

# **ESE5001 Environmental Engineering Principles**

## **Lecture Notes Chemical Principles**

# Introduction

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# Concentrations and Units of Measurement

**Concentrations:** Quantity of species per volume

**Common Units:**

1. Moles per Volume

Eg.  $M = \frac{mol}{L}$  (in H<sub>2</sub>O, generally not apply in air)

where mole = Avogadro's number of elements:

$$N_{av} = 6.02 \times 10^{23}$$

# Concentrations and Units of Measurement

## 2. Mass per Volume

- Common concentration units for contaminants in water.
- Eg. mg/L,  $\mu\text{g}/\text{m}^3$
- Milli- :  $10^{-3}$
- Micro- :  $10^{-6}$

# Concentrations and Units of Measurement

## Density

### – Mass conc. Summed over all constituents.

- Fresh water:  $1 \text{ g cm}^{-3}$
- Salt water:  $1.03 \text{ g cm}^{-3}$ 
  - Pressure has very little influence on density of water
  - Temperature (Yes)

$$\rho = \frac{M}{V}$$

### – Air (293K, 1 atm): $1.2 \text{ kg m}^{-3}$

– 273K: 20°C

$1.2 \text{ mg cm}^{-3}$

Air ~ 1000 x less dense than water

$$pV = nRT$$

# Concentrations and Units of Measurement

## 3. Mass or Mole Fraction

– Quantity of species per quantity of base material, both expressed with same measure.

- $\text{ppm} \equiv 10^{-6} = 1 \text{ part per } 10^6 \text{ parts solution (fluid plus species).}$
- $\text{ppb} \equiv 10^{-9} = 1 \text{ part per } 10^9 \text{ parts solution}$
- $\text{ppt} \equiv 10^{-12} = 1 \text{ part per } 10^{12} \text{ parts solution}$
- $\% \equiv 10^{-2} = 1 \text{ part per } 100 \text{ parts solution}$
- $\text{‰} \equiv 10^{-3} = 1 \text{ part per } 1000 \text{ parts solution}$
- In Air always means mole Fraction
- In Water always means mass Fraction

# Concentrations and Units of Measurement Example

Example 1 (1.C.1 of text): One gram of table salt (NaCl) is dissolved in pure water to make 1 L of solution. Determine mass fraction, mass concentration and molarity of  $\text{Na}^+$  in solution.

Soln:  $\text{MW of NaCl} = 23 + 35.5 = 58.5 \text{ g/mole}$

$$1 \text{ g of NaCl} = \frac{1}{58.5} = 0.017 \text{ mole of Na}^+$$

$$\text{molarity of Na}^+ = 0.017 \text{ M or } \boxed{17 \text{ mM}}$$

$$\text{mass conc of Na}^+ = 0.017 \times 23 \frac{\text{g Na}^+}{\text{mole}} = \boxed{0.39 \frac{\text{g}}{\text{L}} \text{ Na}^+}$$

$$\text{mass fraction: } \frac{\text{mass of Na}^+}{\text{mass of soln}} = \frac{0.39}{1000} = 0.39 \times 10^{-3} \left(\frac{\text{g}}{\text{g}}\right) = \boxed{390 \text{ ppm}}$$

# Concentrations and Units of Measurement Example

aqueous soln

Example 2: A solution contains 8  $\mu\text{g/L}$  Lead (Pb, atomic mass 207). Express this concentration as moles per litre, ppm, and the mole fraction of Pb. Assume the solution has a density of 1 g/mL.

Soln

$$M = \frac{\text{mass conc}}{\text{MW}} = \frac{8 \text{ } \mu\text{g/L Pb}}{207 \times 10^6 \frac{\text{mg Pb}}{\text{mole Pb}}} = 3.86 \times 10^{-8} \frac{\text{mole Pb}}{\text{L}}$$

mass fraction : 1  $\mu\text{g/L} = 1 \text{ ppb}$

$$8 \text{ } \mu\text{g/L} = 8 \text{ ppb} = \boxed{0.808 \text{ ppm}}$$

$$\text{mole fraction} = \frac{\text{molar conc of Pb}}{(\text{molar conc of Pb} + \text{molar conc of H}_2\text{O})} = \frac{3.86 \times 10^{-8}}{(3.86 \times 10^{-8} + 55.6)} = \boxed{6.95 \times 10^{-10}}$$

$$\text{molar conc of H}_2\text{O} = \frac{\text{mass conc. of H}_2\text{O}}{\text{MW of H}_2\text{O}} = \frac{1000 \text{ g H}_2\text{O/L}}{18 \text{ g/mole}} = 55.6 \text{ M}$$



# Unit Conversion

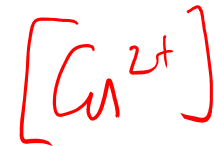
## Mass and Molar Concentrations Conversion:

$$C_i = MW_i [i]$$

where

$MW_i$  = molecular weight of species  $i$

$[i]$  = molar concentration of species  $i$



Eg. Convert 50 mg/L of Benzene ( $C_6H_6$ ) into molar concentration?

$$[C_6H_6] = \frac{C_i}{MW_i} = \frac{50 \text{ mg/L}}{(78 \frac{\text{mg}}{\text{mmole}})} = \boxed{6.41 \times 10^{-4} \text{ M}} \\ \text{or} \\ \boxed{0.641 \text{ mM}}$$

dissolved  
organic  
carbon

## Example

A natural water had DOC concentration of 3.5 mg/L. The average composition of the organic molecules in the solution is  $C_{30}H_{33}O_{18}N$ . Assuming that all the molecules actually have that composition, compute the molar concentration and mass concentration of the molecules in the sample.

Soln:

$$\text{mw of } C_{30}H_{33}O_{18}N = 12 \times 30 + 33 + 18 \times 16 + 14 = 695 \text{ g/mole}$$

$$\text{mass conc} = \frac{3.5 \text{ mg C/L}}{12 \times 30 \frac{\text{g C}}{\text{mole}}} \times 695 \frac{\text{g}}{\text{mole}} = \boxed{6.8 \frac{\text{mg}}{\text{L}}}$$

$$\text{mole conc} = \frac{6.8}{695} \neq \frac{3.5}{12 \times 30} = \boxed{9.7 \times 10^{-6} \text{ M}}$$

= 9.7 ppm  
molar fraction.

# Unit Conversion

In water, species presents are in dilute levels  $\rightarrow$  density of aqueous solution  $\approx$  density of fresh water = 1000 g/L

Therefore:

Mass Conc

1  $\mu\text{g/L}$

1 mg/L

$\equiv$

$\equiv$

Mass Fraction

1 ppb

1 ppm

Eg. Benzene ( $\text{C}_6\text{H}_6$ ): WHO standard in drinking water = 10  $\mu\text{g/L}$ , as mass fraction?

$\hookrightarrow$  10 ppb or 0.01 ppm

Benzene Conc. in air: Singapore outdoor air:  $4 \mu\text{g}/\text{m}^3$ , convert to mole fraction <sup>20°C</sup>

Consider  $1 \text{ m}^3$  of air,

$$\text{mole fraction} = \frac{\text{mole of } \text{C}_6\text{H}_6}{\text{mole of sample}}$$

$$\text{mole of } \text{C}_6\text{H}_6 = \frac{4 \mu\text{g}}{\text{m}^3} \times 1 \text{ m}^3 \times \frac{1}{78 \text{ g/mole}} = 51 \times 10^{-9} \text{ mole of } \text{C}_6\text{H}_6$$

$$n = \frac{pV}{RT} = \frac{(1 \text{ atm})(1 \text{ m}^3)}{8.2 \times 10^{-6} \text{ mol}^{-1} \text{ m}^3 \text{ K}^{-1} \text{ atm} \times 303 \text{ K}} = 41.3 \text{ mole of air}$$

$$\text{mole fraction} = \frac{51 \times 10^{-9}}{(51 \times 10^{-9} + 41.3)} = 1.2 \times 10^{-9} \frac{\text{mole}}{\text{mole}}$$

$$= \boxed{1.2 \text{ ppb}}$$

$$\approx 4.0 \frac{\mu\text{g}}{\text{m}^3}$$

In Air:  $1 \mu\text{g}/\text{m}^3 \sim 1 \text{ ppb}$ ;  $1 \text{ mg}/\text{m}^3 \sim 1 \text{ ppm}$

# Unit Conversion

Mass Fraction to Mass Concentration:

$$C_i = \rho_s X_i$$

where  $\rho_s$  = solution density (with units of mass per volume).

$X_i$  = mass fraction

$C_i$  = mass conc

# Impurities

- Components
- Constituents
- Impurities
- Contaminants
- Pollutants

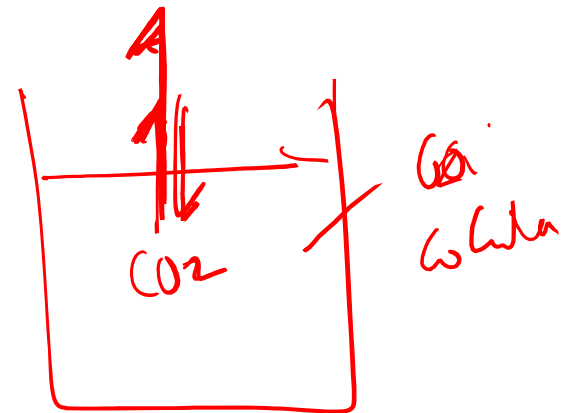
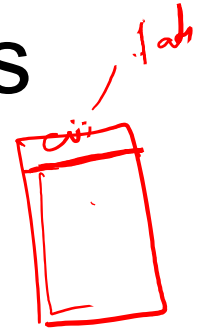
# Impurities

- Inorganic versus Organic ( $\text{H}_2\text{S}$  vs. Benzene)
- Ionic versus nonionic ( $\text{HCO}_3^-$  vs.  $\text{SiO}_2$ )
- Elements versus compounds (Pb vs.  $\text{HCHO}$ )
- Molecular versus particulate ( $\text{O}_2$  vs. clay grain)
- Abiotic versus Biotic (soot vs. bacterium)

# Impurities

Example of impurity classes — Gases in  $\text{H}_2\text{O}$

- Air & water in equilibrium
- $\text{O}_2$  in  $\text{H}_2\text{O}$  depends on amount in air & originally in  $\text{H}_2\text{O}$





# Henry' s Law

1st form:  $C_w = K_{H,g} \times P_g$

(M) (M atm<sup>-1</sup>) (in atm)

2nd form:  $P_g = H_g \times C_w$

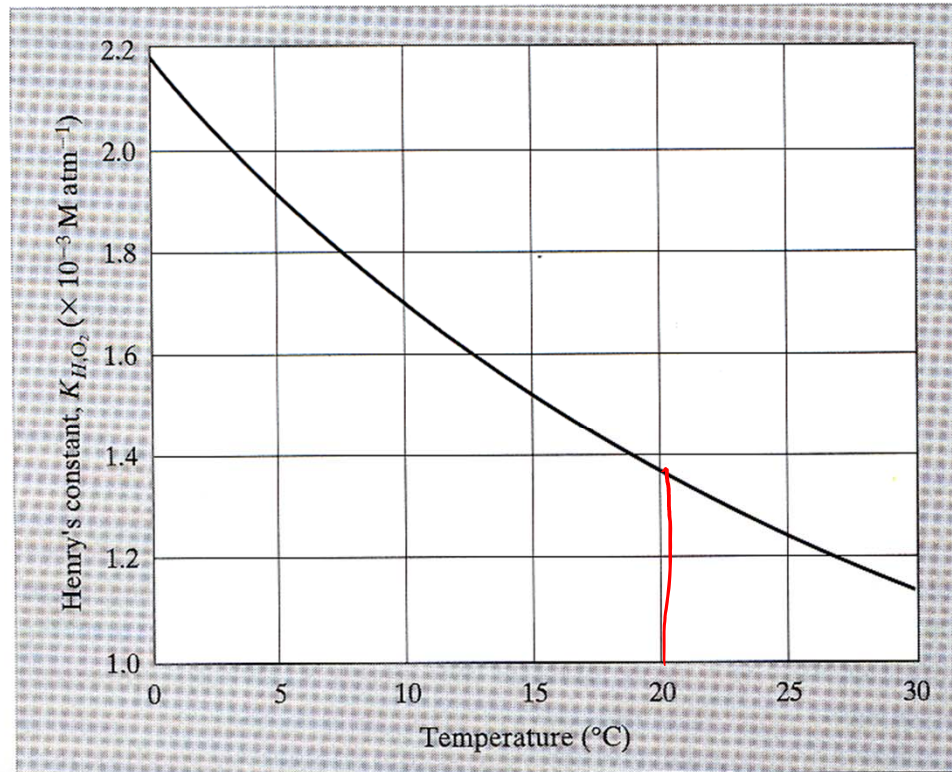
(atm) (atm M<sup>-1</sup>) (M)

i.e. Henry' s law constants relationship:

$$K_{H,g} = H_g^{-1}$$

# Henry's Law Constant for Water

$$[O_2] = K_{H,O_2} \times P_{O_2}$$



**Figure 3.B.2** Henry's law constant for oxygen ( $O_2$ ) in distilled water as a function of temperature (Whipple and Whipple, 1911).

