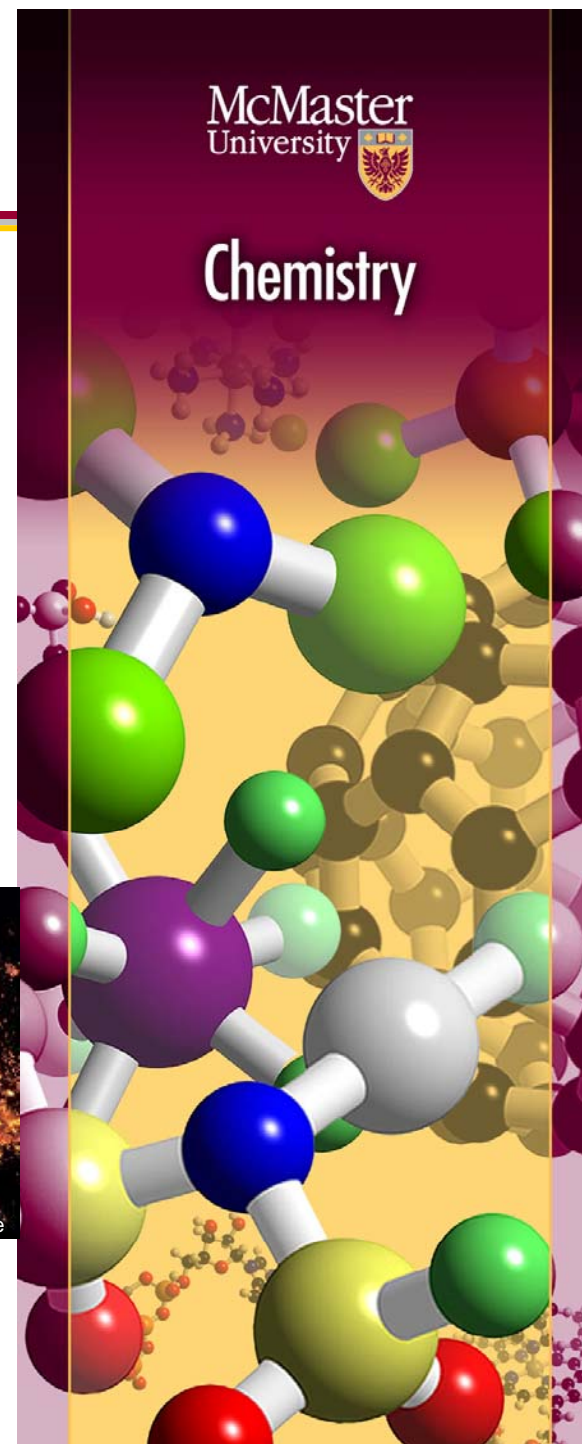
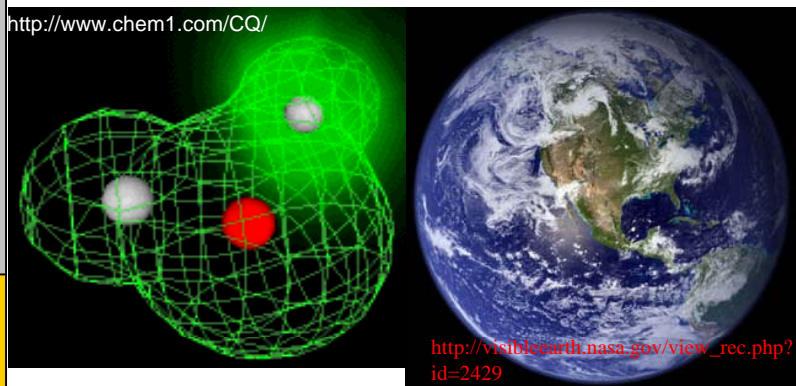


CHEM 1A03: Intro. Chemistry I

Water & Aqueous Chemistry

Ch.5: Reactions in Aqueous Solutions

<http://www.chem1.com/CQ/>



Water: A Vital Natural Resource!

Significance of Water: **Energy, Health & Environment**

“No single measure would do more to reduce disease and save lives in the developing world than bringing safe **water & adequate sanitation to all.”**

UN Secretary-General Kofi Annan, 2003 International Year of Freshwater

“Water** is probably the only natural resource to touch all aspects of human civilization—from agricultural and industrial development to the cultural & religious values embedded in society.”**

Koichiro Matsuura, Director-General, UNESCO



Department of
Chemistry



Water: An Enigmatic Medium!

Unique Macroscopic Properties Essential to Life

1. Unusually **high boiling point (b.p.)** of liquid water at STP:
bp = 100°C at 1 atm (Sea level) → T,P-dependent
2. **Density** of ice (0.92 g/mL) < liquid water (1 g/mL) at 0°C:
Ice expands with freezing: Lower packing density
3. **High specific heat capacity** of water (74 J/mol·K at STP):
Absorbs thermal heat for storage/distribution/release
4. Water **dissolves** a variety of **solutes** as a solvent:
Strong solvation properties for most polar molecules/ions



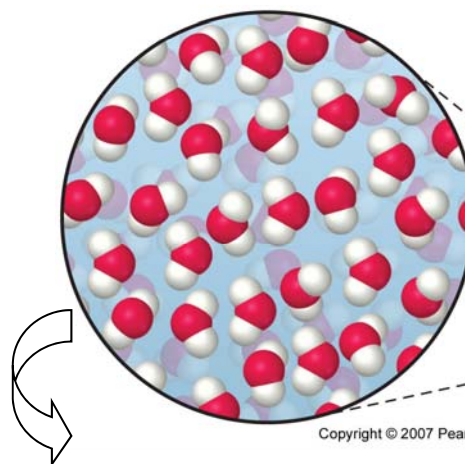
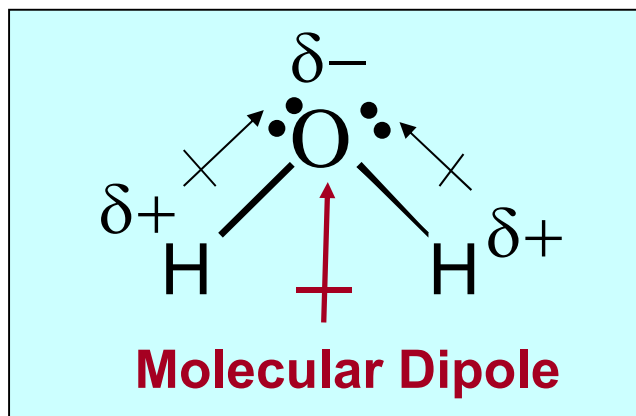
41 Anomalies of Water: <http://www.lsbu.ac.uk/water/anmlies.html>



IClicker Question #1

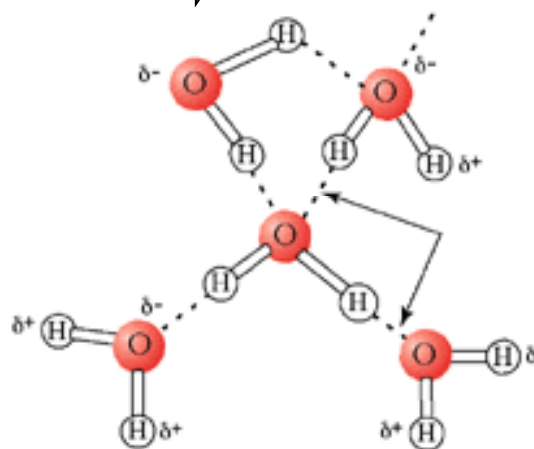
Which **intermolecular force** accounts for water's unusual **high b.p.**?

- (a) Ion-dipole
- (b) Dipole-dipole
- (c) H-bonding
- (d) Van der Waals
- (e) none of the above



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Fig. 5-1a, p. 152 (143, 9th ed.)

