NEPHAR 201
Analytical Chemistry II

Chapter 1

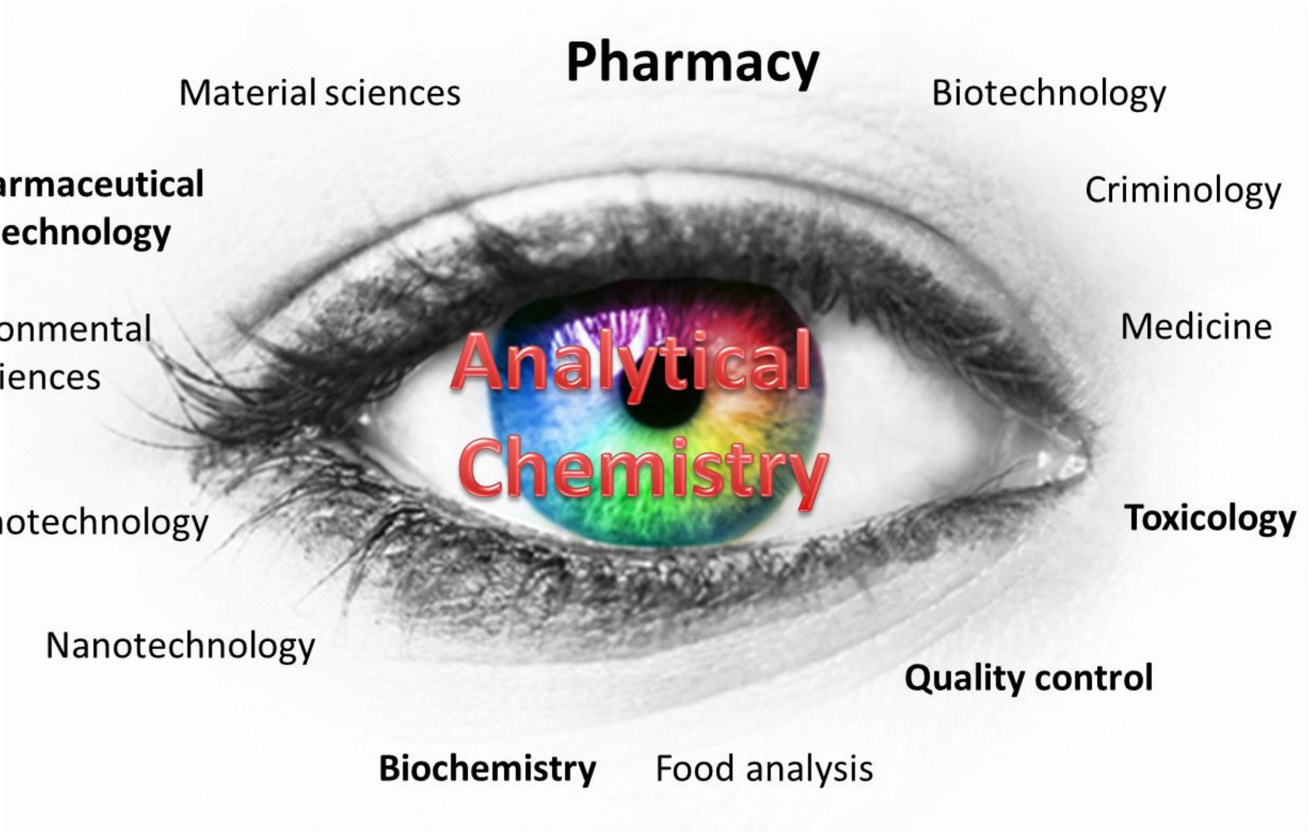
Introduction: Basic concepts and calculations in analytical chemistry

Assist. Prof. Dr. Usama ALSHANA

Analytical chemistry

Analytical chemistry: is the study of the separation, identification, and quantification of the chemical components of natural and artificial materials.

Where is it needed?



Analytical Chemistry

Pharmacy

Material sciences

Biotechnology

Pharmaceutical technology

Criminology

Environmental sciences

Medicine

Nanotechnology

Toxicology

Nanotechnology

Quality control

Biochemistry

Food analysis

Analysis

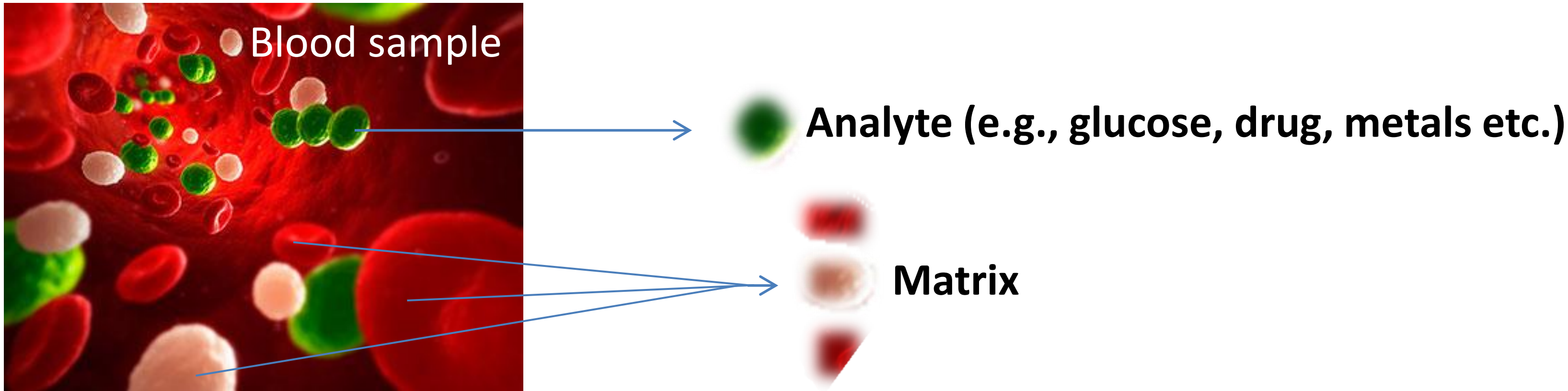
Qualitative

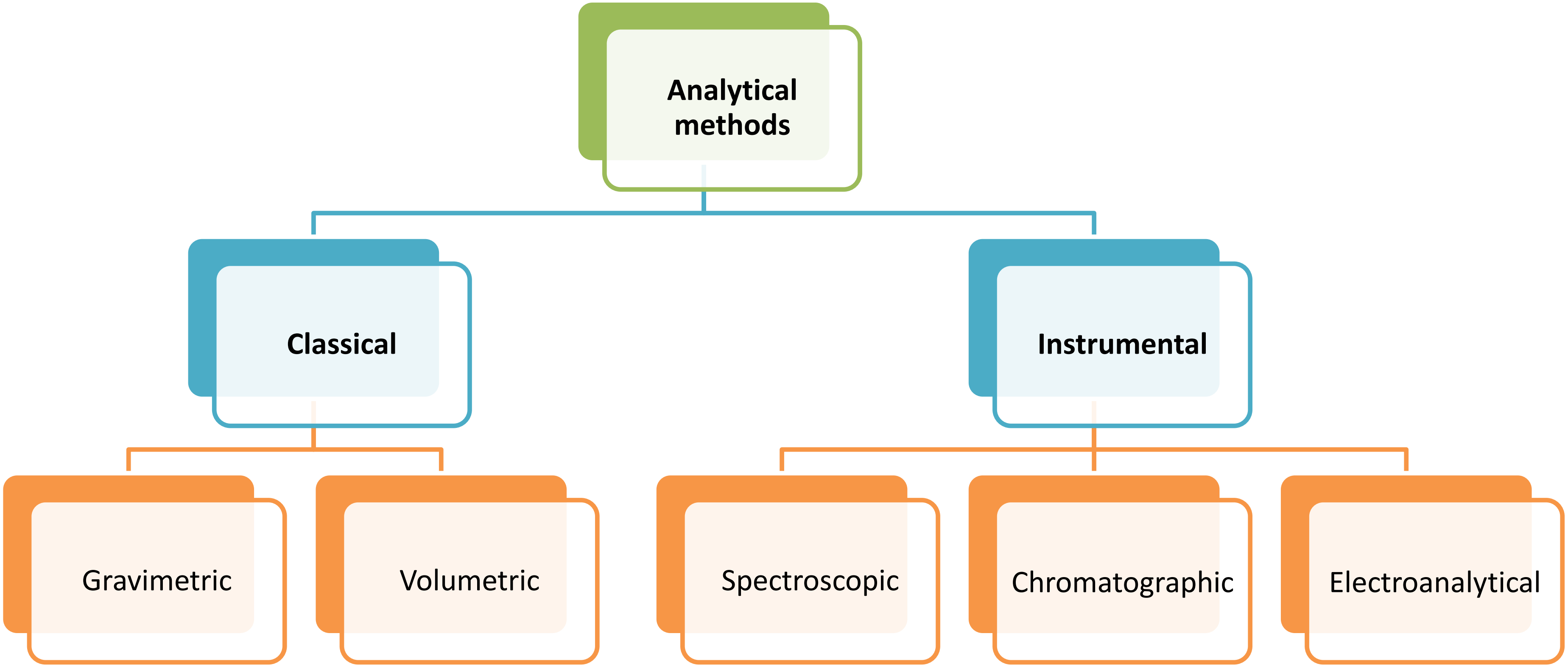
The process of finding out the **identity** of components in a sample (elements or compound)

Quantitative

The process of finding out the **amount** of components in a sample (elements or compound)

- **Sample:** A portion of material selected from a larger quantity of material.
- **Analyte:** The component of a sample (element, ion, compound, etc.) to be determined.
- **Matrix:** all of the components making up the sample containing the analyte.





- **Analytical methods**
  - **Classical**
    - Gravimetric
    - Volumetric
  - **Instrumental**
    - Spectroscopic
    - Chromatographic
    - Electroanalytical

- **Gravimetric analysis:** a method that is based on the measurement of the <u>mass</u> a pure substance with an analytical balance.

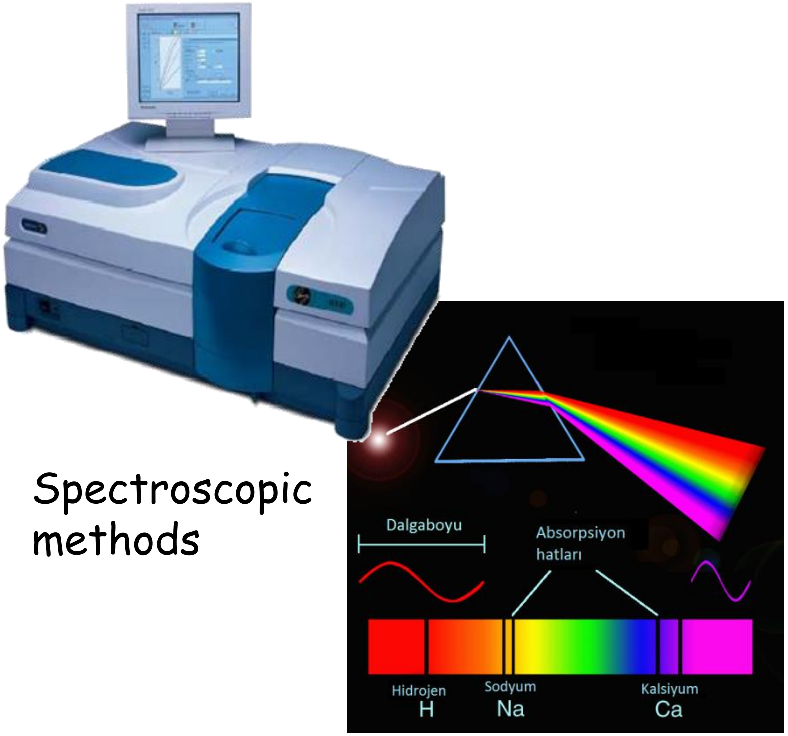
- **Volumetric method:** this method involves the measurement of the <u>volume</u> of a solution of known concentration which is used to determine the concentration of the analyte (e.g. titration).

analytical balance

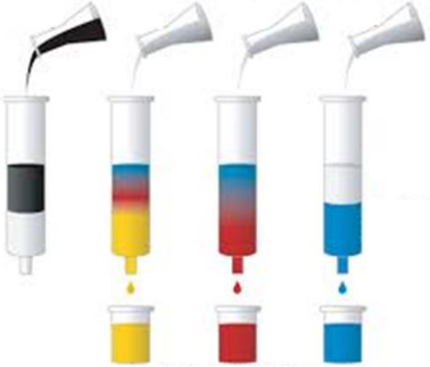
- **Spectroscopic methods:** methods that are based on the measurement of the interaction of the analyte with light such as absorption, emission, scattering etc.

- **Chromatographic methods:** physical methods of separation that distribute components to separate between two phases, one stationary (stationary phase), the other (the mobile phase) moving in a definite direction.

- **Electroanalytical methods:** methods that are based on quantifying the analyte by measuring the potential (volts) and/or current (amperes) in an electrochemical cell containing the analyte.



Spectroscopic methods



Chromatographic methods

Electroanalytical methods

Basic steps in analysis

1. Choice of the technique/method
2. Sampling
3. Sample preparation
4. Eliminating interferences
5. Calibration and measurement of concentration
6. Calculations and validation of the method

SI Units

Measurement	Unit	Symbol
Mass	Kilogram	kg
Distance	Meter	m
Time	Second	s
Temperature	Kelvin	K
Amount of substance	Mole	Mol
Electric current	Amper	A

- **Mole:** the amount of any chemical substance that contains as many elementary entities, e.g., atoms, molecules, ions, or electrons, as there are atoms in 12 grams of pure carbon-12 (^{12}C). This number is expressed by the **Avogadro constant**, which has a value of 6.022×10^{23}.
- **Molar mass (molecular weight, M_r):** the mass (in g) of one mole of any substance.

Prefixes of units

Prefix	Symbol	Meaning
giga-	G	10^9
mega-	M	10^6
kilo-	k	10^3
deci-	d	10^{-1}
centi-	c	10^{-2}
milli-	m	10^{-3}
micro-	µ	10^{-6}
nano-	n	10^{-9}
pico-	p	10^{-12}
femto-	f	10^{-15}

Example

What is the mass (in mg) of a substance having a mass of 5.0 kg?

Solution

$$?\,mg = 5.0\,\cancel{kg} \times \frac{10^3\,\cancel{g}}{1\,\cancel{kg}} \times \frac{10^3\,mg}{1\,\cancel{g}} = 5.0 \times 10^6\,mg$$

Example

How many liters (L) and milliliters (mL) is a solution of 50 µL volume?

Solution

(a) $$? L = 50\ \cancel{\mu L} \times \frac{1\ L}{10^6\ \cancel{\mu L}} = 5.0 \times 10^{-5}\ L$$

(b) $$? mL = 50\ \cancel{\mu L} \times \frac{1\ \cancel{L}}{10^6\ \cancel{\mu L}} \times \frac{10^3\ mL}{1\ \cancel{L}} = 5.0 \times 10^{-2}\ mL$$

Example

What is the mass (in g) of $1.00 \times 10^{-2}\ mol$ HCl?

Solution

$$? g = 1.00 \times 10^{-2}\ \cancel{mol} \times \frac{36.5\ g}{1\ \cancel{mol}} = 0.365\ g$$

or: $$M_r = \frac{m}{n}$$

$$m = M_r \times n = 36.5 \frac{g}{\cancel{mol}} \times 1.00 \times 10^{-2}\ \cancel{mol}$$

$$= 0.365\ g$$

Example

What is the amount (in mol) of 39.6 mg strontium chloride ($SrCl_2$)?

38
Sr
Strontium
87.62

17
Cl
Chlorine
35.453

Solution

$$? \, mol = 39.6 \, \cancel{mg} \times \frac{1 \, mol}{158.52 \, \cancel{g}} \times \frac{1 \, \cancel{g}}{10^3 \, \cancel{mg}} = 2.50 \times 10^{-4} \, mol$$

Concentration units, conversions and solution preparations

- **Concentration units:** the units that express the relative amount of a solute in a known amount (or volume) of the solution.
- **Molarity (M):** is a measure of the concentration of a solute in a solution, or of any chemical species in terms of amount of substance in a given volume. A commonly used unit for molar concentration used in chemistry is mol/L. A solution of concentration 1 mol/L is also denoted as 1 molar (1 M).

$$\boxed{Molarity = \frac{mol \; of \; solute}{volume \; of \; solution}} \Rightarrow \boxed{1M \, (molar) = \frac{1 \, mol}{1 \, L}}$$

Example

What is the molar concentration of 19.8 g strontium chloride ($SrCl_2$, $M_r = 158.52\ g/mol$) in 250 mL of a solution? Describe how this solution is prepared.