# H<sub>2</sub>O Vapor in AIR

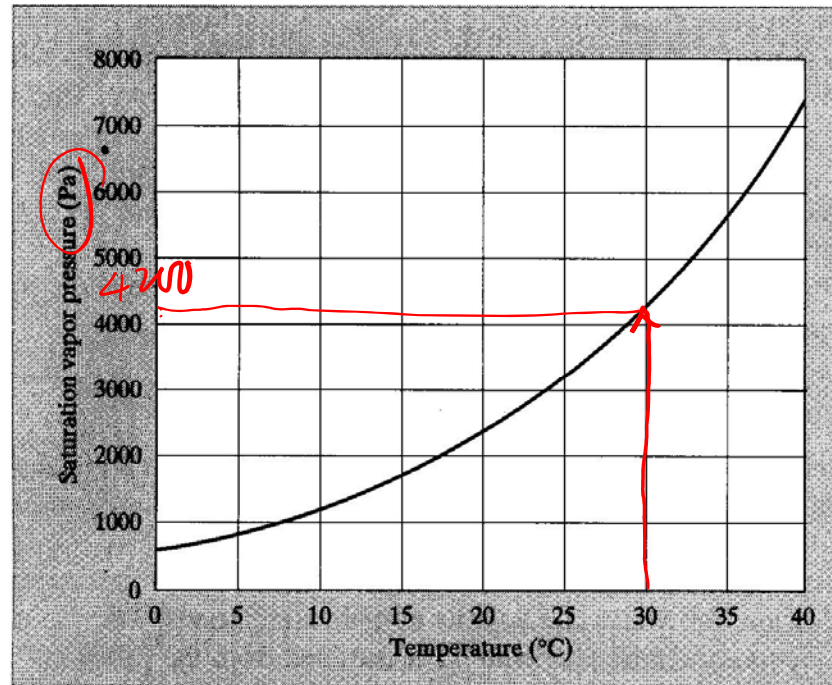


Figure 3.B.1 Saturation vapor pressure of water as a function of temperature.

$$Y_{H_2O} = \frac{P_{H_2O}^o}{P}$$

At  $P = 1 \text{ atm} = 1.01 \times 10^5 \text{ Pa}$  & Temp = 20°C

$$Y_{H_2O} = \frac{4200}{1.01 \times 10^5} = 4\%$$

Relative Humidity = Actual partial pressure/Sat. vapor pressure

# O<sub>2</sub> in H<sub>2</sub>O

At Temp. = 20°C,

$$K_{H, O_2} = 1.4 \times 10^{-3} \text{ M atm}^{-1}$$

$$[O_2] = K_{H, O_2} \times P_{O_2} = 1.4 \times 10^{-3} \text{ M atm}^{-1} \times 0.2 \text{ atm} = 0.3 \times 10^{-3} \text{ M}$$

At sea level:  $P_{O_2} = 0.2 \text{ atm}$ ,

$$[O_2] = 0.3 \times 10^{-3} \text{ M} \equiv \times (16 \times 2) =$$

$$9.6 \frac{\text{mg}}{\text{L}}$$

When bottle opened at Genting Highlands (2 km) above sea level, [O<sub>2</sub>]?

# Ionic Impurities in H<sub>2</sub>O

H<sub>2</sub>O



1.  $K_w = [\text{H}^+][\text{OH}^-] = 10^{-14} \text{ M}^2$

in pure H<sub>2</sub>O, eq. conc. of H<sup>+</sup>, OH<sup>-</sup> ?

2. Relationship:  $[\text{H}^+] = [\text{OH}^-]$

$$\rightarrow [\text{H}^+] = 10^{-7} \text{ M} = [\text{OH}^-]$$

Steps:

1. Unknowns
2. Relationships
3. Solve mathematically

# pH

$$-\log_{10} [10^{-7}] = 7$$

Note:

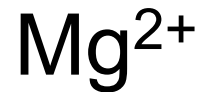
$$\text{pH} \equiv -\log_{10} [\text{H}^+]$$

Except when in highly concentrated solution,  $[\text{H}^+]$  has to be replaced by activity.

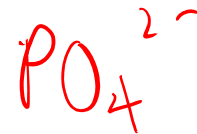
# Ions

## Common Drinking Water Ions:

### Cations



### Anions



# Electroneutrality

- Sum of normalities of cations = sum of normalities of anions

$$\Sigma \text{ cations} = \Sigma \text{ anions} \quad [=] \text{ eq/L}$$

$$\text{Normality} = \text{charge per ion} \times \text{molarity of ion} \\ [=] \text{ eq/L}$$

Note: 1 eq = 1 mole of net elect. Charge

Acceptable Limits for charge balance:

$$|\Sigma \text{anions} - \Sigma \text{cations}| \leq (0.1065 + 0.0155 \Sigma \text{anions})$$

meq/L



# Electroneutrality

Eg. Determine the acceptability of the following water analysis submitted by a commercial analytical lab.

Cation	Conc mg/L		Anion	Conc mg/L
Ca <sup>2+</sup>	93.8		HCO <sub>3</sub> <sup>-</sup>	164.7
Mg <sup>2+</sup>	28.0		SO <sub>4</sub> <sup>2-</sup>	134.0
Na <sup>+</sup>	13.7		Cl <sup>-</sup>	92.5
K <sup>+</sup>	30.2			

Approach:

- Convert all ions concentration into normality
- Check with acceptable limits

# Electroneutrality

Solution:

Cation	Conc mg/L	Conc mM	meq /L	Anion	Conc mg/L	Conc mM	meq/L
Ca <sup>2+</sup>	93.8	2.34	4.68	HCO <sub>3</sub> <sup>-</sup>	167.4	2.74	2.74
Mg <sup>2+</sup>	28.0	1.15	2.30	SO <sub>4</sub> <sup>2-</sup>	134.0	1.39	2.79
Na <sup>+</sup>	13.7	0.60	0.60	Cl <sup>-</sup>	92.5	2.61	2.61
K <sup>+</sup>	30.2	0.77	0.77				
Total			8.35				8.14

Check accuracy:

$$|\Sigma \text{anions} - \Sigma \text{cations}| \leq (0.1065 + 0.0155 \Sigma \text{anions})$$

$$|8.14 - 8.35| \leq [0.1065 + 0.0155(8.14)]$$

$$0.21 \leq (0.2327)$$

Accuracy within allowable limits, water analysis is **acceptable**.

$$\frac{(8.35 - 8.14)}{\frac{(8.35 + 8.14)}{2}} \times 100 = 2.54\% < 5\%$$

# Ionic Strength

- Intensity of electric field in a solution

$$\mu = \frac{1}{2} \sum_i z_i^2 [i] \quad [=] \text{ M}$$

where  $z_i$  = charge of species i

$[i]$  = molarity of species i

# Ionic Strength

Eg. Compute the ionic strength of a solution containing the following concentration of ions:

$[\text{Ca}^{2+}] = 10^{-4} \text{ M}$ ,  $[\text{CO}_3^{2-}] = 10^{-5} \text{ M}$ ,  $[\text{HCO}_3^-] = 10^{-3} \text{ M}$ ,

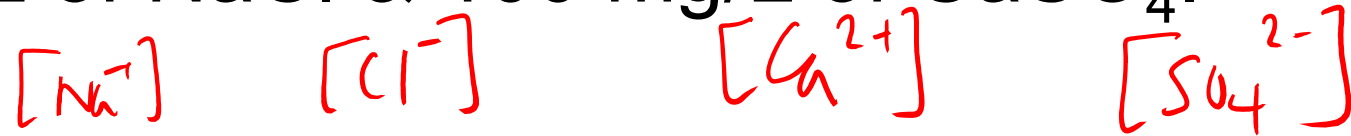
$[\text{SO}_4^{2-}] = 10^{-4} \text{ M}$ ,  $[\text{Na}^+] = 1.02 \times 10^{-3} \text{ M}$

$$I = \frac{1}{2} \left[ (2)^2 (10^{-4}) + (-2)^2 (10^{-5}) + (-1)^2 (10^{-3}) + (-2)^2 (10^{-4}) + (1)^2 (1.02 \times 10^{-3}) \right] \text{ M}$$

$$= 1.43 \times 10^{-3} \text{ M}$$

# Ionic Strength

Find the ionic strength of solution with 50 mg/L of NaCl & 100 mg/L of CaSO<sub>4</sub>.



$$50 \text{ mg/L NaCl} \Rightarrow \frac{50}{58.5} = 0.855 \text{ mM} = [Na^+] = [Cl^-]$$

$$100 \text{ mg/L CaSO}_4 \Rightarrow 0.735 \text{ mM} = [Ca^{2+}] = [SO_4^{2-}]$$

$$I = \frac{1}{2} \sum (z_i^2 [i]) = \frac{1}{2} (1 \times 0.855 + 1 \times 0.855 + 4 \times 0.735 + 4 \times 0.735) = \text{mM}$$



# Ionic Strength

Why need to know ionic strength?

- Used for computation of activity for non-diluted solution.
- As concentration of ions in solution increases, electrostatic interactions between ions also increase and the activity of ions becomes somewhat less than their measured or analytical concentrations

Activity:

$$\{i\} = \gamma_i [i]$$

Where activity coefficient,  $\gamma_i$  (Debye-Hückel relationship):

$$\log \gamma_i = -0.5 Z_i^2 \frac{\sqrt{\mu}}{1 + \sqrt{\mu}}$$

Eg. Calculate the activity coefficients and activities of each ion solution containing 0.01M  $\text{MgCl}_2$  and 0.02 M  $\text{Na}_2\text{SO}_4$ .

Soln: When salts are dissolved:

Ion	C (M)	Z	$CZ^2$
$\text{Mg}^{2+}$	0.01	+2	0.04
$\text{Na}^+$	0.04	+1	0.04
$\text{Cl}^-$	0.02	-1	0.02
$\text{SO}_4^{2-}$	0.02	-2	0.08
		$\Sigma C_i Z_i^2 =$	0.18

Ion	Activity Coefficient ( $\gamma$ )	Activity ( $\gamma C$ )
$\text{Mg}^{2+}$	0.35	0.0035
$\text{Na}^+$	0.77	0.031
$\text{Cl}^-$	0.77	0.015
$\text{SO}_4^{2-}$	0.35	0.007

Ionic strength,  $\mu = 1/2 \Sigma_i C_i Z_i^2 = 0.09$

$$\log \gamma_i = -0.5 Z_i^2 \frac{\sqrt{0.09}}{1 + \sqrt{0.09}} = -0.115 Z_i^2$$



# Hardness

- Hard Waters? Water containing multivalent ions  
→ scales in hot-water pipes, heaters, boilers, teapots & precipitates in soap water.
- Expressed as normality (eq/L or meq/L) or as  $\text{CaCO}_3$
- Each mole of  $\text{CaCO}_3$  (MW=100 g/mol) liberates 2 moles of cationic charge → a hardness of 1 meq/L is the same as a hardness of 50 mg/L as  $\text{CaCO}_3$ .

Classification	Hardness (meq/L)	Hardness (mg/L as $\text{CaCO}_3$ )
Soft	< 1.5	< 75
Moderately hard	1.5 – 3	75 – 150
Hard	3 – 6	150 – 300
Very hard	>6	>300

# Hardness

- Total hardness (TH) = sum of normalities of all multivalent cations.
- Carbonate hardness (CH) associated with  $\text{CO}_3^{2-}$  &  $\text{HCO}_3^-$
- Noncarbonate hardness (NCH): the rest

$$\text{TH} = \Sigma (\text{normalities of multivalent cations})$$

- In DW Treatment, hardness removal (also called softening) refers to removal of calcium ( $\text{Ca}^{2+}$ ) and magnesium ( $\text{Mg}^{2+}$ ).

# Hardness

- To find CH & NCH:
- Compute TH
- $N_c = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]$  [=] eq/L or meq/L
- If  $N_c < \text{TH}$ ,  $\text{CH} = N_c$  &  $\text{NCH} = \text{TH} - \text{CH}$
- If  $N_c > \text{TH}$ ,  $\text{CH} = \text{TH}$  &  $\text{NCH} = 0$

# Alkalinity

- In natural waters, alkalinity is attributable to bases such as  $\text{CO}_3^-$ ,  $\text{HCO}_3^-$  &  $\text{OH}^-$ , ammonia, phosphates, organic bases, etc.
- Refers to the capacity of water to neutralize acids.

$$A = [\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] - [\text{H}^+]$$

- Expressed in equivalent per litre.
- Measured by titration: addition of strong acid to water until pH reaches  $\sim 4.5$ . Amount of acid added per liter of water sample is the measured alkalinity.

# Alkalinity

Eg.  $\text{NaHCO}_3$  dissolved in  $\text{H}_2\text{O}$

Adding vinegar  $\rightarrow$  bubbling due to  $\text{CO}_2$

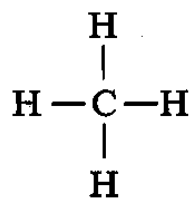
# Organics

- Molecule that has carbon and hydrogen, except carbonate and bicarbonate.