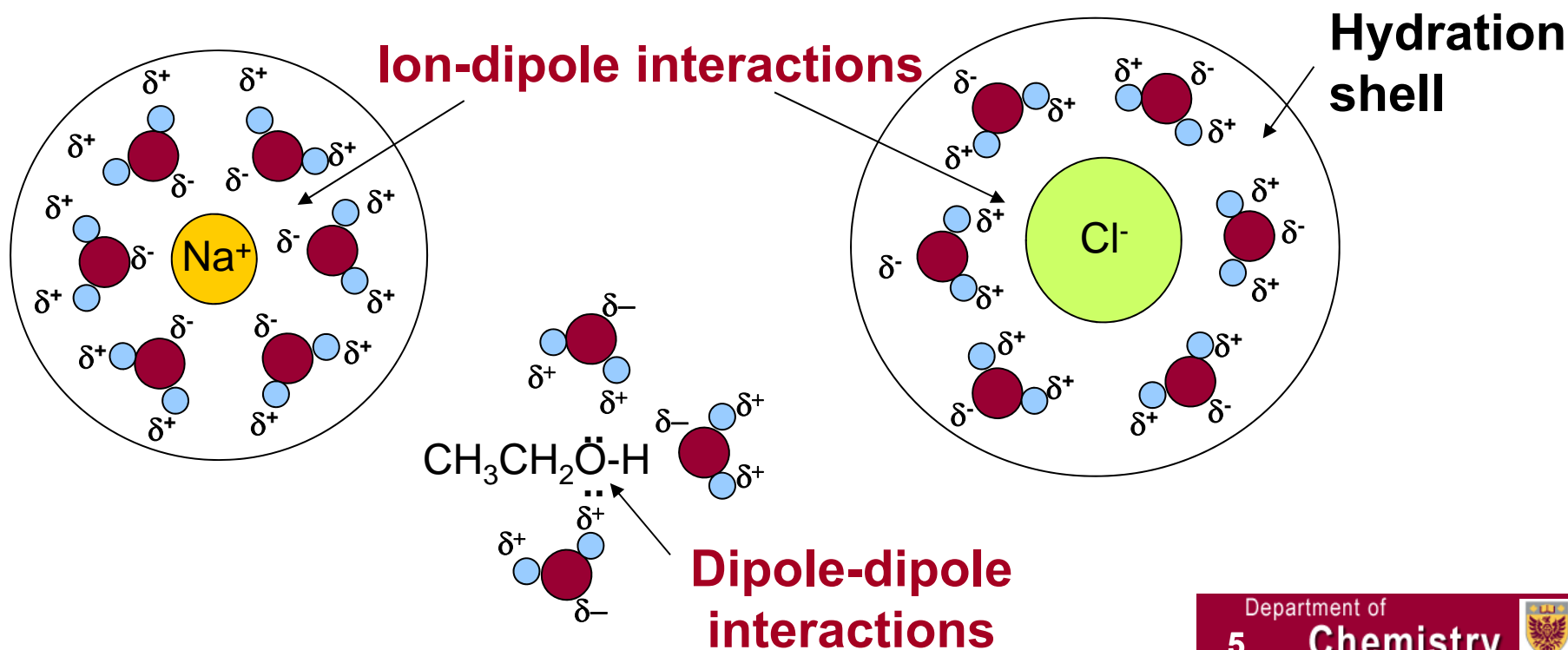


Hydrogen bonds:
possible because
of water's
extreme polarity



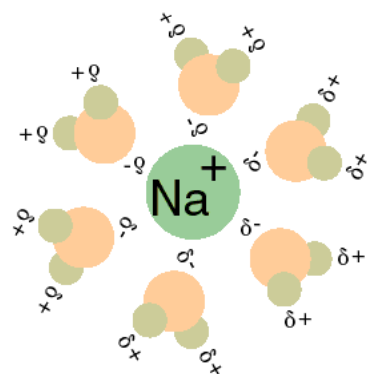
Solute Solvation by Water

- Solubilization of polar/ionic solutes: **Hydration**
- Energetically favorable **H₂O-solute interactions**:
H-bonding (dipole-dipole) with solutes (O-H, N-H, C=O)
+/- ion-dipole forces



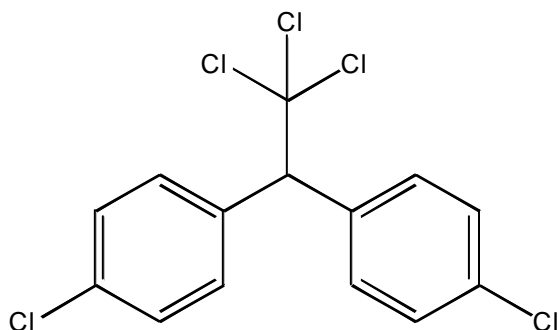
Properties of Water Vital for Molecular Behaviour

Ion Hydration, Sodium Pumps & Ion Transport



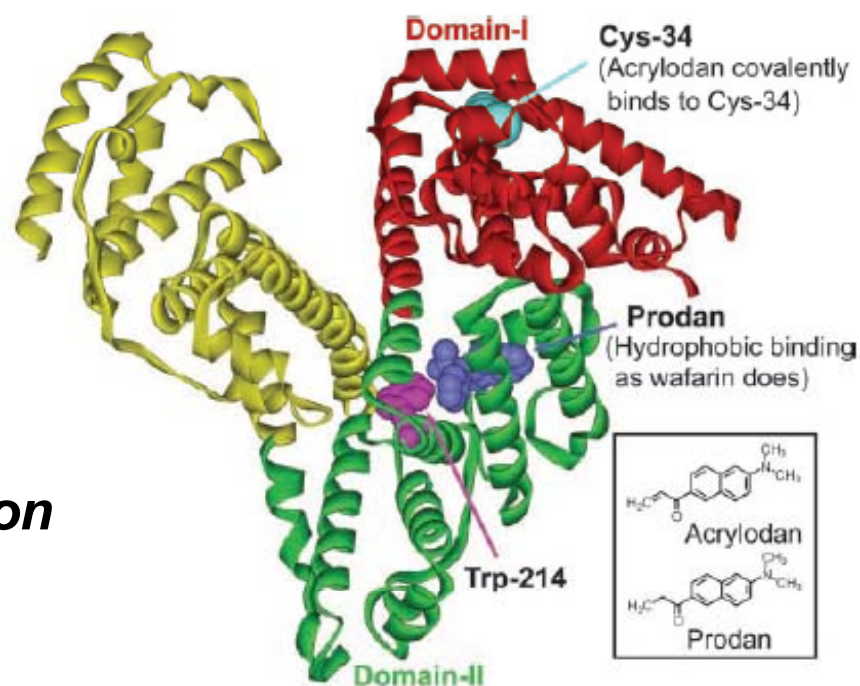
Sodium Ion

Solubility, Toxicity & Bioaccumulation



Dichlorodiphenyl-trichloroethane (DDT)

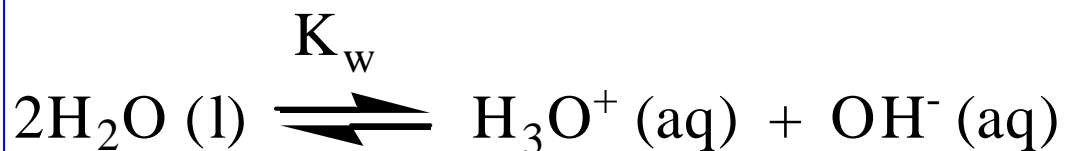
Protein Folding, Activity & Drug Binding