Solution

For the solute: $n = \frac{m}{M_r} = \frac{19.8\ g}{158.52\ g/mol} = 0.125\ mol$

For the solution: $V = 250\ mL \times \frac{1\ L}{10^3\ mL} = 0.250\ L$

⇨ $$M = \frac{n\ (solute, mol)}{V\ (solution, L)} = \frac{0.125\ mol}{0.250\ L} = 0.50\ M\ (or\ \frac{mol}{L})$$

To prepare this solution, 19.8 g strontium chloride ($SrCl_2$), are dissolved in an appropriate amount of water (approx. 125 mL), transferred into a 250-mL volumetric flask and the solution is made up to the mark with deionized water.

Example

How many grams of strontium chloride hexahydrate ($SrCl_2.6H_2O$, $M_r = 266.62\ g/mol$) would be weighed to prepare 250 mL of 0.540 M chloride ions (Cl^-)? Explain how this solution would be prepared.

Solution

For Cl^-: $$M = \frac{n}{V} \Longrightarrow n = M \times V = 0.540\ \frac{mol}{\cancel{L}} \times 0.250\ \cancel{L} = 0.135\ mol\ Cl^-$$

For $SrCl_2.6H_2O$:

$$1\ \text{mol}\ SrCl_2.6H_2O \longrightarrow 2\ \text{mol}\ Cl^-$$

$$x\ \text{mol}\ SrCl_2.6H_2O \longleftarrow 0.135\ \text{mol}\ Cl^-$$

$$x = 0.0675\ mol\ of\ SrCl_2.6H_2O$$

$$M_r = \frac{m}{n} \Longrightarrow m = M_r \times n = 266.62\ \frac{g}{\cancel{mol}} \times 0.0675\ \cancel{mol}$$

$$= 18.0\ g\ SrCl_2.6H_2O$$

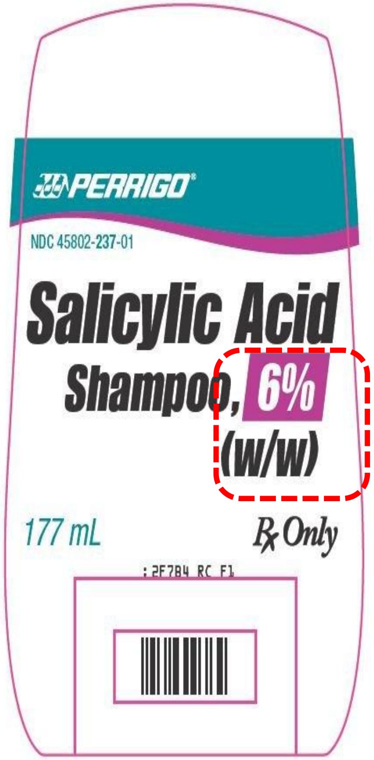
To prepare this solution, 18.0 g strontium chloride hexadydrate ($SrCl_2.6H_2O$) are weighed in a beaker and dissolved in an appropriate amount of deionized water (approx. 125 mL). The solution is transferred into a 250-mL volumetric flask and is made up to the mark with deionized water.

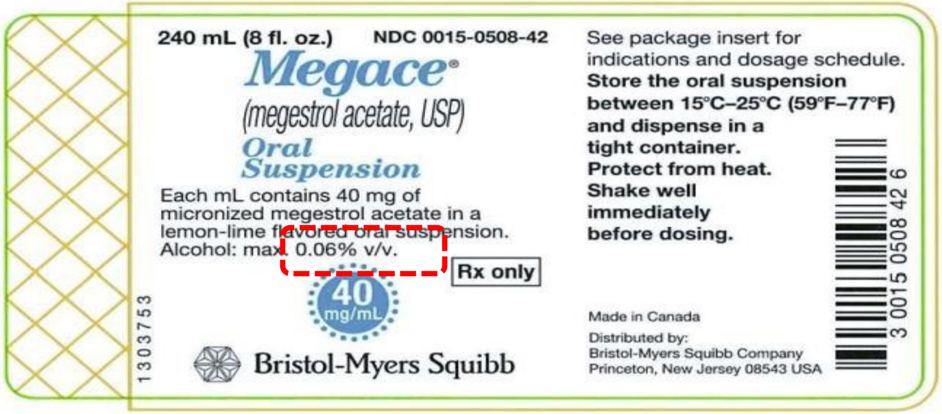
A mass of K_2FeSCN ($M_r = 192\ g/mol$) is dissolved in an appropriate volume of deionized water and the solution is made up to 500 mL. If the final concentration of Fe^{2+} ions is $2{,}0 \times 10^{-3}\ M$, calculate the mass (in g) of K_2FeSCN that has been weighed.

A solution of sodium chloride, NaCl (500 mL) contains 20.0 g of NaCl. What is the molar concentration of NaCl in this solution? Describe how this solution was prepared.

Percentage Concentration

- **Percentage concentration:** expresses the percentage of a solute in a solution.
- **Percentage by weight (w/w)**, **percentage by volume (v/v)** and **percentage by weight/volume (w/v)** are also used to report concentrations. In the International System, “w” and “v” stand for weight and volume, respectively.





240 mL (8 fl. oz.) NDC 0015-0508-42

Megace®

(megestrol acetate, USP)

Oral Suspension

Each mL contains 40 mg of micronized megestrol acetate in a lemon-lime flavored oral suspension. Alcohol: max. 0.06% v/v.

40 mg/mL

Rx only

Bristol-Myers Squibb

1303753

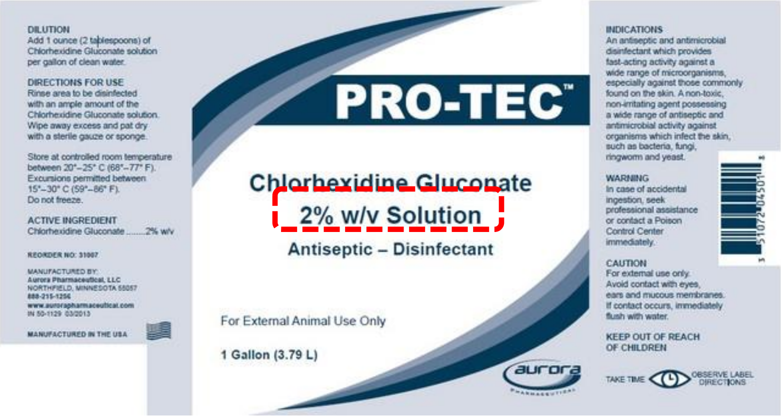
See package insert for indications and dosage schedule.

Store the oral suspension between 15°C–25°C (59°F–77°F) and dispense in a tight container. Protect from heat. Shake well immediately before dosing.

Made in Canada

Distributed by:
Bristol-Myers Squibb Company
Princeton, New Jersey 08543 USA

3 0015 0508 42 6



DILUTION
Add 1 ounce (2 tablespoons) of Chlorhexidine Gluconate solution per gallon of clean water.

DIRECTIONS FOR USE
Rinse area to be disinfected with an ample amount of the Chlorhexidine Gluconate solution. Wipe away excess and pat dry with a sterile gauze or sponge.

Store at controlled room temperature between 20°–25° C (68°–77° F). Excursions permitted between 15°–30° C (59°–86° F). Do not freeze.

ACTIVE INGREDIENT
Chlorhexidine Gluconate ....2% w/v

REORDER NO: 31007

MANUFACTURED BY:
Aurora Pharmaceutical, LLC
NORTHFIELD, MINNESOTA 55057
888-215-1256
www.aurorapharmaceutical.com
IN 50-1129 03/2013

MANUFACTURED IN THE USA

PRO-TEC™

Chlorhexidine Gluconate

2% w/v Solution

Antiseptic – Disinfectant

For External Animal Use Only

1 Gallon (3.79 L)

aurora

INDICATIONS
An antiseptic and antimicrobial disinfectant which provides fast-acting activity against a wide range of microorganisms, especially against those commonly found on the skin. A non-toxic, non-irritating agent possessing a wide range of antiseptic and antimicrobial activity against organisms which infect the skin, such as bacteria, fungi, ringworm and yeast.

WARNING
In case of accidental ingestion, seek professional assistance or contact a Poison Control Center immediately.

CAUTION
For external use only. Avoid contact with eyes, ears and mucous membranes. If contact occurs, immediately flush with water.

KEEP OUT OF REACH OF CHILDREN

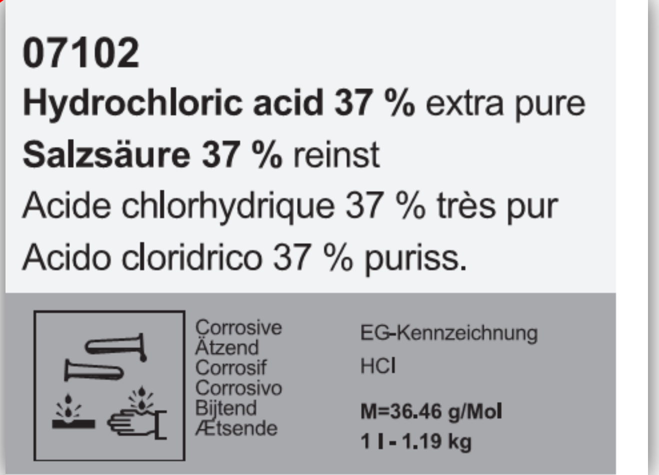
TAKE TIME OBSERVE LABEL DIRECTIONS

- **Percentage by volume (v/v)** is generally used to report the concentration of a liquid solute mixed with another liquid in a solution. For example, a 20 % ethanol (C_2H_5OH) solution is prepared by mixing 20.0 mL of pure ethanol with water and the volume is made up to 100 mL with water.

- **Percentage by weight/volume (w/v)** is generally used to describe the concentration of a solid solute in a solution. For example, 10 % KOH solution is prepared by dissolving 10 g KOH in water and the solution is made up to 100 mL.

- **Percentage by weight (w/w)** can also be used to tell the mass of a solute (in g) in 100 g of a solution. For example, on the label of HCl bottle, 37 % means that there are 37 g of HCl in 100 g of this solution.

For conversions, the density of solutions is generally given on the label, e.g., 1 L = 1.19 kg



07102
Hydrochloric acid 37 % extra pure
Salzsäure 37 % reinst
Acide chlorhydrique 37 % très pur
Acido cloridrico 37 % puriss.

Corrosive
Ätzend
Corrosif
Corrosivo
Bijtend
Ætsende

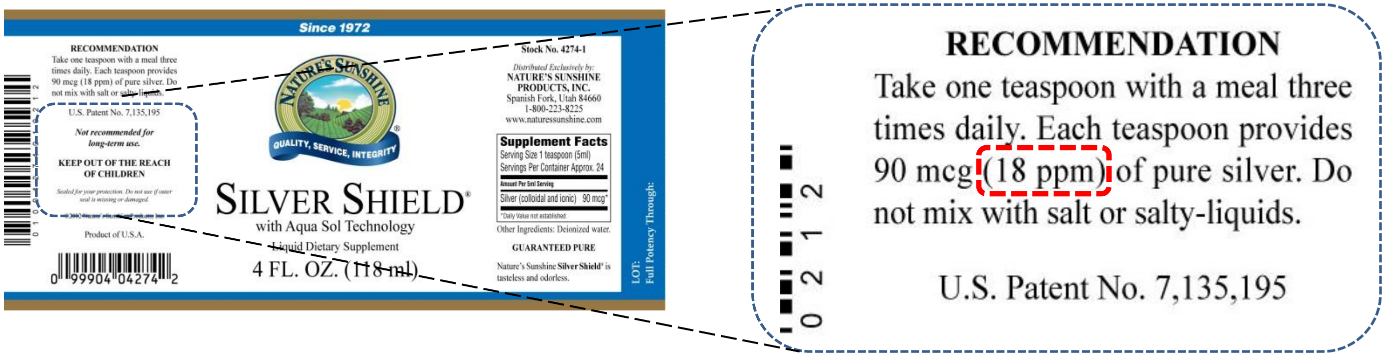
EG-Kennzeichnung
HCl
M=36.46 g/Mol
1 l - 1.19 kg

- **Part per million (ppm), part per billion (ppb) and part per trillion (ppt):** Due to advancement in instruments, scientists also use low concentration expressions such as ppm, ppb and ppt.

$1\ \text{ppm} = 1\ \text{mg L}^{-1}$

$1\ \text{ppb} = 1\ \mu\text{g L}^{-1}$

$1\ \text{ppt} = 1\ \text{ng L}^{-1}$



Since 1972

RECOMMENDATION
Take one teaspoon with a meal three times daily. Each teaspoon provides 90 mcg (18 ppm) of pure silver. Do not mix with salt or salty-liquids.

U.S. Patent No. 7,135,195

Not recommended for long-term use.

KEEP OUT OF THE REACH OF CHILDREN

Sealed for your protection. Do not use if outer seal is missing or damaged.

Product of U.S.A.

NATURE'S SUNSHINE®

QUALITY, SERVICE, INTEGRITY

SILVER SHIELD®
with Aqua Sol Technology
Liquid Dietary Supplement
4 FL. OZ. (118 ml)

Stock No. 4274-1

Distributed Exclusively by:
NATURE'S SUNSHINE PRODUCTS, INC.
Spanish Fork, Utah 84660
1-800-223-8225
www.naturessunshine.com

Supplement Facts
Serving Size 1 teaspoon (5ml)
Servings Per Container Approx. 24
Amount Per 5ml Serving
Silver (colloidal and ionic) 90 mcg*
*Daily Value not established

Other Ingredients: Deionized water.

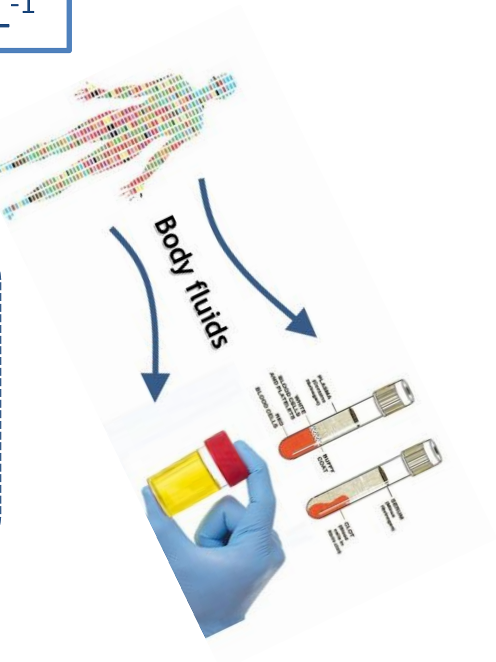
GUARANTEED PURE

Nature's Sunshine **Silver Shield**® is tasteless and odorless.

LOT:
Full Potency Through:

RECOMMENDATION
Take one teaspoon with a meal three times daily. Each teaspoon provides 90 mcg (18 ppm) of pure silver. Do not mix with salt or salty-liquids.

U.S. Patent No. 7,135,195



These concentration units are sometimes used to describe the concentration of analytes in medicines, biological fluids (blood, urine, saliva), water, soil, air samples, etc.

Conversions among concentration units

Example

A commercial HCl solution has a concentration of 37 % (w/w) and a density of 1.19 kg L^{-1}.

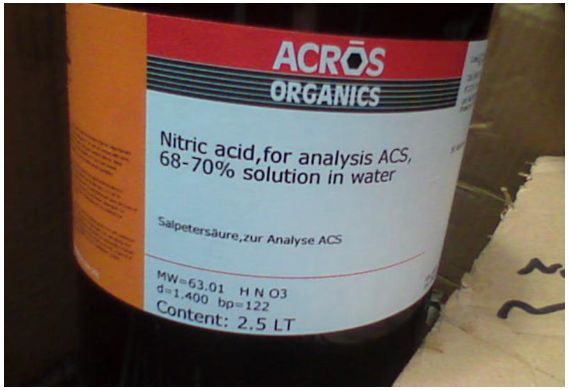
What is the molar concentration of HCl in this solution?