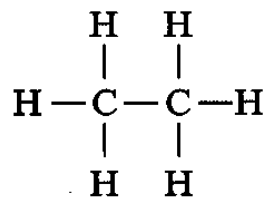
**Table C.1** Number of Bonds Associated with Elements in Organic Molecules

Element	Atomic number	Typical number of bonds
H	1	1
C	6	4
N	7	3
O	8	2
F	9	1
P	15	3
S	16	2
Cl	17	1
Br	35	1
I	53	1

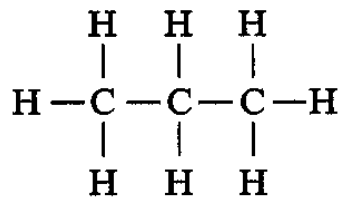
# Organics: Alkanes



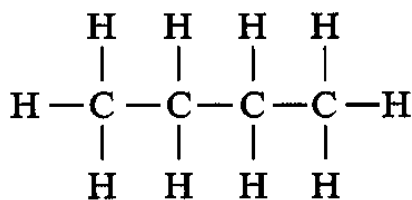
Methane



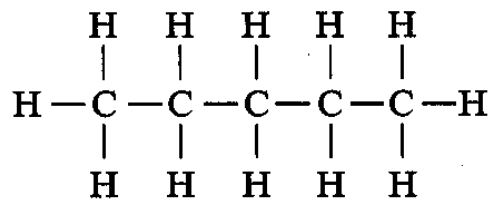
Ethane



Propane



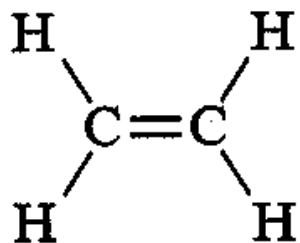
*n*-Butane



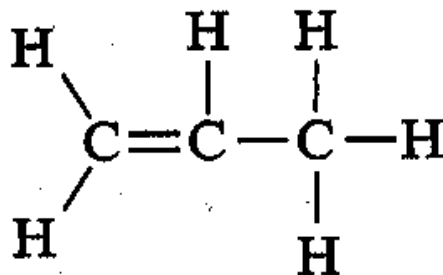
*n*-Pentane

**Figure C.1** Structures and names of straight-chain alkanes with carbon numbers 1–5.

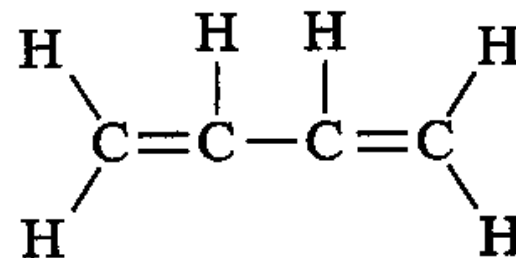
# Organics: Alkenes



Ethene



Propene

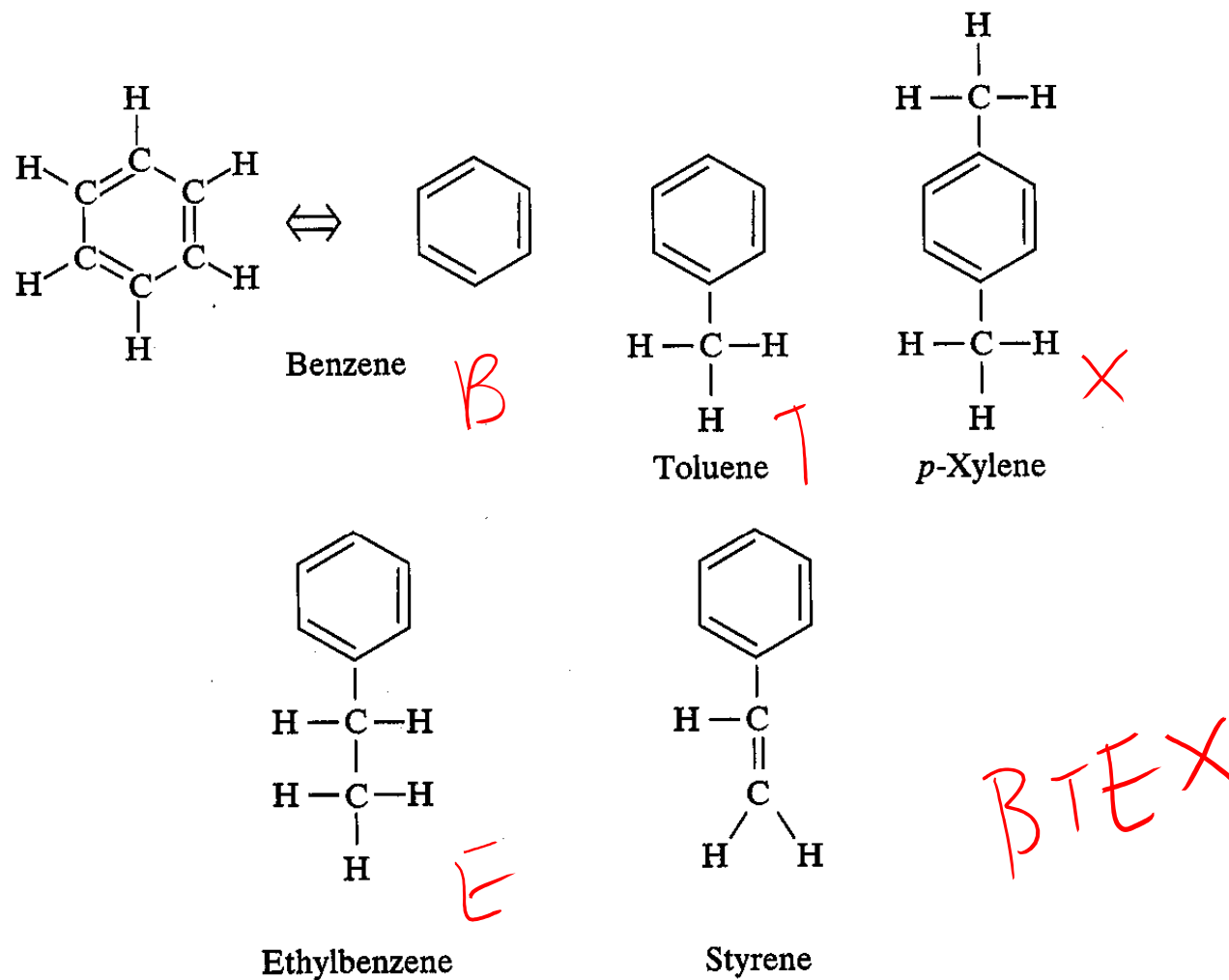


1,3-Butadiene

**Figure C.2** Structures of some alkenes.

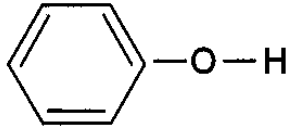


# Organics: Aromatic



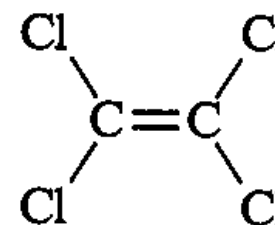
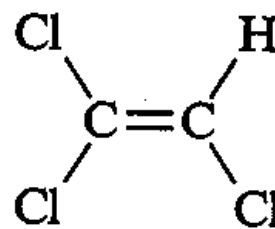
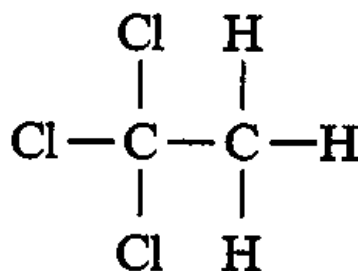
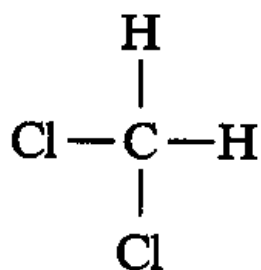
**Figure C.3** Some aromatic compounds.

# Organics: Oxygenated

Class	Structure	Example
Alcohol (aliphatic)	$R-O-H$	$\begin{array}{c} H \\   \\ H-C-O-H \\   \\ H \end{array}$ <u>Methanol</u>
Aldehyde	$R-\overset{\overset{O}{\parallel}}{C}-H$	$\begin{array}{c} H & H & O \\ & \backslash & \parallel \\ & C=C & -C-H \\ & / & \\ H & & \end{array}$ <p><i>formaldehyde</i> (handwritten red text with arrow pointing to the aldehyde group)</p> <u>Acrolein</u>
Ketone	$R-\overset{\overset{O}{\parallel}}{C}-R'$	$\begin{array}{c} H & O & H \\   & \parallel &   \\ H-C & -C & -C-H \\   & &   \\ H & & H \end{array}$ <u>Acetone</u>
Phenol	$\phi-O-H$	 <u>Phenol</u>

**Figure C.4** Representative classes and examples of oxygenated organic compounds of environmental significance.

# Organics: Chlorinated



Dichloromethane    1,1,1-Trichloroethane (TCA)    Trichloroethene (TCE)    Tetrachloroethene (PCE)

**Figure C.5** Chlorinated solvents.

# Organics: Sulfur and Nitrogen Containing

Class	Structure	Example	
Mercaptan	$R-S-H$	$\begin{array}{c} H \\   \\ H-C-S-H \\   \\ H \end{array}$	Methyl mercaptan
Sulfide	$R-S-R'$	$\begin{array}{c} H & H \\   &   \\ H-C-S-C-H \\   &   \\ H & H \end{array}$	Dimethyl sulfide
Amine (primary)	$\begin{array}{c} H \\   \\ R-N \\   \\ H \end{array}$	$\begin{array}{c} H & H \\   &   \\ H-C-N \\   &   \\ H & H \end{array}$	Methyl amine
Nitrosamines	$\begin{array}{c} R \\ \diagdown \\ N-N=O \\ \diagup \\ R' \end{array}$	$\begin{array}{c} H \\   \\ H-C-H \\   \\ N-N=O \\   \\ H-C-H \\   \\ H \end{array}$	N-Nitroso-dimethylamine

NDMA

**Figure C.7** General structures and specific examples of some organic compounds that contain either sulfur or nitrogen.

# Environmental Transformation

- Partitioning
- Stoichiometry
- Equilibrium
- Kinetics

## Partitioning

## Equilibrium

## Relationship (or data)

- 1) Water-gas phase
- 2) Liquid (NAPL)-water
- 3) Solid-water

Henry's Law

Solubility

Solubility

*non-aqueous  
phase  
liquid*

# Vapor Pressure of Some Organic Substances at 25°C

**Table 3.B.1** Vapor Pressure of Some Organic Substances at 25 °C

Species	Chemical formula	Molecular weight (g/mol)	Vapor pressure (Pa)
Acetone	C <sub>3</sub> H <sub>6</sub> O	58	28,600
Benzene	C <sub>6</sub> H <sub>6</sub>	78	12,800
Benzo(a)pyrene	C <sub>20</sub> H <sub>12</sub>	252	$7 \times 10^{-7}$
Chloroform	CHCl <sub>3</sub>	119.4	26,000
Dieldrin	C <sub>12</sub> H <sub>8</sub> Cl <sub>6</sub> O	380	$7 \times 10^{-4}$
Ethylbenzene	C <sub>8</sub> H <sub>10</sub>	106	1,280
Ethylene dibromide	CH <sub>2</sub> Br <sub>2</sub>	176	270
<i>n</i> -Octane	C <sub>8</sub> H <sub>18</sub>	114	1,890
Naphthalene	C <sub>10</sub> H <sub>8</sub>	128	10.6
Phenol	C <sub>6</sub> H <sub>6</sub> O	94	26
2,3,7,8-TCDD	C <sub>12</sub> H <sub>4</sub> O <sub>2</sub> Cl <sub>4</sub>	322	$2 \times 10^{-7}$
Tetrachloroethylene	C <sub>2</sub> Cl <sub>4</sub>	166	2,550
Toluene	C <sub>7</sub> H <sub>8</sub>	92	3,850
1,1,1-Trichloroethane	C <sub>2</sub> H <sub>3</sub> Cl <sub>3</sub>	133.4	16,800
Trichloroethylene	C <sub>2</sub> HCl <sub>3</sub>	131.4	9,900

Source: Schwarzenbach et al., 1993.

# Henry's Constant

**Table 3.B.2** Henry's Law Constants for Selected Species

Species	Formula	$K_H$ (M atm <sup>-1</sup> )	$H_g$ (atm M <sup>-1</sup> )	Temperature (°C)
Ammonia <sup>a</sup>	NH <sub>3</sub>	62	0.016	25
Benzene	C <sub>6</sub> H <sub>6</sub>	0.18	5.6	20
Benzo( <i>a</i> )pyrene	C <sub>20</sub> H <sub>12</sub>	2040	$4.9 \times 10^{-4}$	20
Carbon dioxide <sup>a</sup>	CO <sub>2</sub>	0.034	29	25
Carbon monoxide	CO	0.0010	1000	20
Chloroform	CHCl <sub>3</sub>	0.31	3.2	20
Ethylbenzene	C <sub>8</sub> H <sub>10</sub>	0.11	9.1	20
Formaldehyde	HCHO	6300	$1.6 \times 10^{-4}$	25
Hydrogen sulfide <sup>a</sup>	H <sub>2</sub> S	0.115	8.7	20
Methane	CH <sub>4</sub>	0.0015	670	20
Naphthalene	C <sub>10</sub> H <sub>8</sub>	2.2	0.45	20
Nitric acid <sup>a</sup>	HNO <sub>3</sub>	$2.1 \times 10^5$	$4.8 \times 10^{-6}$	25
Nitrogen	N <sub>2</sub>	0.00067	1500	20
Oxygen	O <sub>2</sub>	0.00138	720	20
Phenol	C <sub>6</sub> H <sub>6</sub> O	2200	$4.5 \times 10^{-4}$	20
Sulfur dioxide <sup>a</sup>	SO <sub>2</sub>	1.24	0.81	25
Tetrachloroethylene	C <sub>2</sub> Cl <sub>4</sub>	0.083	12	20
Toluene	C <sub>7</sub> H <sub>8</sub>	0.15	6.7	20
1,1,1-Trichloroethane	C <sub>2</sub> H <sub>3</sub> Cl <sub>3</sub>	0.055	18	20
Trichloroethylene	C <sub>2</sub> HCl <sub>3</sub>	0.11	9.1	20

<sup>a</sup>These species participate in acid-base reactions when dissolved in water. The coefficients listed refer to the solubility of the unreacted species only.



# Solubility of selected organics

**Table 3.B.3** Water Solubility of Selected Organic Liquids

Species	Solubility (mg/L) <sup>a</sup>
Benzene	1,780
Benzo( <i>a</i> )pyrene	0.0038
Chloroform	8,200
Dieldrin	0.2
Ethylbenzene	152
Ethylene dibromide	4,300
<i>n</i> -Octane <sup>b</sup>	0.72
Naphthalene <sup>b</sup>	31
Phenol	93,000
2,3,7,8-TCDD	0.0002
Tetrachloroethylene	200
Toluene	535
1,1,1-Trichloroethane	4,400
Trichloroethylene	1,100

<sup>a</sup>At 20 °C unless otherwise noted.

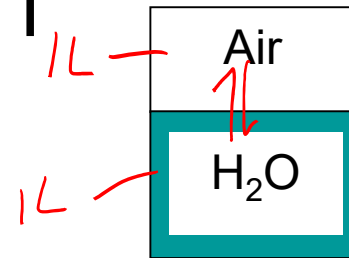
<sup>b</sup>At 25 °C.

Source: Sawyer et al., 1994; LaGrega et al., 1994; Schwarzenbach et al., 1993.

# Water-Gas Partitioning

- Henry's Law:  $[i] = K_{H,i} P_i$

- Eg. 3.11



Given 89 mg/L in gas phase, Find Henry's constant!

