## Fundamental Principles of Environmental Engheering

By Dr. Abdelmeguid E. Aboubaraka


## Process selection

## Contaminant Properties

Source water quality
Removal efficiency

## Reliability

Flexibility
Sustainability and Energy Considerations

## Cost

Utility Experience

## Successful Operating History

Desired finished-water quality


## Life-Cycle Assessment of Water Treatment Facilities

Specific energy consumption during pumping

## plant <br> operation

## operating <br> the treatment

 facility ( $80 \%$ )decommissioning the plant after its useful life(1 \%)

Chemicals
and
consumable

Waste

## Specific energy <br> consumption during pumping

$$
P_{W}=\frac{Q_{F} P}{e}
$$

where $\quad P_{W}=$ power, W (or rate of energy consumption, $\mathrm{kWh} / \mathrm{d}$ )
$Q_{F}=$ feed water flow rate, $\mathrm{m}^{3} / \mathrm{d}$ or ML/d
$P=$ pressure, Pa
$e=$ efficiency

$$
P=\rho g h
$$

$$
\text { where } \begin{aligned}
& \rho=\text { density of fluid, } \mathrm{kg} / \mathrm{m}^{3} \\
& g=\text { gravitational constant }, 9.81 \mathrm{~m} / \mathrm{s}^{2} \\
& h=\text { head }, \mathrm{m}
\end{aligned}
$$

Specific energy consumption is the energy consumed per unit volume of water produced and can be calculated from

$$
E=\frac{P_{W}}{Q_{P}}
$$

where $\quad E=$ specific energy consumption, $\mathrm{kWh} / \mathrm{m}^{3}$

$$
Q_{P}=\text { product water flow rate }, \mathrm{m}^{3} / \mathrm{d} \text { or } \mathrm{ML} / \mathrm{d}
$$

$$
r=\frac{Q_{P}}{Q_{F}}
$$

where $\quad r=$ is the recovery.

Calculate the specific energy consumption of the following cases

A- Reverse osmosis (RO) system designed to produce $19,000 \mathrm{~m}^{3} / \mathrm{d}\left(\mathrm{Q}_{\mathrm{p}}\right)$ ( 5 mgd ) at 80 percent recovery. The RO feed pumps operate at 16 bar ( 232 psi ) and 87 percent efficiency

B- Distribution pumps operating at $3785 \mathrm{~m}^{3} / \mathrm{d}$ ( 1 mgd ), 90 m head $(295 \mathrm{ft})$, and 85 percent efficiency.

Solution
Part 1

1. Calculate the feed water flow using

$$
r=\frac{\mathbf{Q}_{p}}{\mathbf{Q}_{r}}
$$

$$
\mathrm{Q}_{\mathrm{F}}=\mathrm{Q}_{\mathrm{p}} / \mathrm{r}=\left(19,000 \mathrm{~m}^{3} / \mathrm{d}\right) /(0.80)=23,750 \mathrm{~m}^{3} / \mathrm{d}
$$

Calculate the pump power

$$
\begin{aligned}
& 1 \mathrm{bar}=105 \mathrm{~N} / \mathrm{m}^{2} \\
& 1 \mathrm{~N} \cdot \mathrm{~m}=1 \mathrm{~J}=1 \mathrm{~W} \cdot \mathrm{~s}, \quad P_{\mathrm{w}}=\frac{Q_{F} P}{e}=\frac{\left(23,750 \mathrm{~m}^{3} / \mathrm{d}\right)\left(16 \times 10^{5} \mathrm{~N} / \mathrm{m}^{2}\right)}{0.87(86,400 \mathrm{~s} / \mathrm{d})} \\
& \text { so } 1 \mathrm{kWh}=3.6 \times 10^{6} \mathrm{~N} \cdot \mathrm{~m} \quad=5.06 \times 10^{5} \mathrm{~N} \cdot \mathrm{~m} / \mathrm{s}=506 \mathrm{~kW}
\end{aligned}
$$

Calculate specific energy consumption

$$
E=\frac{P_{W}}{Q_{P}}=\frac{506 \mathrm{~kW}(24 \mathrm{~h} / \mathrm{d})}{19,000 \mathrm{~m}^{3} / \mathrm{d}}=0.64 \mathrm{kWh} / \mathrm{m}^{3}
$$

