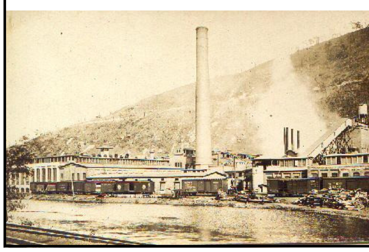
Great Barrier Reef. Images available at http://www.wickedtravel.com.au/Destinations/GreatBarrierReef.aspx (left) and http://ngm.nationalgeographic.com/2011/05/great-barrier-reef/holland-text

$$\mathrm{CaCO_3}(s) + \mathrm{CO_2}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{Ca^{2+}}(aq) + 2\mathrm{HCO_3^-}(aq)$$

Calcium carbonate trapped at treatment plant — Dissolved calcium bicarbonate enters river and neutralizes acid

$$\mathrm{HCO_3^-}(aq) + \mathrm{H^+}(aq) \xrightarrow{\text{neutralization}} \mathrm{CO_2}(g) + \mathrm{H_2O}(l)$$

Bicarbonate — Acid in river



Papermill near the Potomac. Image available at http://www.rootsweb.ancestry.com/~mdallegh/Luke.htm

1

Coral reefs are large underwater structures composed of the skeletons of coral, which are marine invertebrate animals. The coral species that build coral reefs are known as hermatypic or "hard" corals because they extract calcium carbonate from seawater to create a hard, durable exoskeleton that protects their soft, sac-like bodies. (http://www.livescience.com/40276-coral-reefs.html)

For the past 30 years the Great Barrier Reef in Australia lost 50 percent of its coral cover. Worldwide coral reefs are being covered by seaweed meadows that do not support the biodiversity that is necessary for reefs to function. These reefs are flood protection from surge storms, income from tourism and many other critical ecosystems services that are the lifeblood of tropical island nations. The loss is caused by overfishing, global change, ocean acidification, pollution and coral

Picture: http://scientistatwork.blogs.nytimes.com/2011/10/12/a-disappearing-underwater-world/?scp=10&sq=marine%20science&st=cse by Ana Maria Garcia

2

Chapter 6: CHEMICAL EQUILIBRIA

3

What is chemical equilibrium?

Consider the balanced equation **$2NO_2\ (g) \longrightarrow N_2O_4\ (g)$**

- Using stoichiometry: Mass of product can be calculated from the given mass of NO_2 reactant
- Single arrow: Assumes reaction goes to completion

Does the reaction really go to completion?

- Many reactions do not go to completion
  - They stop short at an *intermediate state* before all the reactants are consumed
    - Reaches a state of chemical equilibrium

4

What is chemical equilibrium?

Chemical equilibrium refers to a situation where:

(1) A reaction proceeds in the forward and reverse direction = a *reversible reaction*

Use of double arrows for reversible reactions:

$$2NO_2\,(g) \rightleftharpoons N_2O_4\,(g)$$

(2) Rate of forward reaction = Rate of reverse reaction

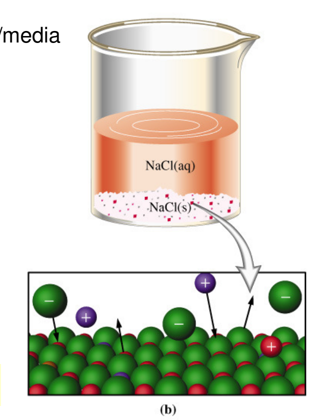
(3) These two opposing reactions never stop (unless the system is disturbed) = a *dynamic process*

5

Equilibrium is a dynamic process

Illustration of a dynamic process

Source: http://cwx.prenhall.com/bookbind/pubbooks/hillchem3/medialib/media_portfolio/14.html



Saturated NaCl solution: Although nothing seems to be happening:

- Solid NaCl redissolves, forming Na^+ and Cl^- ions
- Dissolved Na^+ and Cl^- come out of solution (precipitation)

$$\underbrace{\text{Rate of dissolution = rate of precipitation}}_{\text{No net change!}}$$

6

The Equilibrium Expression

For the general reaction: $aA_{(g)} + bB_{(g)} \rightleftharpoons cC_{(g)} + dD_{(g)}$

The **equilibrium expression** is:

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

K_c or K_{eq} is the equilibrium constant; it varies with temperature

- Notice that the *product* terms appear on the numerator
- The *reactant* terms appear on the denominator
- The coefficients (#moles) appear as exponents

7

The Equilibrium Expression

Exercise 1: Write the equilibrium expression for the reaction

$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$

Answer:

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

Product conc. raised to its coefficient

Reactant conc. raised to its coefficient; each reactant term multiplied

Exercise 2: Write the equilibrium expression for the reaction

$2NOCl\,(g) \rightleftharpoons 2NO\,(g) + Cl_2\,(g)$

$$Keq = \frac{[NO]^2\,[Cl_2]}{[NOCl]^2}$$

8

Equilibrium Expressions for Gas Phase Reactions

Rule #1: For reactions involving gases, the partial pressure of each gaseous component is used instead of molar concentration

Thus, for the reaction $N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$

The K_{eq} expression can be rewritten as:

$$\boxed{K_{\mathbf{eq}} = \frac{P^2_{NH3}}{P_{N2}\;P^3_{H2}} = K_p}$$

Note: K_p is used instead of K_{eq} when all the species in the expression are gases

9

Equilibrium Expressions for Heterogeneous Reactions

Heterogeneous reactions are those that involve more than one phase

For example, consider the solid-gas equilibrium reaction:

$$CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)$$

How do we write the equilibrium expression for this heterogeneous reaction?

Rule #2: Pure solids (s) and pure liquids or solvents (l) do not appear in the Keq expression

10

Equilibrium Expressions for Heterogeneous Reactions

K_{eq} for the reaction **$CaCO_3$ (s) $\rightleftharpoons$ CaO (s) + CO_2 (g)**

is written as:

Replaces solid CaO product

A gas, so we'll use K_P in place of K_{eq}

$$K_{eq} = \frac{1 \times [CO_2]}{1} = [CO_2] = P_{CO_2}$$

Replaces solid $CaCO_3$ reactant

Since pure solids (s) do not appear in the K_{eq} expression

Thus, for the reaction above,

$$\boxed{K_P = P_{CO_2}}$$

11

Equilibrium Expressions for Heterogeneous Reactions

Consider another heterogeneous reaction involving the dissolution of a salt, called **solubility equilibria**:

AgCl (s) $\rightleftharpoons$ Ag^+ (aq) + Cl^- (aq)

Write the equilibrium expression for this solubility equilibrium.

$$\boxed{K_{eq} = [Ag^+][Cl^-]}$$

Remember: Solids do not appear in the K_{eq} expression

Challenge: Write the K_{eq} expression for

HCO_2H (aq) + H_2O (l) $\rightleftharpoons$ HCO_2^- (aq) + H_3O^+ (aq)

Formic acid — Formate ion — Hydronium ion

Answer: $\boxed{Keq = \frac{[HCO_2^-][H_3O^+]}{[HCO_2H]}}$

12

The Magnitude of Equilibrium Constants

Equilibrium constants can be very large (K_{eq} >>1) or very small (K_{eq} <<1).

What is the importance of the magnitude of K_{eq}?

Keq >>1: Equilibrium lies to the right; **products** predominate

Recall: $K_{eq} = \frac{\text{Product term}}{\text{Reactant term}}$

Thus, K_{eq} > 1 favors products

Keq <<1: Equilibrium lies to the left; **reactants** predominate

Thus, K_{eq} < 1 favors reactants

13

The Magnitude of Equilibrium Constants

Examples:

(1) NH_3 (aq) + H_2O (l) $\rightleftharpoons$ NH_4^+ (aq) + OH^- (aq) $K_{eq} = 1.8 \times 10^{-5}$

Q. What species predominate at equilibrium?

- Small K_{eq} favors reactants: NH_3 and H_2O predominate

(2) Cu^{2+}(aq) + $4NH_3$ (aq) $\rightleftharpoons$ $Cu(NH_3)_4^{2+}$(aq) $K_{eq} = 5.0 \times 10^{12}$

Q. What species predominate at equilibrium?

- Large K_{eq} favors products: $Cu(NH_3)_4^{2+}$ predominate

14

Manipulating Equilibrium Expressions

Case 1: Reversing a reaction

What happens to the new K_{eq}?

- When a reaction is reversed, the new K_{eq}, K_{eq}', is the reciprocal of the original, i.e.

$$\boxed{K_{eq}' = 1/K_{eq}}$$

Given the equilibrium reaction: **$PCl_3\,(g) + Cl_2\,(g) \rightleftarrows PCl_5\,(g)$**

Write the K_{eq} expression for the reverse reaction

Answer: The reverse reaction is:

$PCl_5\,(g) \rightleftarrows PCl_3\,(g) + Cl_2\,(g)$

$$\text{So } K_{eq}' = \frac{[PCl_3]\,[Cl_2]}{[PCl_5]}$$

Convince yourself that this is true by writing the Keq expression for the forward reaction

$$= \frac{1}{K_{eq}}$$

15

Manipulating K_{eq} - *Cont.*

Case 2: Adding reactions

What is the new K_{eq} when reactions are added?

