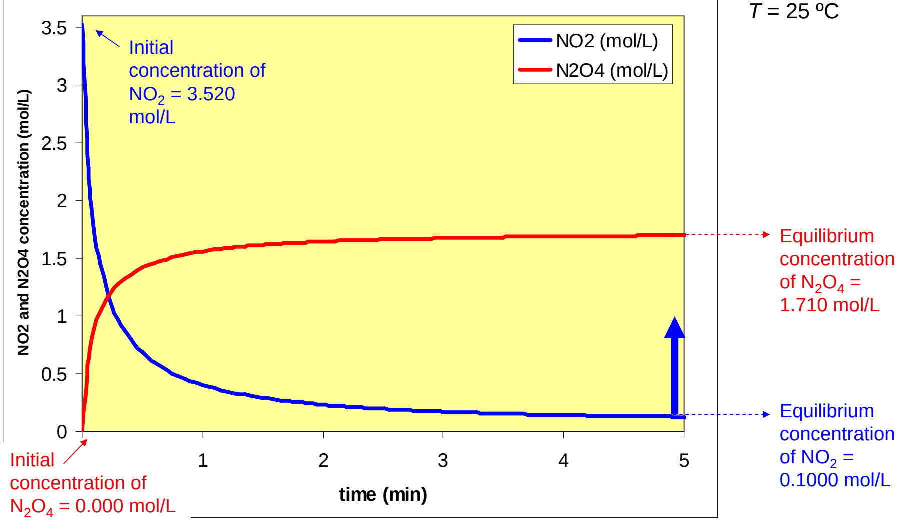
- Some outside forces cause the equilibrium to shift and others don't
- What does "shift" mean?

- Outside forces that do not change the value of K
  - Addition or removal of a reactant or product
  - Volume change (for gas phase reaction)
  - Addition or removal of an inert gas (for gas phase reaction)
- Outside force that changes the value of K
  - Temperature change

Let's begin with a system that achieves equilibrium

$2\ NO_2 \leftrightarrows N_2O_4$ $\qquad K_c = \frac{[N_2O_4]}{[NO_2]^2} = 171$

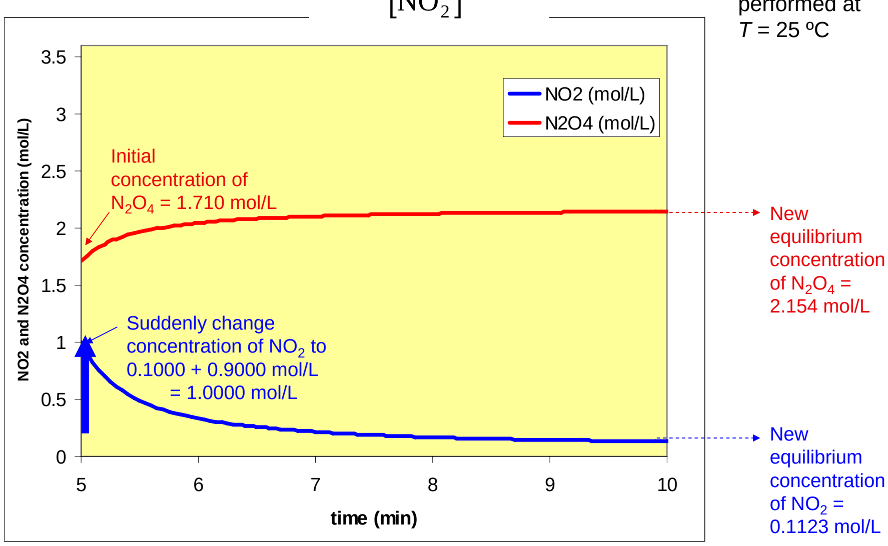
Experiment performed at *T* = 25 ºC



Then, once it is at equilibrium, add some NO_2 to the flask

$2\ NO_2 \leftrightarrows N_2O_4$ $\qquad K_c = \frac{[N_2O_4]}{[NO_2]^2} = 171$

Experiment performed at *T* = 25 ºC



Mathematically, what happened?

$$K_c = \frac{[N_2O_4]}{[NO_2]^2} = 171$$ at this temperature

Initially at equilibrium:

$2\ NO_2 \leftrightarrows N_2O_4$

Add some NO_2

	$2\ NO_2\ (g)$	$\leftrightarrows$	$N_2O_4\ (g)$	
Initial (non-eq)	3.52 M		0 M	$Q = \frac{[N_2O_4]}{[NO_2]^2} = \frac{0}{(3.52)^2} = 0$
First change	$-\ 2x$		$+\ x$	
First equilibrium	0.100 M		1.71 M	$K = \frac{[N_2O_4]}{[NO_2]^2} = \frac{1.71}{(0.100)^2} = 171$
Disturbance creates new initial (non-eq)	0.100+0.900 =1.000 M		1.71 M	$Q = \frac{[N_2O_4]}{[NO_2]^2} = \frac{1.71}{(1.00)^2} = 1.71$
Second change	$-\ 2x$		$+\ x$	
Second equilibrium	0.112 M		2.15 M	$K = \frac{[N_2O_4]}{[NO_2]^2} = \frac{2.15}{(0.112)^2} = 171$

Conclusion: Equilibrium is re-established. The system reacted to partially un-do the disturbance, using up some of the NO_2 that was added.

