

# Basic Chemistry Concepts I

# Basic chemistry concepts I

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- Chemistry – basics of the basics
- Chemical reactions
- Equilibrium chemistry

# Mole & molarity

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- Mole = Avogadro's number ( $6.02 \times 10^{23}$ ) of molecules
- Molarity (M) = number of moles per liter of solution (mole/L)  
cf) molality (m) = number of moles per kg of solvent

# Activity

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- Determines the tendency for a reaction to occur
- Represented by  $\{ \}$  (cf. molarity by  $[ ]$ )
- In dilute aqueous solutions, the ions do not significantly interact with one another:

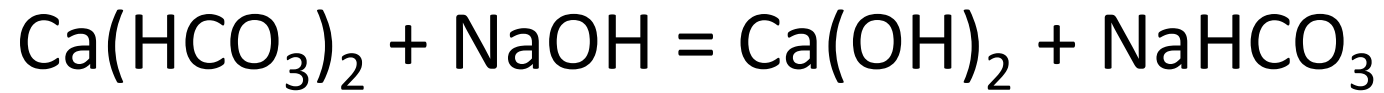
$$\{i\} \approx [i]$$

- As concentration increases, the ion-ion interaction becomes more significant:

$$\{i\} = \gamma_i \cdot [i] \quad \text{where } \gamma_i = \text{activity coefficient}$$

# Balancing chemical reactions

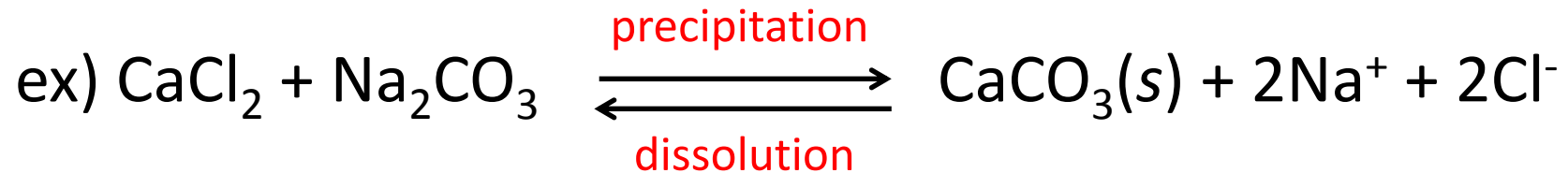
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# Types of chemical reactions

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- Precipitation-dissolution reactions

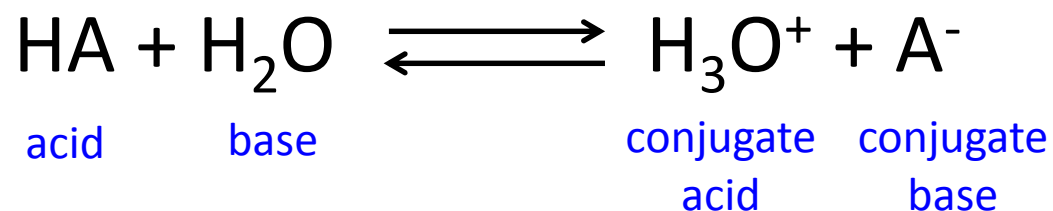


Usage: softening, phosphorous removal, heavy metal removal

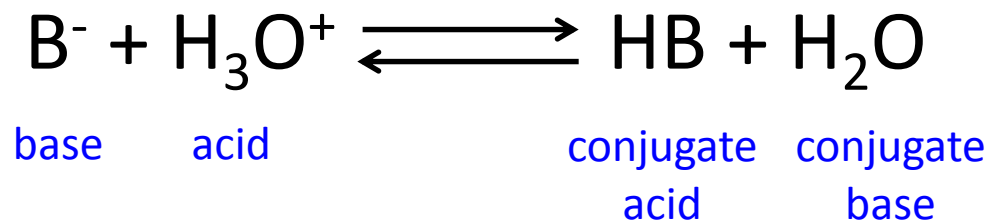
# Acid-base reactions

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- Brønsted-Lowry acid: any substance that can donate a proton (i.e., proton donor)



- Brønsted-Lowry base: any substance that can accept a proton (i.e., proton acceptor)



