

ESE5001 Environmental Engineering Principles

Lecture Notes Chemical Principles

Introduction

- *Lecturer:*
Associate Prof. Ng How Yong
E2-02-21
Tel: 65164777
Email: howyongng@nus.edu.sg

Concentrations and Units of Measurement

Concentrations: Quantity of species per volume

Common Units:

1. Moles per Volume

Eg. $M = \frac{mol}{L}$ (in H₂O, 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 g cm^{-3}
- Salt water: 1.03 g cm^{-3}
 - Pressure has very little influence on density of water
 - Temperature (Yes)

– Air (293K, 1 atm): 1.2 kg m^{-3}

1.2 mg cm^{-3}

Air ~ 1000 x less dense than water

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 _____ Fraction
- In Water always means _____ 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 Na^+ in solution.

Soln:

Concentrations and Units of Measurement Example

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 $1\ \text{g/mL}$.

Soln

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?

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:

Unit Conversion

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

Therefore:

<u>Mass Conc</u>		<u>Mass Fraction</u>
1 $\mu\text{g/L}$	\equiv	1 ppb
1 mg/L	\equiv	1 ppm

Eg. Benzene (C_6H_6): WHO standard in drinking water = 10 $\mu\text{g/L}$, as mass fraction?

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

Consider 1 m^3 of air,

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

Unit Conversion

Mass Fraction to Mass Concentration:

$$C_i = \rho_s X_i$$

where ρ_s = solution density (with units of
mass per volume).

X_i = mass fraction

Impurities

- Components
- Constituents
- Impurities
- Contaminants
- Pollutants

Impurities

- Inorganic versus Organic (H_2S vs. Benzene)
- Ionic versus nonionic (HCO_3^- vs. SiO_2)
- Elements versus compounds (Pb vs. HCHO)
- Molecular versus particulate (O_2 vs. clay grain)
- Abiotic versus Biotic (soot vs. bacterium)

Impurities

Example of impurity classes — Gases in H_2O

- Air & water in equilibrium
- O_2 in H_2O depends on amount in air & originally in H_2O

Henry's Law

1st form: $C_w = K_{H,g} \times P_g$
(M) (M atm⁻¹) (in atm)

2nd form: $P_g = H_g \times C_w$
(atm) (atm M⁻¹) (M)

i.e. Henry's law constants relationship:

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

Henry's Law Constant for Water

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

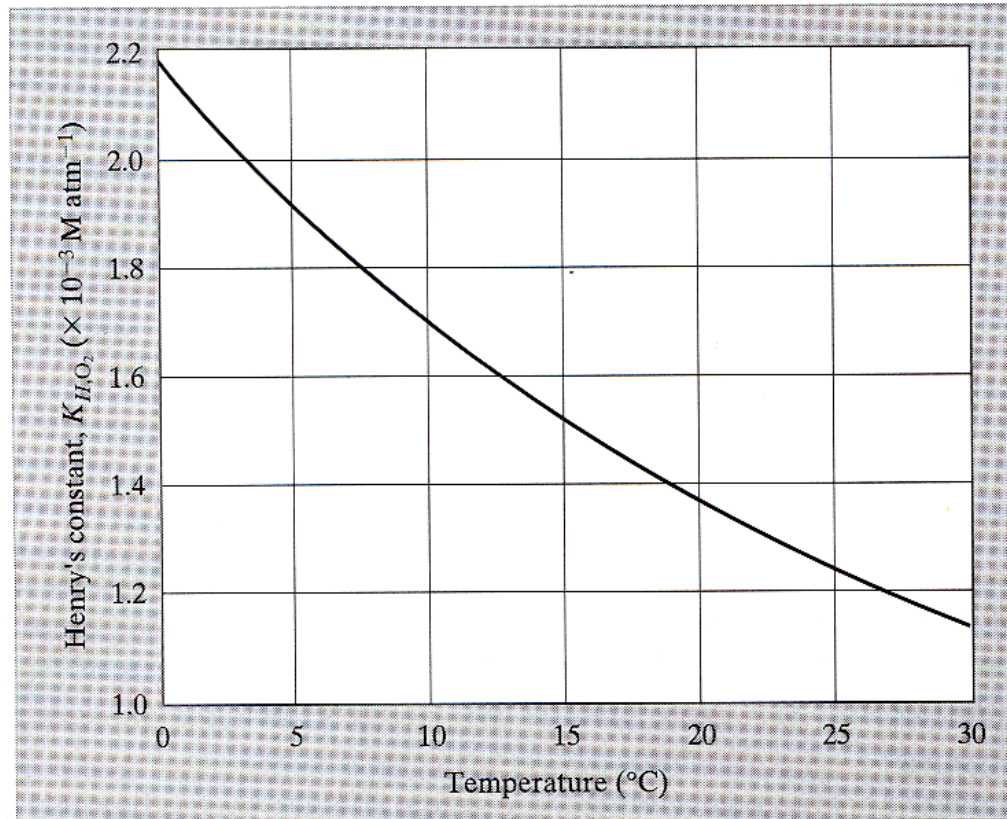
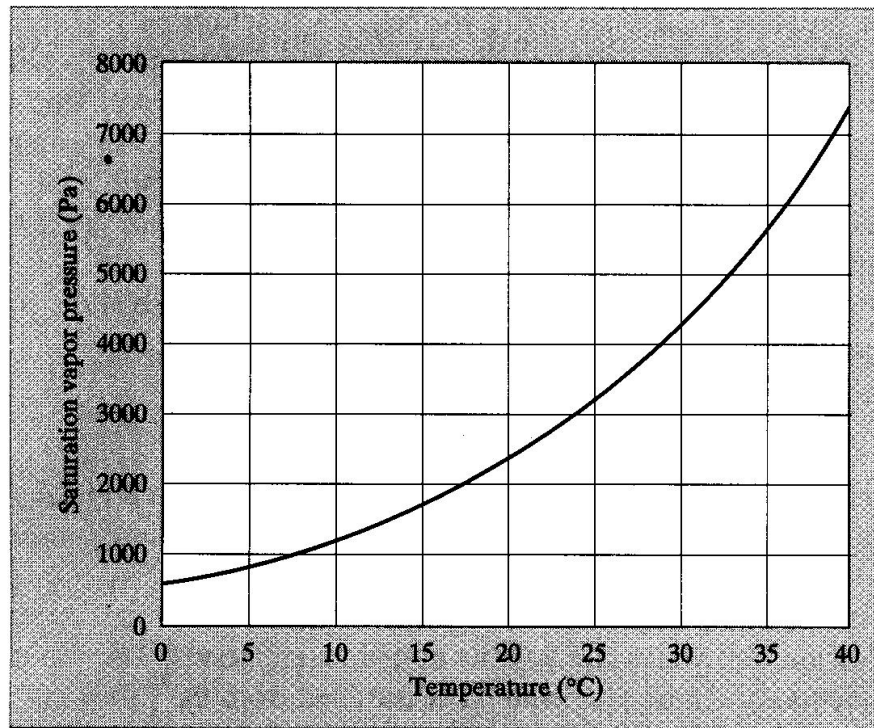


Figure 3.B.2 Henry's law constant for oxygen (O_2) in distilled water as a function of temperature (Whipple and Whipple, 1911).