Add 1 g of CHCl<sub>3</sub> in 2 L vessel

$$MW \times [i] \times (1L) + \left( \frac{89 \text{ mg/L}}{1000 \text{ mg/g}} \right) (1 \times L) = 1 \text{ g}$$

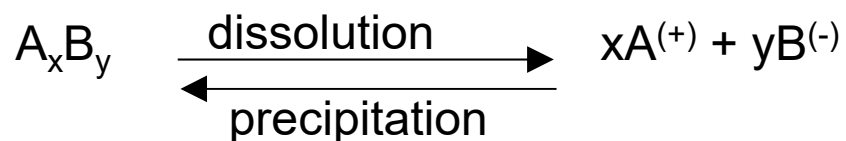
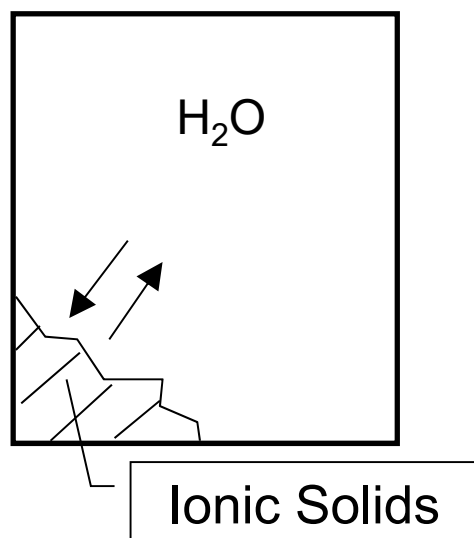


$$[i] = ?$$

$$[i] = K_{H,i} P_i$$

$$P_i = \frac{nRT}{V}$$

# Solid Solubility



$$K_{\text{sp}} = [\text{A}^{(+)}]^x [\text{B}^{(-)}]^y$$

Note: Valid only if solid is present at Equilibrium!



Al can also be in (+2) or (+4) state, but not common.

$$K_{\text{sp}} = [\text{Al}^{3+}][\text{OH}^-]^3$$

# Solubility Product

**Table 3.B.4** Solubility Products for Some Ionic Solids at  $T = 25\text{ }^{\circ}\text{C}$

Compound	Equilibrium relationship	$K_{sp}^a$	$K_{sp}^b$
Aluminum hydroxide	$\text{Al(OH)}_3 \rightleftharpoons \text{Al}^{3+} + 3 \text{OH}^-$	$1 \times 10^{-32} \text{ M}^4$	$2 \times 10^{-32} \text{ M}^4$
Cadmium hydroxide	$\text{Cd(OH)}_2 \rightleftharpoons \text{Cd}^{2+} + 2 \text{OH}^-$	$2 \times 10^{-14} \text{ M}^3$	$5.9 \times 10^{-15} \text{ M}^3$
Calcium carbonate	$\text{CaCO}_3 \rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{2-}$	$5 \times 10^{-9} \text{ M}^2$	$8.7 \times 10^{-9} \text{ M}^2$
Calcium fluoride	$\text{CaF}_2 \rightleftharpoons \text{Ca}^{2+} + 2 \text{F}^-$	$3 \times 10^{-11} \text{ M}^3$	$4 \times 10^{-11} \text{ M}^3$
Calcium hydroxide	$\text{Ca(OH)}_2 \rightleftharpoons \text{Ca}^{2+} + 2 \text{OH}^-$	$8 \times 10^{-6} \text{ M}^3$	$5.5 \times 10^{-6} \text{ M}^3$
Calcium phosphate	$\text{Ca}_3(\text{PO}_4)_2 \rightleftharpoons 3 \text{Ca}^{2+} + 2 \text{PO}_4^{3-}$	$1 \times 10^{-27} \text{ M}^5$	$2.0 \times 10^{-29} \text{ M}^5$
<u>Calcium sulfate</u>	<u><math>\text{CaSO}_4 \rightleftharpoons \text{Ca}^{2+} + \text{SO}_4^{2-}</math></u>	<u><math>2 \times 10^{-5} \text{ M}^2</math></u>	$1.9 \times 10^{-4} \text{ M}^2$
Chromium(III) hydroxide	<u><math>\text{Cr(OH)}_3 \rightleftharpoons \text{Cr}^{3+} + 3 \text{OH}^-</math></u>	$6 \times 10^{-31} \text{ M}^4$	$6 \times 10^{-31} \text{ M}^4$
Iron(II) hydroxide	$\text{Fe(OH)}_2 \rightleftharpoons \text{Fe}^{2+} + 2 \text{OH}^-$	$5 \times 10^{-15} \text{ M}^3$	$8 \times 10^{-16} \text{ M}^3$
Iron(III) hydroxide	$\text{Fe(OH)}_3 \rightleftharpoons \text{Fe}^{3+} + 3 \text{OH}^-$	$6 \times 10^{-38} \text{ M}^4$	$4 \times 10^{-38} \text{ M}^4$
Magnesium carbonate	$\text{MgCO}_3 \rightleftharpoons \text{Mg}^{2+} + \text{CO}_3^{2-}$	$4 \times 10^{-5} \text{ M}^2$	$1 \times 10^{-5} \text{ M}^2$
Magnesium hydroxide	$\text{Mg(OH)}_2 \rightleftharpoons \text{Mg}^{2+} + 2 \text{OH}^-$	$9 \times 10^{-12} \text{ M}^3$	$1.2 \times 10^{-11} \text{ M}^3$
Nickel hydroxide	$\text{Ni(OH)}_2 \rightleftharpoons \text{Ni}^{2+} + 2 \text{OH}^-$	$2 \times 10^{-16} \text{ M}^3$	$6.5 \times 10^{-18} \text{ M}^3$

<sup>a</sup>Sawyer et al., 1994, p. 38.

<sup>b</sup>Benefield and Morgan, 1990.

# Solid Solubility



At Equilibrium,

$$K_{\text{sp}} = 2 \times 10^{-5} \text{ M}^2 = [\text{Ca}^{2+}][\text{SO}_4^{2-}]$$

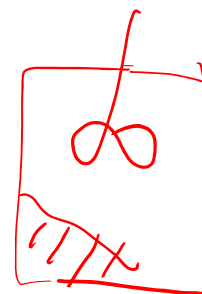
$$[\text{Ca}^{2+}] = [\text{SO}_4^{2-}]$$

$$K_{\text{sp}} = [\text{Ca}^{2+}]^2 = [\text{SO}_4^{2-}]^2 = 2 \times 10^{-5}$$

$$\Rightarrow [\text{Ca}^{2+}] = [\text{SO}_4^{2-}] = \sqrt{K_{\text{sp}}} = 4.5 \times 10^{-3} \text{ M}$$

$\times 136 \frac{\text{g}}{\text{mole}}$

$$\Rightarrow \textcircled{0.612 \text{ g/L}} \text{ CaSO}_4^{2-}$$



# Stoichiometry

- A chemical reaction must conserve the number of atoms for each element involved in the reaction and the electrical charge associated with ions.
- Eg.



$$\begin{array}{rclcl}
 \text{C:} & \frac{LHS}{3} & = & \frac{RHS}{b} & \\
 \text{H:} & 6 & = & 2c + d & \\
 \text{a:} & 2 & = & d & \\
 \text{O:} & 2a & = & 2b + c & 
 \end{array}
 \left. \vphantom{\begin{array}{rclcl} \text{C:} & \frac{LHS}{3} & = & \frac{RHS}{b} & \\ \text{H:} & 6 & = & 2c + d & \\ \text{a:} & 2 & = & d & \\ \text{O:} & 2a & = & 2b + c & } \right\}
 \begin{array}{l}
 a = 4 \\
 b = 3 \\
 c = 2 \\
 d = 2
 \end{array}$$

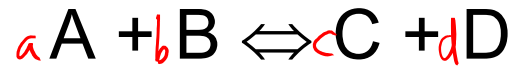
# Chemical Equilibrium

Equilibrium:

1. Not vary with time.
2. Internally uniform.
3. NO net flows of mass, heat, or species within system or between system and its surroundings.
4. Net rate of chemical reactions is ZERO.



# Chemical Equilibrium



- 1) Rate of reaction in forward direction:

$$R_f = k_f [A]^a [B]^b$$

- 2) Rate of reaction in reverse direction:

$$R_r = k_r [C]^c [D]^d$$

At equilibrium:  $R_f = R_r$

$$\rightarrow k_f [A]^a [B]^b = k_r [C]^c [D]^d$$

or

$$\frac{[C]^c [D]^d}{[A]^a [B]^b} = \frac{k_f}{k_r} = K$$

where  $K = \text{equilibrium constant}$  of the reaction



# Acid-Base Reaction

• pH =  $-\log_{10} [\text{H}^+]$

A generic expression:



$$K_A = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

# Strength of Acid

Define

$$\underline{p}K_A = -\log_{10}(K_A)$$

- Strong acid:  $pK_A \leq 1$  (fully dissociate)
- Weak acid:  $pK_A \geq 1$  (partially dissociate)



$$K_{HCl} = \frac{[H^+][Cl^-]}{[HCl]}$$

$$\underbrace{-\log_{10} K_{HCl}}_{pK_A} = -\log_{10} \left( \frac{[H^+][Cl^-]}{[HCl]} \right)$$

$$\begin{aligned} pH &= -5 \\ -\log_{10}[H^+] &= -5 \\ [H^+] &= 10^{-5} M \end{aligned}$$

# Acid Dissociation Constants

**Table 3.C.1** Acid Dissociation Constants ( $T = 25\text{ }^{\circ}\text{C}$ )

Species	Chemical formula	$\text{p}K_A$
Perchloric acid	$\text{HClO}_4$	-7
Hydrochloric acid	$\text{HCl}$	-3
Sulfuric acid	$\text{H}_2\text{SO}_4$	-3
Nitric acid	$\text{HNO}_3$	-1.2
Sulfonic acid	$\text{H}_2\text{SO}_3$	1.89
Bisulfate	$\text{HSO}_4^-$	1.92
Phosphoric acid	$\text{H}_3\text{PO}_4$	2.12
Acetic acid	$\text{CH}_3\text{COOH}$	4.7
Butyric acid	$\text{C}_3\text{H}_7\text{COOH}$	4.8
Propionic acid	$\text{C}_2\text{H}_5\text{COOH}$	4.9
Carbonic acid	$\text{H}_2\text{CO}_3$	6.35
Hydrogen sulfide	$\text{H}_2\text{S}$	7.1
Dihydrogen phosphate	$\text{H}_2\text{PO}_4^-$	7.21
Bisulfite	$\text{HSO}_3^-$	7.22
Hypochlorous acid	$\text{HOCl}$	7.6
Hydrogen cyanide	$\text{HCN}$	9.2
Ammonium	$\text{NH}_4^+$	9.23
Bicarbonate	$\text{HCO}_3^-$	10.33
Hydrogen phosphate	$\text{HPO}_4^{2-}$	12.32
Bisulfide	$\text{HS}^-$	12.9

$$\text{p}K_A = 7.6 \Rightarrow K_A = 10^{-7.6}$$

$$K_A = \frac{[\text{H}^+][\text{OCl}^-]}{[\text{HOCl}]}$$

$10^{-7.6} =$

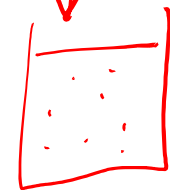
# Acid-Base Reaction

- $pK_A = pH \rightarrow 50\%$  of acid is dissociated.

$$\begin{aligned}
 pH &= pK_A \\
 \Rightarrow -\log_{10} [H^+] &= -\log_{10} K_A \\
 \Rightarrow [H^+] &= K_A
 \end{aligned}$$

$$\frac{[H^+][OAc^-]}{[HOAc]} = K_A = [H^+] \Rightarrow [OAc^-] = [HOAc]$$

HOCl?



e equilibrium

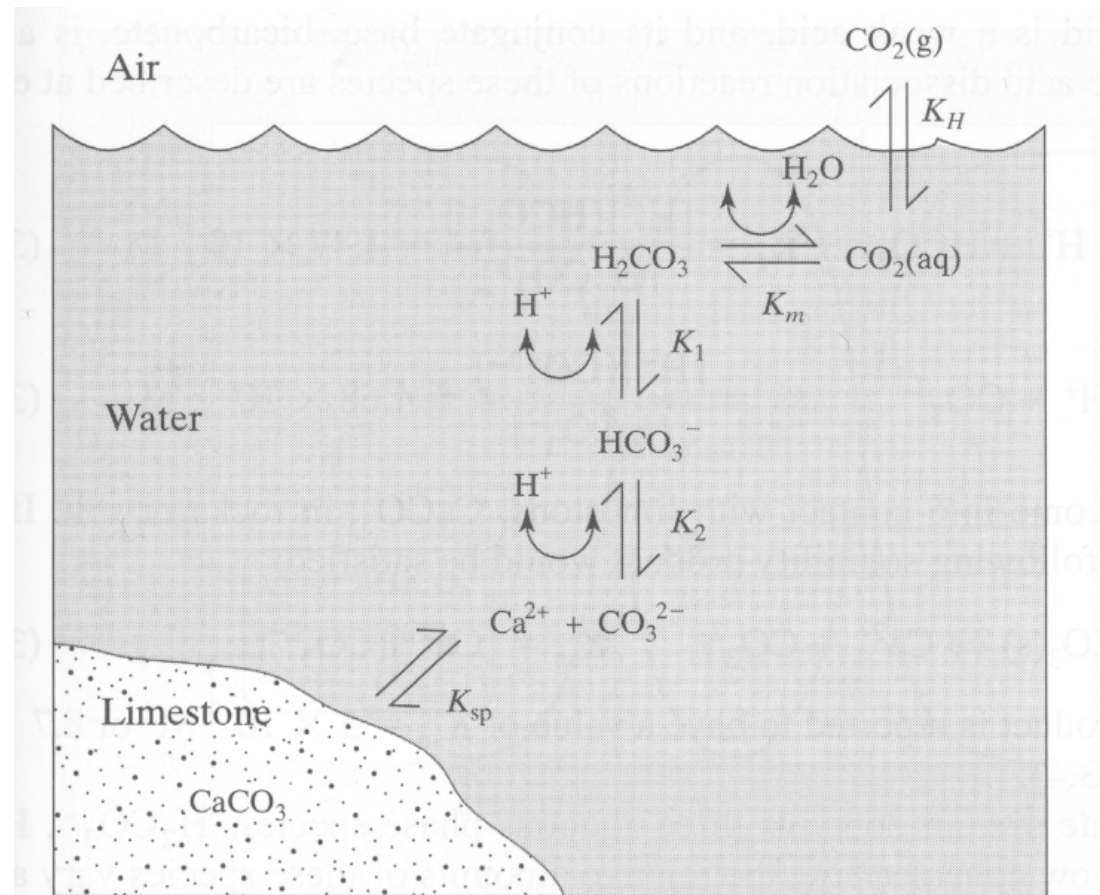
- If  $pH \gg pK_A$ , acid is fully dissociated  $[OAc^-] = [HOAc]$