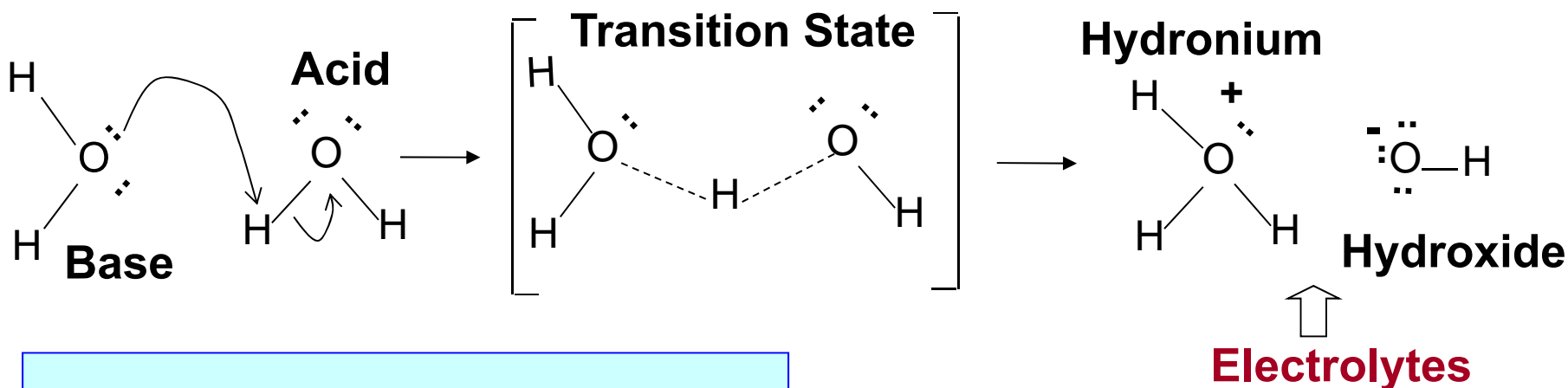
Human Serum Albumin (HSA)

Auto-ionization of Water

- Water auto-ionization: Water is **amphoteric & conductive**



**Water acts as acid
& base with itself!**



$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1 \times 10^{-14} (25^\circ\text{C})$$

Why isn't $[\text{H}_2\text{O}]$ included in equilibrium expression?

Purified De-ionized Water:

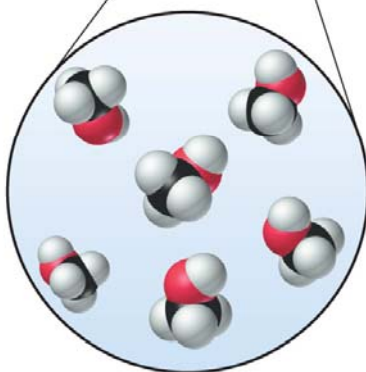
$$\text{pH} = -\log[\text{H}_3\text{O}^+] = 7.0$$

Low conductivity since $[\text{H}_3\text{O}^+]$ & $[\text{OH}^-] = 0.1 \mu\text{M}$



Solute Properties & Electrolytes

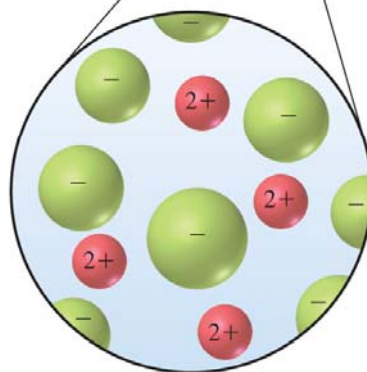
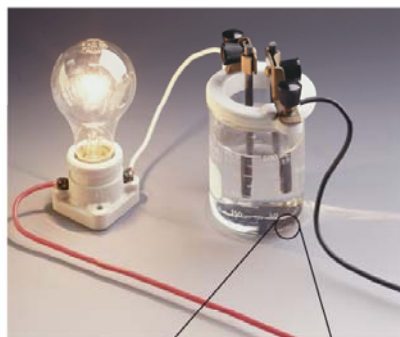
Non-electrolyte



(a)

Neutral molecule

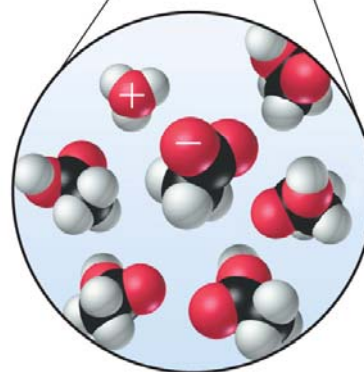
Strong electrolyte



(b)

Fully charged ions

Weak electrolyte



(c)

Partially ionized
molecule

Degree of ionization of an electrolyte in aqueous solution!



Solutes as Electrolytes

1. Strong electrolyte (Ionic)

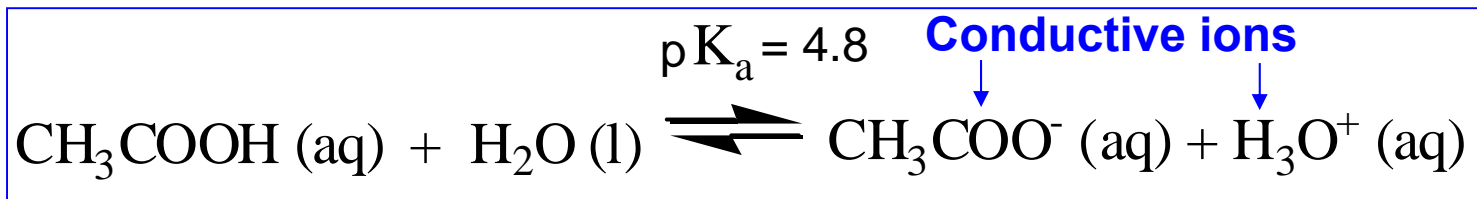
Sodium Chloride:



Intravenous supply of electrolytes

2. Weak electrolyte (Weakly Ionic)

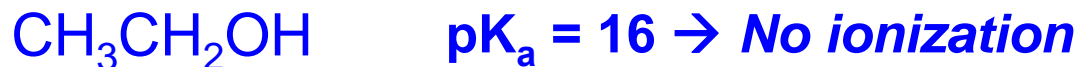
Acetic Acid: Vinegar (5-8% w)



Preservative/Sour

3. Non-electrolyte (Neutral)

Ethanol: Vodka (> 40% v)



Spirit, Depressant & Diuretic



iClicker Question #2

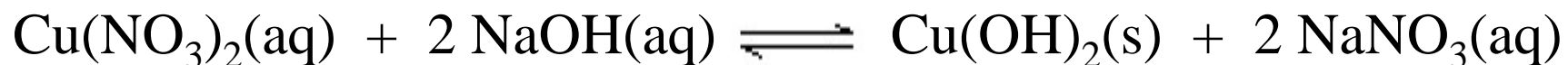
Which of the following would be the **strongest conductor** of electricity?

- (a) NaBr (aq, 1M)
- (b) CH₃OH (l)
- (c) CH₃COOH (aq, 1M)
- (d) (NH₄)₂SO₄ (aq, 1M)
- (e) H₂O (l)



Major Types of Aqueous Chemical Reactions

- **1. Solubility or Precipitation Reactions: (ion transfer)** Lab 2



- **2. Reduction-Oxidation (Redox) Reactions: (electron transfer)**



- **3. Acid-Base Reactions: (proton transfer)**



K is a measure of extent of chemical reaction & transformation!



Solubility: Qualitative Guidelines

TABLE 5.1 Solubility Guidelines for Common Ionic Solids

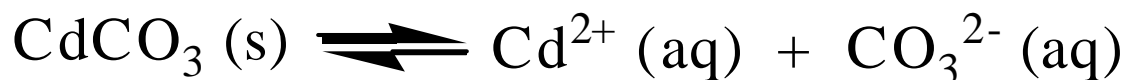
Follow the lower-numbered guideline when two guidelines are in conflict. This leads to the correct prediction in most cases.

1. Salts of group 1 cations (with some exceptions for Li^+) and the NH_4^+ cation are soluble.
2. Nitrates, acetates, and perchlorates are soluble.
3. Salts of silver, lead, and mercury(I) are insoluble.
4. Chlorides, bromides, and iodides are soluble.
5. Carbonates, phosphates, sulfides, oxides, and hydroxides are insoluble (sulfides of group 2 cations and hydroxides of Ca^{2+} , Sr^{2+} , and Ba^{2+} are slightly soluble).
6. Sulfates are soluble except for those of calcium, strontium, and barium.