Part Calculate the pressure produced by the pump $1 \mathrm{~N}=1 \mathrm{~kg} \cdot \mathrm{~m} / \mathrm{s}^{2}$
2

$$
P=\rho g h=\left(1000 \mathrm{~kg} / \mathrm{m}^{3}\right)\left(9.81 \mathrm{~m} / \mathrm{s}^{\mathrm{z}}\right)(90
$$

$$
\mathrm{m})=8.83 \times 10^{5} \mathrm{~N} / \mathrm{m}^{2}
$$

Calculate specific energy consumption Note that QF = QP so the flow cancels out

$$
E=\frac{P}{e}=\frac{8.83 \times 10^{5} \mathrm{~N} / \mathrm{m}^{2}}{0.85}\left(\frac{1 \mathrm{kWh}}{3.6 \times 10^{6} \mathrm{~N} \cdot \mathrm{~m}}\right)=0.29 \mathrm{kWh} / \mathrm{m}^{3}
$$

# Fundamental Principles of Environmental Engineering 

## A-Units of Expression for

 Chemical Concentrations
## Mass concentration

is expressed as units of mass of a component per volume of solution.

$$
88 \mathrm{~kg}=88 \mathrm{~kg}\left(1000 \frac{\mathrm{~g}}{\mathrm{~kg}}\right)\left(1000 \frac{\mathrm{mg}}{\mathrm{~g}}\right)\left(1000 \frac{\mu \mathrm{~g}}{\mathrm{mg}}\right)=88,000,000,000 \mu \mathrm{~g}
$$

kg to $\mu \mathrm{g}$, the sequence might be any one of the following:

$$
\begin{gathered}
\mathrm{kg} \Rightarrow \mathrm{~g} \Rightarrow \mathrm{mg} \Rightarrow \mu \mathrm{~g} \\
\mathrm{~kg} \Rightarrow \mu \mathrm{~g}
\end{gathered}
$$

## A-Units of Expression for Chemical Concentrations

- Molar concentration is preferred, particularly when working with chemical stoichiometry or when the basis for the mass is not clear.
- can be converted to mass concentrations if the molecular weight is known:

$$
[\mathrm{A}](\mathrm{MW})=C_{\mathrm{A}}
$$

## Molar concentration

(gram moles per liter)
(gmmols/L).
or molarity [A] Molarity is the number of gram moles of solute per liter of solution

Gram moles = the mass in grams/
the molecular mass
where $\quad[\mathrm{A}]=$ molar concentration of component $\mathrm{A}, \mathrm{mol} / \mathrm{L}$ MW $=$ molecular weight of component $\mathrm{A}, \mathrm{g} / \mathrm{mol}$
$C_{A}=$ mass concentration of component $\mathrm{A}, \mathrm{g} / \mathrm{L}$

Consider calcium carbonate. This substance has a mass density equals $2.6 \mathrm{~g} / \mathrm{cc}$. Suppose, 35 mg is dissolved in a liter of water, find the corresponding molarity.

- The answer
- The mass of 35 mg is 0.035 g .
- Calcium carbonate has a molecular weight of $100 \mathrm{~g} / \mathrm{mol}$;
- thus, 0.035 g is $0.035 / 100=0.00035$ gmol.
- The volume corresponding to 0.35 g is $0.035 / 2.6=0.0135 \mathrm{cc}=0.0000135 \mathrm{~L}$
- the total volume of the mixture is 1.0000135 L .
- the corresponding molarity of 35 mg dissolved in one liter of water is
$\Rightarrow \quad 0.00035 / 1.0000135=0.00035 \mathrm{M}$.


## A-Units of Expression for Chemical Concentrations

## Mole fraction or mass fraction

- is the ratio of the amount or mass of a given component to the total amount or mass of all components
- are most suitable for concentrated solutions.

$$
X_{A}=\frac{n_{\mathrm{A}}}{\sum_{i=1}^{N} n_{i}}
$$

$$
C_{\mathrm{A}}=\frac{m_{\mathrm{A}}}{\sum_{i=1}^{N} m_{i}}
$$

where
$X_{A}=$ mole fraction of component $A$
$n_{A}, n_{i}=$ amounts of component $A$ and component $i$,
$C_{A}=$ mass fraction of component $A$
$m_{A}, m_{i}=$ mass of component $A$ and component $i, \mathrm{~kg}$
$N=$ number of components