- If  $pH \ll pK_A$ , acid is fully non-dissociated

$$\begin{aligned}
 -\log_{10} [H^+] &\ll -\log_{10} (K_A) \\
 [H^+] &\gg K_A
 \end{aligned}$$

$$\frac{[H^+][OAc^-]}{[HOAc]} = K_A \Rightarrow \frac{[H^+]}{K_A} = \frac{[HOAc]}{[OAc^-]}$$

# Acid-Base Reaction Example: Carbonate System

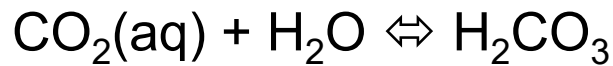


**Figure 3.C.1** Species and transformations for the carbonate system in natural air-water-limestone environments.

# Acid-Base Reaction Example: Carbonate System

Species involved:  $\text{CO}_{2(g)}$ ,  $\text{H}_2\text{CO}_3^*$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ .

$$[\text{CO}_2(\text{aq})] = K_H P_{\text{CO}_2}$$

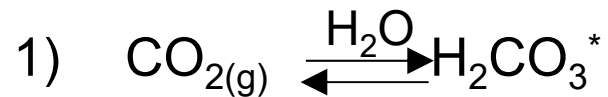


$$[\text{H}_2\text{CO}_3]/[\text{CO}_2(\text{aq})] = K_m = 1.58 \times 10^{-3}$$

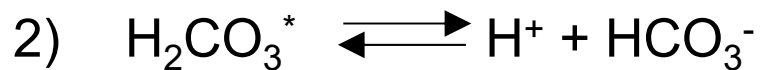
Define

$$[\text{H}_2\text{CO}_3^*] = [\text{CO}_2(\text{aq})] + [\text{H}_2\text{CO}_3] = [\text{CO}_2(\text{aq})](1 + K_m)$$

$$[\text{H}_2\text{CO}_3] = K_m [\text{CO}_2(\text{aq})]$$



$$[\text{H}_2\text{CO}_3^*] = (1 + K_m) K_H P_{\text{CO}_2}$$



$$K_{c1} = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3^*]}$$



$$K_{c2} = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$$

# Eg. Carbonate System

What is the pH of soda "Coca-Cola" (when it is still haven't been opened)?

Assume  $P_{\text{CO}_2} = 2 \text{ atm}$

Unknowns (5):  $[\text{H}^+]$ ,  $[\text{OH}^-]$ ,  $[\text{HCO}_3^-]$ ,  $[\text{H}_2\text{CO}_3^*]$ ,  $[\text{CO}_3^{2-}]$

$$\textcircled{1} \quad [\text{H}^+][\text{OH}^-] = K_w = 10^{-14}$$

$$\textcircled{2} \quad K_{a1} = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3^*]} = 10^{-6.35}$$

$$\textcircled{3} \quad K_{a2} = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = 10^{-10.33}$$

$$\textcircled{4} \quad [\text{H}_2\text{CO}_3^*] = K_H P_{\text{CO}_2}$$

$$\textcircled{5} \quad \text{E.N.:} \quad [\text{H}^+] = [\text{HCO}_3^-] + [\text{OH}^-] + 2[\text{CO}_3^{2-}]$$

Solve using algorithm:

- 1) Use one equation (EN) and pick one variable  $[H^+]$
- 2) Transform that equation in terms of one unknown.  
e.g.,  $[H^+]$



# Chemical Equilibrium

Coca-cola Example:

- EN + equilibrium:

$$[H^+] = \frac{K_w}{[H^+]} + \frac{K_{c1} K_H P_{CO_2}}{[H^+]} + 2 \frac{K_{c1} K_{c2} P_{CO_2} K_H}{[H^+]^2}$$

$\underbrace{\hspace{1.5cm}}_{[OH^-]}$ 
 $\underbrace{\hspace{1.5cm}}_{[HCO_3^-]}$ 
 $\underbrace{\hspace{1.5cm}}_{[CO_3^{2-}]}$

Where do we get the parameters?

- $P_{CO_2}$ : 2 atm (given)
- $K_{H,CO_2}$ : Table 3.B.2:  $K_{H,CO_2} = 0.034 \text{ M atm}^{-1}$  (25°C)

# Chemical Equilibrium

Where do we get the parameters?

$$K_{C1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3^*]} \quad (H_2CO_3^* \rightleftharpoons H^+ + HCO_3^-)$$

Table 3.C.1: For  $H_2CO_3$ ,  $pK_A = 6.35$

$$pK_A = -\log_{10} (K)$$

$$K_A = 10^{-6.35}$$

$$K_{C2} = 10^{-10.33}$$

# Henry's Constants

**Table 3.B.2** Henry's Law Constants for Selected Species

Species	Formula	$K_H$ (M atm <sup>-1</sup> )	$H_g$ (atm M <sup>-1</sup> )	Temperature (°C)
Ammonia <sup>a</sup>	NH <sub>3</sub>	62	0.016	25
Benzene	C <sub>6</sub> H <sub>6</sub>	0.18	5.6	20
Benzo(a)pyrene	C <sub>20</sub> H <sub>12</sub>	2040	$4.9 \times 10^{-4}$	20
Carbon dioxide <sup>a</sup>	CO <sub>2</sub>	0.034	29	25
Carbon monoxide	CO	0.0010	1000	20
Chloroform	CHCl <sub>3</sub>	0.31	3.2	20
Ethylbenzene	C <sub>8</sub> H <sub>10</sub>	0.11	9.1	20
Formaldehyde	HCHO	6300	$1.6 \times 10^{-4}$	25
Hydrogen sulfide <sup>a</sup>	H <sub>2</sub> S	0.115	8.7	20
Methane	CH <sub>4</sub>	0.0015	670	20
Naphthalene	C <sub>10</sub> H <sub>8</sub>	2.2	0.45	20
Nitric acid <sup>a</sup>	HNO <sub>3</sub>	$2.1 \times 10^5$	$4.8 \times 10^{-6}$	25
Nitrogen	N <sub>2</sub>	0.00067	1500	20
Oxygen	O <sub>2</sub>	0.00138	720	20
Phenol	C <sub>6</sub> H <sub>6</sub> O	2200	$4.5 \times 10^{-4}$	20
Sulfur dioxide <sup>a</sup>	SO <sub>2</sub>	1.24	0.81	25
Tetrachloroethylene	C <sub>2</sub> Cl <sub>4</sub>	0.083	12	20
Toluene	C <sub>7</sub> H <sub>8</sub>	0.15	6.7	20
1,1,1-Trichloroethane	C <sub>2</sub> H <sub>3</sub> Cl <sub>3</sub>	0.055	18	20
Trichloroethylene	C <sub>2</sub> HCl <sub>3</sub>	0.11	9.1	20

<sup>a</sup>These species participate in acid-base reactions when dissolved in water. The coefficients listed refer to the solubility of the unreacted species only.

# pK<sub>A</sub>

**Table 3.C.1** Acid Dissociation Constants ( $T = 25\text{ }^{\circ}\text{C}$ )

Species	Chemical formula	pK <sub>A</sub>
Perchloric acid	HClO <sub>4</sub>	-7
Hydrochloric acid	HCl	-3
Sulfuric acid	H <sub>2</sub> SO <sub>4</sub>	-3
Nitric acid	HNO <sub>3</sub>	-1.2
Sulfonic acid	H <sub>2</sub> SO <sub>3</sub>	1.89
Bisulfate	HSO <sub>4</sub> <sup>-</sup>	1.92
Phosphoric acid	H <sub>3</sub> PO <sub>4</sub>	2.12
Acetic acid	CH <sub>3</sub> COOH	4.7
Butyric acid	C <sub>3</sub> H <sub>7</sub> COOH	4.8
Propionic acid	C <sub>2</sub> H <sub>5</sub> COOH	4.9
Carbonic acid	H <sub>2</sub> CO <sub>3</sub>	6.35
Hydrogen sulfide	<del>H<sub>2</sub>S</del>	<del>7.1</del>
Dihydrogen phosphate	H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	7.21
Bisulfite	HSO <sub>3</sub> <sup>-</sup>	7.22
Hypochlorous acid	HOCl	7.6
Hydrogen cyanide	HCN	9.2
Ammonium	NH <sub>4</sub> <sup>+</sup>	9.23
Bicarbonate	HCO <sub>3</sub> <sup>-</sup>	10.33
Hydrogen phosphate	HPO <sub>4</sub> <sup>2-</sup>	12.32
Bisulfide	HS <sup>-</sup>	12.9

# Chemical Equilibrium

- How to solve using a spread sheet?

0

$$[H^+] = \frac{K_w}{[H^+]} + \frac{K_{c1} K_H P_{CO2}}{[H^+]} + 2 \frac{K_{c1} K_{c2} P_{CO2}}{[H^+]^2} - [H^+]$$

# What is the pH of water in a carbonated beverage? (Using a spread sheet)

KHC	0.034	M/atm			
pCO2	2	atm			
H2CO3*	0.068	M			
Kc1	4.47E-07	M			
Kc2	4.68E-11	M			
Kw	1.00E-14	M			
pH	[H+]	[OH-]	[HCO3-]	[CO32-]	EN
1	1.00E-01	1.00E-13	3.04E-07	1.42E-16	1.00E-01
2	1.00E-02	1.00E-12	3.04E-06	1.42E-14	1.00E-02
<b>3</b>	<b>1.00E-03</b>	<b>1.00E-11</b>	<b>3.04E-05</b>	<b>1.42E-12</b>	<b>9.70E-04</b>
<b>4</b>	<b>1.00E-04</b>	<b>1.00E-10</b>	<b>3.04E-04</b>	<b>1.42E-10</b>	<b>-2.04E-04</b>
5	1.00E-05	1.00E-09	3.04E-03	1.42E-08	-3.03E-03
6	1.00E-06	1.00E-08	3.04E-02	1.42E-06	-3.04E-02
7	1.00E-07	1.00E-07	3.04E-01	1.42E-04	-3.04E-01
8	1.00E-08	1.00E-06	3.04E+00	1.42E-02	-3.07E+00
9	1.00E-09	1.00E-05	3.04E+01	1.42E+00	-3.32E+01
10	1.00E-10	1.00E-04	3.04E+02	1.42E+02	-5.88E+02
11	1.00E-11	1.00E-03	3.04E+03	1.42E+04	-3.15E+04
12	1.00E-12	1.00E-02	3.04E+04	1.42E+06	-2.88E+06
13	1.00E-13	1.00E-01	3.04E+05	1.42E+08	-2.85E+08
14	1.00E-14	1.00E+00	3.04E+06	1.42E+10	-2.85E+10

pH	[H+]	[OH-]	[HCO3-]	[CO32-]	EN
3	1.00E-03	1.00E-11	3.04E-05	1.42E-12	9.70E-04
3.1	7.94E-04	1.26E-11	3.83E-05	2.25E-12	7.56E-04
3.2	6.31E-04	1.58E-11	4.82E-05	3.57E-12	5.83E-04
3.3	5.01E-04	2.00E-11	6.06E-05	5.66E-12	4.41E-04
3.4	3.98E-04	2.51E-11	7.64E-05	8.98E-12	3.22E-04
3.5	3.16E-04	3.16E-11	9.61E-05	1.42E-11	2.20E-04
3.6	2.51E-04	3.98E-11	1.21E-04	2.25E-11	1.30E-04
<b>3.7</b>	<b>2.00E-04</b>	<b>5.01E-11</b>	<b>1.52E-04</b>	<b>3.57E-11</b>	<b>4.72E-05</b>
<b>3.8</b>	<b>1.58E-04</b>	<b>6.31E-11</b>	<b>1.92E-04</b>	<b>5.66E-11</b>	<b>-3.33E-05</b>
3.9	1.26E-04	7.94E-11	2.41E-04	8.98E-11	-1.16E-04

3.7	2.00E-04	5.01E-11	1.52E-04	3.57E-11	4.72E-05
3.71	1.95E-04	5.13E-11	1.56E-04	3.74E-11	3.91E-05
3.72	1.91E-04	5.25E-11	1.60E-04	3.92E-11	3.10E-05
3.74	1.82E-04	5.50E-11	1.67E-04	4.30E-11	1.49E-05
<b>3.75</b>	<b>1.78E-04</b>	<b>5.62E-11</b>	<b>1.71E-04</b>	<b>4.50E-11</b>	<b>6.90E-06</b>
<b>3.76</b>	<b>1.74E-04</b>	<b>5.75E-11</b>	<b>1.75E-04</b>	<b>4.71E-11</b>	<b>-1.13E-06</b>
3.78	1.66E-04	6.03E-11	1.83E-04	5.16E-11	-1.72E-05
3.79	1.62E-04	6.17E-11	1.87E-04	5.41E-11	-2.52E-05

**Answer: pH = 3.76**

# Chemical Equilibrium Example

- Hypochlorous acid (HOCl), a weak acid, can be used for disinfecting water. If 1 mg of HOCL is added to pure water to make up 1 L of liquid volume, what is the equilibrium pH?