H₂O Vapor in AIR



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

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

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

$Y_{H_2O} =$

Relative Humidity = Actual partial pressure/Sat. vapor pressure

O₂ in H₂O

At Temp. = 20°C,

$$K_{H, O_2} = \quad \text{M atm}^{-1}$$

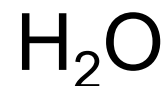
$$[O_2] = K_{H, O_2} \times P_{O_2}$$

At sea level: $P_{O_2} =$,

$$[O_2] =$$

When bottle opened at Genting Highlands (2 km) above sea level, $[O_2]$?

Ionic Impurities in H₂O



1. $K_w = [\text{H}^+][\text{OH}^-] = 10^{-14} \text{ M}^2$
in pure H₂O, eq. conc. of H⁺, OH⁻ ?
2. Relationship: $[\text{H}^+] = [\text{OH}^-]$
→ $[\text{H}^+] = 10^{-7} \text{ M}$

Steps:

1. Unknowns
2. Relationships
3. Solve mathematically

pH

Note:

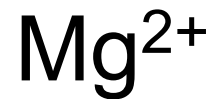
$$\text{pH} \equiv -\log_{10} [\text{H}^+]$$

Except when in highly concentrated solution,
[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:

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

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 ²⁺	93.8		HCO ₃ ⁻	164.7
Mg ²⁺	28.0		SO ₄ ²⁻	134.0
Na ⁺	13.7		Cl ⁻	92.5
K ⁺	30.2			

Approach:

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

Electroneutrality

Solution:

Cation	Conc mg/L	Conc M	meq /L	Anion	Conc mg/L	Conc mM	meq/L
Ca ²⁺	93.8	2.34	4.68	HCO ₃ ⁻	167.4	2.74	2.74
Mg ²⁺	28.0	1.15	2.30	SO ₄ ²⁻	134.0	1.39	2.79
Na ⁺	13.7	0.60	0.60	Cl ⁻	92.5	2.61	2.61
K ⁺	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**.

Ionic Strength

- Intensity of electric field in a solution

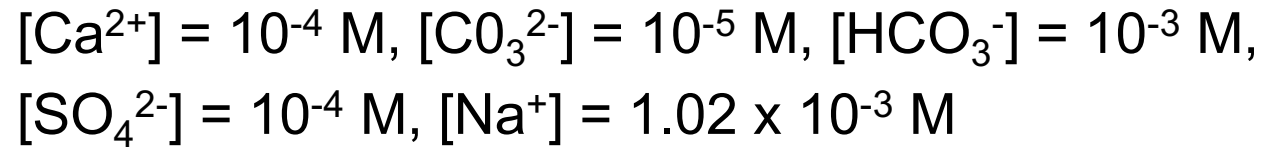
$$\mu = \frac{1}{2} \sum_i z_i^2 [i] \quad [=] \text{ M}$$

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:



Ionic Strength

Find the ionic strength of solution with 50 mg/L of NaCl & 100 mg/L of CaSO_4 .

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, γ_i (Debye-Hückey 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 MgCl_2 and 0.02 M Na_2SO_4 .

Soln: When salts are dissolved:

Ion	C (M)	Z	CZ^2
Mg^{2+}	0.01	+2	0.04
Na^+	0.04	+1	0.04
Cl^-	0.02	-1	0.02
SO_4^{2-}	0.02	-2	0.08
		$\Sigma C_i Z_i^2 =$	0.18

Ion	Activity Coefficient (γ)	Activity (γC)
Mg^{2+}	0.35	0.0035
Na^+	0.77	0.031
Cl^-	0.77	0.015
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 multivalents ions
→ scales in hot-water pipes, heaters, boilers, teapots & precipitates in soap water.
- Expressed as normality (eq/L or meq/L) or as CaCO_3
- Each mole of 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 CaCO_3 .

Classification	Hardness (meq/L)	Hardness (mg/L as CaCO_3)
Soft	< 1.5	< 7.5
Moderately hard	1.5 – 3	75 -100
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 CO_3^{2-} & 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 (Ca^{2+}) and magnesium (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 CO_3^- , HCO_3^- & 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 ~ 4.5 . Amount of acid added per liter of water sample is the measured alkalinity.

Alkalinity

Eg. NaHCO_3 dissolved in H_2O

Adding vinegar \rightarrow bubbling due to CO_2

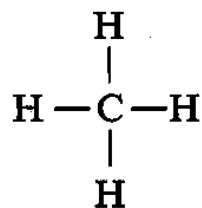
Organics

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

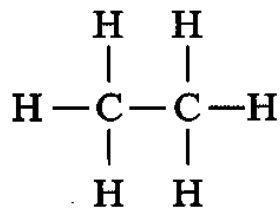
Table C.1 Number of Bonds Associated with Elements in Organic Molecules

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

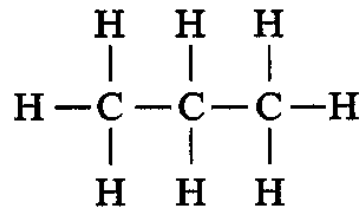
Organics: Alkanes



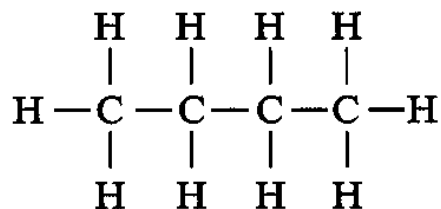
Methane



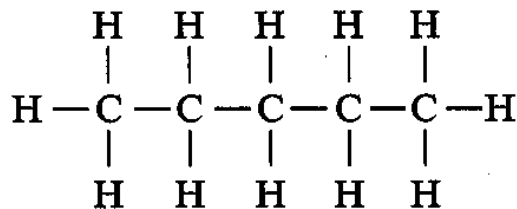
Ethane



Propane



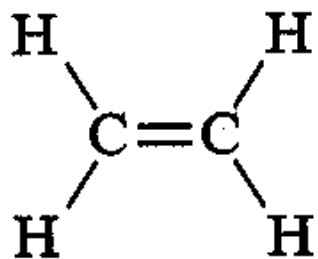
n-Butane



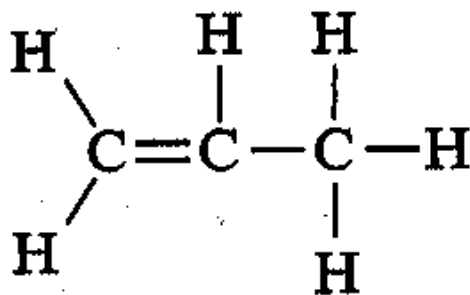
n-Pentane

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

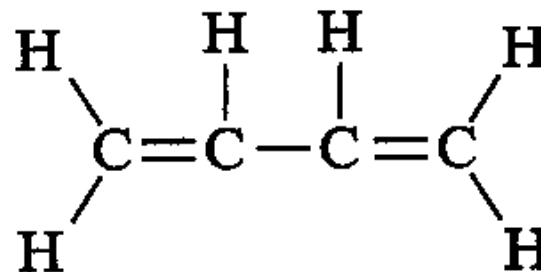
Organics: Alkenes



Ethene



Propene



1,3-Butadiene

Figure C.2 Structures of some alkenes.