***cf) Lewis definition***

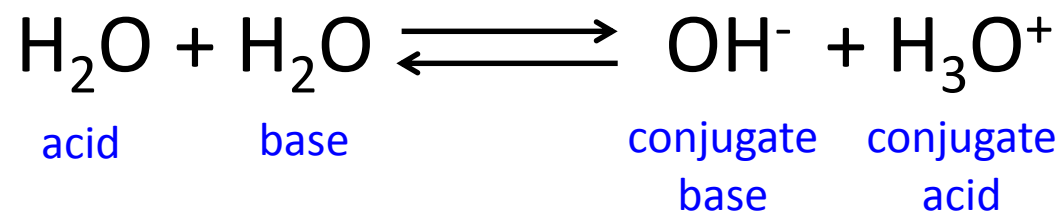
*Lewis acid: electron pair acceptor*

*Lewis base: electron pair donor*

# Water as both acid & base

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- Water is amphoteric – can be either an acid or a base



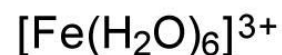
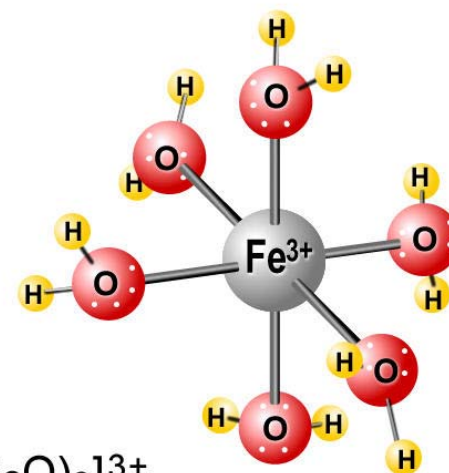
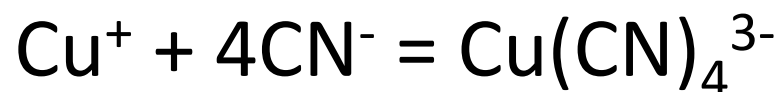
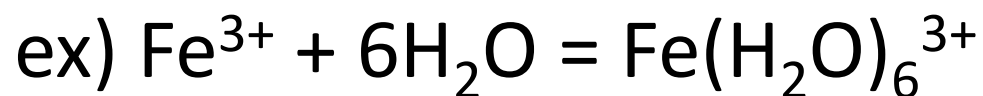
- $\text{pH} = -\log\{\text{H}^+\}$  (“p” denotes “-log”)



# Complexation reactions

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- Coordination of two or more atoms, molecules, or ions resulting in the formation of a more stable product



Octahedral

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- Complex ion = a metal ion (Lewis acid) coordinated with ligands (Lewis bases)

# Complexation reactions - implications

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- Many metal ions exist as complex ions in water (metal aquo complex)  
ex)  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ ,  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ ,  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ ,  
 $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ ,  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ ,  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$
- Environmental significance: complexation of metals affects the uptake, biodegradability, toxicity, and mobility of the metal

# Oxidation-reduction (redox) reactions

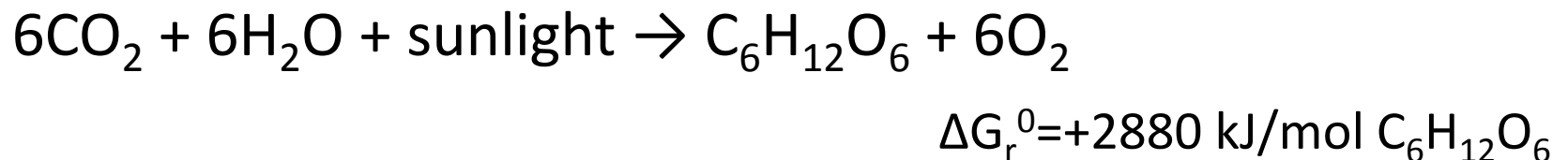
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- Involves changes in the oxidation state
- Essential for life: photosynthesis and respiration are redox reactions!

respiration using glucose:



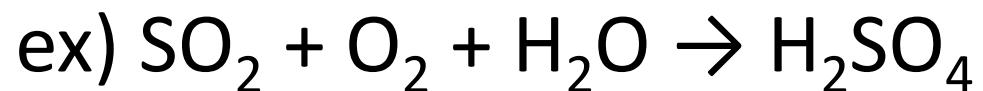
photosynthesis of glucose:



# Balancing redox reactions

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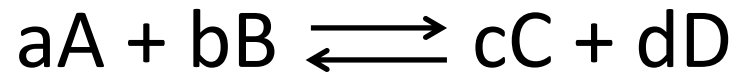
- Have to consider electron balance in addition to atom balance!