Solution

$$? \frac{mol\ HCl}{L\ soln} = \frac{37\ \cancel{g\ HCl}}{100\ \cancel{g\ soln}} \times \frac{1\ mol\ HCl}{36.5\ \cancel{g\ HCl}} \times \frac{1.19 \times 10^3\ \cancel{g\ soln}}{1\ L\ soln}$$

$$= 12.0\ mol/L$$

If the concentration of nitric acid (HNO_3) in a commercial solution is 69 % (w/w) that is equavilanet to 15.3 mol/L. Calculate the density (in kg L^{-1}) of this solution.



Example

A sample of sea water having a density of 1.018 g mL^{-1} contains 19.2 ppm nitrate ions (NO_3^-). What is the molar concentration of nitrate ions in the sample?

7
N
Nitrogen
14.007

8
O
Oxygen
15.999

1 ppm = 1 mg L^{-1}

Solution

$$? \frac{mol\ NO_3^-}{L\ soln} = \frac{19.2\ \cancel{mg}\ NO_3^-}{L\ soln} \times \frac{1\ mol\ NO_3^-}{62\ \cancel{g}\ NO_3^-} \times \frac{1\ \cancel{g}\ NO_3^-}{10^3\ \cancel{mg} NO_3^-} = 3.0 \times 10^{-4}\ mol/L$$

Example

International standards require that the maximum concentration of chloride ions in drinking water not exceed 2.5×10^5ppb. Calculate this concentration in mM.

1 ppb = 1 µg L^{-1}

Solution

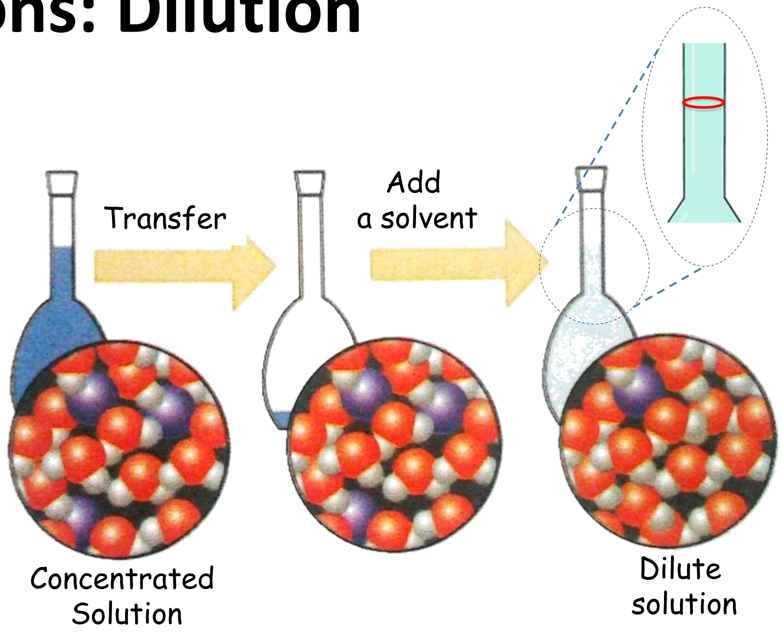
17
Cl
Chlorine
35.453

$$? \frac{mol\ Cl^-}{L\ soln} = \frac{2.5 \times 10^5\ \cancel{\mu g}\ Cl^-}{L\ soln} \times \frac{1\ mol\ Cl^-}{35.45\ \cancel{g}\ Cl^-} \times \frac{1\ \cancel{g}\ Cl^-}{10^6\ \cancel{\mu g}\ Cl^-} = 7.0 \times 10^{-3}\ mol/L$$

$$= 7.0\ mmol/L = 7.0\ mM$$

Preparation of solutions: Dilution

A certain amount (or volume) of the original solution is transferred into another volumetric flask. The solution is then made up to the mark with a solvent (e.g., water). The new solution is more dilute than the original.



Steps of dilution

Calculations

$$\underbrace{M_1V_1}_{\text{Conc. soln}} = \underbrace{M_2V_2}_{\text{dil. soln}}$$

Example

How many mL of 0.152 M $HCl_{(aq)}$ are needed to prepare 100 mL of 5.23×10^{-4} M $HCl_{(aq)}$?

State the steps for preparing this dilute solution.

Solution

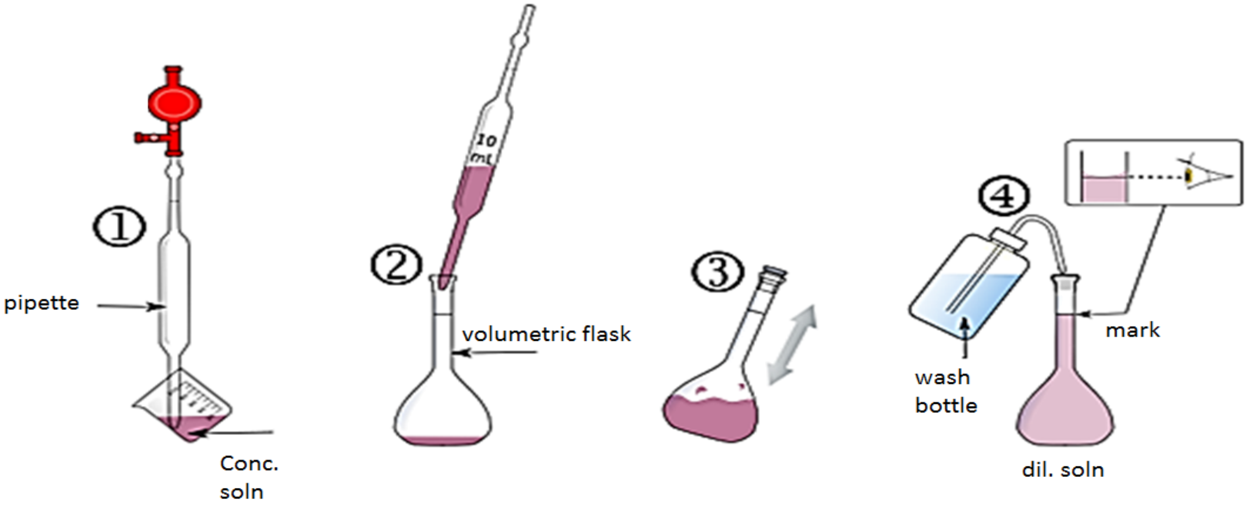
$M_1 = 0.152\ M$
$V_1 = ?$
$M_2 = 5.23 \times 10^{-4}$ M
$V_2 = 100\ mL$

$$\underbrace{\boldsymbol{M_1 V_1}}_{\text{Conc. soln}} = \underbrace{\boldsymbol{M_2 V_2}}_{\text{dil. soln}}$$

$$0.\cancel{1}52\ M \times V_1 = 5.23 \times \cancel{1}0^{-4}\ M \times 100\ mL \Rightarrow V_1 = 0.344\ \text{mL}\ (= 344\ \mu L)$$

① 344 µL of the original concentrated HCl solution are withdrawn into a micropipette (if the volume was larger than 1 mL, a pipette is used) and transferred into a 100-mL volumetric flask ② a small amount of DI water is added ③ the solution is swirled and ④ the solution is made up to the mark with DI water using a wash bottle.

or
micropipette



Example

How many mL would be taken from 1.00 M sulfuric acid [$H_2SO_{4(aq)}$] to prepare 250 mL, 0.02 M $H_2SO_{4(aq)}$ solution? How is this dilute solution prepared?

Solution

$$M_1 = 1.00\ M$$
$$V_1 = ?$$
$$M_2 = 0.02\ \text{M}$$
$$V_2 = 250\ mL$$

$$\underbrace{\boldsymbol{M_1V_1}}_{\text{Conc. soln}} = \underbrace{\boldsymbol{M_2V_2}}_{\text{dil. soln}}$$

$$1.00\ M \times V_1 = 0.02\ M \times 250\ mL \quad \Rightarrow \quad V_1 = 5.00\ \text{mL}$$

⇨ 5.0 mL of the original concentrated H_2SO_4 solution are withdrawn into a pipette and transferred into a 250-mL volumetric flask. A small amount of DI water is added and the solution is swirled. The solution is made up to the mark with DI water using a wash bottle.

Describe how 100 mL, 0.5 M nitric acid [$HNO_{3(aq)}$] would be prepared from 2.00 M $HNO_{3(aq)}$.

Example

Atomic absorption spectrometry (AAS) and atomic emission spectrometry (AES) are used to determine metals in biological and environmental samples at concentrations below ppm. 1000 ppm commercial stock solutions are used to prepare working standard solutions. Describe how a 1.0 ppm, 100 mL lead ions (Pb^{2+}) solution may be prepared starting with the 1000 ppm stock solution.

Solution

$$M_1 = 1000\ ppm$$
$$V_1 = ?$$
$$M_2 = 1.0\ ppm$$
$$V_2 = 100\ mL$$

$$\underbrace{\boldsymbol{M_1V_1}}_{\text{Conc. soln}} = \underbrace{\boldsymbol{M_2V_2}}_{\text{dil. soln}}$$

$$1000\ ppm \times V_1 = 1.0\ ppm \times 100\ mL \quad \Rightarrow \quad V_1 = 0.1\ mL = 100\ \mu L$$

100 µL of the stock Pb^{2+} solution are withdrawn into a micropipette and transferred into a 100-mL volumetric flask. A small amount of DI water is added and the solution is swirled. The solution is made up to the mark with DI water using a wash bottle.

Example

A commercial ammonia (NH_3) solution has a concentration of 28.0 % (w/w) and a density of 0.899 g mL^{-1}. Using this solution, describe how 500 mL, 0.100 M NH_3 solution may be prepared.

Solution

First, convert % (w/w) into M;

$$? \frac{mol\ NH_3}{L\ soln} = \frac{28.0\ g\ \cancel{NH_3}}{100\ g\ \cancel{soln}} \times \frac{0.899\ g\ \cancel{soln}}{1\ \cancel{mL}\ soln} \times \frac{10^3\ \cancel{mL}\ soln}{1\ L\ soln} \times \frac{1\ mol\ NH_3}{17\ g\ \cancel{NH_3}} = 14.8\ mol/L$$

Second;

$$M_1 \times V_1 = M_2 \times V_2$$

$$14.8\ \cancel{\frac{mol}{L}} \times V_1 = 0.100\ \cancel{\frac{mol}{L}} \times 500\ mL$$

⇨ $$V_1 = 3.38\ mL$$

3.38 mL of the stock NH_3 solution are withdrawn into a pipette and transferred into a 500-mL volumetric flask. A small amount of DI water is added and the solution is swirled. The solution is made up to the mark with DI water using a wash bottle.

End-Of-Section Questions

How many moles are there in 38.1 mg of sodium tetraborate decahydrate ($Na_2B_4O_7.10H_2O$)? How many moles of boron (B) does this sample contain?

(Na:22.99; B:10.81; O: 16.00; H: 1.00 g/mol)

If 400 mg of $K_4Fe(CN)_6$ are dissolved in DI water and the volume is made up to 500 mL, what would the molar concentration of potassium ions (K^+) in the solution be?

(K: 39.10; Fe: 55.85; C: 12.01; N: 14.01 g/mol)

In average, human blood contains 180 ppm of potassium ions (K^+), what is the molar concentration of K^+?

(K: 39.10 g/mol)

How many grams of oxalic acid ($H_2C_2O_4.2H_2O$) are required to prepare 500 mL, 0.300 M? Describe how this solution is prepared.

(H: 1.00; C: 12.01; O: 16.00 g/mol)

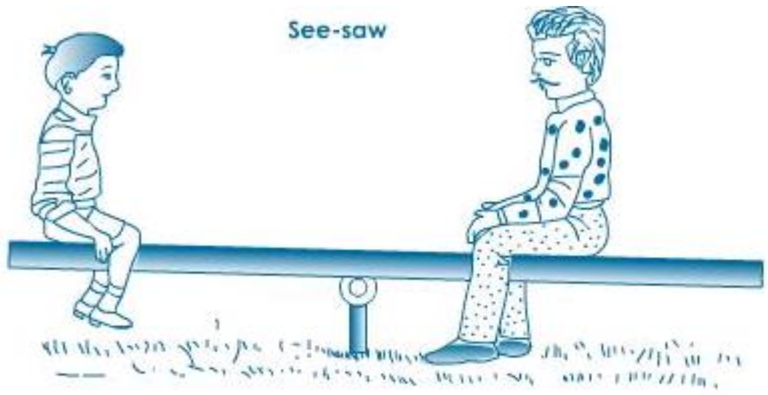
A commercial sulfuric acid (H_2SO_4) solution has a density of 1.84 g/mL and a concentration of 96 % (w/w). What is the molar concentration of H_2SO_4 in this solution?

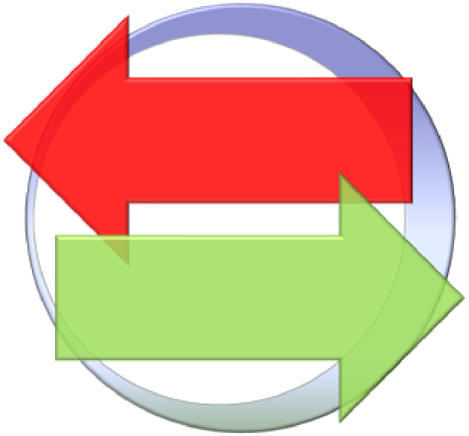
(H: 1.00; O: 16.00; S: 32.00 g/mol)

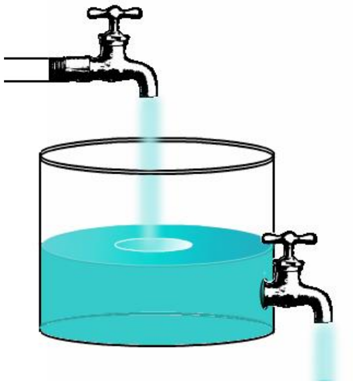
Describe how 250 mL, 3.00 M phosphoric acid (H_3PO_4) may be prepared from the commercial H_3PO_4 solution having a density of 1.70 g mL^{-1} and a concentration of 85 % (w/w).

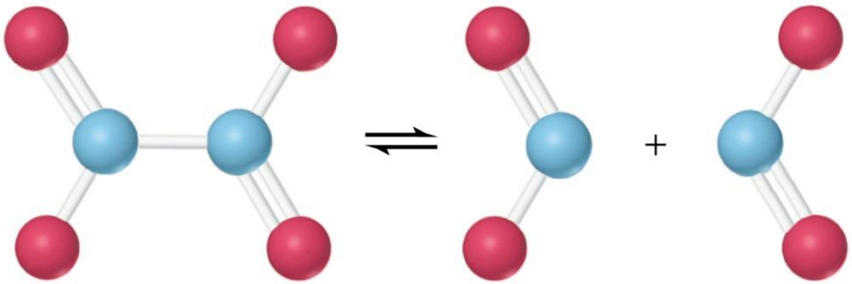
(H: 1.00; P: 30.97; O: 16.00 g/mol)

Chemical Equilibria









Solutes

Ionic

- Found as ions,
- Are called electrolytes,
- Conduct electricity,
- Ex. NaCl, MgI_2, NaOH, K_2SO_4

Molecular

- Found as molecules,
- Are not called electrolytes,
- Do not conduct electricity,
- Ex. Sugar ($C_6H_{12}O_6$), methanol (CH_3OH)

Electrolytes

Strong

A solute that **completely**, or almost completely, ionizes or dissociates in a solution. Ex. NaCl, HNO_3, KOH

Weak

A solute that does not fully dissociate into ions in solution. These substances only **partially** ionize in solution. Ex. H_2CO_3, NH_3, AgCl

Reactions

Irreversible **Reversible**

Irreversible reactions:

- Proceed in one direction. Reactants cannot be obtained from products,
- The reaction proceed till the reactants are completely consumed up,
- No equilibrium is formed during the reaction,
- In reality, no reaction is completely irreversible. However, reactions proceeding so much to the right (product side) are said to be irreversible.