## Example

The results of an analysis in a sample of water are shown in the table below. Calculate the mole fractions of the respective species.

| lons | Conc (mg/L) |
| :--- | :---: |
|  |  |
| $\mathrm{Ca}\left(\mathrm{HCO}_{3}\right)_{2}$ | 150 |
| $\mathrm{Mg}\left(\mathrm{HCO}_{3}\right)_{2}$ | 12.0 |
| $\mathrm{Na}_{2} \mathrm{SO}_{4}$ | 216.0 |


| lons | Conc <br> $(\mathbf{m g} / \mathbf{L})$ | Molecular Mass | Moles/Liter | Mole <br> Fraction |
| :--- | :---: | ---: | :---: | :---: |
| $\mathrm{Ca}\left(\mathrm{HCO}_{3}\right)_{2}$ | 150 | $40.1(2)+2\{1+12+3(16)\}=202.2$ | $0.74^{\mathrm{a}}$ | $0.32^{\mathrm{b}}$ |
| $\mathrm{Mg}\left(\mathrm{HCO}_{3}\right)_{2}$ | 12.0 | $24.3(2)+2\{1+12+3(16)\}=170.6$ | 0.07 | 0.03 |
| $\mathrm{Na}_{2} \mathrm{SO}_{4}$ | 216.0 | $23(2)+32.1+4(16)=142.1$ | 1.52 | 0.65 |
|  |  | Sum $=\Sigma$ | 2.33 | 1.00 |

a $\frac{150}{202.2}=0.74$
b $\frac{0.74}{2.33}=0.32$

## A-Units of Expression for Chemical Concentrations

## Mass concentration

Stoichiometric Factors
" $X$ " is a common method of expressing concentration in environmental engineering because water quality parameters are often composed of multiple constituents.

- nitrogen can be present in water as $\mathrm{NH}_{3}, \mathrm{NH}^{+}, \mathrm{NO}^{3-}$, or $\mathrm{NO}^{2-}$, each of which has a different molecular weight
- The concentration of hardness, alkalinity
mg/L chloride as $\mathrm{NaCl}=\frac{\mathrm{mg} \mathrm{Cl}^{-}}{\mathrm{L}} \times \frac{\text { formula weight of sodium chloride }}{\text { formula weight of chlorine }}$


## A- Units of Expression for Chemical Concentrations

Normality ( N ) or equivalents/volume (eq/L)
of analyte dissolved and diluted to a 1-L volume, designated by

$$
N=\frac{m_{\mathrm{A}}}{(\mathrm{EW}) V}
$$

where $\quad N=$ normality of component A, eq/L
$m_{\mathrm{A}}=$ mass of component A, g
$\mathrm{EW}=$ equivalent weight of component $\mathrm{A}, \mathrm{g} / \mathrm{eq}$
$V=$ volume of solution, L

The equivalent weight is expressed as

$$
\mathrm{EW}=\frac{\mathrm{MW}}{z}
$$

where $z$ is the equivalents per mole of the component.
For ionic species in water,
$z$ is equal to the valence; for oxidation-reduction reactions,
$z$ is equal to the number of electrons transferred; and for acid/base reactions,
$z$ is equal to the number of replaceable hydrogen atoms or their equivalent.

Equivalent mass based on ionic charge $\mathrm{Fe}\left(\mathrm{HCO}_{3}\right)_{2}+2 \mathrm{Ca}(\mathrm{OH})_{2} \rightarrow \mathrm{Fe}(\mathrm{OH})_{2}+2 \mathrm{CaCO}_{3}$ $+2 \mathrm{H}_{2} \mathrm{O}$ the equivalent mass $\mathrm{OF} \mathrm{Fe}\left(\mathrm{HCO}_{3}\right)_{2}$ is MW of $\mathrm{Fe}\left(\mathrm{HCO}_{3}\right)_{2} / 2$

Equivalent mass based on acid-base reactions
$\mathrm{H}_{3} \mathrm{PO}_{4}+2 \mathrm{NaOH} \rightarrow 2 \mathrm{Na}^{+}+\mathrm{HPO}_{4}^{2-}+2 \mathrm{H}_{2} \mathrm{O}$
The equivalent mass of $\mathrm{H}_{3} \mathrm{PO}_{4}$ is MW of $\mathrm{H}_{3} \mathrm{PO}_{4} / 2$
equivalent mass of NaOH is $\mathrm{MW} \mathrm{NaOH} / 1$