Changing the volume (in a gaseous equilibrium)

- Consider the same NO_2 and N_2O_4 system
- http://myphlip.pearsoncmg.com/altproducts/demo/ab2page.cfm?vbcid=9018&vid=10000#oa213641 (works if you have ActiveX)

Initially at equilibrium:

$2\ NO_2 \leftrightarrows N_2O_4$

Decrease in volume
Causes increase in pressures and concentrations of NO_2 and N_2O_4
BUT by an EQUAL factor

$$Q = \frac{[N_2O_4]}{[NO_2]^2} = \frac{3.42}{(0.200)^2} = 85.5$$

	$2\ NO_2\ (g)$	$\leftrightarrows$	$N_2O_4\ (g)$
First equilibrium	0.100 M		1.71 M
Disturbance creates new initial (non-eq)	0.200 M		3.42 M
Change	$-\ 2x$		$+\ x$
Second equilibrium	0.142 M		3.45 M

Conclusion: Equilibrium is re-established. The system reacted to partially un-do the disturbance. The reaction proceeded in the direction that reduces the pressure by decreasing the number of molecules.

Changing the pressure by adding an inert gas

- Consider what would happen if the total pressure in the previous example were increased not by changing the volume but instead by adding an inert gas
- Mathematically, neither the concentrations nor the partial pressures of each gas change in this case

	$2\ NO_2\ (g)$	$\leftrightarrows$	$N_2O_4\ (g)$
First equilibrium	0.100 M		1.71 M
Disturbance creates no change	0.100 M		1.71 M

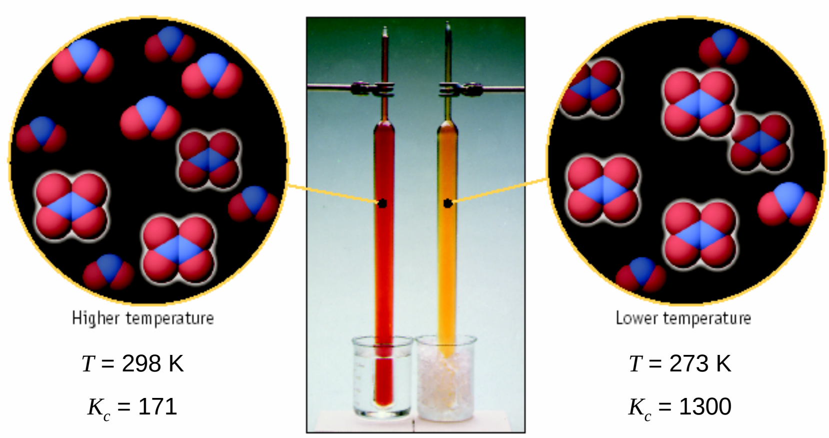
Temperature change

$2\ NO_2\ (g) \leftrightarrows N_2O_4\ (g)$

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

N_2O_4 is colorless

NO_2 is brown



T = 298 K

K_c = 171

T = 273 K

K_c = 1300

Temperature change

- Think of heat energy as a reactant or product
- Changing from lower temperature to higher temperature caused the equilibrium to shift in favor of NO_2
- Which one of these correctly describes this behavior?

Initially at equilibrium:

$2\ NO_2 + heat \leftrightarrows N_2O_4$

Add some heat

OR

Initially at equilibrium:

$2\ NO_2 \leftrightarrows N_2O_4 + heat$

Add some heat

Conclusions:

- The reaction must be ___________________________
- As the temperature increases, the value of K __________________

Example: Disturbing a chemical equilibrium

Similar to Practice Exercises on pp. 655-656.

Explain the effect in each case. Assume each system is at equilibrium before the disturbance occurs.

a) $2\ NOCl\ (g) \leftrightarrows 2\ NO\ (g) + Cl_2\ (g)$ $\Delta H^o_{rxn} = +77.1 kJ$

What would happen if the temperature were decreased?

b) $H_2\ (g) + CO_2\ (g) \leftrightarrows H_2O\ (g) + CO\ (g)$

What would happen if the volume were increased?

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

What would happen if suddenly more CO_2 were added? More C?

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

An increase in temperature causes the CO concentration to increase. What is the sign of ΔH?

Summary of le Chatelier's principle

If you take a system that is at equilibrium and then disturb it, it will come back to equilibrium in a special way: It will partially un-do the disturbance

- If you add a chemical that is involved in the equilibrium, the new equilibrium will be shifted toward the direction that uses up some of the new chemical that was added (K_{eq} will not change)
- If you change the pressure or the volume in a gas phase reaction, the new equilibrium will shift in the direction that reduces the disturbance (K_{eq} will not change)
- If you add heat, the new equilibrium will be shifted toward the direction that uses up some of the heat that was added and the value of K_{eq} will also change, since you changed T

Important equilibria

- Weak acids and weak bases (ch. 16)
- Buffers, acid-base titrations (ch. 17)
- Solubility equilibria (ch. 17)
- Oxidation-reduction, separated so as to generate voltage (ch. 20)