Ex. $CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(g)}$

Reversible reactions:

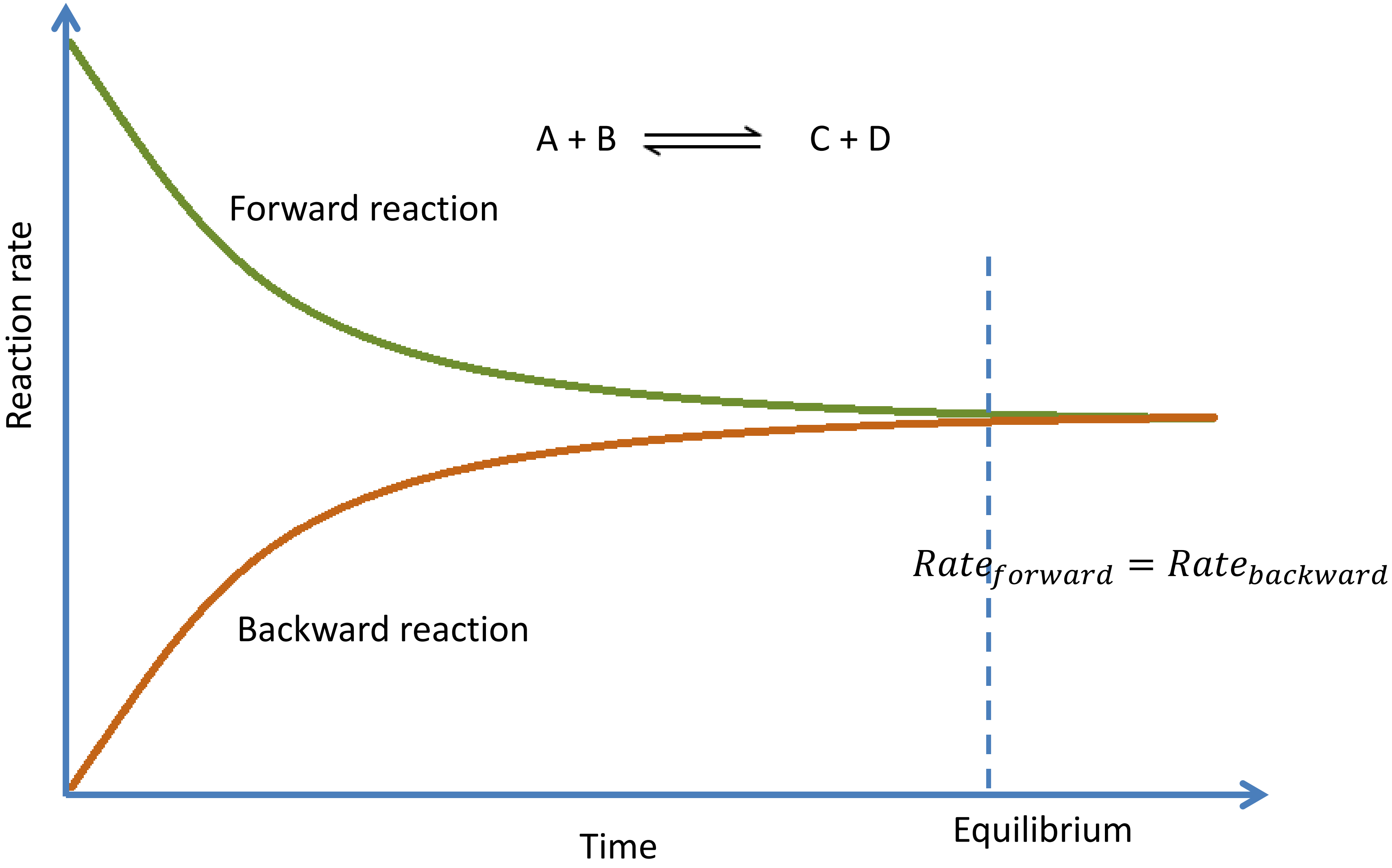
- Proceed in two directions. Products are obtained from reactants (forward reaction) and reactants from products (backward reaction),
- When the rate of the forward reaction equals the rate of the backward reaction, the reaction is said to have reached **dynamic equilibrium**.
- At equilibrium, the concentrations of reactants and products are constant (but do not have to be equal).

Ex. $3N_{2(g)} + 2H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

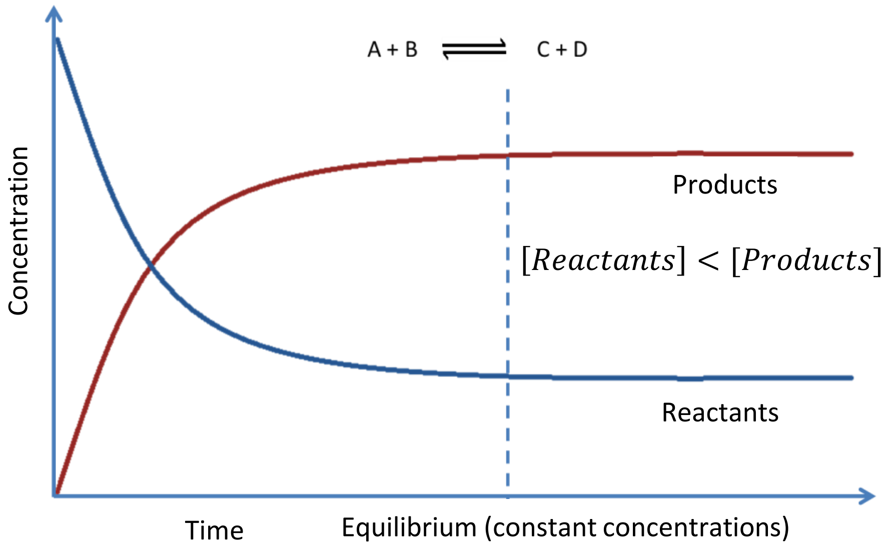
$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$

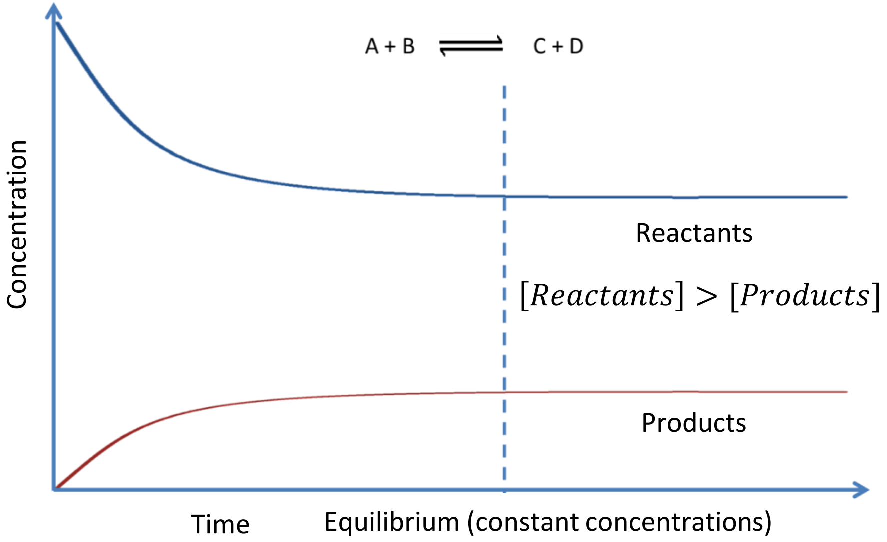
$CuSO_4.5H_2O_{(k)} \rightleftharpoons CuSO_{4(k)} + 5H_2O_{(g)}$

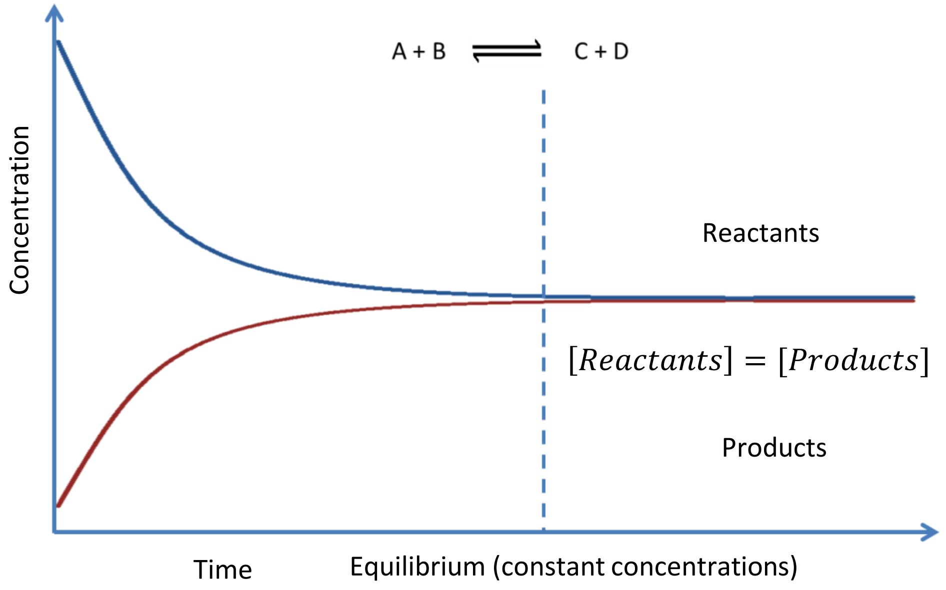
Rate-time relationship in equilibrium reactions



Concentration-time relationship in equilibrium reactions







EQUILIBRIUM CONSTANT (K_c)

- **Equilibrium constant**

$$aA + bB \rightleftharpoons cC + dD$$

Forward reaction $\quad aA + bB \longrightarrow cC + dD$

$$rate_f = k_f \times [A]^a \times [B]^b$$

Backward reaction $\quad cC + dD \longrightarrow aA + bB$

$$rate_b = k_b \times [C]^c \times [D]^d$$

At equilibrium, the rates are equal:

$$k_f \times [A]^a \times [B]^b = k_b \times [C]^c \times [D]^d$$

Therefore;

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

This ratio is expressed as the **equilibrium constant (*K*$_c$)**. Therefore, for the general reaction written above:

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

Example

Writing equilibrium constant expressions

Write the equilibrium constant expressions for the following reactions:

a) $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$

b) $4NH_{3(g)} + 5O_{2(g)} \rightleftharpoons 4NO_{(g)} + 6H_2O_{(g)}$

c) $CH_3COOH_{(s)} + CH_3OH_{(s)} \rightleftharpoons CH_3COOCH_{3(s)} + H_2O_{(s)}$

Solution

a) $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$

$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$

b) $4NH_{3(g)} + 5O_{2(g)} \rightleftharpoons 4NO_{(g)} + 6H_2O_{(g)}$

$$K_c = \frac{[NO]^4[H_2O]^6}{[NH_3]^4[O_2]^5}$$

c) $CH_3COOH_{(s)} + CH_3OH_{(s)} \rightleftharpoons CH_3COOCH_{3(s)} + H_2O_{(s)}$

$$K_c = \frac{[CH_3COOCH_3][H_2O]}{[CH_3COOH][CH_3OH]}$$

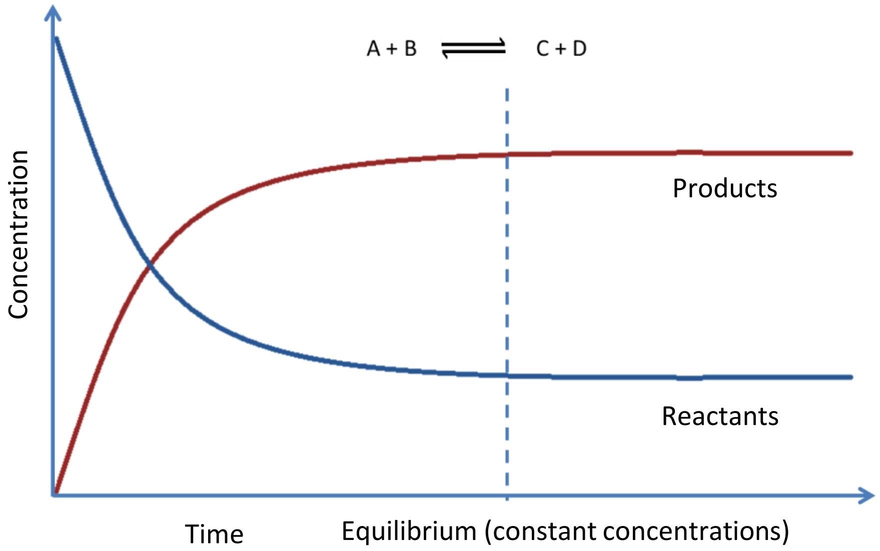
Comparison of equilibrium constants

Case 1

$H_{2(g)} + Cl_{2(g)} \rightleftharpoons 2HCl_{(g)}$ $\quad K_c = 4.0 \times 10^{31}$ $\quad T = 300\ K$

$$K_c = \frac{[HCl]^2}{[H_2][Cl_2]} = 4.0 \times 10^{31}$$

$$\underbrace{[HCl]^2}_{\text{product}} \gg \underbrace{[H_2][Cl_2]}_{\text{reactants}}$$



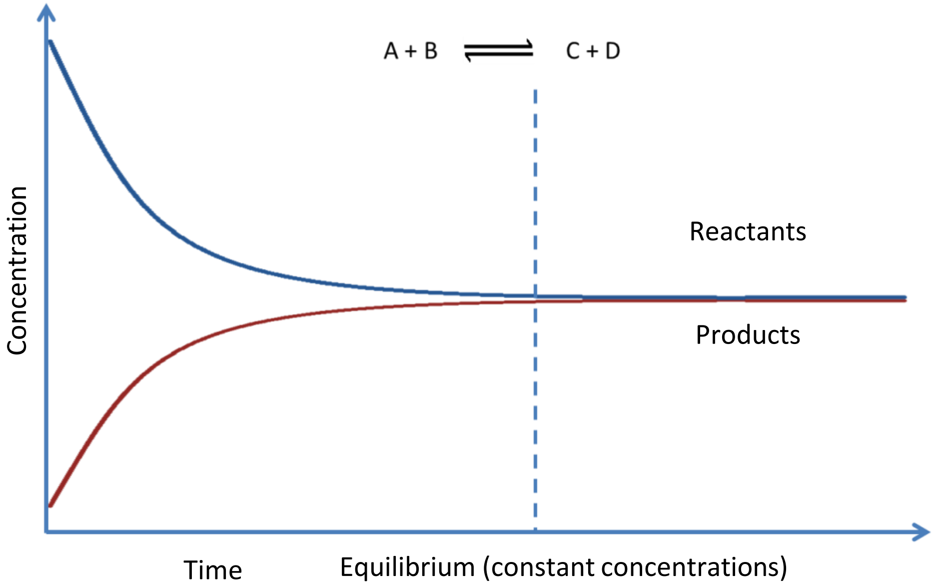
Comparison of equilibrium constants

Case 2

$$2HD_{(g)} \rightleftharpoons H_{2(g)} + D_{2(g)} \qquad K_c = 0.52 \qquad T = 100\ K$$

$$K_c = \frac{[H_2][D_2]}{[HD]^2} = 0.52$$

$$\underbrace{[H_2][D_2]}_{\text{products}} \cong \underbrace{[HD]^2}_{\text{reactant}}$$



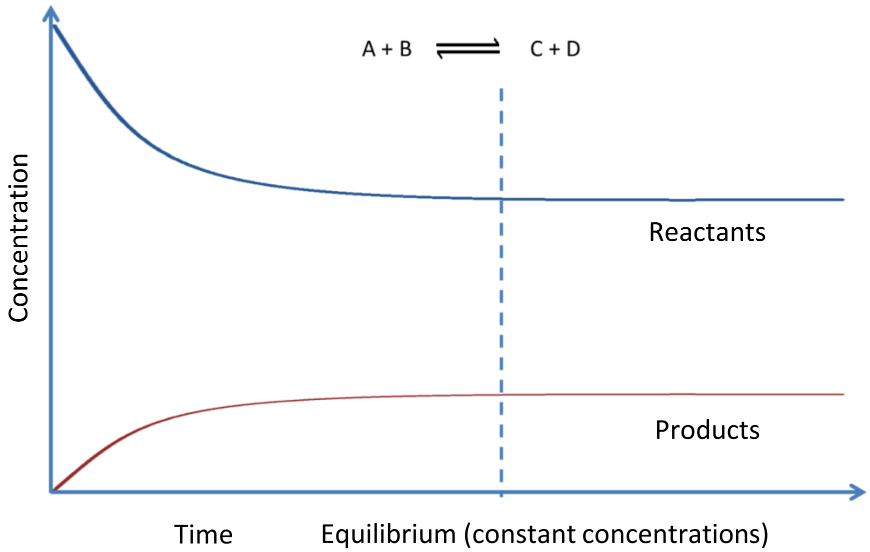
Comparison of equilibrium constants

Case 3

$F_{2(g)} \rightleftharpoons 2F_{(g)}$ $\quad K_c = 7.3 \times 10^{-13}$ $\quad T = 500\ K$

$$K_c = \frac{[F]^2}{[F_2]} = 7.3 \times 10^{-13}$$

$$\underbrace{[F_2]}_{\text{reactant}} \gg \underbrace{[F]^2}_{\text{product}}$$



Determination and use of equilibrium constants

Example Determination of the equilibrium constant

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

At equil. 0.305 M 0.324 M 0.796 M

Calculate K_c for the above equilibrium.