- Equivalent mass based on oxidationreduction reactions


## $4 \mathrm{Fe}(\mathrm{OH})_{2}+\mathrm{O}_{2}+2 \mathrm{H}_{2} \mathrm{O} \rightarrow 4 \mathrm{Fe}(\mathrm{OH})_{3}$

- The ferrous is oxidized to the ferric form from an oxidation state of +2 to +3.
- equivalent mass of $\mathrm{Fe}(\mathrm{OH})_{2}$ is then $4 \mathrm{MW} \mathrm{Fe}(\mathrm{OH})_{2} / 4$.
- the equivalent mass of oxygen is MW $\mathrm{O}_{2} / 4$


## Equivalent concentration and normality.

- first convert the molar concentration to mass concentration by multiplying it by the molecular mass (MM).
- the equivalent concentration, [C] eq, is
- The concentration expressed as geq/L is the normality.
- Example : The concentration of $\mathrm{Ca}\left(\mathrm{HCO}_{3}\right)_{2}$ is $0.74 \mathrm{gmol} / \mathrm{L}$. Convert this concentration to geq/L.

$$
\begin{aligned}
{[C]_{\mathrm{eq}} } & =\frac{[C](M M)}{\mathrm{eq} \cdot \mathrm{mass}} \\
{[C] } & =0.74 \mathrm{gmol} / \mathrm{L} \\
M M & =40.1(2)+2\{1+12+3(16)\}=202.2
\end{aligned}
$$

Therefore, eq. mass $=\frac{\mathrm{Ca}\left(\mathrm{HCO}_{3}\right)_{2}}{2}=\frac{202.2}{2}$
$[C]_{\text {eq }}=\frac{0.74(202.2)}{\frac{202.2}{2}}=1.48 \mathrm{geq} / \mathrm{L}$

## A- Units of Expression for Chemical Concentrations

## Log molar concentrations

are used because concentrations often vary
by many orders of magnitude, making
logarithms convenient.
$[\mathrm{C}]=2 \times 10^{-5} \mathrm{~mol} / \mathrm{L}$,
then $\log [C]=-4.7$ and
$[C]=10^{-4.7} \mathrm{~mol} / \mathrm{L}$.

## The $p$ notation

the negative of the base-10 log of the value:

$$
p C=-\log (C)
$$

$C=$ is the concentration of a constituent in solution (in mol/L).

The pH of a solution is defined as
$\mathrm{pH}=-\log \left[\mathrm{H}^{+}\right]$
The p notation can be used for any value, not just concentrations.


## Ghendcel



The most important reaction:

- acids and bases,
- precipitation of solids,


## Chemical reactions

- complexation of metals,
- oxidation of reduced species
used in water treatment to change the physical, chemical, and biological nature of water to accomplish water quality objectives.

$$
\mathrm{C}+\mathrm{D} \rightarrow \mathrm{~A}+\mathrm{B}
$$

Irreversible reactions consume reactants and form products until one of the reactants is totally consumed. Oxidationreduction reactions
$\mathrm{A}+\mathrm{B} \rightleftharpoons \mathrm{C}+\mathrm{D}$
At equilibrium, both bicarbonate and carbonate can be present in solution and the relative concentration of each will depend on the solution pH

## $\mathrm{HCO}_{3}{ }^{-} \rightleftarrows \mathrm{H}^{+}+\mathrm{CO}_{3}{ }^{2-}$

Reversible reactions are those that proceed until an equilibrium condition is reached; at this equilibrium, both reactants and products may be present.