Soluble: Strong Electrolytes ($K_{\text{sp}} \gg 1$)



Insoluble: Weak Electrolytes ($K_{\text{sp}} \ll 1$)



↑
“slightly soluble”
= soluble

Table 5-1; p. 156-159
(146-149, 9th ed.)



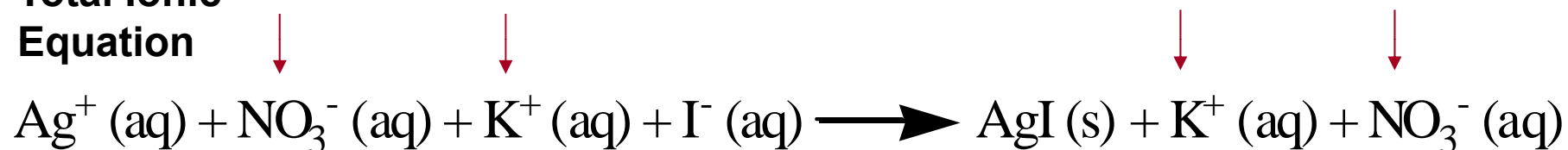
Net Ionic Reaction

Precipitation of AgI (s)



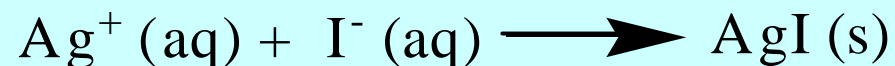
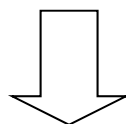
or

Total Ionic
Equation



*Spectator Ions
Derived from Strong
Electrolytes*

Net Ionic Equation

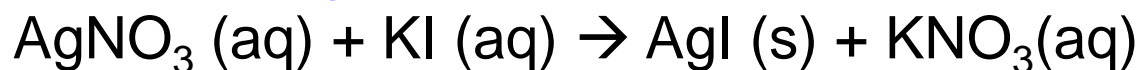


Practice Exercise & Solution

Practice Question:

Determine the mass of KI needed to precipitate 0.1 mM of AgNO_3 in a 20 mL sample solution.

Balanced equation:



Moles of AgNO_3 present in solution:

$$(1 \times 10^{-4} \text{ moles/L}) \times (2 \times 10^{-2} \text{ L}) = 2 \times 10^{-6} \text{ moles of } \text{AgNO}_3$$

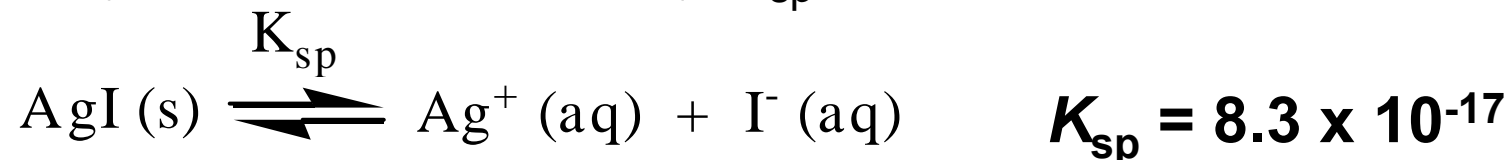
moles of KI = moles of AgNO_3 , from the balanced reaction.

$$\text{Mass of KI} = 2 \times 10^{-6} \text{ moles} \times 166.0 \text{ g/mol} = 0.3 \text{ mg}$$



Solubility & Precipitation: Demo#1

Solubility Product (defined by K_{sp})



Precipitation



$\text{AgNO}_3 (\text{aq})$



NaI (aq)

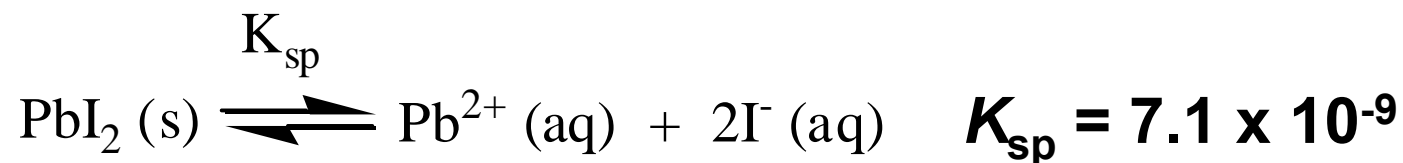


$\text{AgI (s)} + \text{NaNO}_3 (\text{aq})$

Fig. 5-7 (5-4 9th ed.)



Solubility & Precipitation: Demo#2



iClicker Question #3

What would be the impact of dissolving PbI_2 in a 1.0 M solution of $\text{Pb}(\text{NO}_3)_2$?

- a. Increase the solubility
- b. Decrease the solubility
- c. No effect on equilibrium



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Fig. 18-1, pg 752



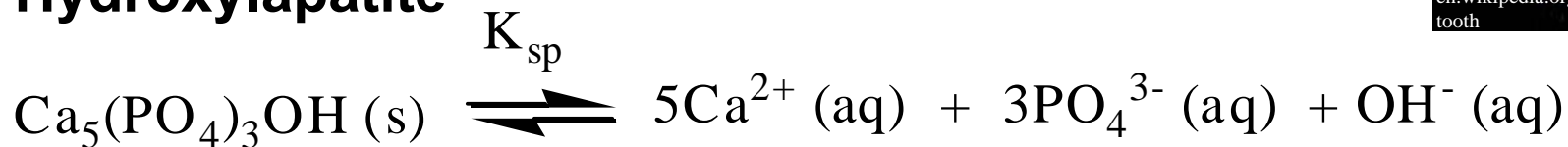
Solubility Product for Salts: K_{sp}

- Measure of the **intrinsic solubility** of a salt in aqueous solution → Also temp., pH, ionic strength dependent; K_{sp} in pure water
- A **low $K_{sp} \ll 1$** implies a sparingly soluble or highly insoluble salt

Which form of apatite is **least soluble & most resistant** to demineralization (tooth decay)?

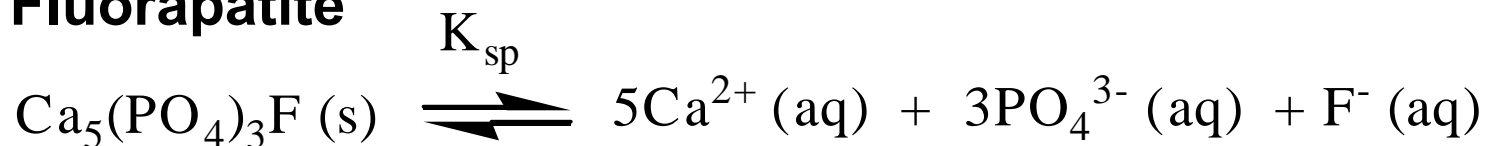


Hydroxylapatite



$$K_{sp} = [\text{Ca}^{2+}]^5 [\text{PO}_4^{3-}]^3 [\text{OH}^-] = 1.0 \times 10^{-36}$$

Fluorapatite

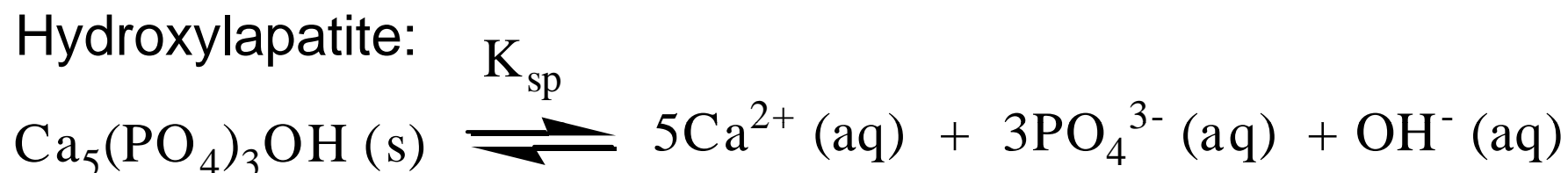


$$K_{sp} = [\text{Ca}^{2+}]^5 [\text{PO}_4^{3-}]^3 [\text{F}^-] = 1.0 \times 10^{-60}$$