# Chemical equilibrium

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- For a reversible reaction



at chemical equilibrium,

$$\text{rate}(\text{forward rxn}) = \text{rate}(\text{reverse rxn})$$

- Equilibrium constant,  $K$

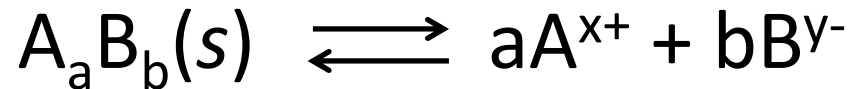
$$K = \frac{\{C\}^c \{D\}^d}{\{A\}^a \{B\}^b}$$

*For pure solid, activity = 1*  
*For gases, activity = partial pressure*

# Chemical equilibrium: solubility

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- For a precipitation-dissolution reaction



$$K = \frac{\{A^{x+}\}^a \{B^{y-}\}^b}{\{A_a B_b\}}$$

as  $\{A_a B_b\} = 1$  (pure solid),  $K = \{A^{x+}\}^a \{B^{y-}\}^b$

- Solubility product,  $K = \{A^{x+}\}^a \{B^{y-}\}^b$

# Ionic strength

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- In most cases we want to know [ ] at equilibrium, not { }
- Recall {i} =  $\gamma_i[i]$ :

$$K_s = \{A^{x+}\}^a \{B^{y-}\}^b = (\gamma_A[A^{x+}])^a \cdot (\gamma_B[B^{y-}])^b$$

- $\gamma_i < 1$  in concentrated solutions because of ion-ion interactions
- Ionic strength,  $I$  : measure of interaction among ions in a solution

$$I = \frac{1}{2} \sum C_i z_i^2$$

$C_i$  = molarity of the  $i^{\text{th}}$  ion

$z_i$  = charge of the  $i^{\text{th}}$  ion

# Calculating activity coefficients

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- Davies equation (for  $I < 0.5 \text{ M}$ ):

$$\log \gamma_i = -Az_i^2 \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2I \right)$$

$A \approx 0.5$  for water at  $25^\circ\text{C}$

$z_i = \text{charge of the ion}$

*There are many approximations available, verified at different ranges of ionic strength. Let's use Davies equation for this class.*



# Selected solubility products (@ 25°C)

Substance	Equilibrium Reaction	pK <sub>s</sub>	Application
Aluminum hydroxide	$\text{Al(OH)}_3 (s) \rightleftharpoons \text{Al}^{3+} + 3\text{OH}^-$	32.9	Coagulation
Aluminum phosphate	$\text{AlPO}_4 (s) \rightleftharpoons \text{Al}^{3+} + \text{PO}_4^{3-}$	22.0	Phosphate removal
Calcium carbonate (aragonite)	$\text{CaCO}_3 (s) \rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{2-}$	8.34	Softening, corrosion control
Ferric hydroxide	$\text{Fe(OH)}_3 (s) \rightleftharpoons \text{Fe}^{3+} + 3\text{OH}^-$	38.57	Coagulation, iron removal
Ferric phosphate	$\text{FePO}_4 (s) \rightleftharpoons \text{Fe}^{3+} + \text{PO}_4^{3-}$	21.9	Phosphate removal
Magnesium hydroxide	$\text{Mg(OH)}_2 (s) \rightleftharpoons \text{Mg}^{2+} + 2\text{OH}^-$	11.25	Removal of calcium and magnesium
Dolomite (CaMg(CO <sub>3</sub> ) <sub>2</sub> ) (ordered)	$\text{CaMg(CO}_3)_2 \rightleftharpoons \text{Ca}^{2+} + \text{Mg}^{2+} + 2\text{CO}_3^{2-}$	17.09	Weathering of dolomitic minerals
Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 6\text{H}^+ \rightleftharpoons 2\text{Al}^{3+} + 2\text{Si(OH)}_4 + \text{H}_2\text{O}$	7.44	Weathering of kaolinite clays
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \rightleftharpoons \text{Ca}^{2+} + \text{SO}_4^{2-} + 2\text{H}_2\text{O}$	4.58	Weathering of gypsum minerals