Species:  $[H^+]$ ,  $[OH^-]$ ,  $[HOCl]$ ,  $[OCl^-]$

$$(1) [H^+][OH^-] = K_w = 10^{-14}$$

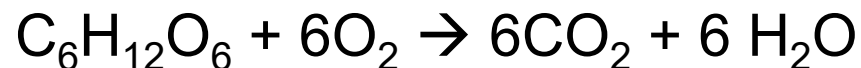
$$(2) K_A = \frac{[H^+][OCl^-]}{[HOCl]} = 10^{-7.6}$$

$$(3) E.N.: [H^+] = [OH^-] + [OCl^-]$$

$$(4) \text{ mass balance: } [HOCl]_T = [HOCl] + [OCl^-] + \cancel{[H^+]}$$

# Chemical Kinetics

- Time scale for reaction to achieve equilibrium is “large”  
→ Kinetics.
- Example: Glucose in oxygenated water



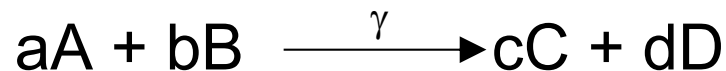
- Glucose in sterile (no bugs) distilled  $\text{H}_2\text{O}$  at pH 7 in contact with air is stable “forever”, i.e., a kinetic barrier to its oxidation.
- When pH is  $> 13$ , oxidation will occur.
- Methylene Blue (MeB) is a redox indicator which is blue when  $\text{O}_2$  is present and colourless when  $\text{O}_2$  is absent.  
 $\text{H}_2\text{O} + \text{Glucose} + \text{O}_2 + \text{MeB} @ \text{pH} > 7 \rightarrow \text{blue}$   
 $\text{H}_2\text{O} + \text{Glucose} + \text{O}_2 + \text{MeB} @ \text{pH} > 13 \rightarrow \text{colourless}$



# Chemical Kinetics

## Definitions

- An ~~e~~ *elementary reaction* is one that proceeds as stoichiometrically written.
- Rate law for irreversible elementary reaction:



$$R_{\gamma} = \cancel{\theta} \frac{1}{a} \left( \frac{d[A]}{dt} \right) = \cancel{\theta} \frac{1}{b} \left( \frac{d[B]}{dt} \right) = \frac{1}{c} \left( \frac{d[C]}{dt} \right) = \frac{1}{d} \left( \frac{d[D]}{dt} \right)$$

&  $\frac{d[A]}{dt} = \frac{(A_2 - A_1)}{(t_2 - t_1)} \quad \Bigg| \quad R_{\gamma} = k_{\gamma} [A]^a [B]^b$

where a,b,c,d = constants = stoichiometric coefficients

$k_{\gamma}$  = reaction rate constant

# Chemical Kinetics

- Example of Rate Calculations: Reaction of disinfectant HOCL (hypochlorous acid) with  $\text{NH}_3$  (ammonia) to form  $\text{NH}_2\text{Cl}$  (monochloramine):



$$k = 5.1 \times 10^6 \text{ l/mole, sec at } 25^\circ\text{C}$$

If initial  $\text{NH}_3$  and HOCL concentrations are both  $10^{-3} \text{ M}$ , what is the overall reaction rate?

$$\text{Rate Law: } R = -\frac{1}{1} \frac{d[\text{NH}_3]}{dt} = -\frac{1}{1} \frac{d[\text{HOCl}]}{dt} = k [\text{NH}_3] [\text{HOCl}]$$

$$\begin{aligned} \text{Initial rate} &= (5.1 \times 10^6) (10^{-3}) (10^{-3}) \\ &= \boxed{5.1 \frac{\text{mole}}{\text{L} \cdot \text{s}}} \end{aligned}$$

# Chemical Kinetics

## Batch Reactor

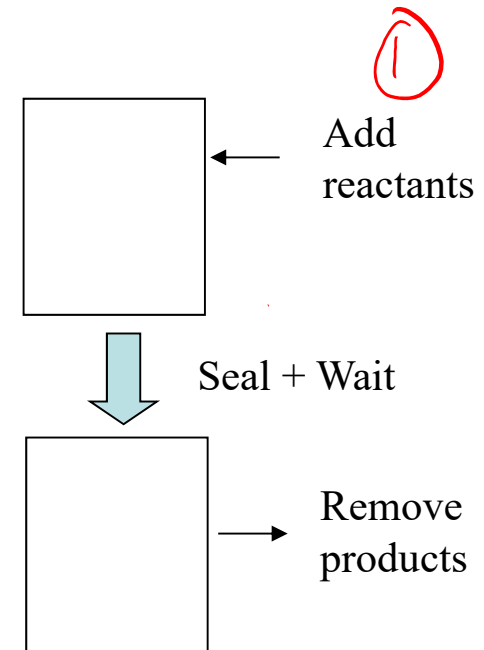
Consider chemical reaction in batch reactor.

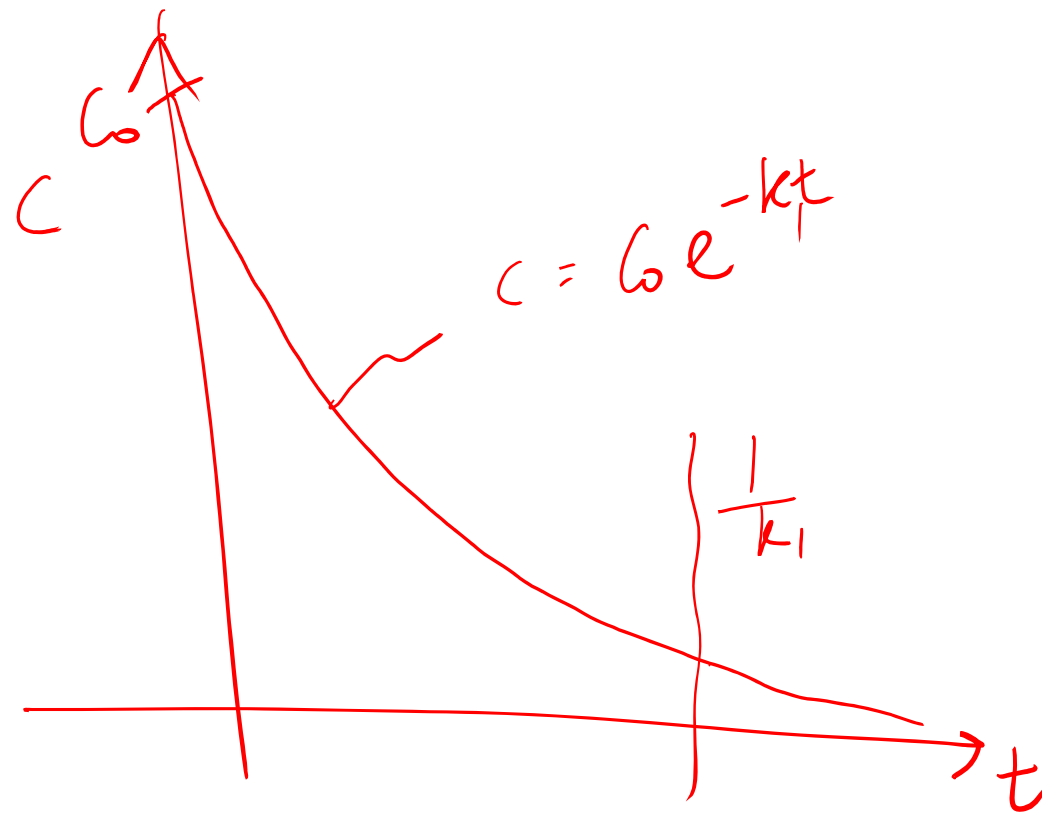
1<sup>st</sup> order decay rxn.:  $A \xrightarrow{1} \text{products}$

Rate Law:  $R_1 = k_1[A]$

In a batch reactor with only rxn. 1 occurring:

$$\frac{d[A]}{dt} = -R_1 = -k_1[A]$$





# Chemical Kinetics

## 1) 1<sup>st</sup> Order Decay Reaction

Consider chemical reaction in batch reactor.

1<sup>st</sup> order decay rxn.:  $A \xrightarrow{1} \text{products}$

Rate Law:  $R_1 = k_1[A]$

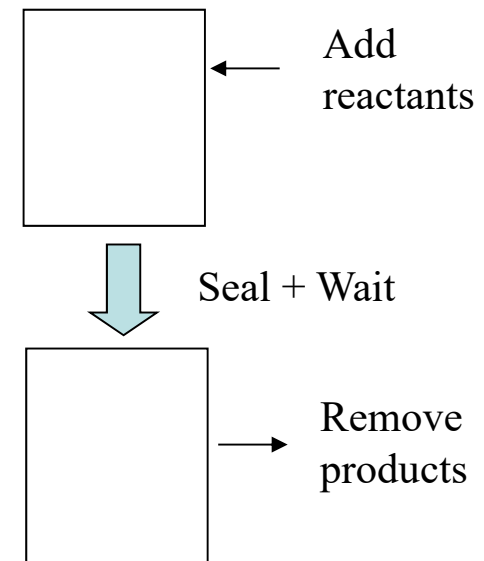
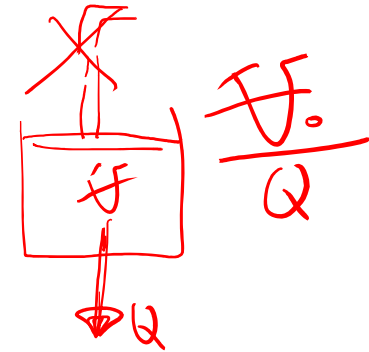
$$\frac{d[A]}{dt} = -R_1 = -k_1[A]$$

$$[A](t) = A_o e^{-k_1 t}$$

Characteristics time,

$$\tau = \frac{\text{Stock}}{\text{Outflow Rate}}$$

$$\tau \sim \frac{\cancel{A_o}}{k_1 \cancel{A_o}} = \frac{1}{k_1}$$

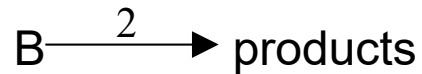


# Chemical Kinetics

Other variations:

2) 0<sup>th</sup> Order Decay Reaction:

(provided  $[B] \gg 0$ )



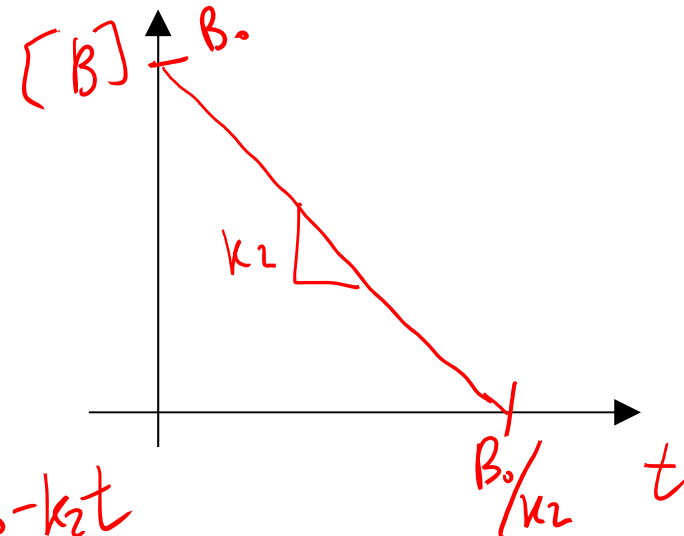
Rate Law:  $R_2 = k_2$  &  $[B](t=0) = B_0$

In a batch reactor,

$$\frac{d[B]}{dt} = -R_2 = -k_2$$

$$\int_{B_0}^B d[B] = \int_0^t k_2 dt$$

$$[B] = B_0 - k_2 t$$



- Characteristics time,

$$\tau = \frac{\text{Stock}}{\text{Outflow Rate}}$$

$$\tau \simeq \frac{B_0}{k_2}$$

Valid for  $t < B_0/k_2$ ;  $[B](t) = 0$  for  $t \geq B_0/k_2$

# Chemical Kinetics

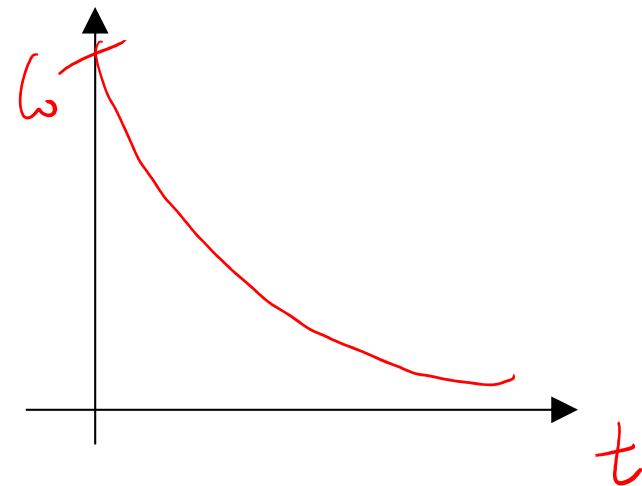
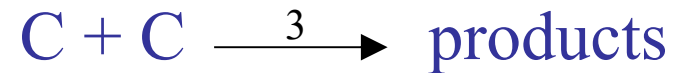
3) i) 2<sup>th</sup> Order Decay Reaction:

Rate Law:  $R_3 = k_3[C]^2$

$$\frac{1}{2} \frac{d[C]}{dt} = -R_3 = -k_3[C]^2$$

$$\int_{C_0}^C \frac{dC}{[C]^2} = \int_0^t -2k_3 dt$$

$$C[t] = \frac{C_0}{1 + 2k_3 t C_0}$$



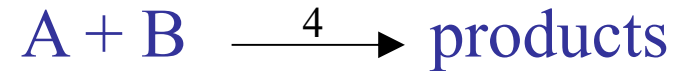
- Characteristics time,

$$\tau = \frac{\text{Stock}}{\text{Outflow Rate}}$$

$$\tau \sim \frac{C_0}{2k_3 C_0^2} = \frac{1}{2k_3 C_0}$$

# Chemical Kinetics

## 3. ii) 2<sup>th</sup> Order Decay Reaction:



Rate Law:  $R_4 = k_4[A][B]$  Note: 1<sup>st</sup> order in [A] & [B]; 2<sup>nd</sup> order over all.