Organics: Aromatic

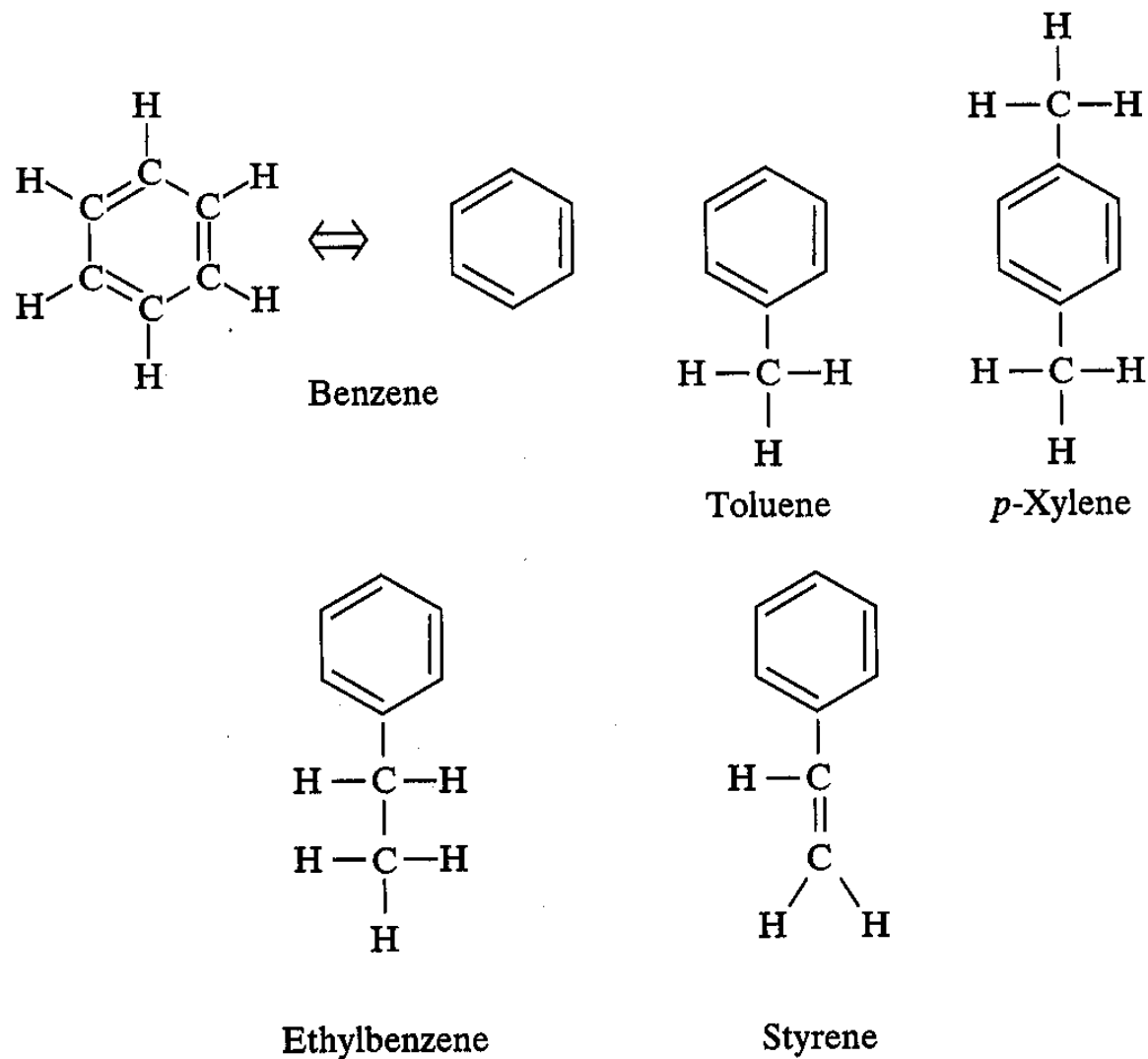


Figure C.3 Some aromatic compounds.

Organics: Oxygenated

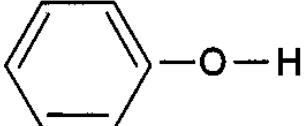
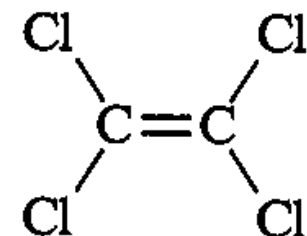
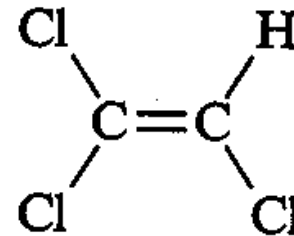
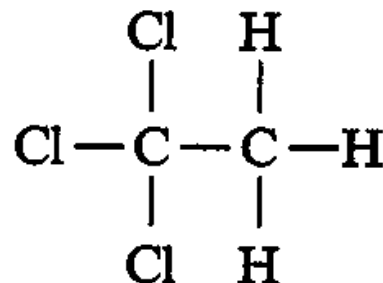
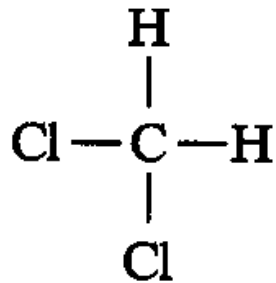
Class	Structure	Example	
Alcohol (aliphatic)	$R-O-H$	$ \begin{array}{c} H \\ \\ H-C-O-H \\ \\ H \end{array} $	Methanol
Aldehyde	$ \begin{array}{c} O \\ \\ R-C-H \end{array} $	$ \begin{array}{c} H \quad H \quad O \\ \diagdown \quad \quad \\ C=C-C-H \\ \diagup \\ H \end{array} $	Acrolein
Ketone	$ \begin{array}{c} O \\ \\ R-C-R' \end{array} $	$ \begin{array}{c} H \quad O \quad H \\ \quad \quad \\ H-C-C-C-H \\ \quad \quad \\ H \quad \quad H \end{array} $	Acetone
Phenol	$\phi-O-H$		Phenol

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}{ccc} H & & H \\ & & \\ H-C-S-C-H \\ & & \\ H & & H \end{array} $ Dimethyl sulfide
Amine (primary)	$ \begin{array}{c} H \\ \diagup \\ R-N \\ \diagdown \\ H \end{array} $	$ \begin{array}{ccc} H & & H \\ & & \diagup \\ H-C-N \\ & & \diagdown \\ 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} $ <i>N</i> -Nitroso-dimethylamine