- If a reaction can be expressed as the sum of 2 or more reactions, K_{eq} for the overall reaction is the product of the K_{eq}'s of the individual reactions, i.e. if

Reaction 3 = Reaction 1 + Reaction 2

$$\boxed{K_{eq\,3} = K_{eq\,1} \times K_{eq\,2}}$$

16

Manipulating K_{eq} - *Cont.*

Example: At 100 ^{0}C the following reactions have the K_{eq}'s noted on the right of their equations:

(1) $2NOBr_{(g)} \rightleftarrows 2NO_{(g)} + Br_{2\,(g)}$ $K_{eq\,1} = 0.42$

(2) $Br_{2\,(g)} + Cl_{2\,(g)} \rightleftarrows 2BrCl_{(g)}$ $K_{eq\,2} = 7.2$

Use these data to calculate K_{eq} for the reaction

$\mathbf{2NOBr_{(g)} + Cl_{2\,(g)} \rightleftarrows 2NO_{(g)} + 2BrCl_{(g)}}$ $\mathbf{K_{eq}}$ = ?

Analysis:

First, inspection of the overall reaction reveals that it is indeed the sum of reactions 1 and 2

17

Manipulating Equilibrium Expressions

Adding reactions 1 and 2 gives:*

(1) $2NOBr_{(g)} \rightleftarrows 2NO_{(g)} + \cancel{Br_2}_{(g)}$ $K_{eq\,1} = 0.42$

(2) $\cancel{Br_2}_{(g)} + Cl_{2\,(g)} \rightleftarrows 2BrCl_{(g)}$ $K_{eq\,2} = 7.2$

$\mathbf{2NOBr_{(g)} + Cl_{2\,(g)} \rightleftarrows 2NO_{(g)} + 2BrCl_{(g)}}$ $\mathbf{K_{eq\,3}}$ = ?

$\mathbf{K_{eq\,3}} = K_{eq\,1} \times K_{eq\,2}$

$\mathbf{K_{eq\,3}} = 0.42 \times 7.2 = \mathbf{3.0}$

*Cancel equimolar amounts of identical species on left and right side of the equations

18

Manipulating K_{eq} - *Cont.*

Case 3: Reactions with different coefficients

What is the new K_{eq} when the coefficients (mole ratios) are changed?

➢ If the coefficients in a balanced equation are multiplied by a factor n, the equilibrium constant is raised to the nth power, i.e.

$$\boxed{K_{eq}' = (K_{eq})^n}$$

Example: At 25 ^{0}, the equilibrium constant for the reaction $\mathbf{N_2\,(g) + O_2\,(g) \rightleftarrows 2NO\,(g)}$ is 4.2×10^{-31}. Calculate K_{eq} for the reaction $\mathbf{\frac{1}{2} N_2\,(g) + \frac{1}{2} O_2\,(g) \rightleftarrows NO\,(g)}$

19

Answer:

Reaction 1: $\mathbf{N_2\,(g) + O_2\,(g) \rightleftarrows 2NO\,(g)}$ $K_{eq} = 4.2 \times 10^{-31}$.

Reaction 2: $\mathbf{\frac{1}{2} N_2\,(g) + \frac{1}{2} O_2\,(g) \rightleftarrows NO\,(g)}$ $K_{eq}' = ?$

Inspection of these reactions shows that the second reaction is derived by multiplying the coefficients in the first reaction by ½, so:

$$K_{eq}' = (K_{eq})^{1/2}$$

$$\mathbf{K_{eq}'} = (4.2 \times 10^{-31})^{1/2} = \mathbf{6.5 \times 10^{-16}}$$

20

LeChâtelier's Principle

LeChâtelier's principle

If a stress or disturbance is applied to a system in equilibrium, the system shifts to the direction that relieves the stress

What factors disturb (or stress) equilibrium systems?

21

Factors that affect equilibria

- Changing concentration by adding or removing a reactant or product
- Changing the temperature of the system
- Changing the partial pressure of gaseous reactant or product

- Each disturbance change equilibrium differently
  - How does the system go back to equilibrium? (Needs to be determined)

22

LeChâtelier's Principle – *Cont.*

Example involving change of concentration:
In the equation

$$2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)}$$

- If you add more NO (g) the equilibrium shifts to the right producing more NO_2 (g) – WHY?
- If you add more NO_2(g) the equilibrium shifts to the left producing more NO(g) and O_2(g) – WHY?
- Where will the reaction shift if you remove the product?