Differential Solubility of Salts

Determine the Relative Decrease in Solubility of Fluorapatite vs. Hydroxylapatite



$$K_{\text{sp}} = [\text{Ca}^{2+}]^5 [\text{PO}_4^{3-}]^3 [\text{OH}^-] = 1.0 \times 10^{-36}$$

Let $x = [\text{OH}^-]$ formed upon dissolution

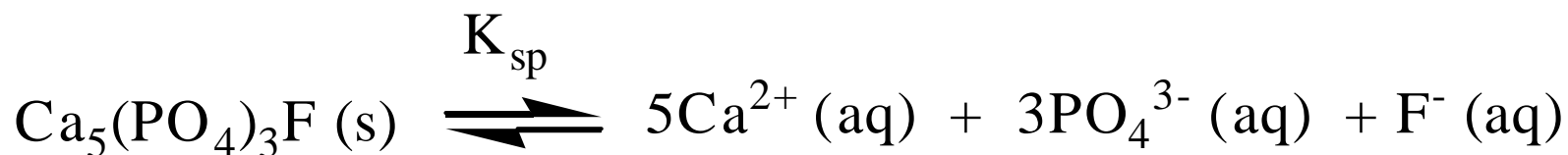
$$K_{\text{sp}} = (5x)^5 (3x)^3 (x) = 84375 x^9$$

$$x = [K_{\text{sp}}/84375]^{1/9} = 2.84 \times 10^{-5} \text{ M} \quad \leftarrow \text{Molar solubility of hydroxylapatite}$$



Differential Solubility of Salts...contd

Similarly, for Fluorapatite:



$$K_{\text{sp}} = [\text{Ca}^{2+}]^5 [\text{PO}_4^{3-}]^3 [\text{F}^{-}] = 1.0 \times 10^{-60}$$

Let $x = [\text{F}^{-}]$ formed upon dissolution

$$K_{\text{sp}} = (5x)^5 (3x)^3 (x) = 84375 x^9$$

$$x = [K_{\text{sp}}/84375]^{1/9} = 6.11 \times 10^{-8} \text{ M}$$

$$\frac{2.84 \times 10^{-5} \text{ M}}{6.11 \times 10^{-8} \text{ M}} = 460$$

Hydroxylapatite 460-fold
more soluble than
fluorapatite



Take Home Problem

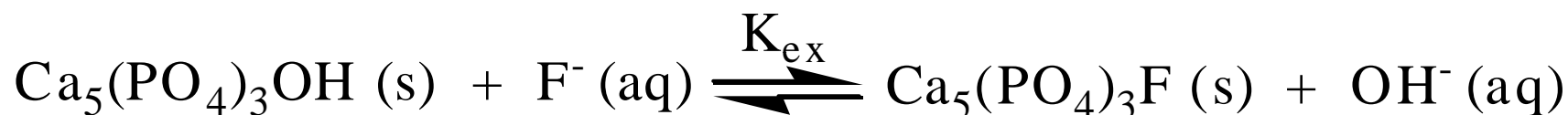
What is the molar solubility of cobalt (II) hydroxide ($K_{sp} = 1.6 \times 10^{-15}$)?

- a. 6.1×10^{-6}
- b. 9.3×10^{-6}
- c. 8.7×10^{-6}
- d. 7.4×10^{-6}
- e. 1.1×10^{-6}

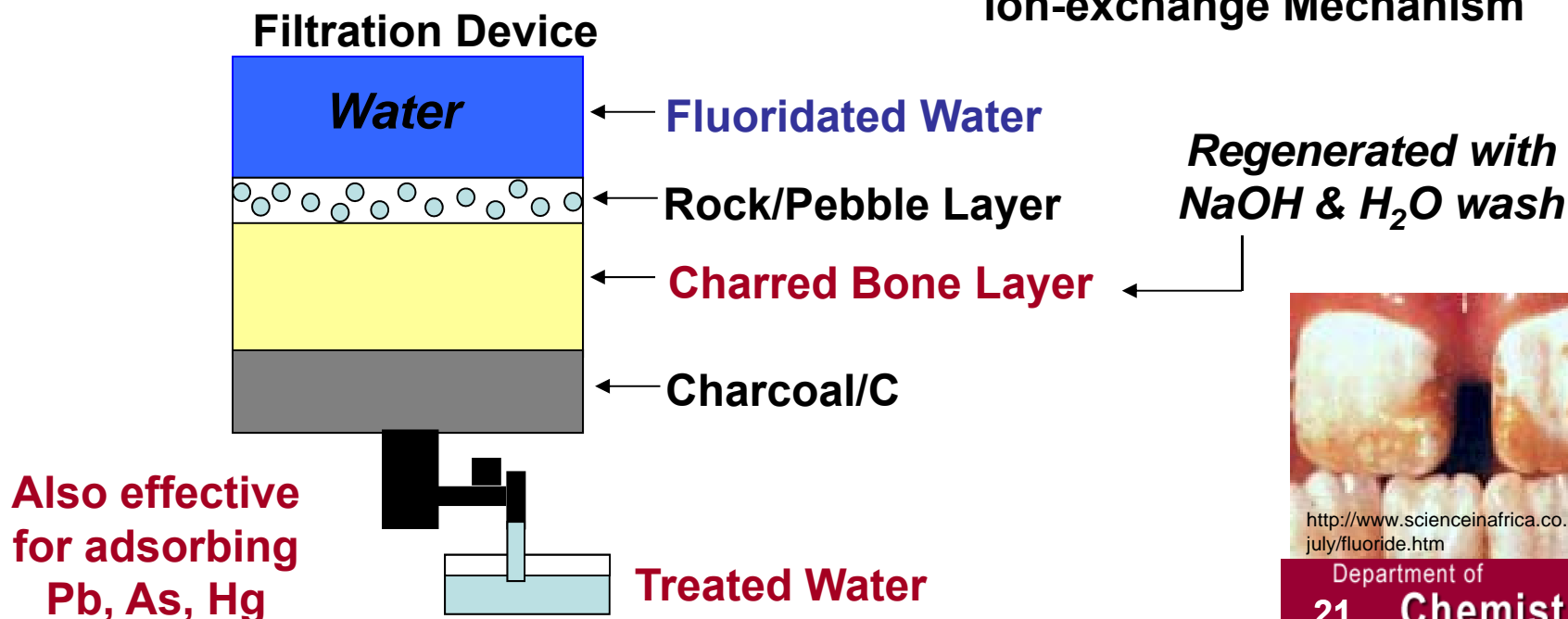


Application: Low Cost Defluoridation Method

- Inexpensive, renewable and low cost method needed for **defluoridation** of drinking water in villages of developing countries
- **Ion-exchange process** uses **charred animal bone** that is pulverized, filtered & washed for defluoridation via **F⁻ adsorption**

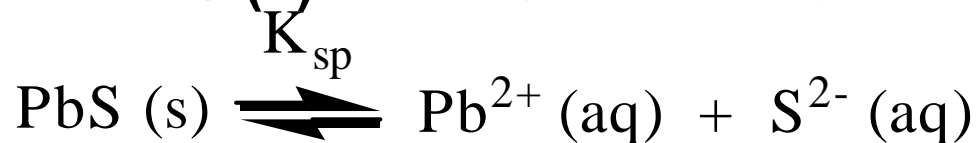


Ion-exchange Mechanism



Q vs K_{sp} : Practice Question

Precipitation of PbS (s): Lead Contamination



$$K_{sp} = [\text{Pb}^{2+}] [\text{S}^{2-}] = 3.0 \times 10^{-29}$$



<http://www.sxc.hu/photo/158242>

Will a precipitate form if 0.50 mL of 10 μM of K_2S is mixed with 250 mL of 0.10 μM $\text{Pb}(\text{NO}_3)_2$?