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

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

Equilibrium

Relationship (or data)

Henry' s Law

Solubility

Solubility

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 ₃ H ₆ O	58	28,600
Benzene	C ₆ H ₆	78	12,800
Benzo(a)pyrene	C ₂₀ H ₁₂	252	7×10^{-7}
Chloroform	CHCl ₃	119.4	26,000
Dieldrin	C ₁₂ H ₈ Cl ₆ O	380	7×10^{-4}
Ethylbenzene	C ₈ H ₁₀	106	1,280
Ethylene dibromide	CH ₂ Br ₂	176	270
<i>n</i> -Octane	C ₈ H ₁₈	114	1,890
Naphthalene	C ₁₀ H ₈	128	10.6
Phenol	C ₆ H ₆ O	94	26
2,3,7,8-TCDD	C ₁₂ H ₄ O ₂ Cl ₄	322	2×10^{-7}
Tetrachloroethylene	C ₂ Cl ₄	166	2,550
Toluene	C ₇ H ₈	92	3,850
1,1,1-Trichloroethane	C ₂ H ₃ Cl ₃	133.4	16,800
Trichloroethylene	C ₂ HCl ₃	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 ⁻¹)	H_g (atm M ⁻¹)	Temperature (°C)
Ammonia ^a	NH ₃	62	0.016	25
Benzene	C ₆ H ₆	0.18	5.6	20
Benzo(<i>a</i>)pyrene	C ₂₀ H ₁₂	2040	4.9×10^{-4}	20
Carbon dioxide ^a	CO ₂	0.034	29	25
Carbon monoxide	CO	0.0010	1000	20
Chloroform	CHCl ₃	0.31	3.2	20
Ethylbenzene	C ₈ H ₁₀	0.11	9.1	20
Formaldehyde	HCHO	6300	1.6×10^{-4}	25
Hydrogen sulfide ^a	H ₂ S	0.115	8.7	20
Methane	CH ₄	0.0015	670	20
Naphthalene	C ₁₀ H ₈	2.2	0.45	20
Nitric acid ^a	HNO ₃	2.1×10^5	4.8×10^{-6}	25
Nitrogen	N ₂	0.00067	1500	20
Oxygen	O ₂	0.00138	720	20
Phenol	C ₆ H ₆ O	2200	4.5×10^{-4}	20
Sulfur dioxide ^a	SO ₂	1.24	0.81	25
Tetrachloroethylene	C ₂ Cl ₄	0.083	12	20
Toluene	C ₇ H ₈	0.15	6.7	20
1,1,1-Trichloroethane	C ₂ H ₃ Cl ₃	0.055	18	20
Trichloroethylene	C ₂ HCl ₃	0.11	9.1	20

^aThese 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) ^a
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 ^b	0.72
Naphthalene ^b	31
Phenol	93,000
2,3,7,8-TCDD	0.0002
Tetrachloroethylene	200
Toluene	535
1,1,1-Trichloroethane	4,400
Trichloroethylene	1,100

^aAt 20 °C unless otherwise noted.

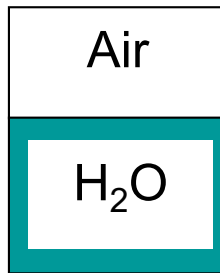
^bAt 25 °C.

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

Water-Gas Partitioning

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

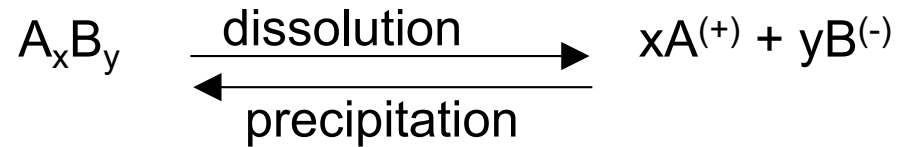
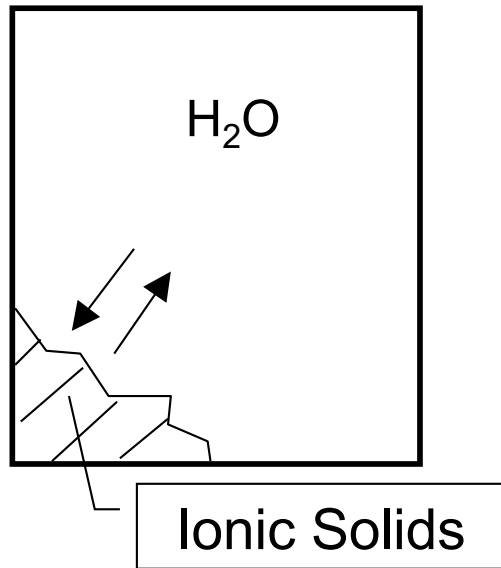
- Eg. 3.11



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

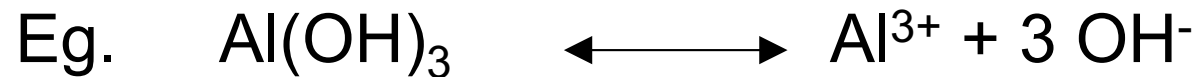
← Add 1 g of CHCl₃ in 2 L vessel

Solid Solubility



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

Note: Valid only if solid is present at Equilibrium!



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

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

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	$\text{Al}(\text{OH})_3 \rightleftharpoons \text{Al}^{3+} + 3 \text{OH}^-$	$1 \times 10^{-32} \text{ M}^4$	$2 \times 10^{-32} \text{ M}^4$
Cadmium hydroxide	$\text{Cd}(\text{OH})_2 \rightleftharpoons \text{Cd}^{2+} + 2 \text{OH}^-$	$2 \times 10^{-14} \text{ M}^3$	$5.9 \times 10^{-15} \text{ M}^3$
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	$\text{Ca}(\text{OH})_2 \rightleftharpoons \text{Ca}^{2+} + 2 \text{OH}^-$	$8 \times 10^{-6} \text{ M}^3$	$5.5 \times 10^{-6} \text{ M}^3$
Calcium phosphate	$\text{Ca}_3(\text{PO}_4)_2 \rightleftharpoons 3 \text{Ca}^{2+} + 2 \text{PO}_4^{3-}$	$1 \times 10^{-27} \text{ M}^5$	$2.0 \times 10^{-29} \text{ M}^5$
Calcium sulfate	$\text{CaSO}_4 \rightleftharpoons \text{Ca}^{2+} + \text{SO}_4^{2-}$	$2 \times 10^{-5} \text{ M}^2$	$1.9 \times 10^{-4} \text{ M}^2$
Chromium(III) hydroxide	$\text{Cr}(\text{OH})_3 \rightleftharpoons \text{Cr}^{3+} + 3 \text{OH}^-$	$6 \times 10^{-31} \text{ M}^4$	$6 \times 10^{-31} \text{ M}^4$
Iron(II) hydroxide	$\text{Fe}(\text{OH})_2 \rightleftharpoons \text{Fe}^{2+} + 2 \text{OH}^-$	$5 \times 10^{-15} \text{ M}^3$	$8 \times 10^{-16} \text{ M}^3$
Iron(III) hydroxide	$\text{Fe}(\text{OH})_3 \rightleftharpoons \text{Fe}^{3+} + 3 \text{OH}^-$	$6 \times 10^{-38} \text{ M}^4$	$4 \times 10^{-38} \text{ M}^4$
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	$\text{Mg}(\text{OH})_2 \rightleftharpoons \text{Mg}^{2+} + 2 \text{OH}^-$	$9 \times 10^{-12} \text{ M}^3$	$1.2 \times 10^{-11} \text{ M}^3$
Nickel hydroxide	$\text{Ni}(\text{OH})_2 \rightleftharpoons \text{Ni}^{2+} + 2 \text{OH}^-$	$2 \times 10^{-16} \text{ M}^3$	$6.5 \times 10^{-18} \text{ M}^3$

^aSawyer et al., 1994, p. 38.