| Symbol | Description | Comments |
| :---: | :---: | :---: |
| $\rightarrow$ | Irreversible reaction | Single arrow points from the reactants to the products, e.g., $\mathrm{A}+\mathrm{B} \rightarrow \mathrm{C}$. |
| $\rightleftarrows$ | Reversible reaction | Double arrows used to show that the reaction can proceed in the forward or reverse direction, depending on the solution characteristics. |
| [] | Brackets | Concentration of a chemical species in standard units ( $\mathrm{mol} / \mathrm{L}$ for aqueous phase). |
| \{\} | Braces | Activity of a chemical constituent. |
| (s) | Solid phase | Designates a chemical species present in solid phase, e.g., calcium carbonate, $\mathrm{CaCO}_{3}(\mathrm{~s})$. |
| (I) | Liquid phase | Designates a chemical species present in liquid phase, e.g., liquid benzene, $\mathrm{C}_{6} \mathrm{H}_{6}$ (I). |
| (aq) | Aqueous (dissolved) | Designates a chemical species dissolved in water, e.g., ammonia in water, $\mathrm{NH}_{3}(\mathrm{aq})$. |
| (g) | Gas | Designates a chemical species present in gas phase, e.g., chlorine gas, $\mathrm{Cl}_{2}(\mathrm{~g})$. |
| $\xrightarrow{\text { x }}$ | Catalysis | Chemical species, represented by $x$, catalyzes reaction, e.g, cobalt ( Co ) is the catalyst in the reaction $\mathrm{SO}_{3}{ }^{2-}+0.5 \mathrm{O}_{2} \xrightarrow{\mathrm{CO}} \mathrm{SO}_{4}{ }^{2-}$. |
| $\uparrow$ | Volatilization | Arrow directed up following a component is used to show volatilization of given component, e.g., $\mathrm{CO}_{3}{ }^{2-}+2 \mathrm{H}^{+} \rightleftarrows \mathrm{CO}_{2}$ (g) $\uparrow+\mathrm{H}_{2} \mathrm{O}$. |
| $\downarrow$ | Precipitation | Arrow directed down following a component is used to show precipitation of given component, e.g., $\mathrm{Ca}^{2+}+\mathrm{CO}_{3}{ }^{2-} \rightleftarrows \mathrm{CaCO}_{3}(\mathrm{~s}) \downarrow$. |

## Example

A groundwater used as a drinking water supply contains $2.6 \mathrm{mg} / \mathrm{L}$ of $\mathrm{Fe}^{2+}$

Calculate the amount of $\mathrm{O}_{2}$ that will be needed to oxidize it and the amount of $\mathrm{Fe}(\mathrm{OH})_{3}$ that will be produced.

Assume that the reaction proceeds to completion.

## - The answer

> removing $\mathrm{Fe}^{2+}$ from water is to oxidize it with oxygen to produce insoluble ferric hydroxide $\left[\mathrm{Fe}(\mathrm{OH})_{3}\right.$ ] according to the following reaction:

$$
4 \mathrm{Fe}^{2+}+\mathrm{O}_{2}+10 \mathrm{H}_{2} \mathrm{O} \rightarrow 4 \mathrm{Fe}(\mathrm{OH})_{3}+8 \mathrm{H}^{+}
$$

- 1 mol of $\mathrm{O}_{2}$ is capable of oxidizing 4 mol of $\mathrm{Fe}^{2}+$;
- it will form 4 mol of $\mathrm{Fe}(\mathrm{OH})_{3}$ and 8 mol of $\mathrm{H}+$.
- Using reaction stoichiometry and the molecular weight of the chemical species to calculate the mass of reactants and products participating in a reaction


## The answer

- Determine the molecular weight of each species from the atomic weights
- MW of $\mathrm{Fe}^{2+}=55.8 \mathrm{~g} / \mathrm{mol}$

MW of $\mathrm{O}_{2}=(2) 16.0 \mathrm{~g} / \mathrm{mol}=32.0 \mathrm{~g} / \mathrm{mol}$ MW of $\mathrm{Fe}(\mathrm{OH})_{3}=55.8+(3)(1.0)+$ (3) $(16.0)=106.8 \mathrm{~g} / \mathrm{mol}$

- Calculate the concentration of oxygen required to oxidize the iron.

$$
=(32 * 2.6) /(56 * 4)=0.37 \mathrm{mg} / \mathrm{L} 02
$$

- Therefore, $0.37 \mathrm{mg} / \mathrm{L}$ of $\mathrm{O}_{2}$ is capable of oxidizing $2.6 \mathrm{mg} / \mathrm{L}$ of $\mathrm{Fe}^{2+}$
- Calculate the concentration $\mathrm{Fe}(\mathrm{OH})_{3}$ that will be produced. $=2.6^{*} 106.8 / 56=4.98 \mathrm{mg} / \mathrm{L} \mathrm{Fe}(\mathrm{OH})_{3}$
- Therefore, $4.98 \mathrm{mg} / \mathrm{L}$ of $\mathrm{Fe}(\mathrm{OH})_{3}$ will be produced when $2.6 \mathrm{mg} / \mathrm{L}$ of $\mathrm{Fe}^{2+}$ is oxidized