Solution

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

$$K_c = \frac{(0.796\ M)^2}{(0.324\ M)^3(0.305\ M)} = 61.0\ M^{-2}$$

Example

Determination of the equilibrium constant

$$2CO_{(g)} + 2H_{2(g)} \rightleftharpoons CH_{4(g)} + CO_{2(g)}$$

At equil. $4.3 \times 10^{-6}\ M$ $1.15 \times 10^{-5}\ M$ $5.14 \times 10^{-4}\ M$ $4.12 \times 10^{-4}\ M$

Calculate K_c for the above equilibrium.

Solution

$$K_c = \frac{[CH_4][CO_2]}{[H_2]^2[CO]^2}$$

$$K_c = \frac{(5.14 \times 10^{-4}\ M)\ \times (4.12 \times 10^{-4}\ M)}{(4.3 \times 10^{-6}\ M)^2 \times (1.15 \times 10^{-5}\ M)^2}$$

$$= 8.66 \times 10^{13}\ M^{-2}$$

Example

Calculating equilibrium composition

	$H_{2(g)}$	+	$Cl_{2(g)}$	$\rightleftharpoons$	$2HCl_{(g)}$	$K_c = 4.0 \times 10^{31}$
At equil.	$2.0 \times 10^{-16}\ M$		$1.0 \times 10^{-17}\ M$		$?\ M$	

Calculate the concentration of HCl at equilibrium.

Solution

$$K_c = \frac{[HCl]^2}{[H_2][Cl_2]} = 4.0 \times 10^{31}$$

⇨ $$\frac{x^2}{(2.0 \times 10^{-16}\ M) \times (1.0 \times 10^{-17}\ M)} = 4.0 \times 10^{31}$$

⇨ $$x = [HCl] = 0.28\ M$$

Example

Calculating equilibrium composition

$$F_{2(g)} \rightleftharpoons 2F_{(g)} \qquad K_c = 7.3 \times 10^{-13}$$

At equil. $\quad ?\ M \qquad 8.55 \times 10^{-7}\ M$

Calculate the concentration of F_2 at equilibrium.

Solution

$$K_c = \frac{[F]^2}{[F_2]} = 7.3 \times 10^{-13}$$

$$\Rightarrow \quad \frac{(8.55 \times 10^{-7}\ M)^2}{x} = 7.3 \times 10^{-13}$$

$$\Rightarrow \quad x = [F_2] = 1.00\ M$$

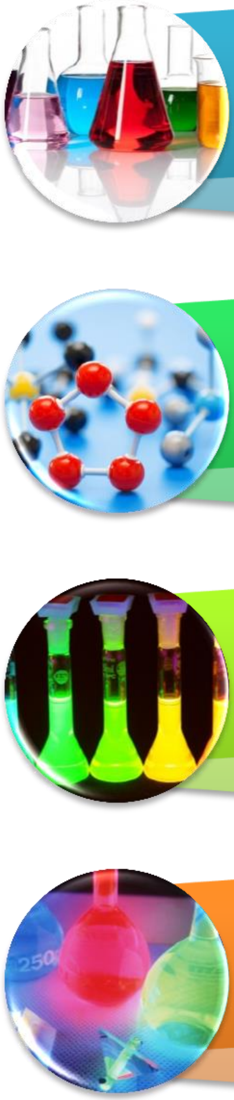
0.500 M nitrogen (N_2) and 0.800 M hydrogen (H_2) are allowed to react till equilibrium is reached. At equilibrium, the concentration of ammonia (NH_3) was found as 0.150 M. Calculate the concentration of N_2 and H_2 at equilibrium and find the equilibrium constant.

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

1.50 mol of PCl_5 is left in a 500-mL flask at 250 °C and allowed to reach equilibrium with its decomposition products of PCl_3 and Cl_2. If $K_c = 1.80$, calculate the equilibrium composition for this reaction.

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$

Factors that affect equilibrium position



- Removing/adding reactants/products
- Pressure
- Temperature
- Using a catalyst

Le Chatelier's Principle

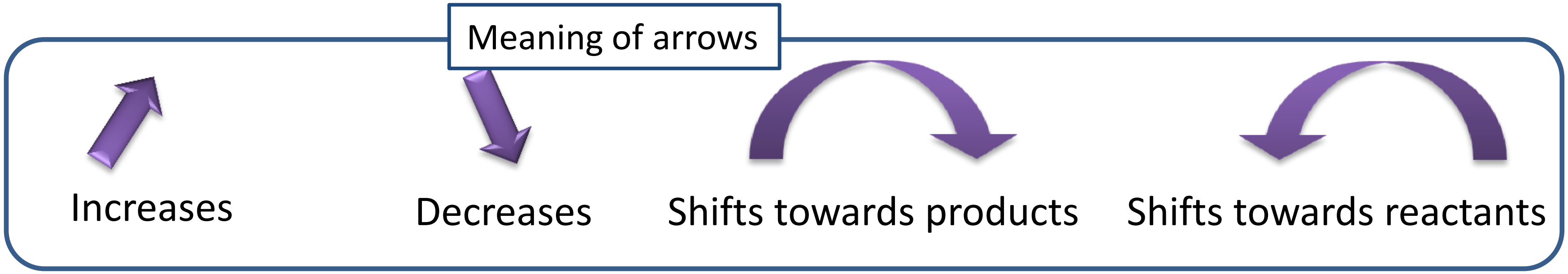
When a system at equilibrium is subjected to change in concentration, temperature, volume, or pressure, then the system readjusts itself to (partially) counteract the effect of the applied change and a new equilibrium is established.

Hanri Le Chatelier
(1850-1936)

Removing/adding reactants/products

To a system at equilibrium:

- if a **reactant** is added, the equilibrium shifts towards the **products** side.
- if a **reactant** is removed, the equilibrium shifts towards the **reactants** side.
- if a **product** is added, the equilibrium shifts towards the **reactants** side.
- if a **product** is removed, the equilibrium shifts towards the **products** side.



Meaning of arrows

Increases

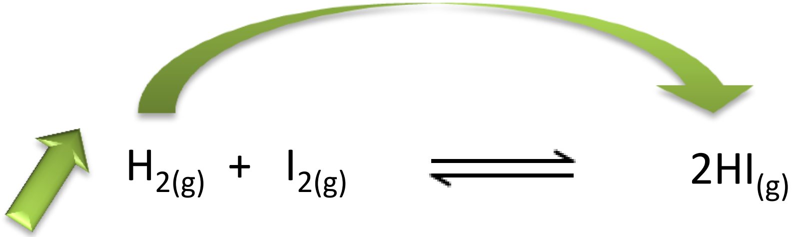
Decreases

Shifts towards products

Shifts towards reactants

- If a **reactant** is added to a system at equilibrium, the equilibrium shifts towards the **products** side.

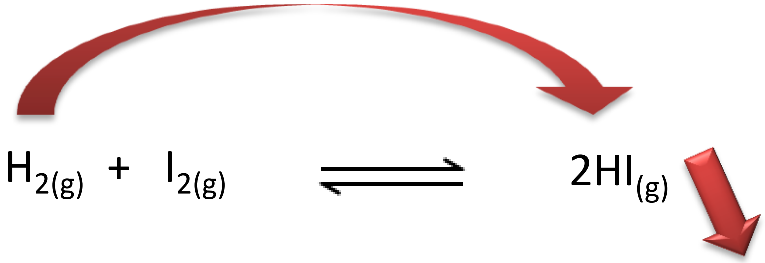
Ex.



$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

- If a **product** is removed from a system at equilibrium, the equilibrium shifts towards the **products** side.

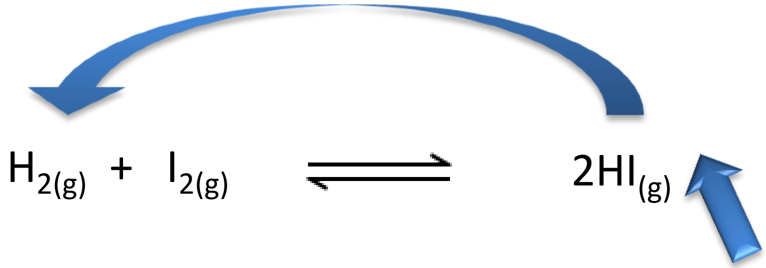
Ex.



$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

- If a **product** is added to a system at equilibrium, the equilibrium shifts towards the **reactants** side.

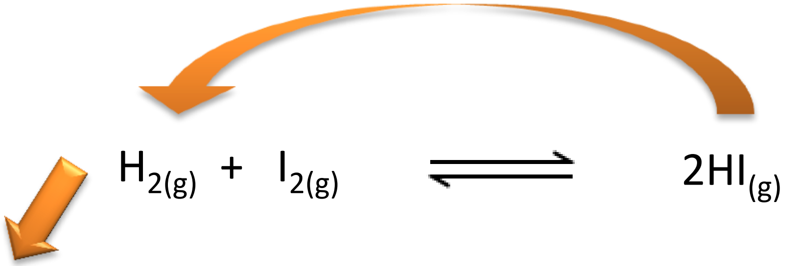
Ex.



$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

- If a **reactant** is removed from a system at equilibrium, the equilibrium shifts towards the **reactants** side.

Ex.



$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

Example

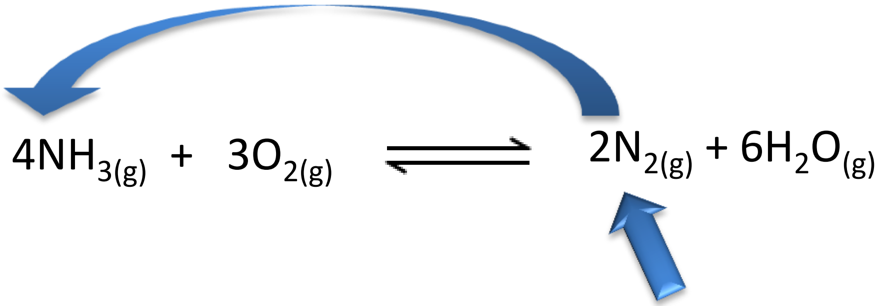
Applying Le Chatelier’s Principle

$$4NH_{3(g)} + 3O_{2(g)} \rightleftharpoons 2N_{2(g)} + 6H_2O_{(g)}$$

Considering the above equilibrium, predict the effect on equilibrium position of (a) adding N_2, (b) removing NH_3 and (c) removing H_2O.

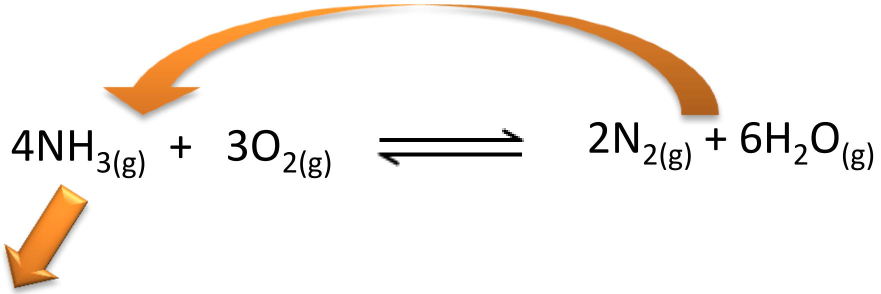
Solution

(a)

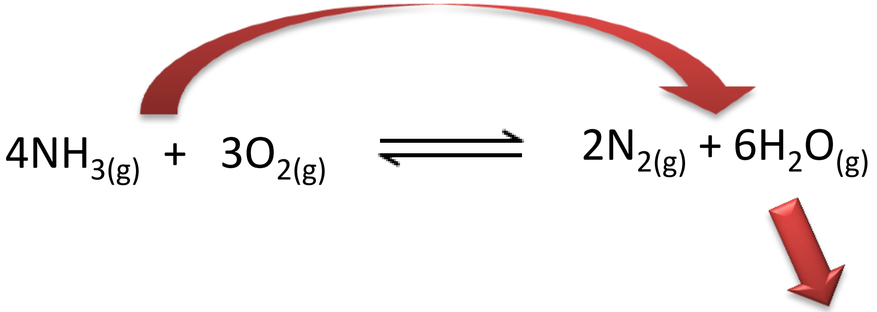


$$4NH_{3(g)} + 3O_{2(g)} \rightleftharpoons 2N_{2(g)} + 6H_2O_{(g)}$$

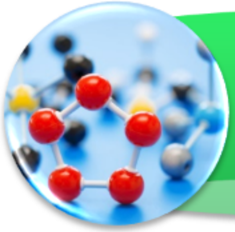
(b)



$$4NH_{3(g)} + 3O_{2(g)} \rightleftharpoons 2N_{2(g)} + 6H_2O_{(g)}$$



(c) $4NH_{3(g)} + 3O_{2(g)} \rightleftharpoons 2N_{2(g)} + 6H_2O_{(g)}$



Pressure

- Molecules comprising solids and liquids are more regularly packed and very small gaps exist between them as compared to gases. Therefore, in solids and liquids, pressure has no effect on equilibrium position.
- If the pressure is increased by decreasing the volume of a reaction mixture, the equilibrium shifts in the direction of fewer moles of gas.