^bBenefield and Morgan, 1990.

Solid Solubility



At Equilibrium,

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

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.

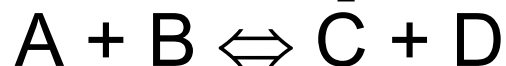


Chemical Equilibrium

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:

$$R_f = k_f [A][B]$$

2) Rate of reaction in reverse direction:

$$R_r = k_r [C][D]$$

At equilibrium: $R_f = R_r$

$$\rightarrow k_f [A][B] = k_r [C][D]$$

or

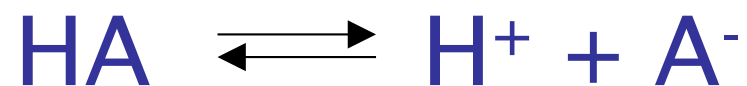
$$\frac{[C][D]}{[A][B]} = \frac{k_f}{k_r} = K$$

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

Acid-Base Reaction

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

A generic expression:



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

Strength of Acid

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

- Strong acid: $\text{p}K_A \leq 1$ (fully dissociate)
- Weak acid: $\text{p}K_A \geq 1$ (partially dissociate)

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	HClO_4	-7
Hydrochloric acid	HCl	-3
Sulfuric acid	H_2SO_4	-3
Nitric acid	HNO_3	-1.2
Sulfonic acid	H_2SO_3	1.89
Bisulfate	HSO_4^-	1.92
Phosphoric acid	H_3PO_4	2.12
Acetic acid	CH_3COOH	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	H_2CO_3	6.35
Hydrogen sulfide	H_2S	7.1
Dihydrogen phosphate	H_2PO_4^-	7.21
Bisulfite	HSO_3^-	7.22
Hypochlorous acid	HOCl	7.6
Hydrogen cyanide	HCN	9.2
Ammonium	NH_4^+	9.23
Bicarbonate	HCO_3^-	10.33
Hydrogen phosphate	HPO_4^{2-}	12.32
Bisulfide	HS^-	12.9

Acid-Base Reaction

- $pK_A = pH \rightarrow 50\%$ of acid is dissociated.
- If $pH \gg pK_A$, acid is fully _____
- If $pH \ll pK_A$, acid is fully _____

Acid-Base Reaction Example: Carbonate System

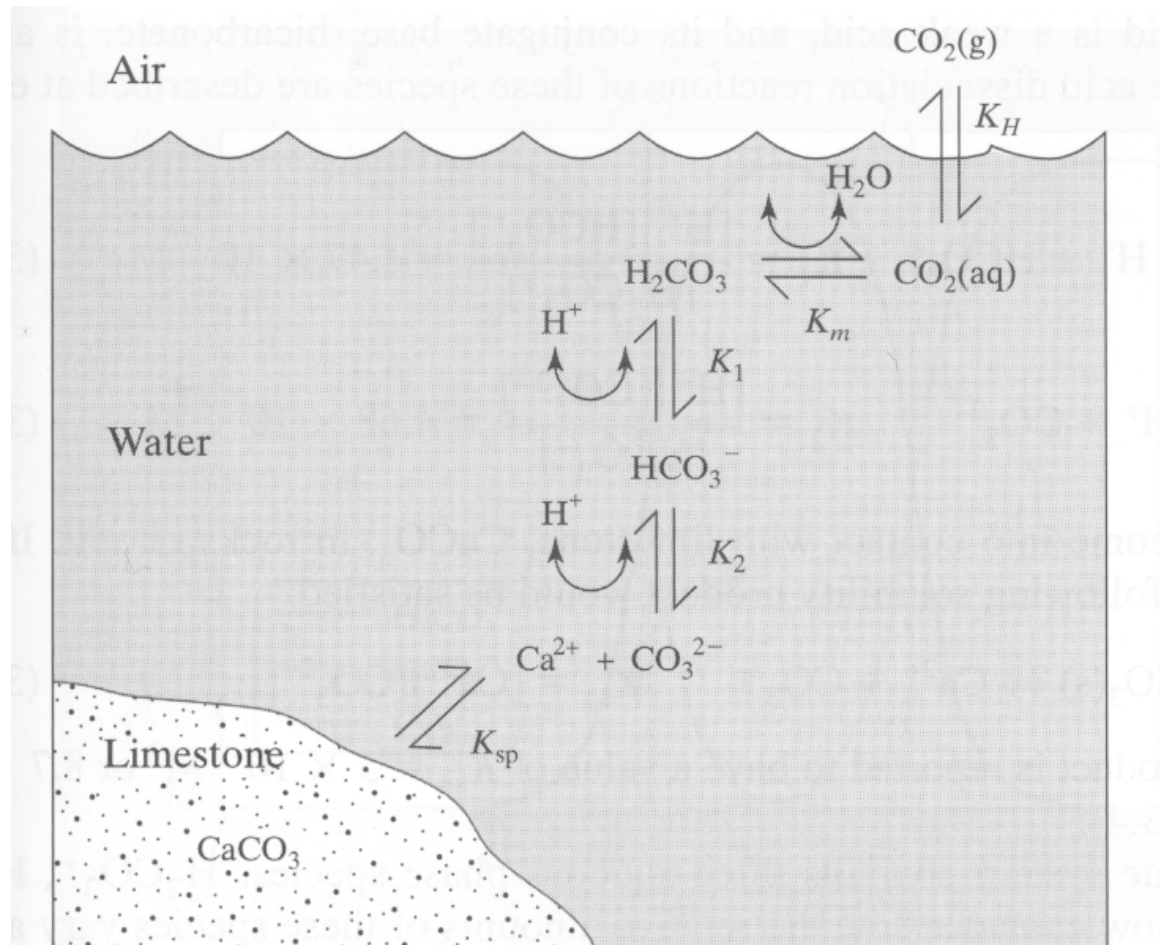
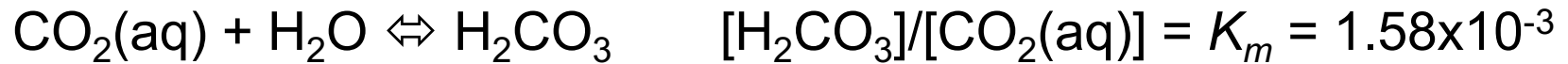


Figure 3.C.1 Species and transformations for the carbonate system in natural air-water-limestone environments.