## Concentration and Activity

| The ability of a |
| :--- |
| species to participate in chemical reactions |
| depends on its chemical activity |
| At equilibrium, the amounts of reactants and |
| products present will depend |
| on the activity of each species |
| The activity of a species is related to its |
| concentration by an activity coefficient: |
| $\{A\}=\gamma[A]$ |
| where $\{A\}=$ activity of species A |
| $Y=$ activity coefficient for species A |
| $[A]=$ concentration of species A |

$\rightarrow$ The activity coefficient for ionic species depends on the overall ionic content of the solution, which is characterized by the ionic strength.

The ionic strength is calculated using the equation

$$
I=\frac{1}{2} \sum_{i} C_{i} z_{i}^{2}
$$

where $\quad I=$ ionic strength of solution, $\mathrm{mol} / \mathrm{L}$
$C_{i}=$ concentration of species $i, \mathrm{~mol} / \mathrm{L}$
$z_{i}=$ charge (valence) on species $i$, unitless

$$
\begin{aligned}
& I=\left(2.5 \times 10^{-5}\right)(\mathrm{TDS}) \\
& I=\left(1.6 \times 10^{-5}\right)(\mathrm{EC})
\end{aligned}
$$

where TDS $=$ total dissolved solids, $\mathrm{mg} / \mathrm{L}$ $\mathrm{EC}=$ electrical conductivity,$\mu \mathrm{S} / \mathrm{cm}$

## Example

For water with an ionic strength of 5 mM (corresponding to TDS of about $200 \mathrm{mg} / \mathrm{L}$ ), calculate the activity coefficients of $\mathrm{Na}+$ and $\mathrm{Ca}^{2+}$ at $25^{\circ} \mathrm{C}$.

For solutions up to $\mathrm{I} \leq 0.5 \mathrm{M}$, Davies equation

$$
\log (\gamma)=-A z^{2}\left(\frac{\sqrt{I}}{1+\sqrt{I}}-0.3 I\right)
$$

where $A=$ constant (for water at $25^{\circ} \mathrm{C}, A=0.50$ )

- the activity coefficients for $\mathrm{Na}+$

$$
5 \mathrm{mM}=0.005 \mathrm{M}
$$

$$
\begin{aligned}
\log \left(\gamma_{\mathrm{Na}^{+}}\right) & =-0.50(1)^{2}\left[\frac{\sqrt{0.005}}{1+\sqrt{0.005}}-0.3(0.005)\right]=-0.0323 \\
\gamma_{\mathrm{Na}^{+}} & =10^{-0.0323}=0.93
\end{aligned}
$$

- the activity coefficient for $\mathrm{Ca}^{2+}$

$$
\begin{aligned}
\log \left(\gamma_{\mathrm{Ca}^{2+}}\right) & =-0.50(2)^{2}\left[\frac{\sqrt{0.005}}{1+\sqrt{0.005}}-0.3(0.005)\right]=-0.129 \\
\gamma_{\mathrm{Ca}^{2+}} & =10^{-0.129}=0.74
\end{aligned}
$$

The charge on the species has a large influence on the value of the activity coefficient.

## Equilibrium Constants

$$
a \mathrm{~A}+b \mathrm{~B} \rightleftharpoons c \mathrm{C}+d \mathrm{D}
$$

where $a, b, c, d=$ stoichiometric coefficients of species A, B, C, D, respectively, unitless

$$
K=\frac{\{\mathrm{C}\}^{c}\{\mathrm{D}\}^{d}}{\{\mathrm{~A}\}^{a}\{\mathrm{~B}\}^{b}}
$$

where
$K=$ equilibrium constant
$\}=$ activity of species
$a, b, c, d=$ stoichiometric coefficients of species A, B, C, D, respectively

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

$$
\mathrm{p} K=-\log (K)
$$

- Example

Calculating concentrations using equilibrium constants

- Sodium hypochlorite ( NaOCl ) is added to water as a disinfectant.