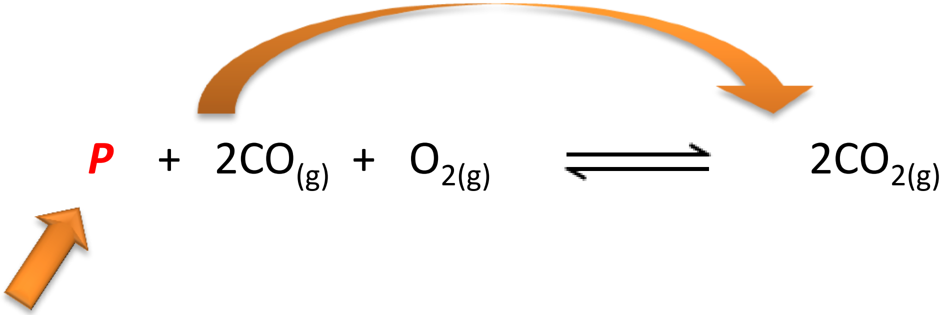
Gas equations

$n_{reactants} > n_{products}$ $n_{reactants} < n_{products}$ $n_{reactants} = n_{products}$

❶ $\boldsymbol{n_{reactants} > n_{products}}$

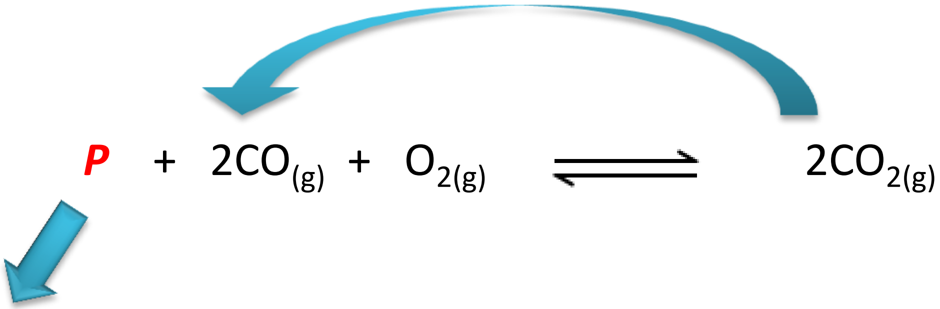
$$\underbrace{2CO_{(g)} + O_{2(g)}}_{3\,mol} \rightleftharpoons \underbrace{2CO_{2(g)}}_{2\,mol}$$

⇨ $\color{red}{\boldsymbol{P}} + 2CO_{(g)} + O_{2(g)} \rightleftharpoons 2CO_{2(g)}$



$$\color{red}{P} + 2CO_{(g)} + O_{2(g)} \rightleftharpoons 2CO_{2(g)}$$

⇨

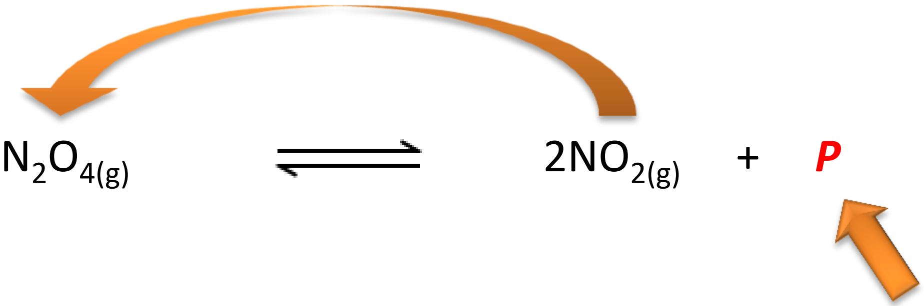


$$\color{red}{P} + 2CO_{(g)} + O_{2(g)} \rightleftharpoons 2CO_{2(g)}$$

❷ $n_{reactants} < n_{products}$

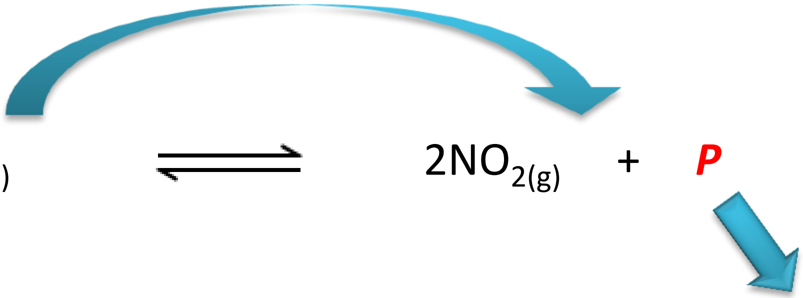
$$\underbrace{N_2O_{4(g)}}_{1\,mol} \rightleftharpoons \underbrace{2NO_{2(g)}}_{2\,mol}$$

⇨ $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)} + P$



$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)} + P$

⇨



$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)} + P$

❸ $n_{reactants} = n_{products}$

$$\underbrace{H_{2(g)} + I_{2(g)}}_{2\,mol} \rightleftharpoons \underbrace{2HI_{(g)}}_{2\,mol}$$

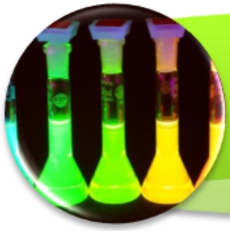
⇨ No effect of pressure on equilibrium position

Predict the effect of increasing (a) the pressure and (b) the volume on the equilibrium position in the following equilibria:

(a) $CO_{(g)} + 3H_{2(g)} \rightleftharpoons CH_{4(g)} + H_2O_{(g)}$

(b) $C_{(s)} + CO_{2(g)} \rightleftharpoons 2CO_{(g)}$

(c) $2Fe_{(s)} + 3H_2O_{(g)} \rightleftharpoons Fe_2O_{3(s)} + 3H_{2(g)}$



Temperature

Equilibria

Exothermic

ΔH_{rxn} $negative$

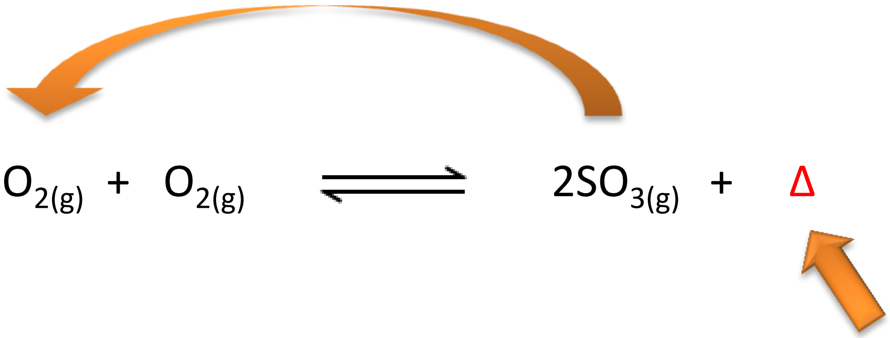
Endothermic

ΔH_{rxn} $positive$

❶ **_Exothermic equilibria_**

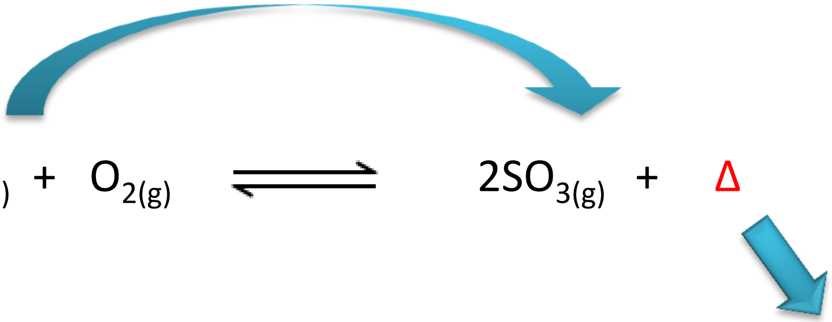
Ex. $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$ $\Delta H_{rxn} = -197{,}78\ kJ$

⇨ $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} + \Delta$



$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} + \Delta$

⇨

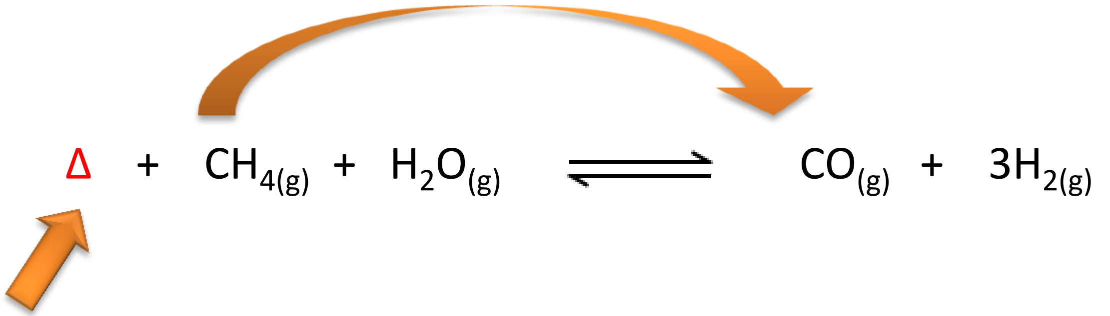


$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} + \Delta$

❷ *Endothermic equilibria*

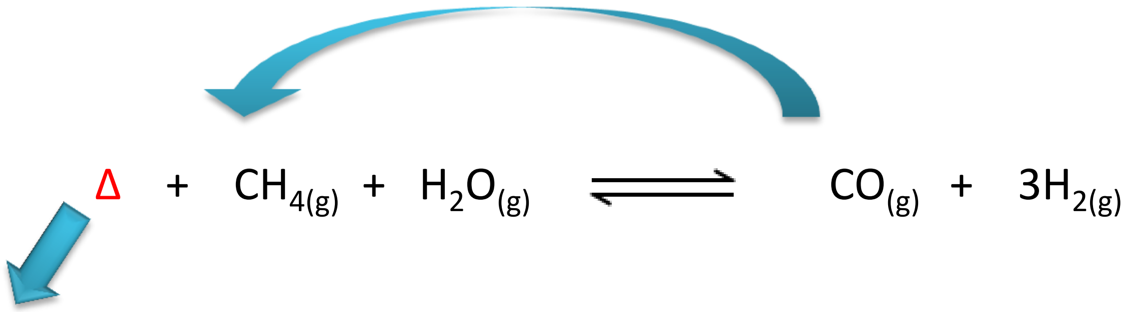
$$CH_{4(g)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + 3H_{2(g)} \qquad \Delta H_{rxn} = +206\ kJ$$

⇨ $$\Delta + CH_{4(g)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + 3H_{2(g)}$$



$$\Delta + CH_{4(g)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + 3H_{2(g)}$$

⇨



$$\Delta + CH_{4(g)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + 3H_{2(g)}$$

Using a catalyst

A catalyst is a substance that speeds up a reaction by lowering the activation energy. In equilibrium reactions, it speeds up both directions and thus has no net effect on the equilibrium position.

$$2SO_{2(g)} + O_{2(g)} \xrightleftharpoons{V_2O_5} 2SO_{3(g)}$$

⇨ The catalyst (V_2O_5) has no effect on the equilibrium position.

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

⇨ The catalyst (Fe) has no effect on the equilibrium position.

ACIDS AND BASES

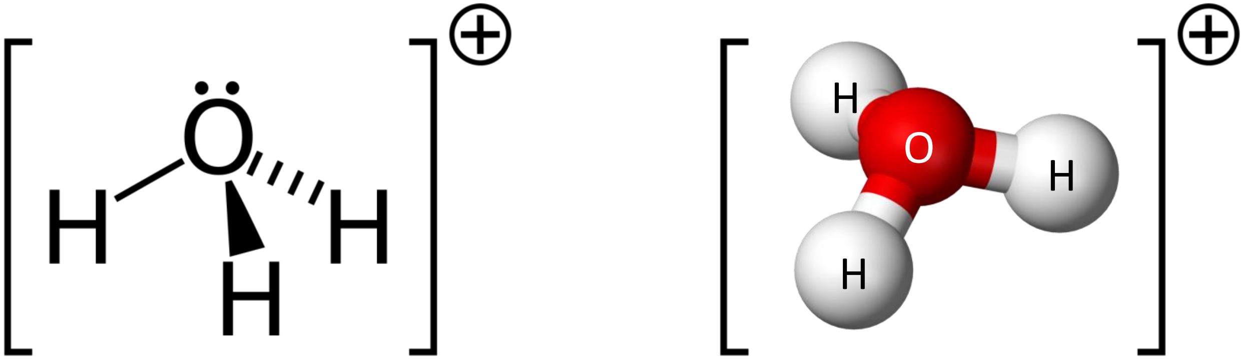
- Acid: a substance that turns litmus paper red and behaves as a proton donor.
- Base: a substance that turns litmus paper blue and behaves as a proton acceptor.

Acid-base definitions

❶ Arrhenius acid-base definition:

Acid: Arrhenius acid is a substance that dissociates in water to form hydrogen ions (H^+), or hydronium ion (H_3O^+)

Base: Arrhenius base is a substance that dissociates in water to form hydroxide ions (OH-).



Hydronium ion

Hydronium ion:
A species forms
when H^+ binds
covalently to a water
(H_2O) molecule.

Acids and Bases

Strong

Dissociates **completely** in water

$\rightarrow$

Weak

Dissociates **partially** in water

$\rightleftharpoons$

$$HCl_{(aq)} \longrightarrow H^+_{(aq)} + Cl^-_{(aq)}$$

or

$$HCl_{(aq)} + H_2O_{(s)} \longrightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$$

Strong acid

$$CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + H^+_{(aq)}$$

or

$$CH_3COOH_{(aq)} + H_2O_{(s)} \rightleftharpoons CH_3COO^-_{(aq)} + H_3O^+_{(aq)}$$

Weak acid

Acids

$$NaOH_{(aq)} \longrightarrow Na^+_{(aq)} + OH^-_{(aq)}$$

Strong base

$$NH_{3(aq)} + H_2O_{(s)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-_{(aq)}$$

Weak base

Bases

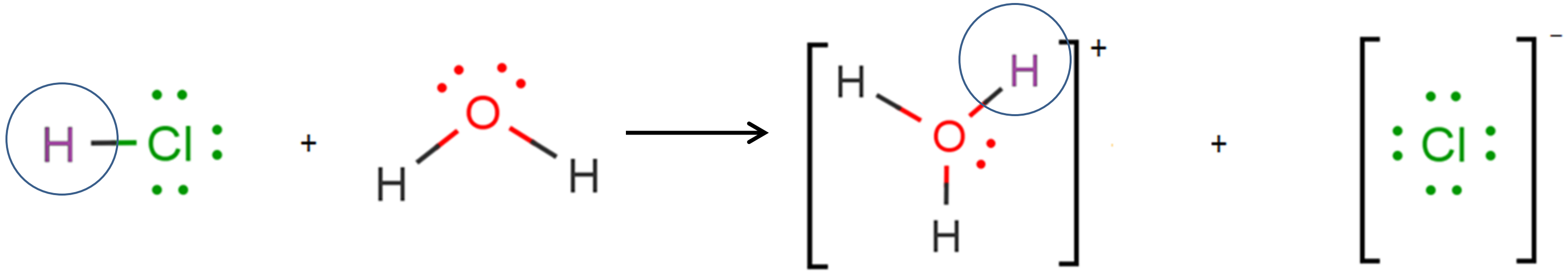
❷ Brønsted-Lowery acid-base definition:

Acid: Proton (or H^+) donor,

Base: Proton (or H^+) acceptor.

Example

$$HCl_{(aq)} + H_2O_{(s)} \longrightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$$

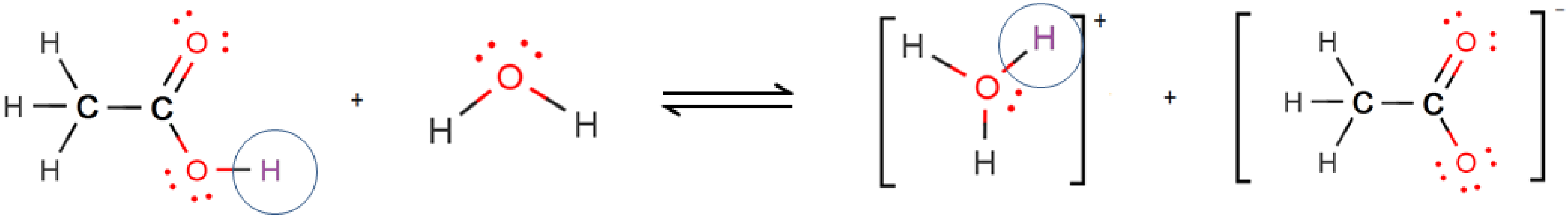


Acid
(proton donor)

Base
(proton acceptor)

Example

$$CH_3COOH_{(aq)} + H_2O_{(s)} \rightleftharpoons CH_3COO^-_{(aq)} + H_3O^+_{(aq)}$$

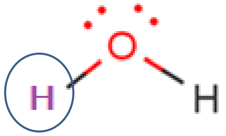


Acid
(proton donor)

Base
(proton acceptor)

Example

$$HCl_{(aq)} + NaOH_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(aq)}$$

$H{-}Cl_{(aq)} + NaOH_{(aq)} \longrightarrow NaCl_{(aq)} +$  (aq)

Acid
(proton donor)

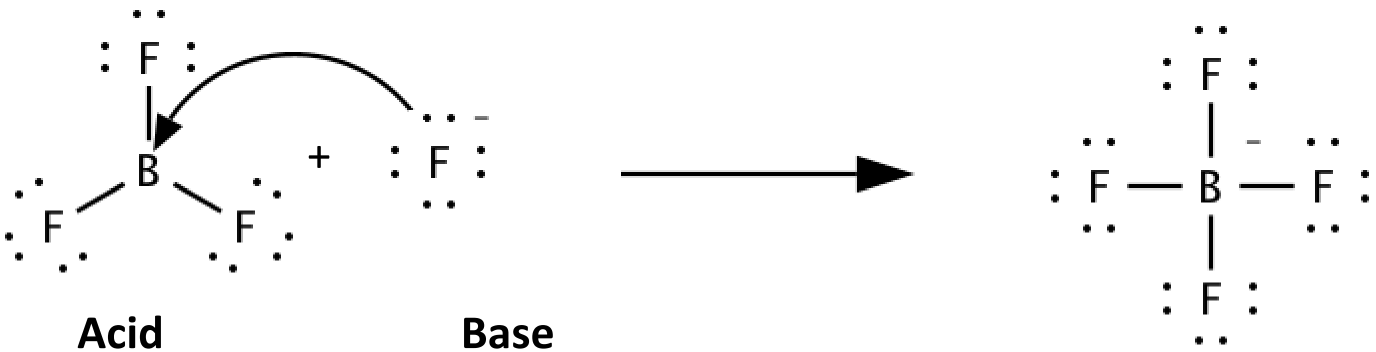
Base
(proton acceptor)

❸ Lewis acid-base definition:

Acid: Electron acceptor,

Base: Electron donor.