Video: Effect of change of concentration on equilibrium:
http://www.youtube.com/watch?v=ZOYyCTvLa9E

23

LeChâtelier's Principle – *Cont.*

Examples involving change of temperature:

- The equilibrium shift depends on whether the reaction is endothermic (+ΔH) or exothermic (- ΔH)

Cool demo on NO_2-N_2O_4 equil:
http://www.youtube.com/watch?v=0XQVXFL4uoo

Exothermic reactions = heat is released to the surrounding; Treat "heat" as a product

Example of an exothermic reaction***:***

$$C_{(s)} + O_{2(g)} \rightleftharpoons CO_{2(g)} + \textbf{heat} \qquad (-\Delta H)$$

Q. What is the effect of increasing temperature on the system?

A. For exothermic reactions, ↑T ≈ ↑[product]. Thus, it results to a <u>shift to the left</u>, forming more reactants (= lower yield of products)

24

LeChâtelier's Principle – *Cont.*

Endothermic reactions = heat is absorbed from the surrounding (+ΔH); Treat "heat" as a reactant

Example of an endothermic reaction:

$$NH_4NO_3\,(s) + \text{heat} \rightleftharpoons NH_4^+\,(aq) + NO_3^-\,(aq) \qquad (+\Delta H)$$

↑T; equilibrium shifts to the ________ **(right)**

↓T; equilibrium shifts to the ________ **(left)**

Summary: Temperature effect on equilibria

For an exothermic reaction (-ΔH), K decreases as T increases

For an endothermic reaction (+ΔH), K increases as T increases

LeChâtelier's Principle – *Cont.*

Example involving change of pressure:

In the equation

$$2NO\,(g) + O_2\,(g) \rightleftharpoons 2NO_2\,(g)$$

- If the pressure is increased (by compressing the system, thus ↓ V), equilibrium shifts to the right. Why?
- If the pressure is decreased (by expanding the system), equilibrium shifts to the left. Why?

When the total pressure of a system in equilibrium is increased (compressed), the equilibrium shifts in the direction that *decreases the total number of molecules*

- The converse is true when the pressure is decreased

LeChâtelier's Principle – *Cont.*

First, let's count the number of molecules:

$$2NO\,(g) + O_2\,(g) \rightleftharpoons 2NO_2\,(g)$$

2 molecules + 1 molecule Total: **3 molecules** (Reactant side)	**2 molecules** total (Product side)

↑**P** (compression) causes a shift to the right. Why?

- Fewer molecules on the right (product) side = less crowding
- The converse is true when the pressure is decreased (expansion to larger V) = larger volume or space can accommodate more molecules

27

Calculations involving K_{eq}

28

1. Calc. K_{eq} from equilibrium concentrations

Example:

$2NOCl\ (g) \rightleftharpoons 2NO\ (g) + Cl_2\ (g)$

The partial pressure of NOCl in a closed container is 2.00 atm. At equilibrium 0.66 atm of NO was detected. Calculate K_P.

Solution: First set up a table of concentrations (or partial P's) like this:

	P_{NOCl}	$\rightleftharpoons$	P_{NO}	P_{Cl2}
Initial	2.00 atm		0	0
Change*	- x		+ x	+ ½ x
Equilibrium	?		0.66 atm	?

* The unknown x is proportional to the reaction stoichiometry. A - sign is used for reactants, as they are used up (reduced by x), and + sign for products as they are produced in the reaction

Determining K_{eq} - *Cont.*

Next, figure out what **x** is by inspection of the table and the reaction stoichiometry

❖ The column for P_{NO} is the only one with sufficient info to allow us to solve for x:

For NO: **0 + x = 0.66 atm, so x = 0.66 atm and ½ x = 0.33 atm**

NOTE: Equilibrium conc. = Initial + Change

Finally, complete the table and calculate K_P.

	P_{NOCl}	$\rightleftharpoons$	P_{NO}	P_{Cl2}
Initial	2.00 atm		0	0
Change	**- 0.66**		**+ 0.66**	**+ 0.33**
Equilibrium	**1.34 atm**		0.66 atm	**0.33 atm**

$$K_P = \frac{P^2_{NO} \times P_{Cl2}}{P^2_{NOCl}}$$

Substituting equilibrium P's gives:

$$K_P = \frac{(0.66)^2\,(0.33)}{(1.34)^2} \Rightarrow K_P = 0.080$$

Remember that K's have no unit!