# Chemical equilibrium: solubility

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**Q:** You added 30 g of  $\text{CaCO}_3$  in water of make 1.00 L solution containing 0.01 M NaCl. Assuming  $\text{Ca}^{2+}$  in solution is at equilibrium with  $\text{CaCO}_3(s)$ , what would be the  $\text{Ca}^{2+}$  concentration?

( $T = 25^\circ\text{C}$ ,  $pK_s$  for  $\text{CaCO}_3 = 8.48$ )

# Reading assignment

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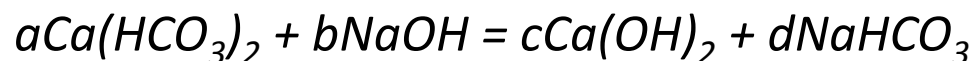
- Textbook Ch2 p. 32-51

# Balancing chemical reactions

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## ***Slide#5 solution)***

*Basic rule: conservation of matter (atoms)*



$$\text{Ca: } a = c \quad (1)$$

$$\text{Na: } b = d \quad (2)$$

$$\text{H: } 2a + b = 2c + d \quad (3)$$

$$\text{C: } 2a = d \quad (4)$$

$$\text{O: } 6a + b = 2c + 3d \quad (5)$$

*Four unknowns → three equations needed (obtain the ratio of each)*

*e.g., use (1), (2) & (4):  $2a = 2c = b = d$  (satisfies (3) & (5) as well)*

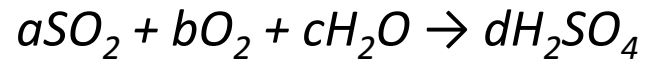


# Balancing redox reactions

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## **Slide#12 solution)**

Basic rule: conservation of matter (atoms + electrons)



$$\text{S: } a = d \quad (1)$$

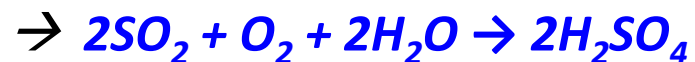
$$\text{O: } 2a + 2b + c = 4d \quad (2)$$

$$\text{H: } 2c = 2d \quad (3)$$

$$e^-: (\text{O}_2 [0] + 4e^- \rightarrow 2\text{O}^{2-}) \times b; \quad (\text{S}^{4+} \rightarrow \text{S}^{6+} + 2e^-) \times a$$

$$4b = 2a \quad (4)$$

e.g., use (1), (2) & (4):  $a = 2b = c = d$  (satisfies (2) as well)



# Chemical equilibrium: solubility

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## **Slide#18 solution)**

i) Assume ionic strength is negligible (activity = molarity)

$$[Ca^{2+}] = [CO_3^{2-}]$$

$$K_s = 10^{-8.48} = [Ca^{2+}][CO_3^{2-}] = [Ca^{2+}]^2$$

$$[Ca^{2+}] = 5.75 \times 10^{-5} M$$

ii) Without the assumption

Let's assume NaCl is a sole contributor of ionic strength

$$I = \frac{1}{2} [(0.01 M) \cdot (1^2) + (0.01 M) \cdot (1^2)] = 0.01 M$$

$$\log \gamma_{Ca} = \log \gamma_{CO_3} = -0.5 \cdot 2^2 \left( \frac{\sqrt{0.01 M}}{1 + \sqrt{0.01 M}} - 0.2 \cdot 0.01 M \right) = -0.175$$

$$\gamma_{Ca} = \gamma_{CO_3} = 10^{-0.175} = 0.664$$

$$\gamma_{Ca} [Ca^{2+}] = 5.75 \times 10^{-5} M$$

$$[Ca^{2+}] = 8.66 \times 10^{-5} M \text{ (valid if within 5% error is accepted)}$$