Initial Concentration of K_2S
After Mixing Solutions:

$$\begin{aligned} &= (1 \times 10^{-5} \text{ mol/L} \times 5 \times 10^{-4} \text{ L}) / 2.505 \times 10^{-1} \text{ L} \\ &= 1.996 \times 10^{-8} \text{ M} \end{aligned}$$

Initial Concentration of $\text{Pb}(\text{NO}_3)_2$
After Mixing Solutions:

$$\begin{aligned} &= (1 \times 10^{-7} \text{ mol/L} \times 2.50 \times 10^{-1} \text{ L}) / 2.505 \times 10^{-1} \text{ L} \\ &= 9.980 \times 10^{-8} \text{ M} \end{aligned}$$

$$Q = [\text{Pb}^{2+}][\text{S}^{2-}] = (9.98 \times 10^{-8})(1.996 \times 10^{-8}) = 2.0 \times 10^{-15} \gg K_{sp}$$

Therefore, precipitate of PbS (s) will form!



iClicker Questions #4 & #5

What is the value for Q_{sp} if 0.500 mL of 1.50M $BaCl_2$ is mixed with 0.600 mL of 0.20M $NaOH$?

- a. 8.1×10^{-3}
- b. 7.7×10^{-3}
- c. 2.3×10^{-3}
- d. 9.1×10^{-2}
- e. 7.4×10^{-2}

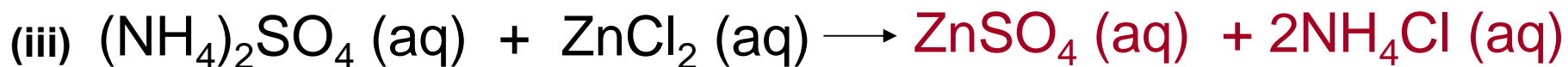
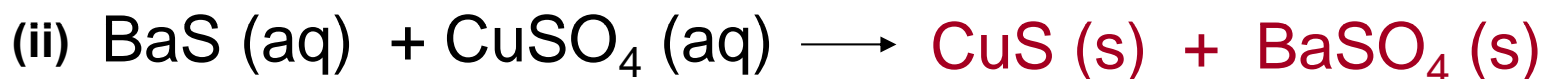
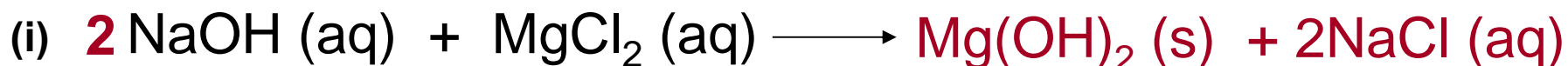
If the K_{sp} for $Ba(OH)_2$ is 5×10^{-3} , will a precipitate form?

- a. Yes
- b. No



Take Home Problem

Which of the following reactions will result in formation of a precipitate?



(A) i

(D) i and ii

(B) ii

(E) ii and iii

(C) iii

Note that precipitation reactions involve an **ion-exchange** process **without** changes in oxidation state of any species

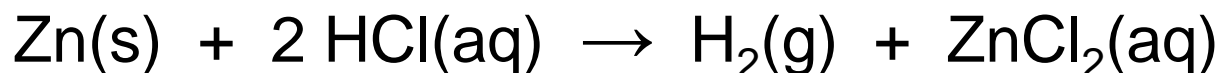


Reduction-Oxidation Reactions (Redox)

- A redox reaction can be identified by changes in oxidation numbers (O.N.) in the reactants and products
- The **reducing agent** **loses electrons** and is **oxidized**
- The **oxidizing agent** **gains electrons** and is **reduced**

Example (Lab 2):

LEO says GER or OIL RIG



O.N. 0 +1 -1 0 +2 -1

Zn(s) is **oxidized** (loses 2 e⁻)

Zn is the reducing agent

H⁺(aq) is **reduced** (each H⁺ gains 1 e⁻)

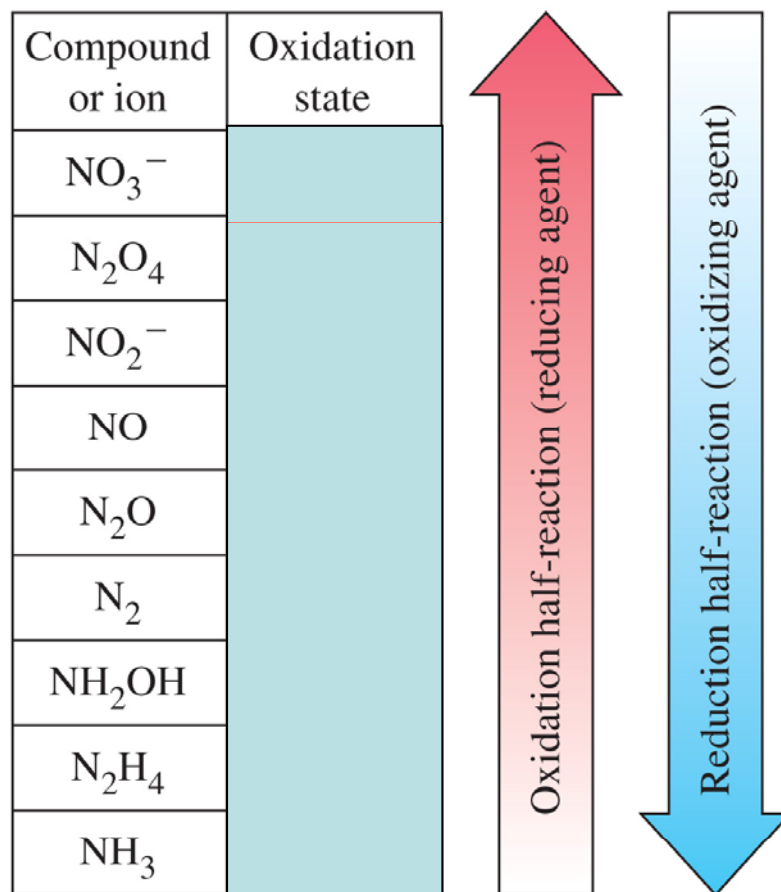
H⁺ is the oxidizing agent



Concept Check: Oxidation States of Nitrogen

N Biogeochemical Cycle

Compound or ion	Oxidation state
NO_3^-	
N_2O_4	
NO_2^-	
NO	
N_2O	
N_2	
NH_2OH	
N_2H_4	
NH_3	



The diagram illustrates the N Biogeochemical Cycle. It features a table with two columns: 'Compound or ion' and 'Oxidation state'. The compounds listed are NO_3^- , N_2O_4 , NO_2^- , NO , N_2O , N_2 , NH_2OH , N_2H_4 , and NH_3 . To the right of the table are two large vertical arrows. The left arrow is red and points upwards, labeled 'Oxidation half-reaction (reducing agent)'. The right arrow is blue and points downwards, labeled 'Reduction half-reaction (oxidizing agent)'.

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Fig. 5-15, p. 176 (5-9, p 162, 9th ed.)



iClicker Question #6

What is the oxidation number for phosphorous in Na_2HPO_4 ?

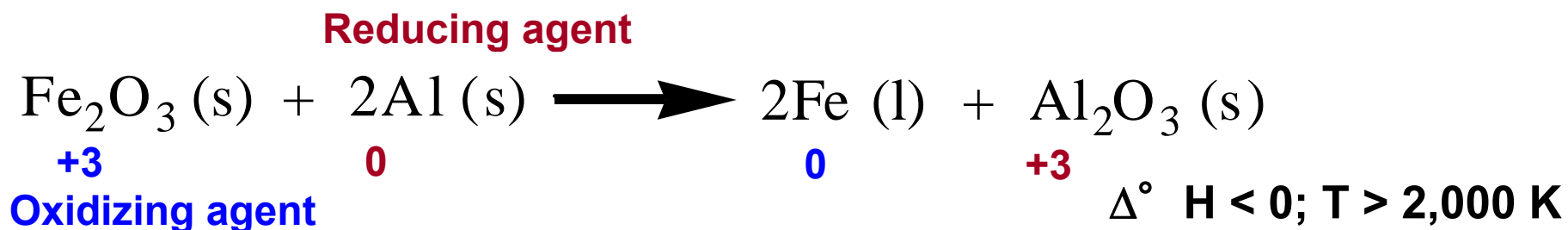
- a. 0
- b. +3
- c. -2
- d. +5



Redox Reactions

Thermite Reaction (or Goldschmidt reaction, 1893)

- A classic **redox reaction** involving hematite (rust) and aluminum for welding applications/pyrotechnics



Highly Exothermic!