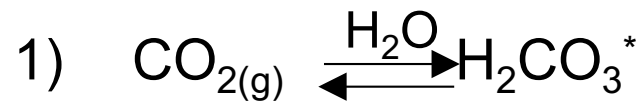
Acid-Base Reaction Example: Carbonate System

Species involved: $\text{CO}_{2(g)}$, H_2CO_3^* , HCO_3^- , CO_3^{2-} .

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



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



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



$$K_{C1} = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3^*]}$$



$$K_{C2} = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$$

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): $[\text{H}^+]$, $[\text{OH}^-]$, $[\text{HCO}_3^-]$,

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:

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

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

^aThese species participate in acid-base reactions when dissolved in water. The coefficients listed refer to the solubility of the unreacted species only.

pK_A

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

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

Chemical Equilibrium

- How to solve using a spread sheet?

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

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
3	1.00E-03	1.00E-11	3.04E-05	1.42E-12	9.70E-04
4	1.00E-04	1.00E-10	3.04E-04	1.42E-10	-2.04E-04
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
3.7	2.00E-04	5.01E-11	1.52E-04	3.57E-11	4.72E-05
3.8	1.58E-04	6.31E-11	1.92E-04	5.66E-11	-3.33E-05
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
3.75	1.78E-04	5.62E-11	1.71E-04	4.50E-11	6.90E-06
3.76	1.74E-04	5.75E-11	1.75E-04	4.71E-11	-1.13E-06
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

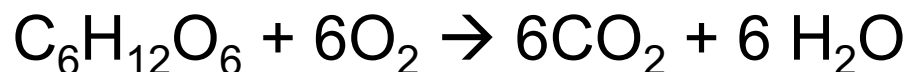
Answer: pH = 3.76

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?

Chemical Kinetics

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

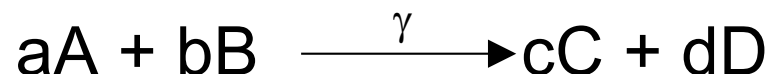


- Glucose in sterile (no bugs) distilled H_2O at pH 7 in contact with air is stable “forever”, i.e., a kinetic barrier to its oxidation.
- When pH is > 13 , oxidation will occur.
- Methylene Blue (MeB) is a redox indicator which is blue when O_2 is present and colourless when O_2 is absent.
 $\text{H}_2\text{O} + \text{Glucose} + \text{O}_2 + \text{MeB} @ \text{pH} > 7 \rightarrow \text{blue}$
 $\text{H}_2\text{O} + \text{Glucose} + \text{O}_2 + \text{MeB} @ \text{pH} > 13 \rightarrow \text{colourless}$

Chemical Kinetics

Definitions

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



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

&

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

k_{γ} = reaction rate constant

Chemical Kinetics

- Example of Rate Calculations: Reaction of disinfectant HOCL (hypochlorous acid) with NH_3 (ammonia) to form NH_2Cl (monochloramine):



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

If initial NH_3 and HOCL concentrations are both 10^{-3} M , what is the overall reaction rate?

Chemical Kinetics

Batch Reactor

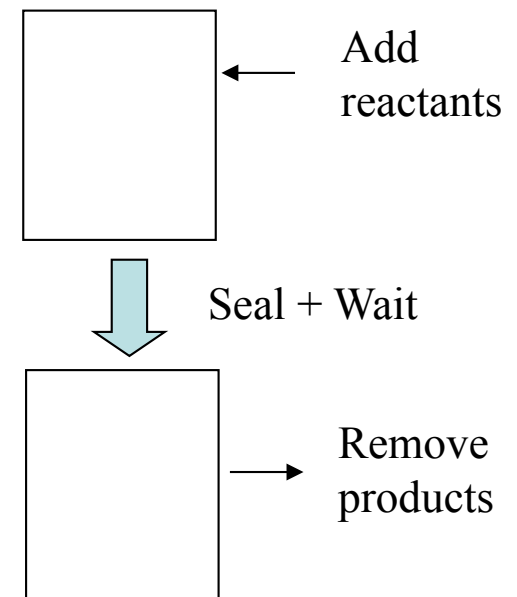
Consider chemical reaction in batch reactor.

1st 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) 1st Order Decay Reaction

Consider chemical reaction in batch reactor.

1st order decay rxn.: $A \xrightarrow{1} \text{products}$

Rate Law: $R_1 = k_1[A]$

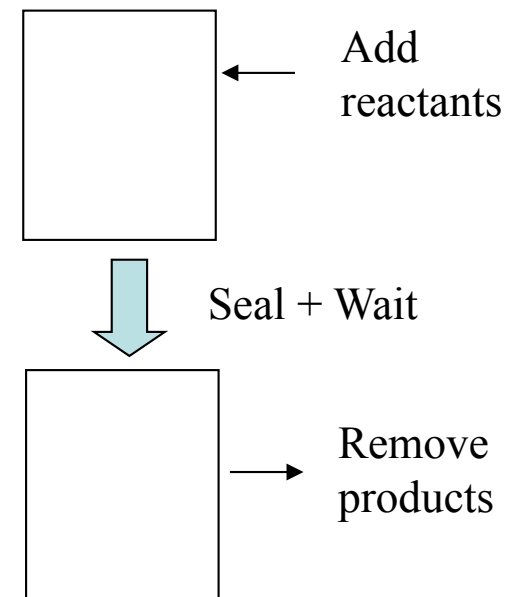
$$\frac{d[A]}{dt} = -R_1 = -k_1[A]$$

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

Characteristics time,

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

$$\tau \sim \frac{A}{k_1 A_0} = \frac{1}{k_1}$$

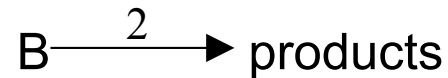


Chemical Kinetics

Other variations:

2) 0th Order Decay Reaction:

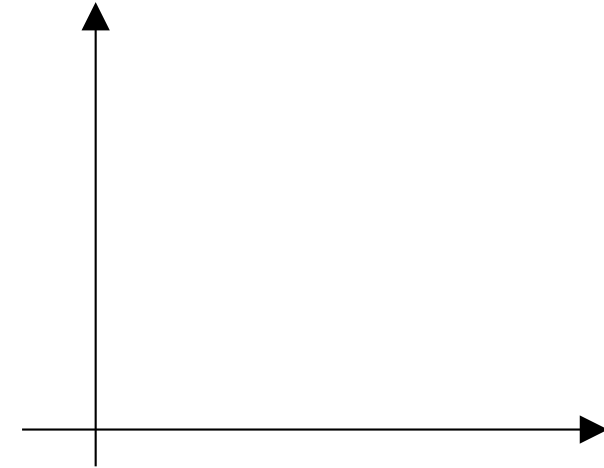
(provided $[B] \gg 0$)