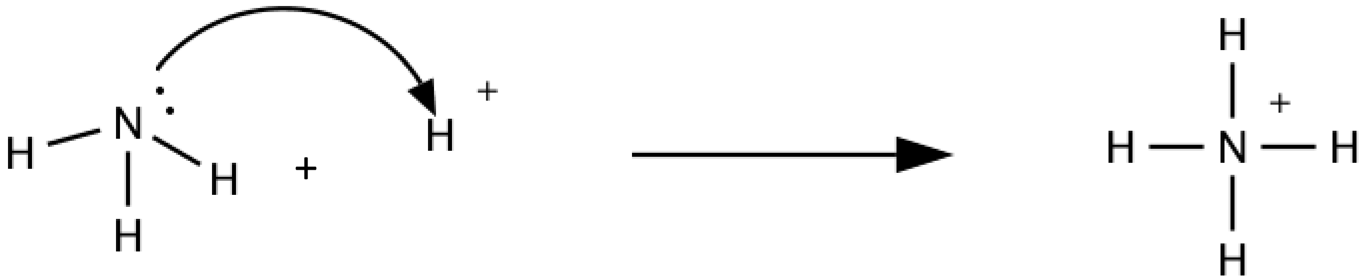
Example



Acid
(electron acceptor)

Base
(electron donor)

Example



Base
(electron donor)

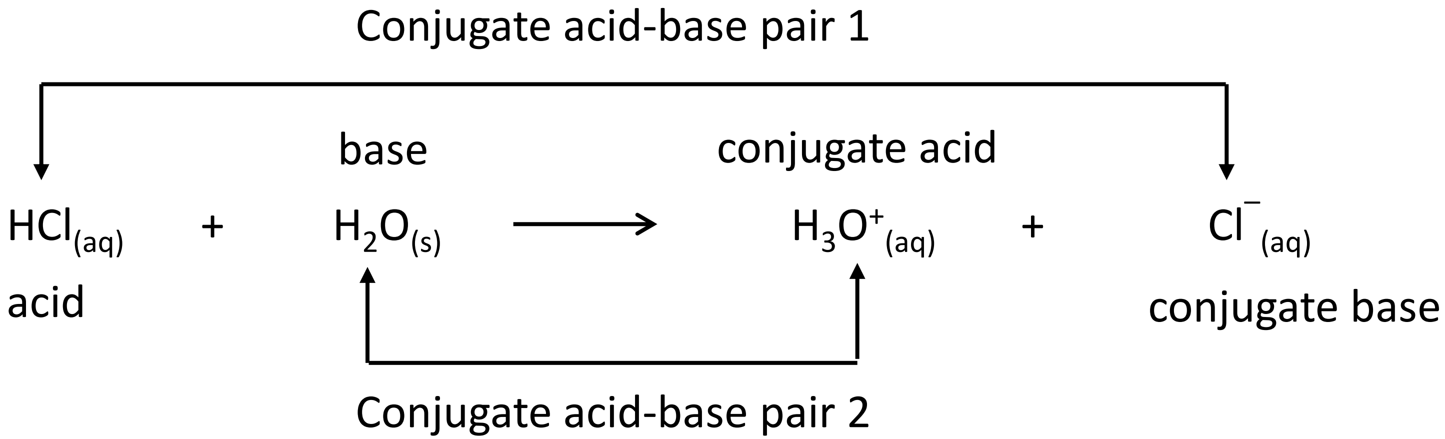
Acid
(electron acceptor)

Conjugate acid-base pairs

- A conjugate pair refers to acids and bases with common features. These common features are the equal loss/gain of protons between the pairs. Conjugate acids and conjugate bases are characterized as the acids and bases that lose or gain protons.

$$\text{Acid + Base} \longrightarrow \text{Conjugate Base + Conjugate Acid}$$

Example

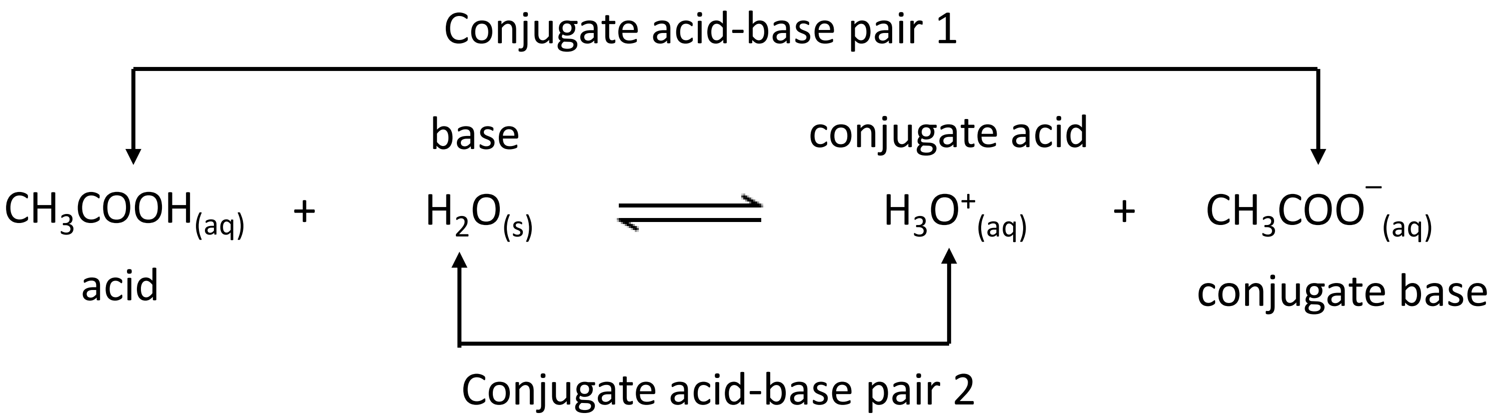


Conjugate acid-base pair 1

$$\underset{\text{acid}}{HCl_{(aq)}} + \overset{\text{base}}{H_2O_{(s)}} \longrightarrow \overset{\text{conjugate acid}}{H_3O^+_{(aq)}} + \underset{\text{conjugate base}}{Cl^-_{(aq)}}$$

Conjugate acid-base pair 2

Example



Conjugate acid-base pair 1

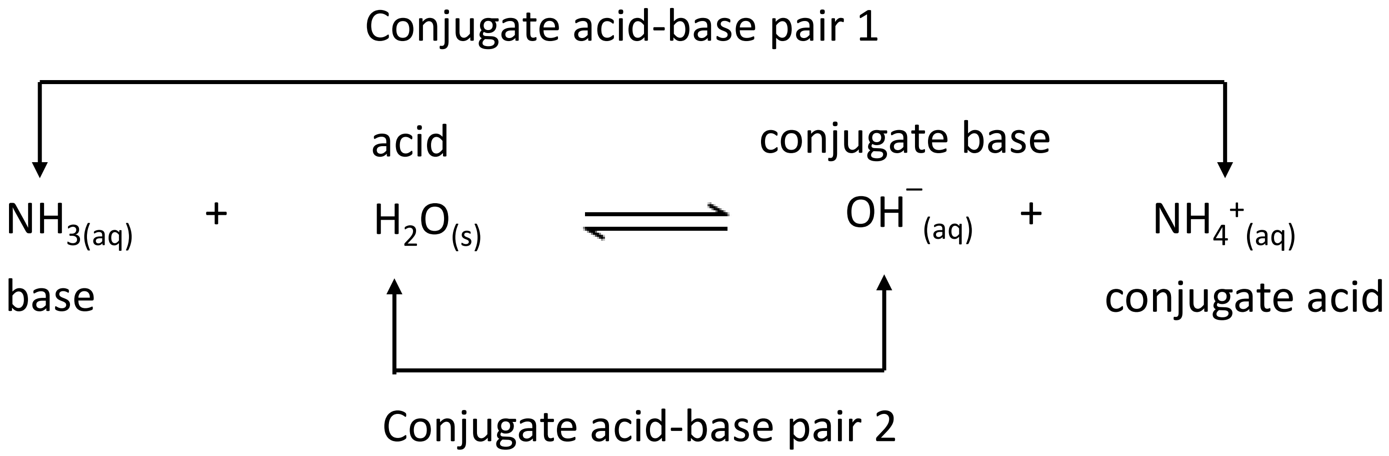
base conjugate acid

$$CH_3COOH_{(aq)} + H_2O_{(s)} \rightleftharpoons H_3O^+_{(aq)} + CH_3COO^-_{(aq)}$$

acid conjugate base

Conjugate acid-base pair 2

Example



Conjugate acid-base pair 1

acid conjugate base

$$NH_{3(aq)} + H_2O_{(s)} \rightleftharpoons OH^-_{(aq)} + NH_4^+{}_{(aq)}$$

base conjugate acid

Conjugate acid-base pair 2

Amphoteric substance: a molecule or ion that can react as an **acid** as well as a **base**.

Example

$$HCl_{(aq)} + H_2O_{(s)} \longrightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$$

$HCl_{(aq)}$	$H_2O_{(s)}$
acid	base

$$NH_{3(aq)} + H_2O_{(s)} \rightleftharpoons OH^-_{(aq)} + NH_4^+{}_{(aq)}$$

$NH_{3(aq)}$	$H_2O_{(s)}$
base	acid

➡ H_2O is an amphoteric substance.

Example

$$3HCl + Al(OH)_3 \longrightarrow AlCl_3 + 3H_2O$$

$3HCl$	$Al(OH)_3$
acid	base

$$NaOH + Al(OH)_3 \longrightarrow Na[Al(OH)_4]$$

$NaOH$	$Al(OH)_3$
base	acid

➡ $Al(OH)_3$ is an amphoteric substance.

Strength of acids and bases

- **Substance**
  - Acid
    - Strong
      - HCl (hydrochloric)
      - HBr (hydrobromic)
      - HI (hydroiodic)
      - HNO_3 (nitric)
      - H_2SO_4 (sulfuric)
      - $HClO_3$ (chloric)
      - $HClO_4$ (perchloric)
    - Weak
      - H_3PO_4 (phosphoric)
      - H_2CO_3 (carbonic)
      - HCOOH (formic)
      - CH_3COOH (acetic)
  - Base
    - Strong
      - Group 1 and 2 hydroxides e.g., NaOH, KOH $Ca(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$
    - Weak
      - NH_3 (ammonia), amines e.g., CH_3NH_2 (methylamine), $C_6H_5NH_2$ (phenylamine)

Attention

Dissociation of strong acids and bases is irreversible and thus a single arrow (→) is used, while dissociation of weak acids and bases is reversible, thus an equilibrium arrow (⇌) is used.

Example

$HCl_{(aq)} + H_2O_{(s)} \longrightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$ **Strong acid** →

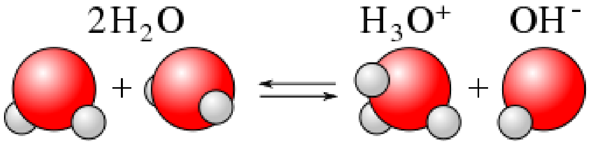
$CH_3COOH_{(aq)} + H_2O_{(s)} \rightleftharpoons CH_3COO^-_{(aq)} + H_3O^+_{(aq)}$ **Weak acid** ⇌

$NaOH_{(aq)} \longrightarrow Na^+_{(aq)} + OH^-_{(aq)}$ **Strong base** →

$NH_{3(aq)} + H_2O_{(s)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-_{(aq)}$ **Weak base** ⇌

Self-ionization of water and ion-product constant (K_w)

- Although pure water is considered a nonelectrolyte, precise measurements show a very small conduction which is due to self-ionization of water. Two water molecules react to to give hydronium (H_3O^+) and hydroxide (OH^-) ions.



or simply, $H_2O_{(s)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$

Equilibrium constant expression:

$$K_c = \frac{[H^+][OH^-]}{\cancel{[H_2O]}}$$

constant

➡ $$K_c[H_2O] = [H^+][OH^-]$$

$$Constant = K_w$$ **(Ion-product for water)**

➡ $$\boxed{K_w = [H^+][OH^-]}$$

at 25 °C $K_w = 1.00 \times 10^{-14}$

	H_2O	$\rightleftharpoons$	H^+	+	OH^-
Start			—		—
Equilibrium			x		x

$$\boxed{K_w = [H^+][OH^-] = 1.00 \times 10^{-14}}$$

$\Rightarrow$ $x^2 = 1.00 \times 10^{-14}$

$\Rightarrow$ $x = 10^{-7}$

$[H^+] = 1.00 \times 10^{-7}$ and $[OH^-] = 1.00 \times 10^{-7}$

Example

$[H^+]$ and $[OH^-]$ in strong acid-base solutions

Calculate $[H^+]$ and $[OH^-]$ in 0.050 M HCl solution.

Solution

HCl is a strong acid

	$HCl_{(aq)}$	$\longrightarrow$	$H^+_{(aq)}$	+	$Cl^-_{(aq)}$
Start	$0.05\ M$		—		—
End	—		$0.05\ M$		$0.05\ M$

$$[H^+] = 0.05\ M$$

$$[H^+][OH^-] = 1.00 \times 10^{-14}$$

$$0.05 \times [OH^-] = 1.00 \times 10^{-14}$$

$$[OH^-] = 2.00 \times 10^{-13} M$$

Example

[H$^+$] and [OH$^-$] in strong acid-base solutions

Calculate [H$^+$] ve [OH$^-$] in 0.050 M NaOH solution.