Consider Half-Reactions

- $\text{Fe}^{3+} (\text{s}) + 3\text{e}^- \longrightarrow \text{Fe} (\text{l})$ **Reduction (Gains e^-)**
- $\text{Al} (\text{s}) \longrightarrow \text{Al}^{3+} (\text{s}) + 3\text{e}^-$ **Oxidation (Loses e^-)**

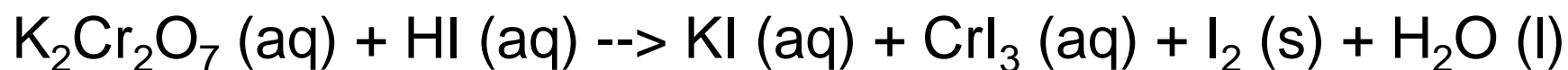
A redox reaction is an **electron transfer** process!

http://www.youtube.com/watch?v=Yex063_Fblk



iClicker Question #7

Identify the oxidizing agent in the following redox reaction:



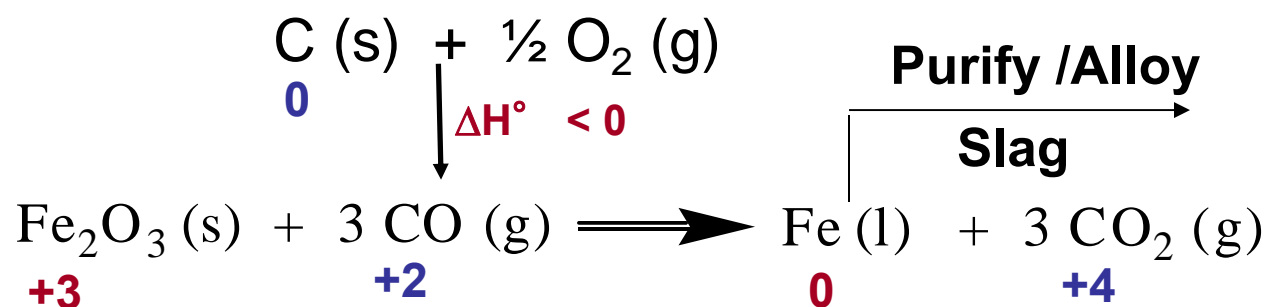
- a. I^-
- b. $\text{Cr}_2\text{O}_7^{2-}$
- c. K^+
- d. Cr^{3+}
- e. H_2O



From the Iron Age to Post-Modern Age

Reduction of Iron Oxide

- Steel and related **iron-based alloys** are widely used in construction
- Smelting of iron ore** in a blast furnace → Chemical **reduction** method for iron (Fe) extraction; Feedstocks: C, Fe₂O₃, CaCO₃



Purify /Alloy
Slag

**Steel & Steel
Alloys**

Fe₂O₃ (s)



Fe (l)



**Stainless
steel
Fe (Cr, Ni)**



Hamilton: Steel City

U. S. Steel Canada (Stelco) &
ArcelorMittal Dofasco Inc.

Blast Furnace: Continuous Generation of Fe (I)

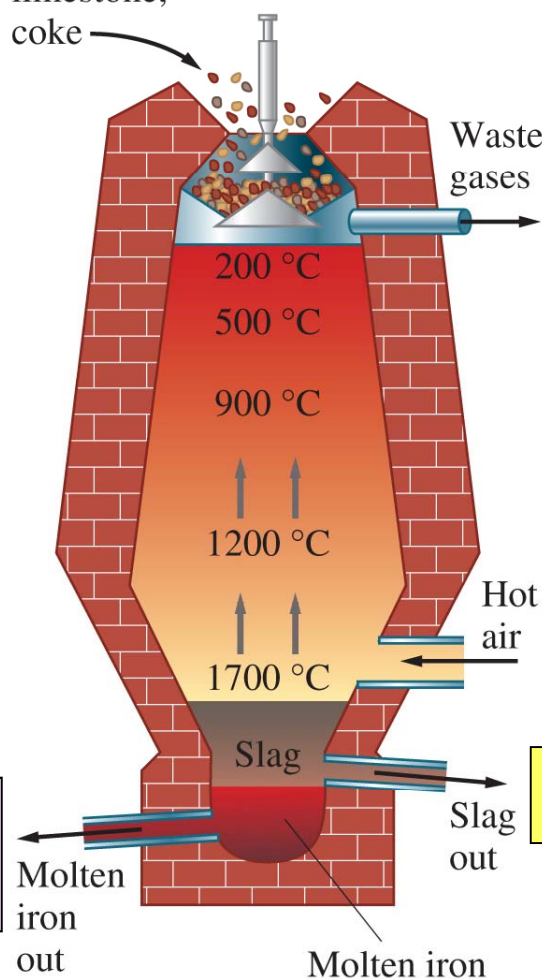
C, Fe₂O₃, CaCO₃

Ore,
limestone,
coke

Fig 23-9 p. 1044 (Fig
23.8, pg 976, 9th ed.)

Steel: Fe < 1% C

**Pig Iron, Fe (I)
3 - 4 % C**



**Waste Gases:
CO₂, CO, SO₂, NO_x, H₂O**

Scrubbing of waste gases
needed to reduce emissions
& lower energy costs!

Hot Air Injection

Slag (Silicates)



Balancing Redox Reactions: Half-reactions

1. Deduce the **oxidation numbers** for all species → This will identify the oxidizing and reducing agents
2. Write reduction and oxidation skeleton **half-reactions**
3. **Balance** the redox atoms (usually not O, H unless they are participating in the redox chemistry)
4. Add the correct number of **electrons** to each half-reaction
- 5a. If **acidic conditions**: Balance O by adding H_2O then H by H^+
- 5b. If **basic conditions**: Balance as if in acidic conditions, then add OH^- to balance the H^+ (making water), then cancel the H_2O (or balance the negative charges by adding OH^- , then balance O & H by adding H_2O)
6. **Check atoms and charges**. Multiply half-reactions by a factor, if needed, to make the number of electrons transferred match.
7. **Write the net redox reaction!**

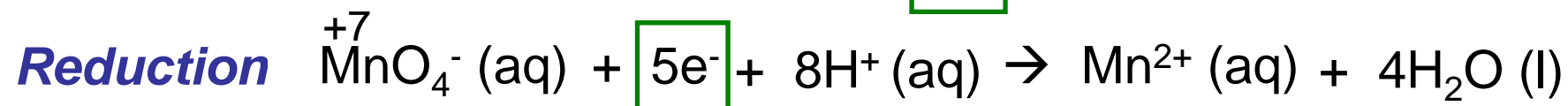
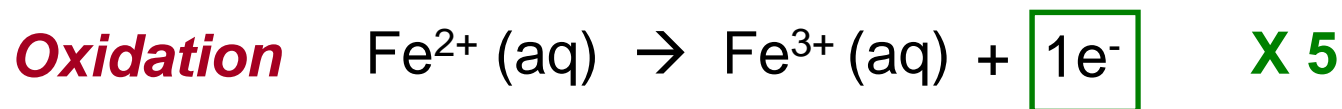


Balancing Redox Reactions: Acidic Conditions

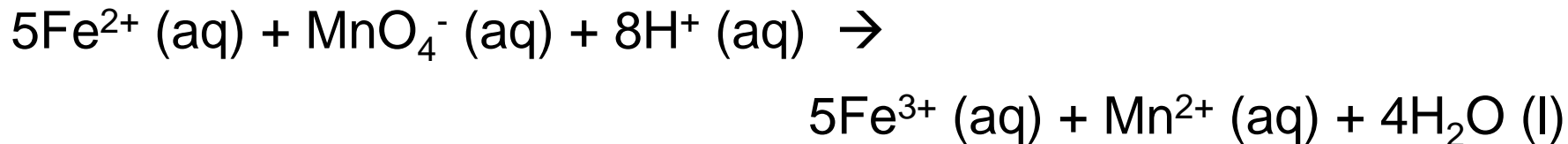
Balance the following reaction under acidic conditions:



Half-cell Reactions:

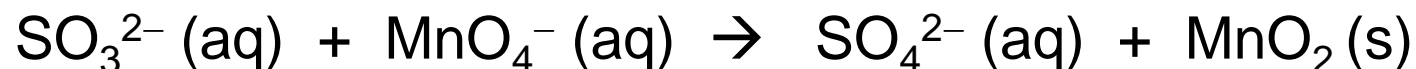


Net Balanced Redox Reaction

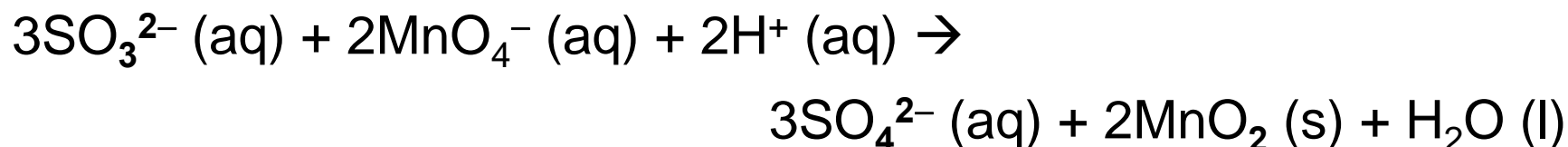
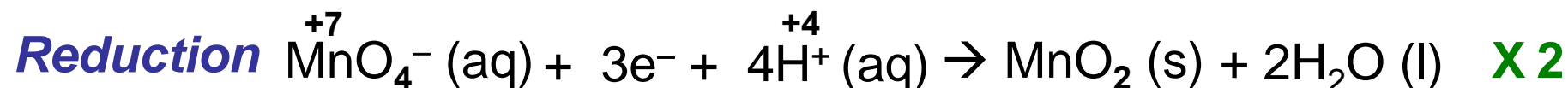
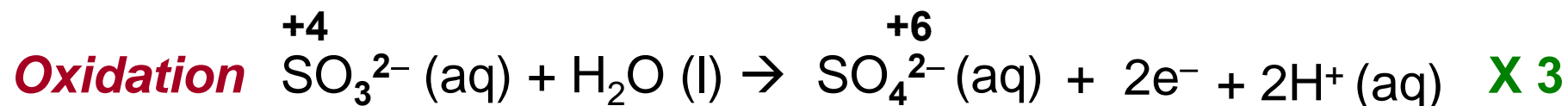


Balancing Redox Reactions: Basic Conditions

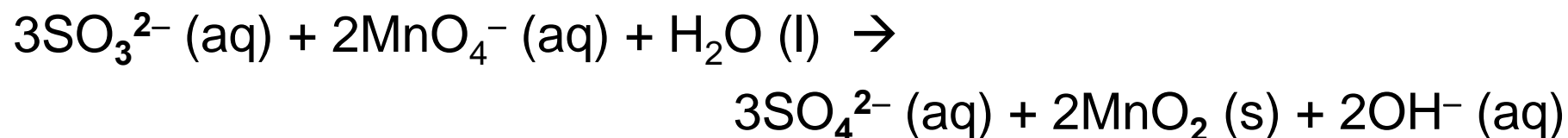
Balance the following reaction under basic conditions:



Half-cell Reactions:



Net Balanced Redox Reaction



iClicker Question #8

When the following is balanced in a basic solution:



The coefficient in front of CO_3^{2-} is:

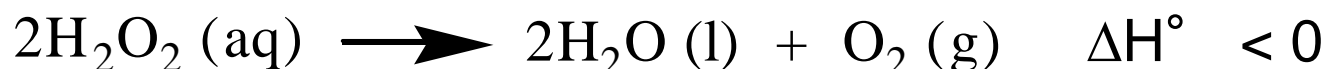
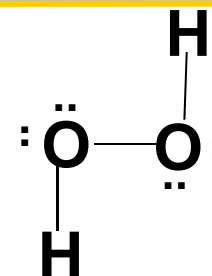
- a. 1
- b. 2
- c. 3
- d. 4
- e. 6



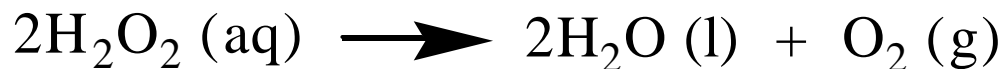
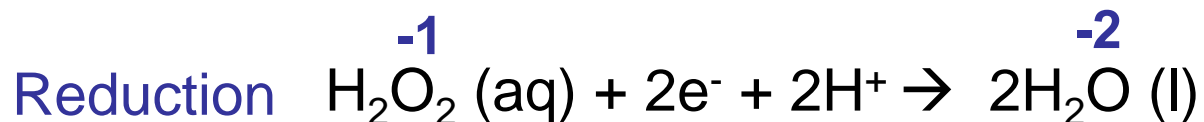
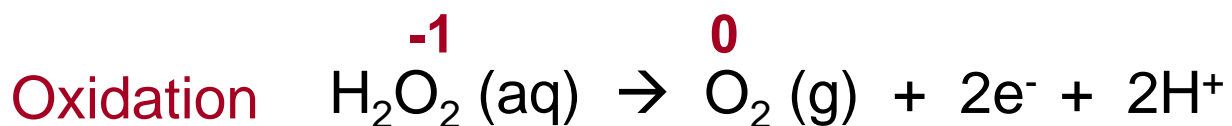
Disproportionation Reactions

Hydrogen Peroxide (H₂O₂)

- Reactive molecule because of **weak O-O** single bond
- One reactant (H₂O₂) acts as **both** reducing and oxidizing agent



Half-Reactions



3% H₂O₂ as disinfectant



Topical antiseptic as H₂O₂ can oxidize microbes

p. 174 (p. 160, 9th ed.)

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Department of
36 Chemistry



REDOX Chemical Reactions: Demo

- Observe and predict the outcome of these two reactions

Redox Chemical Reactions



As in Lab 2



Observations...



A Closer Look...



(a)



(b)



(c)

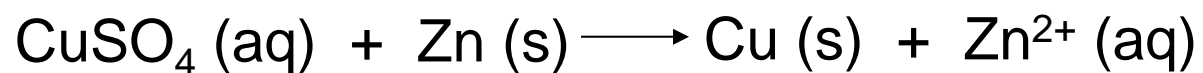
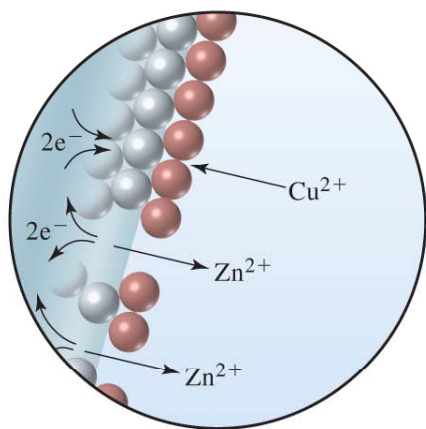


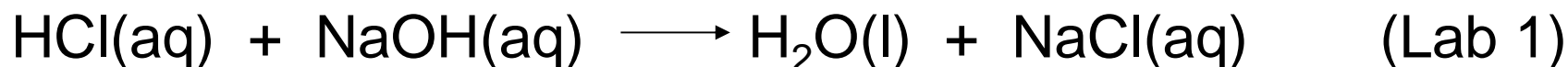
Fig 5-12, p. 167 (Fig 5-7, p. 155)



Acid-Base Reactions

- Involve proton (H^+) transfer (Bronsted-Lowry definition)

Example:



Acid **Base (OH^-)**

H^+ donor **H^+ acceptor**

- The focus of an upcoming section (Ch 16)