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

In a batch reactor,

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



- Characteristics time,

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

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

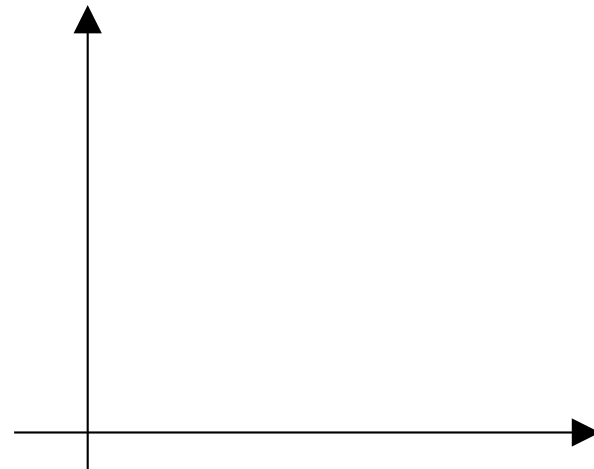
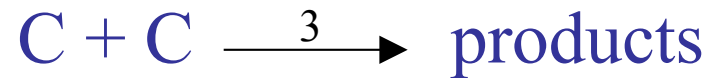
$$\tau \sim \frac{B_0}{k_2}$$

Chemical Kinetics

3) i) 2th Order Decay Reaction:

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

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



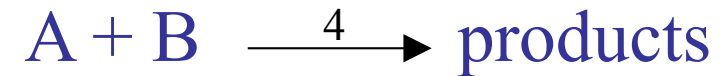
- Characteristics time,

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

$$\tau \sim$$

Chemical Kinetics

3. ii) 2th Order Decay Reaction:



Rate Law: $R_4 = k_4[A][B]$ Note: 1st order in [A] & [B]; 2nd 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:
$$\tau \sim \frac{\min(A_o, B_o)}{k_4 A_o B_o}$$

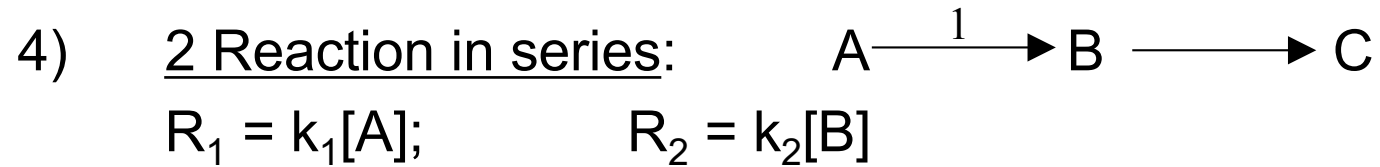
If $A_o = B_o$, all A_o and B_o will be consumed.

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

Case 2: (Function of A but not B)

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

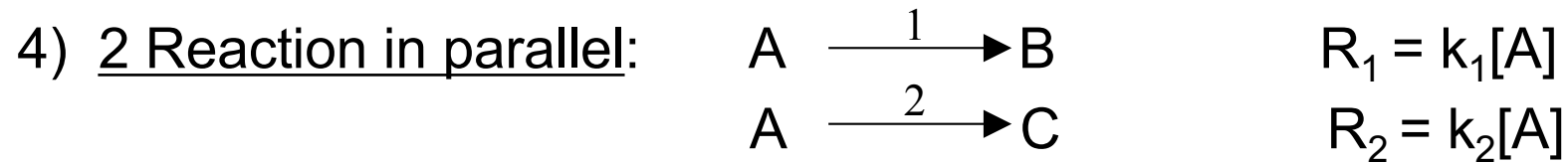
Chemical Kinetics



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

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

Chemical Kinetics



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

Given $[A](t=0) = A_0$, $[A](t) =$

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

$$\frac{d[B]}{dt} =$$

Chemical Kinetics

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

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

- 2nd 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, O₂ and H₂
2. Sum of oxidation state for compound = ionic charge (element or molecule)
3. O in compound is -II
4. H in compound is +I

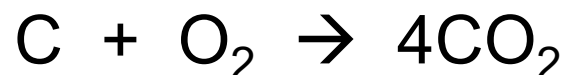
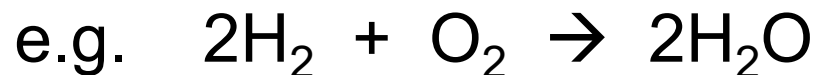
Oxidation State

Example: Determine the oxidation number of C in

i) CO_2 , ii) CO_3^{2-} , iii) HCO_3^- and iv) $\text{C}_2\text{H}_4\text{O}_2$

Oxidation/Reduction

- Involve a change in oxidation state of reactants



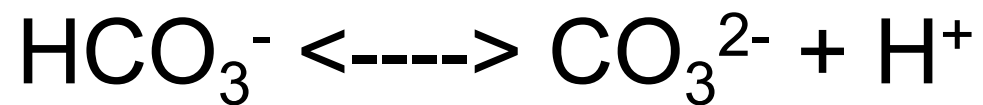
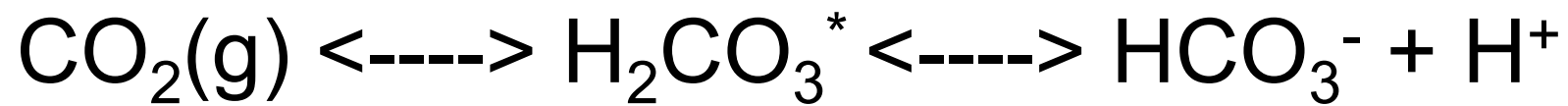
Note: sum of oxidation states on both sides of equations are equal – a requirement for a balanced redox reaction.

In last equation,

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

Cl_2 is an **oxidizing agent**; it gains e^- ; it becomes reduced.

Considering C in:



Balancing Redox Reaction – Electron Balancing Method

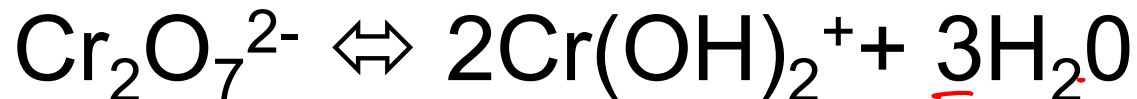
- Consist of two half reactions – an oxidation half-reaction and a reduction half reaction
- Steps:
 1. For each $\frac{1}{2}$ rxn, balance major species (anything but O & H)
 2. For each $\frac{1}{2}$ rxn, balance any O with H_2O
 3. For each $\frac{1}{2}$ rxn, balance any H with H^+
 4. For each $\frac{1}{2}$ rxn, balance charge with e^-
 5. Balance both $\frac{1}{2}$ rxns by eliminating e^-
 6. If solution is alkaline (high pH), cancel out any H^+ by adding OH^- to both side of rxn; sum up H_2O