Upon addition, it immediately dissociates according to the following reaction:

$$
\mathrm{NaOCl} \rightarrow \mathrm{Na}++\mathrm{OCl}-
$$

The hypochlorite then participates in the following reversible acidbase reaction:
$\mathrm{HOCl} \rightleftarrows \mathrm{H}++\mathrm{OCl}-\quad \mathrm{pKa}=7.6$
The strength of hypochlorite as a disinfectant depends on which species is present; thus, it is important to know how much is present as HOCl and how much as OCl - at equilibrium.

- If $2 \mathrm{mg} / \mathrm{L}$ of NaOCl is added,
- Determine how much is present as each species at pH 7.0.


## Solution

Calculate the molar concentration of NaOCl
the MW of NaOCl can be determined to be $74.5 \mathrm{~g} / \mathrm{mol}$

Total OCl- $=[\mathrm{NaOCl}]=2 \mathrm{mg} / \mathrm{L} /(74.5$ $\mathrm{g} / \mathrm{mol})\left(10^{3} \mathrm{mg} / \mathrm{g}\right)=2.68 \times 10^{-5} \mathrm{M}$
pKa $=7.6=-\log 7.6=10-7.6$
$\mathrm{Ka}=\frac{[\mathrm{H}+]\left[\mathrm{OCl}^{-}\right]}{[\mathrm{HOCl}]}=10-7.6$

- Determine the ratio of [ $\mathrm{OCl}-$ ] to [ HOCl ] at $\mathrm{pH}=7.0$.
at $\mathrm{pH} 7=-\log 7=10-7$
- hydrogen ion concentration $[\mathrm{H}+$ ] at pH 7.0 is equal to $10^{-7} .0 \mathrm{M}$
$\frac{[\mathrm{OCl}-]}{[\mathrm{HOCl}]}=\frac{\mathrm{Ka}}{[\mathrm{H}+]}=\frac{10^{-76}}{10^{-7}}=10^{-.06}=0.25$
- At $\mathrm{pH}=7.0,25$ percent of the total hypochlorite added is present as $\mathrm{OCl}-$ and the rest is present as HOCl .
- $[\mathrm{OCl}-]=0.25\left(2.68 \times 10^{-5} \mathrm{M}\right)=6.71 \times$ $10^{-6} \mathrm{M}=6.71 \mu \mathrm{M}$
- $[\mathrm{HOCl}]=0.75\left(2.68 \times 10^{-5} \mathrm{M}\right)=2.01 \times$ $10^{-5} \mathrm{M}=20.1 \mu \mathrm{M}$


## Chemical Kinetics

Chemical kinetics is the study of the rate at which chemical reactions take place, that is, the speed at which reactants are consumed and products are formed.


$$
a \mathrm{~A}+b \mathrm{~B} \rightarrow \text { products }
$$

The rate equation for the reaction in Eq. $4-25$ is

$$
r_{\mathrm{A}}=-k\{\mathrm{~A}\}^{m}\{\mathrm{~B}\}^{n}
$$

where $\quad k=$ reaction rate constant, units vary (see below) $m, n=$ reaction order constants, unitless

## Two common forms of rate equations :

First-order reactions depend on the activity of only one species and have the rate equation

$$
r A=-k\{A\}
$$

where $k=$ first-order reaction rate constant, $\mathrm{s}^{-1}$
Second-order reactions depend on collisions of two molecules of the same species or on collisions between molecules of two different species

$$
\begin{aligned}
& r_{\mathrm{A}}=-k\{\mathrm{~A}\}^{2} \\
& r_{\mathrm{A}}=-k\{\mathrm{~A}\}\{\mathrm{B}\}
\end{aligned}
$$

where $k=$ second-order reaction rate constant, $\mathrm{L} / \mathrm{mol} \cdot \mathrm{s}$

## Reactions Used in Water Treatment



## Acid-base reactions

- Acid-base reactions involve the transfer of a hydrogen ion, or proton, between two species.

$$
\mathrm{HA} \rightleftarrows \mathrm{H}^{+}+\mathrm{A}^{-}
$$

where $\mathrm{HA}=$ acid species
$\mathrm{H}^{+}=$hydrogen ion (hydrated proton, i.e., $\mathrm{H}_{3} \mathrm{O}^{+}$)
$\mathrm{A}^{-}=$conjugate base species
-
the carbonate system is one of the most important acid-base systems in natural waters and loses two protons

$$
\begin{aligned}
& \mathrm{H}_{2} \mathrm{CO}_{3} \rightleftarrows \mathrm{H}^{+}+\mathrm{HCO}_{3}^{-} \\
& \mathrm{HCO}_{3}^{-} \rightleftarrows \mathrm{H}^{+}+\mathrm{CO}_{3}^{2-}
\end{aligned}
$$