31

2. Equilibrium concentrations from K_{eq}

Phosgene, a toxic gas used in World War I as a choking (pulmonary) agent, is a major industrial chemical used to make plastics and pesticides. It dissociates according to the equation:
[Facts from http://www.bt.cdc.gov/agent/phosgene/basics/facts.asp]

$$COCl_2\,(g) \rightleftharpoons CO\,(g) + Cl_2\,(g)$$

At 1000 ^{0}C the equilibrium constant for this reaction is 0.12. If 2.00 moles of this gas is placed in a 5.00-L closed container at 1000 ^{0}C what are the equilibrium concentrations of all three gases?

Solution:

First, recognize that moles are given, so even though the species are gaseous, we will have to use molar concentrations.

32

Equilibrium Concentrations from K_{eq} – *Cont.*

Solution (Cont.):

Given: $K_{eq} = 0.12$

Initial $[COCl_2]$ = (2.00 mol/5.00 L) = 0.400 M

Do not confuse this with equil. concentration. This is the [ ] prior to equilibrium

Now we can set up a table similar to the one we worked on earlier:

33

Solution (Cont.):

	$COCl_2$ (g)	$\rightleftharpoons$	CO (g)	+	Cl_2 (g)
Initial	0.400 M		0		0
Change*	- x		+ x		+ x
Equilibrium	(0.400 – x)		x		x

= Initial + Change

* Recall: The unknown x is proportional to the reaction stoichiometry. A - sign is used for reactants, as they are used up (reduced by x), and + sign for products as they are produced in the reaction

34

Equilibrium Concentrations from K_{eq}

Finally, substitute the given K and equilibrium concentrations (in terms of x, the equilibrium [ ]) into the K_{eq} expression:

$$K_{eq} = \frac{[CO] \times [Cl_2]}{[COCl]} \Rightarrow 0.12 = \frac{(x)(x)}{(0.400 - x)}$$

$$(0.12)(0.400 - x) = x^2$$

$$0.048 - 0.12x = x^2$$

Rearranging into a quadratic* form gives: $x^2 + 0.12x - 0.048 = 0$

* A separate handout for solving quadratic equations is provided

35

Equilibrium Concentrations from K_{eq}

$$\mathbf{x^2 + 0.12x - 0.048 = 0}$$

This is in the quadratic form:

$$\mathbf{ax^2 + bx + c = 0}$$

Where: $a = 1$ $b = 0.12$ $c = -0.048$

Quadratic solution: (See handout)

$$x = \frac{-0.12 \pm \sqrt{0.12^2 - 4(1)(-0.048)}}{2(1)}$$

$x = -0.28$ or $x = 0.16$ **Choose the one that's (+)**

36

Equilibrium Concentrations from K_{eq} – *Cont.*

But what is the meaning of x? Numerically, **x = 0.160**

Recall that x = [CO] = [Cl_2] at equilibrium, so we go back to the table and enter or solve for the equil. concentrations:

	$COCl_2$ (g)	$\rightleftharpoons$	**CO (g)**	**+**	**Cl_2 (g)**
Initial	0.400 M		0		0
Change*	**- x**		**+ x**		**+ x**
Equilibrium	**(0.400 – x)**		**x**		**x**

Thus, at equilibrium: **[CO] = [Cl_2] = 0.16 M**
and **[$COCl_2$]** = (0.400 – 0.160) = **0.24 M**

37

The Systematic Method

	$COCl_2$ $\rightleftharpoons$	CO +	Cl_2
i	0.400	0	0
c	-x	+x	+x
e	0.400 - x	x	x

Equilibrium expression:

$$K_c = \frac{[CO][Cl_2]}{[COCl_2]} \qquad 0.12 = \frac{x^2}{(0.400 - x)}$$

$x^2 + 0.12\,x - 0.048 = 0$

x = -0.28, 0.16 [CO] = [Cl_2] = 0.16 M

[$COCl_2$] = 0.24 M

38

The Quadratic Formula

Given: $a\,x^2 + b\,x + c = 0$

$$\boxed{x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}}$$

$x^2 + 0.12\,x - 0.048 = 0$

$a = 1 \qquad b = 0.12 \qquad c = -0.048$

$$x = \frac{-0.12 \pm \sqrt{0.12^2 + 0.19}}{2}$$

$x = -0.060 \pm 0.22$

39