Previous Example

1. Balance major species:



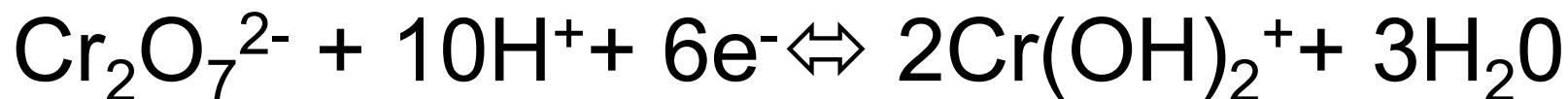
2. Balance any O with H_2O



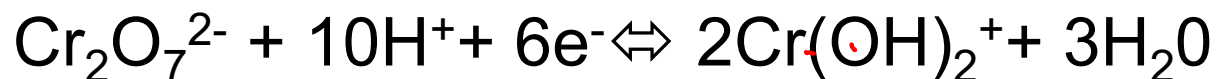
3. Balance any H with H^+



4. Balance charge with e^-



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



Another Example

Balance the reaction in which ferrous iron (Fe^{2+}) is converted to ferric iron (Fe^{3+}) by permanganate (MnO_4^-), which itself is reduced to manganese dioxide ($\text{MnO}_{2(s)}$). The reaction takes place in alkaline solution.

1. Balance major species:



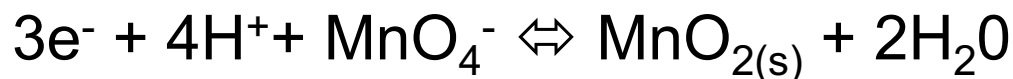
2. Balance any O with H_2O



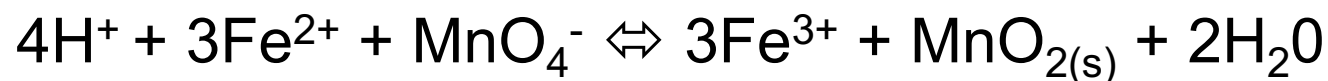
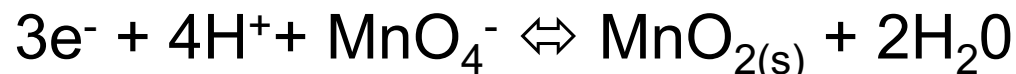
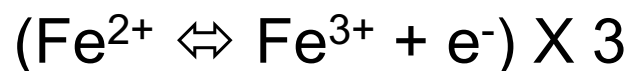
3. Balance any H with H^+



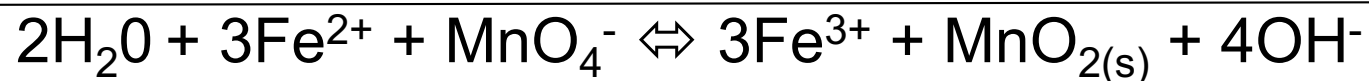
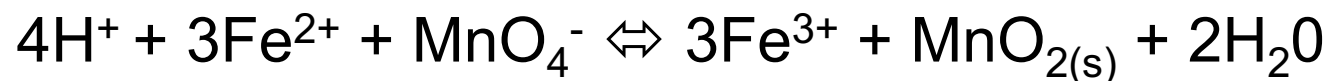
4. Balance charge with e^-



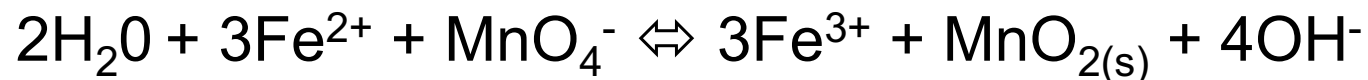
5. Balance both $\frac{1}{2}$ rxns by eliminating e^-



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



7. In alkaline soln, Fe^{3+} will combine with 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 Fe^{3+}

Corrosion



Corrosion

Typical corrosion reaction of metal in oxygen containing H₂O:



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

Consider $\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 \rightarrow 6\text{CO}_2 + 6\text{H}_2\text{O}$

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,

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

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

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

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BOD

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

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

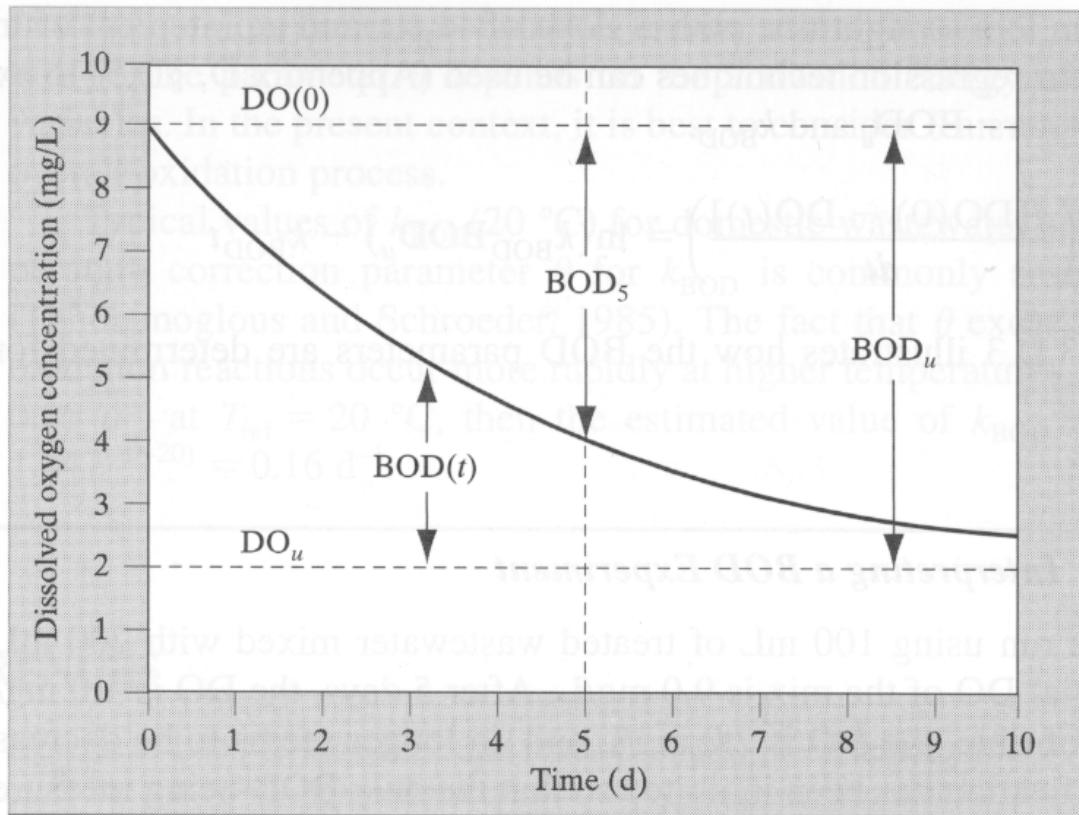


Figure 3.D.5 Idealized decrease in dissolved oxygen concentration in a batch reactor during measurement of BOD.

BOD

How to determine k_{BOD} and 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