Solution

NaOH is a strong base

	$NaOH_{(aq)}$	$\longrightarrow$	$Na^+_{(aq)}$	+	$OH^-_{(aq)}$
Start	$0.05\ M$		—		—
End	—		$0.05\ M$		$0.05\ M$

$$[OH^-] = 0.05\ M$$

$$[H^+][OH^-] = 1.00 \times 10^{-14}$$

$$[H^+] \times 0.05 = 1.00 \times 10^{-14}$$

$$[H^+] = 2.00 \times 10^{-13} M$$

pH and pOH concepts

$\boxed{pH = -\log[H^+]}$ and $\boxed{pOH = -\log[OH^-]}$

$$[H^+][OH^-] = 1.00 \times 10^{-14}$$

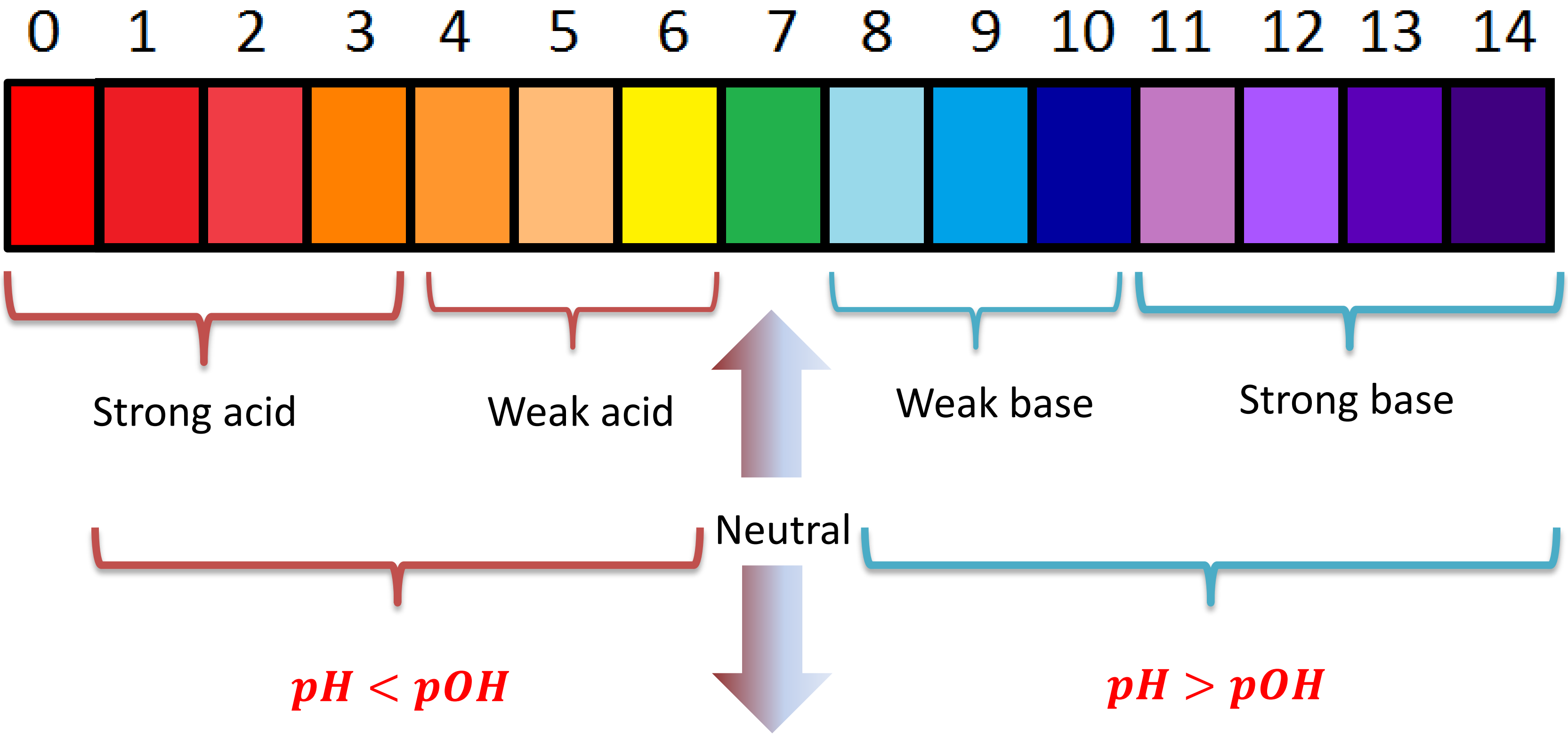
$$-\log([H^+][OH^-]) = -\log(1.00 \times 10^{-14})$$

$$\underbrace{-\log[H^+]}_{pH}\ \underbrace{-\log[OH^-]}_{pOH} = 14$$

$$\Rightarrow \quad \boxed{pH + pOH = 14}$$

pH Scale

- $\boldsymbol{pH}$: is a measure of the acidity or basicity of a solution.



Strong acid

Weak acid

Weak base

Strong base

Neutral

$\boldsymbol{pH < pOH}$

$\boldsymbol{pH > pOH}$

$\boldsymbol{pH = pOH = 7.0}$

$[H^+] > [OH^-]$

$[H^+] = [OH^-] = 10^{-7}$

$[H^+] < [OH^-]$

Example

pH and pOH of strong acid/base solutions

Calculate the pH and pOH of 0.0250 M HCl solution.

HCl is a strong acid $\Rightarrow$

Solution

	$HCl_{(aq)}$	$\rightarrow$	$H^+_{(aq)}$	+	$Cl^-_{(aq)}$
Start	$0.0250\ M$		—		—
End	—		$0.0250\ M$		$0.0250\ M$

$$[H^+] = 0.0250\ M \Rightarrow pH = -\log[H^+] \Rightarrow pH = -\log 0.0250 = 1.60$$

$$[H^+][OH^-] = 1{,}00 \times 10^{-14} \Rightarrow 0.0250 \times [OH^-] = 1.00 \times 10^{-14}$$

$$[OH^-] = 4.00 \times 10^{-13} M \Rightarrow pOH = -\log[OH^-] \Rightarrow pOH = 12.40$$

or, $pH + pOH = 14 \Rightarrow pOH = 14.00 - 1.60 = 12.40$

Calculate $[H^+]$, $[OH^-]$, pH and pOH of the following solutions:

(a) 0.033 M aqueous NaOH solution.

(b) 0.024 M aqueous HNO_3 solution.

(c) 0.011 M aqueous $Ca(OH)_2$ solution.

(d) 0.032 M aqueous H_2SO_4 solution.

Calculate the concentration of the acid or base in the following solutions if:

(a) pH of an aqueous NaOH solution is 11.5.

(b) pOH of aqueous HNO_3 solution is 12.2.

(c) pOH of aqueous $Ca(OH)_2$ solution is 3.5.

(d) pH of aqueous H_2SO_4 solution is 1.5.

Weak acids: Acid dissociation constant (K_a)

$$CH_3COOH_{(aq)} + H_2O_{(s)} \rightleftharpoons CH_3COO^{-}_{(aq)} + H_3O^{+}_{(aq)}$$ **Weak acid**

$$K_c = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]\boxed{[H_2O]}} \longrightarrow \quad \cong constant$$

$$\Rightarrow \quad \boxed{K_c[H_2O]} = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

$$Constant = K_a$$ **Acid dissociation constant**

or,

$$CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^{-}_{(aq)} + H^{+}_{(aq)}$$

$$\Rightarrow \quad K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$ Acid dissociation constant

The general equation for acid dissociation reactions:

$$HA_{(aq)} \rightleftharpoons H^+_{(aq)} + A^-_{(aq)}$$

$$\boxed{K_a = \frac{[H^+][A^-]}{[HA]}}$$

Example pH of weak acidic solutions

Calculate $[CH_3COOH]$, $[CH_3COO^-]$, $[H^+]$ and pH of 0.010 M aqueous acetic acid (CH_3COOH, $K_a = 1.78 \times 10^{-5}$).

CH$_3$COOH is a weak acid

Solution

⇨

	$CH_3COOH_{(aq)}$	$\rightleftharpoons$	$CH_3COO^-_{(aq)}$	+	$H^+_{(aq)}$
Start	$0.010\ M$		—		—
At equilibrium	$0.010 - x$		x		x

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

$$K_a = 1.78 \times 10^{-5} = \frac{x^2}{0{,}010 - x} \qquad \left(\frac{0{,}010}{1.78 \times 10^{-5}} < 1000\right)$$

$$x^2 = 1.78 \times 10^{-7} - 1.78 \times 10^{-5}x \quad \Longrightarrow \quad x^2 + 1.78 \times 10^{-5}x - 1.78 \times 10^{-7} = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4(a)(c)}}{2(a)} \quad \Longrightarrow \quad x = 4.2 \times 10^{-4}\,M$$

	$CH_3COOH_{(aq)}$	$\rightleftharpoons$	$CH_3COO^-_{(aq)}$	+	$H^+_{(aq)}$
Start	$0.010\,M$		—		—
At equil.	$0.010 - x$		x		x
	$= 9.58 \times 10^{-3} M$		$= 4.2 \times 10^{-4}\,M$		$= 4.2 \times 10^{-4}\,M$

$$\Longrightarrow \quad pH = -\log[H^+] = -\log(4.2 \times 10^{-4}) = 3.38$$

Example

pH of weak acidic solutions

Calculate $[C_6H_5COOH]$, $[C_6H_5COO^-]$, $[H^+]$ and pH of 0.130 M aq. benzoic acid (C_6H_5COOH, $K_a = 6.31 \times 10^{-5}$).

Solution

	$C_6H_5COOH_{(aq)}$	$\rightleftharpoons$	$C_6H_5COO^-_{(aq)}$	+	$H^+_{(aq)}$
Start	$0.130\ M$		—		—
At equil.	$0.130 - x$		x		x

$$K_a = \frac{[H^+][C_6H_5COO^-]}{[C_6H_5COOH]} \Longrightarrow K_a = 6.31 \times 10^{-5} = \frac{x^2}{0.130 - x}$$

$$\frac{0.130}{6.31 \times 10^{-5}} \gg 1000 \Longrightarrow 6.31 \times 10^{-5} = \frac{x^2}{0.130 - \cancel{x}}$$

omit

By approximation method

$$\Rightarrow \quad x = 2.86 \times 10^{-3}\ M$$

$$C_6H_5COOH_{(aq)} \rightleftharpoons C_6H_5COO^-_{(aq)} + H^+_{(aq)}$$

Start	$0.130\ M$	—	—
At equil.	$0.130 - x$	x	x
	$= 0.127\ M$	$= 2.86 \times 10^{-3}\ M$	$= 2.86 \times 10^{-3}\ M$

$$\Rightarrow \quad pH = -\log[H^+] = -\log(2.86 \times 10^{-3}) = 2.54$$

What if it were a strong acid, what would the pH be?

$$C_6H_5COOH_{(aq)} \longrightarrow C_6H_5COO^-_{(aq)} + H^+_{(aq)}$$

Start	$0.130\ M$	—	—
End	—	$0.130\ M$	$0.130\ M$

$$\Rightarrow \quad pH = -\log 0.130 = 0.89$$

Compare

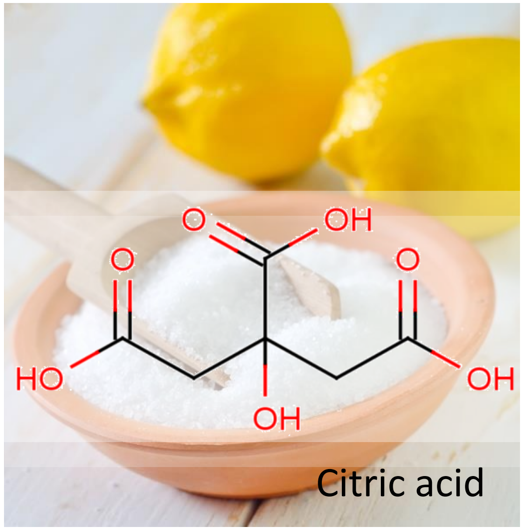
Example

K_a of weak acids

If pH of 0.025 M aq. citric asit (HCit) is 2.41, calculate K_a value of this acid.

Solution

	$HCit_{(aq)}$	$\rightleftharpoons$	$H^+_{(aq)}$	+	$Cit^-_{(aq)}$
Start	$0.025\ M$		—		—
At equil.	$0.025 - x$		x		x

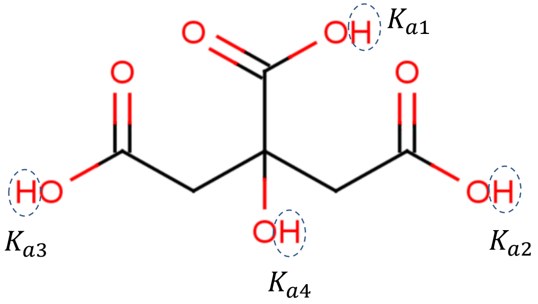


Citric acid

$$pH = -\log[H^+] = 2.41 \quad \Longrightarrow \quad [H^+] = 3.92 \times 10^{-3}\ M$$

	$HCit_{(aq)}$	$\rightleftharpoons$	$H^+_{(aq)}$	+	$Cit^-_{(aq)}$
Start	$0.025\ M$		—		—
At equil.	$0.025 - x$		x		x
	$= 0.021$		$= 3.92 \times 10^{-3}\ M$		$= 3.92 \times 10^{-3}\ M$

$$K_a = \frac{[H^+][Cit^-]}{[HCit]}$$



Citric acid

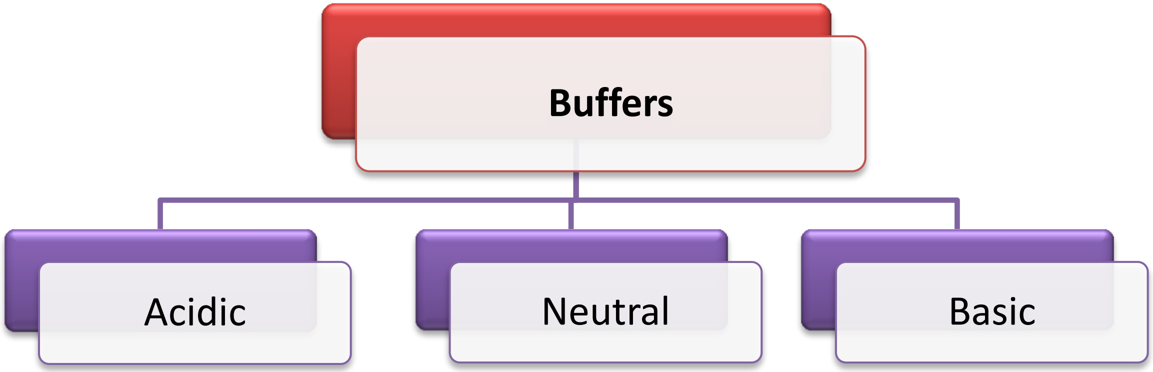
$$\Longrightarrow \quad K_a = \frac{3.92 \times 10^{-3} \times 3.92 \times 10^{-3}}{0.021} = 7.32 \times 10^{-4}$$

Polyprotic acids (K_{a1}, K_{a2}, ...)

# of dissociable H's	Weak acid	Formula	K_a
1	Hydrofluoric	HF	6.92×10^{-4}
	Formic (methanoic)	$HCOOH$	1.78×10^{-4}
	Benzoic	C_6H_5COOH	6.31×10^{-5}
	Acetic (ethanoic)	CH_3COOH	1.82×10^{-5}
	Acetylsalicylic(aspirin)	$C_8H_7O_2COOH$	3.31×10^{-4}
2	Ascorbic	$H_2C_6H_6O_6$	$K_{a1} = 7.94 \times 10^{-5}, K_{a2} = 1.58 \times 10^{-12}$
	Carbonic	H_2CO_3	$K_{a1} = 4.27 \times 10^{-7}, K_{a2} = 5.62 \times 10^{-11}$
3	Phosphoric	H_3PO_4	$K_{a1} = 7.59 \times 10^{-3}, K_{a2} = 6.17 \times 10^{-8},$ $K_{a3} = 2.14 \times 10^{-13}$
4	Citric acid	$C_6H_8O_7$	$K_{a1} = 8.91 \times 10^{-4}, K_{a2} = 2.14 \times 10^{-5},$ $K_{a3} = 4.07 \times 10^{-6}, K_{a4} = 1.20 \times 10^{-14}$

Buffer Solutions

- **A buffer** is a solution that can resist pH change upon the addition of an acidic or basic components. It is able to neutralize small amounts of added acid or base, thus maintaining the pH of the solution relatively stable. This is important for processes and/or reactions which require specific and stable pH ranges.
- Buffer solutions have a **working pH range** and capacity (**buffer capacity**) which dictate how much acid/base can be neutralized before pH changes, and the amount by which it will change.
- To effectively maintain a pH range, a buffer must consist of a **weak conjugate acid-base pair**, meaning either (a) a weak acid and its conjugate base, or (b) a weak base and its conjugate acid.


Buffers

- Acidic
- Neutral
- Basic

Example

pH of buffer solutions

Calculate the pH of a solution composed of 0.400 M acetic acid (CH_3COOH) and 0.500 M acetate ions (CH_3COO^-). $K_a = 1.75 \times 10^{-5}$

Solution

$$CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + H^+_{(aq)}$$

	$CH_3COOH_{(aq)}$	$CH_3COO^-_{(aq)}$	$H^+_{(aq)}$
Start	$0.400\ M$	$0.500\ M$	—
At equil.	$0.400 - x$	$0.500 + x$	x

not zero at the beginning

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

omit

$$\Rightarrow \quad 1.75 \times 10^{-5} = \frac{x(0.500 + \cancel{x})}{(0,400 - \cancel{x})}$$

omit

By approximation method

$$\Longrightarrow \quad 1.75 \times 10^{-5} = \frac{0.500x}{0.400}$$

$$\Longrightarrow \quad x = 1.4 \times 10^{-5}\ M$$

$$CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^{-}_{(aq)} + H^{+}_{(aq)}$$

At equil.	$0.400 - x$	$0.500 + x$	x
	$= 0.400$	$= 0.500$	$= 1.4 \times 10^{-5}$

$$pH = -\log[H^+] = -\log(1.4 \times 10^{-5})$$

$$\Longrightarrow \quad pH = 4.85$$

Calculate the pH of a buffer solution composed of 0.250 M formic acid (HCOOH) and 0.300 M formate ion ($HCOO^-$). $K_a = 1.78 \times 10^{-4}$