- Acid-base reactions are very fast (reaching equilibrium in less than a second), reversible reactions.
- The acid species and the conjugate base can exist simultaneously, depending on the pH of the solution.
- The equilibrium constant for an acid-base reaction is known as the acid dissociation constant, Ka


## Precipitation= Dissolution Reactions

- In water treatment processes, dissolved contaminants can be removed by causing them to precipitate and the removing the solids from water
- The equilibrium constant between a solid and its ions in solution is known as the solubility product.
- EX: Water containing calcium bicarbonate and calcium sulfate is softened using lime and soda ash

$$
\begin{aligned}
& \mathrm{Ca}\left(\mathrm{HCO}_{3}\right)_{2}+\mathrm{Ca}(\mathrm{OH})_{2} \rightarrow 2 \mathrm{CaCO}_{3} \downarrow+2 \mathrm{H}_{2} \mathrm{O} \\
& \mathrm{CaSO}_{4}+\mathrm{Na}_{2} \mathrm{CO}_{3} \rightarrow \mathrm{CaCO}_{3}+\mathrm{Na}_{2} \mathrm{SO}_{4}
\end{aligned}
$$

- The equilibrium constant between a solid and its ions in solution is known as the solubility product.

$$
A_{a} B_{b} \rightleftharpoons a A+b B
$$

$$
K=\frac{\{A\}^{a}\{B\}^{b}}{\left\{A_{a} B_{b}\right\}}
$$

$$
K_{s p}=\{A\}^{a}\{B\}^{b}
$$

At equilibrium, neither reactants nor products increase or decrease with time. Thus, Ksp's, being constants, can be used as indicators whether or not a given solid will form or dissolve in solution.

- For example,
- $\mathrm{CaCO}_{3}$ has a Ksp of $4.8\left(10^{-9}\right)$ at $25^{\circ} \mathrm{C}$. This value decreases to $2.84\left(10^{-9}\right)$ at $60^{\circ} \mathrm{C}$. The equilibrium reaction for this solid is

$$
\mathrm{CaCO}_{3(\mathrm{~s})} \rightleftharpoons \mathrm{Ca}^{2+}+\mathrm{CO}_{3}^{2-}
$$

$$
\begin{aligned}
K_{s p} & =\left\{\mathrm{Ca}^{2+}\right)\left(\mathrm{CO}_{3}^{2-}\right\}=4.8\left(10^{-9}\right) \text { at } 25^{\circ} \mathrm{C} \\
& =\left\{\mathrm{Ca}^{2+}\right)\left(\mathrm{CO}_{3}^{2-}\right\}=2.84\left(10^{-9}\right) \text { at } 60^{\circ} \mathrm{C}
\end{aligned}
$$

- This means that there are fewer particles of the ions existing than required to maintain equilibrium at this higher temperature.
- As a consequence, some of the particles will combine to form a precipitate, the $\mathrm{CaCO}_{3}$ solid.
- The general expression
- OxA + ne- $\rightarrow$ RedA
- where $O x_{A}=$ oxidized species $A$
- $\mathrm{n}=$ number of electrons transferred $\mathrm{e}-=$ electron Red
- Oxidized species A is called an oxidant (or electron acceptor)
- The half reaction for the oxidation of a species
- Redв $\rightarrow$ Охв + ne-
- Oxв $=$ oxidized species $B$
- RedB = reduced species B
- Reduced species B is called a reductant (or electron donor)
- overall oxidation-reduction reaction

$$
\begin{gathered}
\mathrm{OXA}+\mathrm{RedB}_{\mathrm{Cl}} \rightarrow \mathrm{OXB}+\mathrm{Red}_{\mathrm{A}} \\
4 \mathrm{Fe}^{2+}+\mathrm{O}_{2}+10 \mathrm{H}_{2} \mathrm{O} \rightarrow 4 \mathrm{Fe}(\mathrm{OH})_{3}+8 \mathrm{H}^{+}
\end{gathered}
$$