In a batch reactor with  $A_o$ ,  $B_o$  at  $t=0$

Case 1: 
$$\frac{d[A]}{dt} = \frac{d[B]}{dt} = -R_4 = -k_4[A][B]$$

Characteristics Time: 
$$\tau \sim \frac{\min(A_o, B_o)}{k_4 A_o B_o}$$

If  $A_o = B_o$ , all  $A_o$  and  $B_o$  will be consumed.

If  $A_o > B_o$ , all  $B_o$  will be consumed

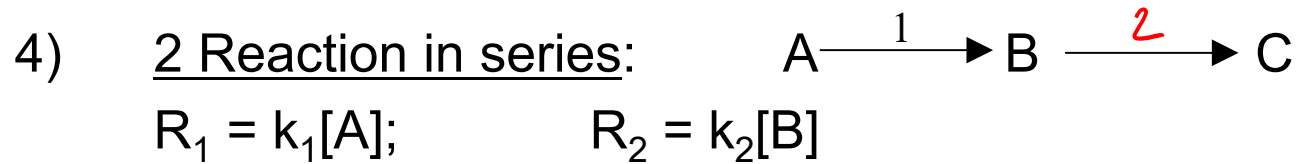
Case 2: (Function of A but not B)

$$\frac{d[A]}{dt} = \frac{d[B]}{dt} = -R_4 = -k_4[A]$$

*pseudo-first order reaction.*



# Chemical Kinetics



i) Seek  $[A](t)$   $\frac{d[A]}{dt} = -R_1 = -k_1[A] \Rightarrow [A] = A_0 e^{-k_1 t}$

ii) Seek  $[B](t)$   $\frac{d[B]}{dt} = R_1 - R_2 = k_1[A] - k_2[B]$

$$\Rightarrow \frac{d[B]}{dt} = k_1 A_0 e^{-k_1 t} - k_2[B]$$

Guess  $[B](t) = (a_1 e^{r_1 t} + a_2 e^{r_2 t})$  — ①

diff ①:  $\frac{d[B]}{dt} = a_1 r_1 e^{r_1 t} + a_2 r_2 e^{r_2 t}$  — #

@t=0  
 $[A] = A_0$   
 $[B] = 0$

$$r_1 a_1 e^{r_1 t} + r_2 a_2 e^{r_2 t} = k_1 A_0 e^{-k_1 t} - k_2 [B]$$

$$\boxed{r_1 a_1 e^{r_1 t} + r_2 a_2 e^{r_2 t}} = \boxed{k_1 A_0 e^{-k_1 t} - k_2 a_1 e^{r_1 t}} - k_2 a_2 e^{r_2 t}$$

Let  $\boxed{r_1 = -k_1}$

$$\Rightarrow -k_1 a_1 e^{-k_1 t} = k_1 A_0 e^{-k_1 t} - k_2 a_1 e^{-k_1 t}$$

$$\Rightarrow -k_1 a_1 = k_1 A_0 - k_2 a_1 \Rightarrow \boxed{a_1 = \frac{k_1 A_0}{k_2 - k_1}}$$

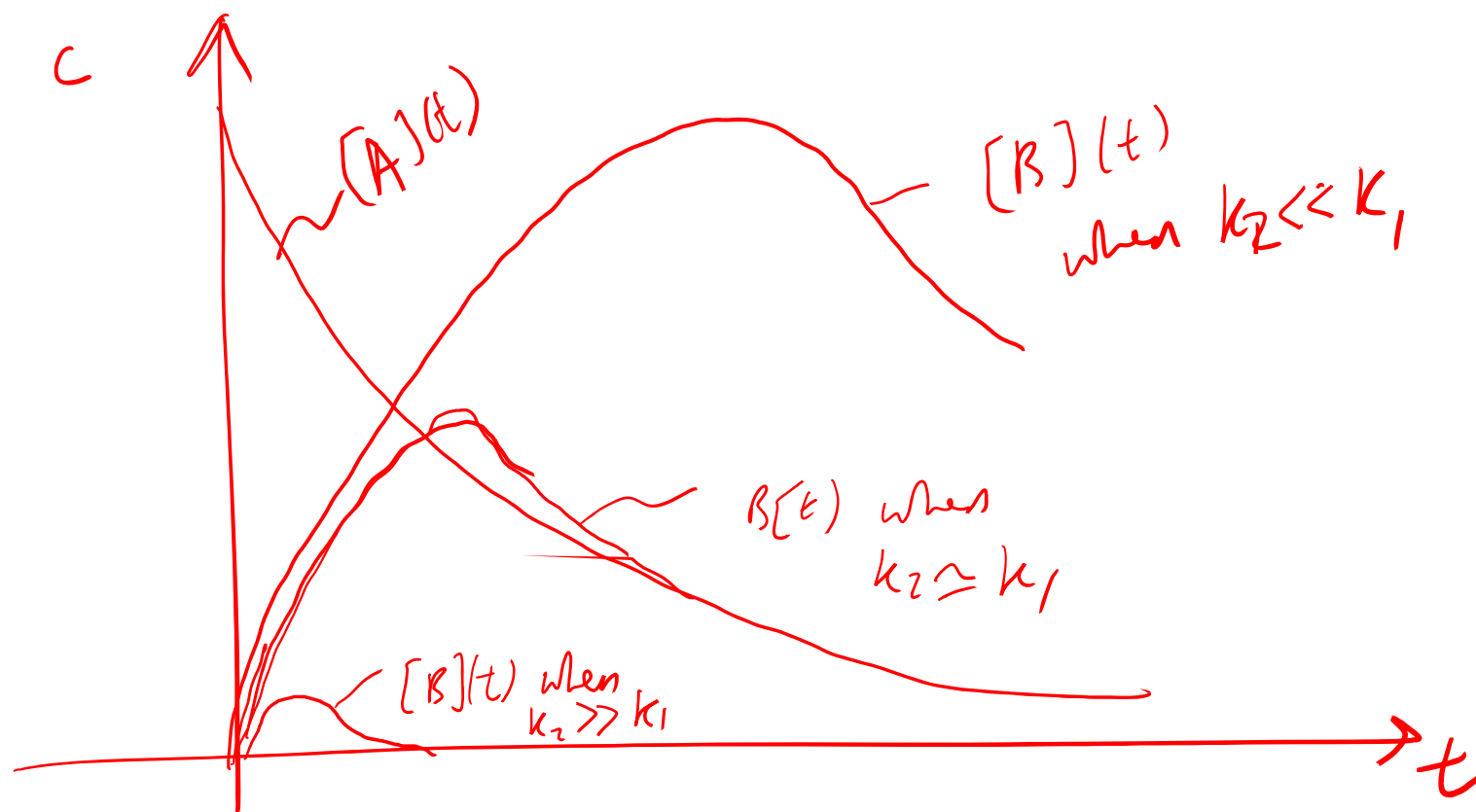
$$r_2 a_2 e^{r_2 t} = -k_2 a_2 e^{r_2 t} \Rightarrow \boxed{r_2 = -k_2}$$

$$\Rightarrow [B](t) = a_1 e^{r_1 t} + a_2 e^{r_2 t} = \frac{k_1 A_0}{k_2 - k_1} e^{-k_1 t} + a_2 e^{-k_2 t}$$

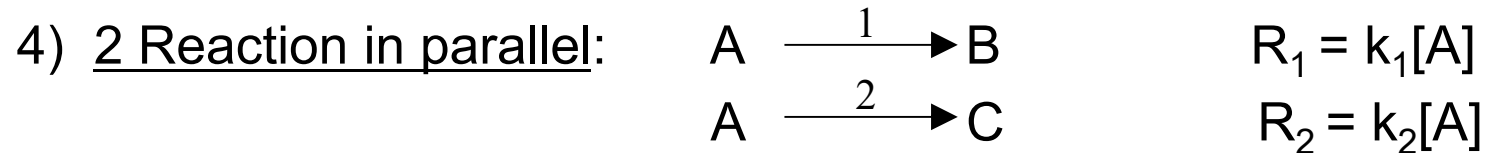
$$\text{@ } t=0, [B]=0 \Rightarrow 0 = \frac{k_1 A_0}{k_2 - k_1} + a_2 \Rightarrow \boxed{a_2 = -\frac{k_1 A_0}{k_2 - k_1}}$$

$$[B](t) = \frac{k_1 A_0}{k_2 - k_1} e^{-k_1 t} - \frac{k_1 A_0}{k_2 - k_1} e^{-k_2 t}$$

$$[A](t) = A_0 e^{-k_1 t}$$



# Chemical Kinetics



$$\frac{d[A]}{dt} = -R_1 - R_2 = -(k_1 + k_2)[A]$$

Given  $[A](t=0) = A_0$ ,  $[A](t) = A_0 e^{-(k_1 + k_2)t}$

$$\frac{d[B]}{dt} = R_1 = k_1[A]$$

$$\frac{d[B]}{dt} = k_1 A_0 e^{-(k_1 + k_2)t}$$

$$\frac{d[C]}{dt} = R_2 = k_2[A] = k_2 A_0 e^{-(k_1 + k_2)t}$$

# Chemical Kinetics

- 0th Order:  $\frac{d[A]}{dt} = -k_0 \quad \tau \sim \frac{A_0}{k_0}$

- 1<sup>st</sup> Order:  $\frac{d[A]}{dt} = -k_1[A] \quad \tau \sim \frac{A_0}{k_1 A_0} = \frac{1}{k_1}$

- 2<sup>nd</sup> Order:

$$\frac{d[A]}{dt} = -2k_{2a}[A]^2 \quad \tau_{2a} \sim \frac{A_0}{2k_{2a}A_0^2} = \frac{1}{2k_{2a}A_0}$$

$$\frac{d[A]}{dt} = \frac{d[B]}{dt} = -k_{2b}[A][B] \quad \tau_{2b} \sim \frac{\min(A_0, B_0)}{k_{2b}A_0B_0}$$

# Redox Reactions

- Chemical species can be characterized by their oxidation state which describes whether they have lost or gained electrons ( $e^-$ ) with respect to a reference state (the element; oxidation state = 0).

E.g.  $Mg^{2+}$  (magnesium ion) has lost  $2e^-$  compared to  $Mg^0$  (magnesium metal)

$Cl^-$  (chloride ion) has gained  $1e^-$  compared to  $1/2Cl_2^0$  (chlorine gas)

- A loss of  $e^-$  is an oxidation
- A gain of  $e^-$  is a reduction

# Rules for determining oxidation state

1. Uncombined elements = 0  
e.g. C, O<sub>2</sub> and H<sub>2</sub>
2. Sum of oxidation state for compound = ionic charge (element or molecule)
3. O in compound is -II
4. H in compound is +I

# Oxidation State

Example: Determine the oxidation number of C in

i)  $\text{CO}_2$ , ii)  $\text{CO}_3^{2-}$ , iii)  $\text{HCO}_3^-$  and iv)  $\text{C}_2\text{H}_4\text{O}_2$

$$\text{i) } \text{CO}_2: 1(x) + 2(-2) = 0 \Rightarrow x = +4$$

$$\text{ii) } \text{CO}_3^{2-}: 1(x) + 3(-2) = -2 \Rightarrow x = +4$$

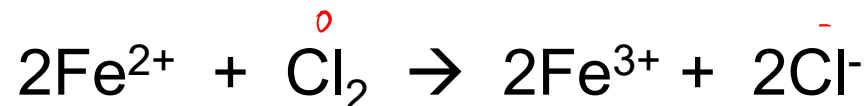
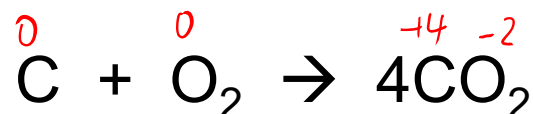
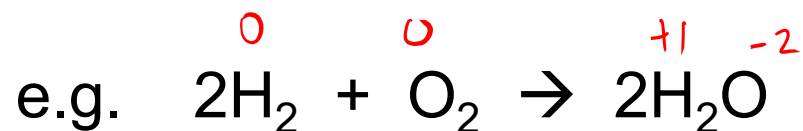
$$\text{iii) } \text{HCO}_3^-: 1 + 1(x) + 3(-2) = -1 \Rightarrow x = +4$$

$$\text{iv) } \text{C}_2\text{H}_4\text{O}_2: 2(x) + 4(1) + 2(-2) = 0 \\ \Rightarrow \underline{\underline{x = 0}}$$



# Oxidation/Reduction

- Involve a change in oxidation state of reactants



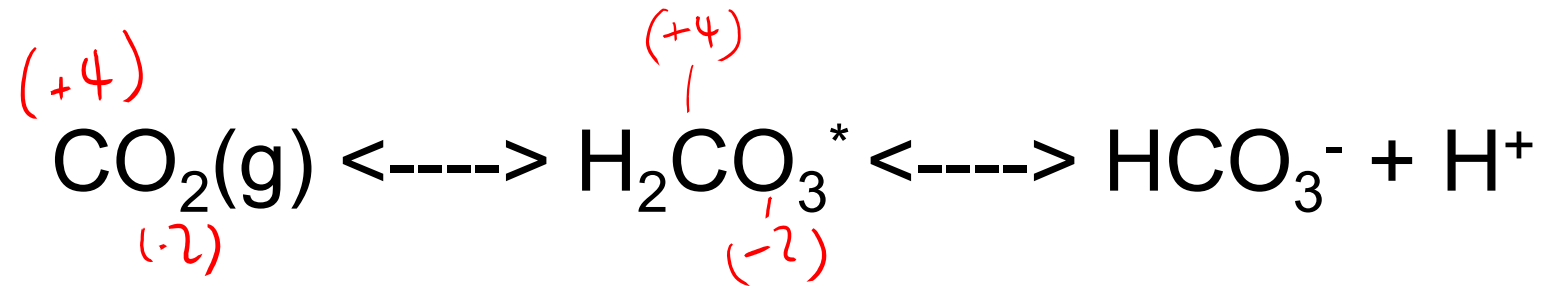
Note: sum of oxidation states on both sides of equations are equal – a requirement for a balanced redox reaction.

In last equation,

$\text{Fe}^{2+}$  is a **reducing agent**; it loses  $\text{e}^-$ ; it becomes oxidized.

$\text{Cl}_2$  is an **oxidizing agent**; it gains  $\text{e}^-$ ; it becomes reduced.

Considering C in:



# Balancing Redox Reaction – Electron Balancing Method

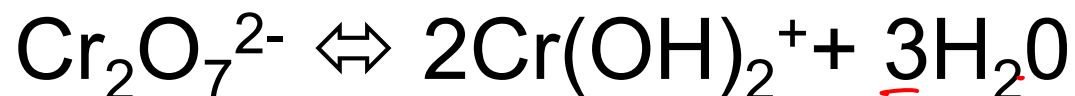
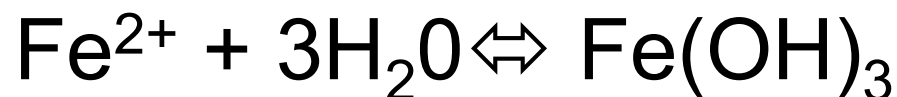
- Consist of two half reactions – an oxidation half-reaction and a reduction half reaction
- Steps:
  1. For each  $\frac{1}{2}$  rxn, balance major species (anything but O & H)
  2. For each  $\frac{1}{2}$  rxn, balance any O with  $\text{H}_2\text{O}$
  3. For each  $\frac{1}{2}$  rxn, balance any H with  $\text{H}^+$
  4. For each  $\frac{1}{2}$  rxn, balance charge with  $\text{e}^-$
  5. Balance both  $\frac{1}{2}$  rxns by eliminating  $\text{e}^-$
  6. If solution is alkaline (high pH), cancel out any  $\text{H}^+$  by adding  $\text{OH}^-$  to both side of rxn; sum up  $\text{H}_2\text{O}$

# Previous Example

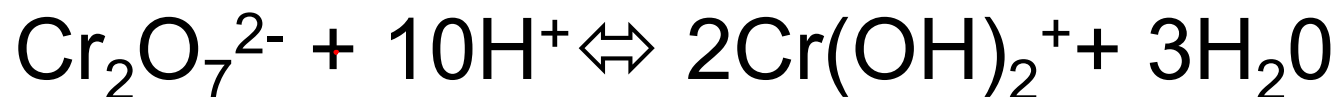
1. Balance major species:



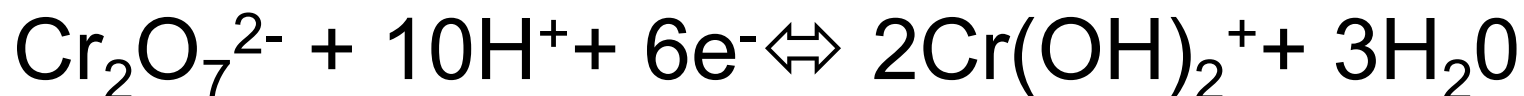
2. Balance any O with  $\text{H}_2\text{O}$



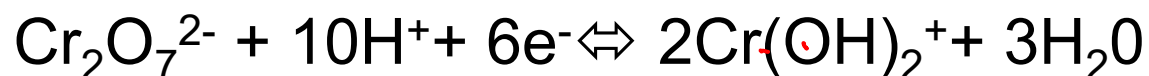
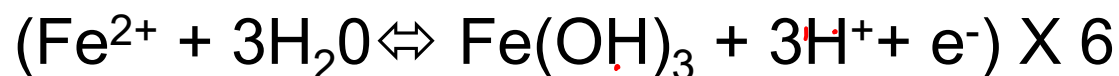
3. Balance any H with  $\text{H}^+$



4. Balance charge with  $e^-$



5. Balance both  $\frac{1}{2}$  rxns by eliminating  $e^-$



# Another Example

Balance the reaction in which ferrous iron ( $\text{Fe}^{2+}$ ) is converted to ferric iron ( $\text{Fe}^{3+}$ ) by permanganate ( $\text{MnO}_4^-$ ), which itself is reduced to manganese dioxide ( $\text{MnO}_{2(s)}$ ). The reaction takes place in alkaline solution.

1. Balance major species:



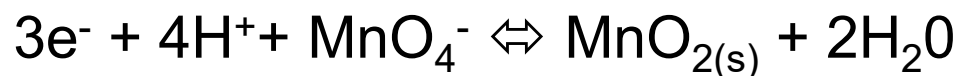
2. Balance any O with  $\text{H}_2\text{O}$



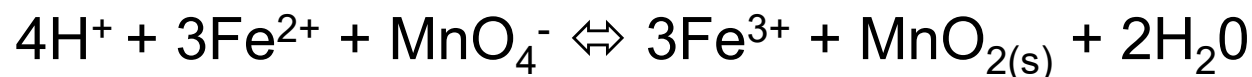
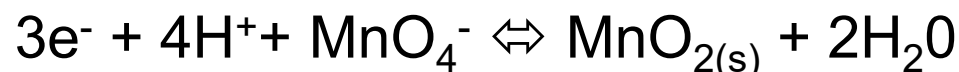
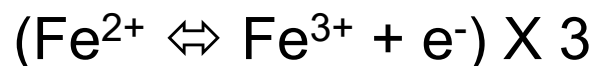
3. Balance any H with  $\text{H}^+$



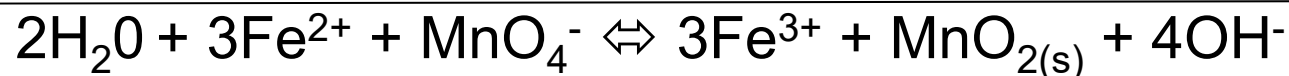
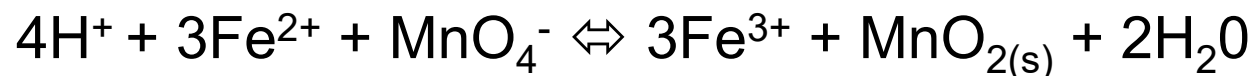
4. Balance charge with  $e^-$



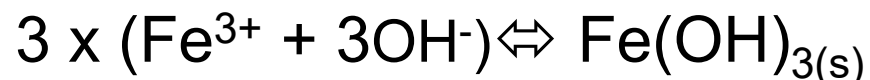
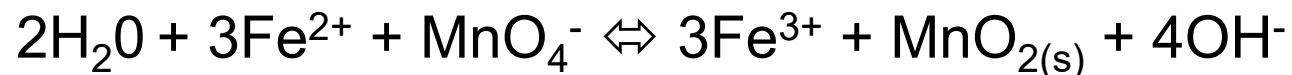
5. Balance both  $\frac{1}{2}$  rxns by eliminating  $e^-$



6. Rxn takes place in alkaline soln, add water dissociation equation to eliminate  $\text{H}^+$  as a reactant:



7. In alkaline soln,  $\text{Fe}^{3+}$  will combine with  $\text{OH}^-$  to form  $\text{Fe}(\text{OH})_{3(s)}$ :



Last step would not have been necessary if in step (1) we had taken  $\text{Fe}(\text{OH})_{3(s)}$  as the product rather than  $\text{Fe}^{3+}$



# Corrosion



# Corrosion

Typical corrosion reaction of metal in oxygen containing H<sub>2</sub>O:

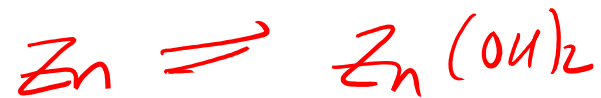


Fe oxidized from 0 to +II

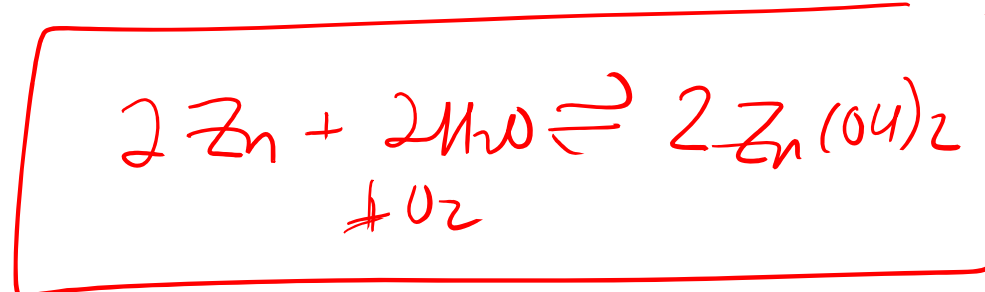
Oxygen reduced from 0 to -II

# Another Corrosion Example

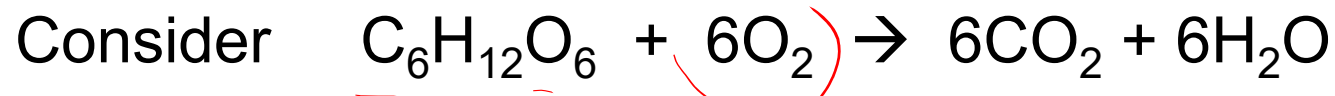
Q3.35 Write a balanced chemical reaction for the corrosion of pure zinc metal by dissolved oxygen in water to produce zinc rust,  $\text{Zn}(\text{OH})_2$ .



⋮



# Theoretical Oxygen Demand



500 mg/L of  $\text{C}_6\text{H}_{12}\text{O}_6$ , what is the theoretical oxygen demand?

$$\begin{aligned} & \downarrow \\ & \frac{500}{(6 \times 12) + (12) + 6(16)} \text{ mM} \times 6 \times 32 \frac{\text{mg O}_2}{\text{L}} \\ & = 533.44 \frac{\text{mg O}_2}{\text{L}} \end{aligned}$$

# Biochemical Oxygen Demand (BOD)

- Microbiologically-mediated degradation of organic material (redox reaction) in water using dissolved oxygen.
- $\text{BOD} + \text{DO} \rightarrow \text{products}$
- Consider a batch reactor,

$$\frac{d[\text{BOD}]}{dt} = -R = -k[\text{BOD}]$$

*Handwritten red annotations: a small 'x' above the second equation, and a red arrow pointing from the crossed-out  $[\text{BOD}]$  term in the first equation to the  $[\text{DO}]$  term in the second equation.*

$$\frac{d[\text{DO}]}{dt} = -R = -k[\text{DO}]$$

where  $[\text{BOD}](t=0) = \text{BOD}_0$ ;  $[\text{DO}](t=0) = \text{DO}_0$



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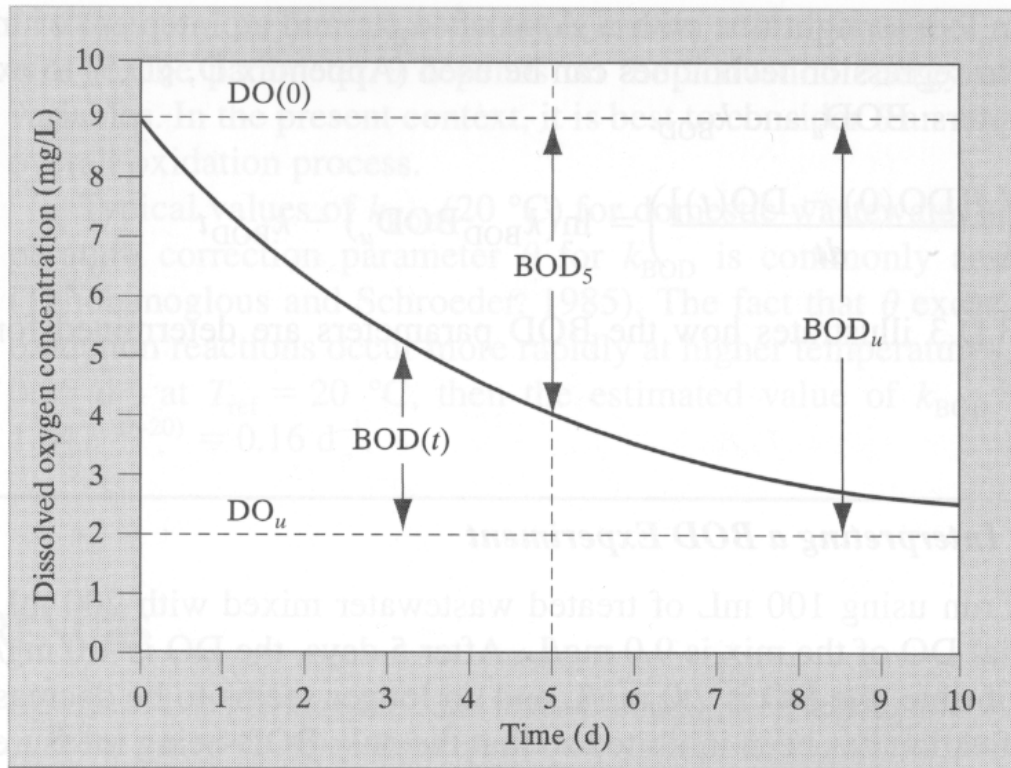




# BOD

$$\text{BOD}(t) = \text{BOD}_u \exp(-k_{\text{BOD}} t)$$

$$\text{DO}(t) = \text{DO}(0) - \text{BOD}_u [1 - \exp(-k_{\text{BOD}} t)]$$



**Figure 3.D.5** Idealized decrease in dissolved oxygen concentration in a batch reactor during measurement of BOD.

# BOD

How to determine  $k_{\text{BOD}}$  and  $\text{BOD}_u$ ?

- Conduct experiment to determine  $\text{DO}(0)$  &  $\text{DO}(t)$ .
- Fit data by plotting natural logarithm of time derivative of  $(\text{DO}(t) - \text{DO}(0))$  against time:

$$\ln\left(\frac{d[\text{DO}(0) - \text{DO}(t)]}{dt}\right) = \ln(k_{\text{BOD}} \text{BOD}_u) - k_{\text{BOD}} t$$

- Slope =  $-k_{\text{BOD}}$
- Y Intercept =  $\ln(k_{\text{BOD}} \times \text{BOD}_u)$

**END**