CHEM 205 section 03

LECTURE #15 Thurs., Feb.28, 2008

LECTURE TOPICS:

TODAY'S CLASS: section 20.1
start Ch.7

MIDTERM EXAM: Tues. March 4th during class
Ch.1-5 (all) but not 20.1
see sample MTs on website

NEXT LECTURE: Thurs. March 6th
continue Ch.7

(1)

Balancing Redox equations: *simple vs. more complex*

1.) **By inspection** - for simple redox reactions

$$Fe_2O_3(s) + 2\,Al(s) \rightarrow 2\,Fe(s) + Al_2O_3(s)$$

(+III) (-II) (0) (0) (+III) (-II)

Oxidation ½ rxn: $2\,Al \rightarrow 2\,Al^{3+} + 6e^-$

Reduction ½ rxn: $2\,Fe^{3+} + 6e^- \rightarrow 2\,Fe$

IMPORTANT to note:
(i) Atoms must balance *...AND...*
(ii) Total change in oxidation states also balance
i.e., no free electrons left over on either side!

2.) **Systematic method:** "Half-reaction method" **Ch.20.1**

useful for reactions in solution (usually acidic or basic)
sometimes solvent is involved, & rxn requires H^+ or OH^-

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Section 20.1: the "half-reaction method"
for balancing redox rxns in acidic / basic solution

In acid: $Fe^{2+}(aq) + MnO_4^-(aq) \rightarrow Fe^{3+}(aq) + Mn^{3+}(aq)$

Ox.: $Fe^{2+} \rightarrow Fe^{3+} + 1e^-$

Ox. ½-rxn: Balance…
- atoms except for H, O
- net ox.# change with e⁻s
- O & H using H_2O, H^+
- check: $charge_{LHS} = charge_{RHS}$

Red.: $MnO_4^- + 4e^- + 8H^+ \rightarrow Mn^{3+} + 4H_2O$

(Mn: +VII → +III)

Red. ½-rxn: Balance…
- atoms except for H, O
- net ox.# change with e⁻s
- O & H using H_2O, H^+
- check: $charge_{LHS} = charge_{RHS}$

Net: $[Fe^{2+} \rightarrow Fe^{3+} + 1e^-] \times 4$

$MnO_4^- + 4e^- + 8H^+ \rightarrow Mn^{3+} + 4H_2O$

$4Fe^{2+} + MnO_4^- + \cancel{4e^-} + 8H^+ \rightarrow 4Fe^{3+} + \cancel{4e^-} + Mn^{3+} + 4H_2O$

Net rxn: Balance e- transfer
- all e⁻s lost by red. agent must be gained by ox. agent
- multiply to yield common # e⁻s

⇨ $4Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 4Fe^{3+} + Mn^{3+} + 4H_2O$

Check final balance at end (atoms AND charge).

Balancing by the Half-Rxn Method: in acidic solution

1. **Separate** into reduction & oxidation half-reactions.
2. **Balance each half-reaction separately:**
   - Balance elements <u>except H & O</u>
   - Balance changes in oxidation state using e^-
   - Balance O using H_2O
   - Balance H using H^+
3. **Now together: account for e^- transfer** *(handed off, not thrown)*
   - # e^- (from reducer) = # e^- (to oxidizer)
   - Multiply half-rxns by appropriate integers
4. **Add half-reactions.**
   - Cancel species appearing on both sides of equation
5. **Check for balance:** elements & charge

In base: $Fe^{2+}(aq) + MnO_4^-(aq) \rightarrow Fe^{3+}(aq) + Mn^{3+}(aq)$

1. Balance as if in acid first:

⇨ $4Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 4Fe^{3+} + Mn^{3+} + 4H_2O$

In basic solution: ~no H^+ around
- for every H^+ in equation, add equal OH^- to both sides
- $H^+ + OH^- \rightarrow H_2O$
- cancel out H_2Os if possible

2. Correct for basic solution:

$4Fe^{2+} + MnO_4^- + 8H^+ + 8OH^- \rightarrow 4Fe^{3+} + Mn^{3+} + 4H_2O + 8OH^-$

$4Fe^{2+} + MnO_4^- + \not{8}H_2O \rightarrow 4Fe^{3+} + Mn^{3+} + \not{4H_2O} + 8OH^-$

⇨ $4Fe^{2+} + MnO_4^- + 4H_2O \rightarrow 4Fe^{3+} + Mn^{3+} + 8OH^-$

Check final balance at end (atoms AND charge).

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Balancing by the Half-Rxn Method: in basic solution

1. Balance as if in acidic solution. *THEN think how BASE differs…*
2. For every H^+: add an OH^- to BOTH sides of rxn eq'n
3. Form water via: $H^+ + OH^- \rightarrow H_2O$
4. Simplify rxn eq'n: cancel out as many H_2O as possible.
5. Check balance: both elements and charges.

Make sure you understand the purpose of steps #2-3:

If the redox reaction **requires H^+**…
- in base, rxn can't find enough dissolved H^+ in solution
- rips H^+ off of H_2O molecules ⇨ leaving OH^- as a product

If the redox reaction **produces H^+**…
- in base, any H^+ produced will react with OH^- ions in sol'n ⇨ leaving H_2O as a product

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Oxidation of sulfite by chromate ion: ***unbalanced; do 1st in acid***

In base: $CrO_4^{2-}(aq) + SO_3^{2-}(aq) \rightarrow Cr(OH)_3(s) + SO_4^{2-}(aq)$

Net in acid: $4H^+ + 2CrO_4^{2-} + 3SO_3^{2-} + H_2O \rightarrow 2Cr(OH)_3 + 3SO_4^{2-}$

Net in base: $2CrO_4^{2-} + 3SO_3^{2-} + 5H_2O \rightarrow 2Cr(OH)_3 + 3SO_4^{2-} + 4OH^-$

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Mining applications… (modified from Kotz Ch5 #117)

Gold can be dissolved from gold-bearing rock by treating the rock with aqueous sodium cyanide in the presence of oxygen:

Unbalanced: $Au(s) + NaCN(aq) + O_2(g) \rightarrow Na[Au(CN)_2](aq)$

(a) What type of reaction is this?

(b) Give the appropriate labels to the reactants (not all apply):

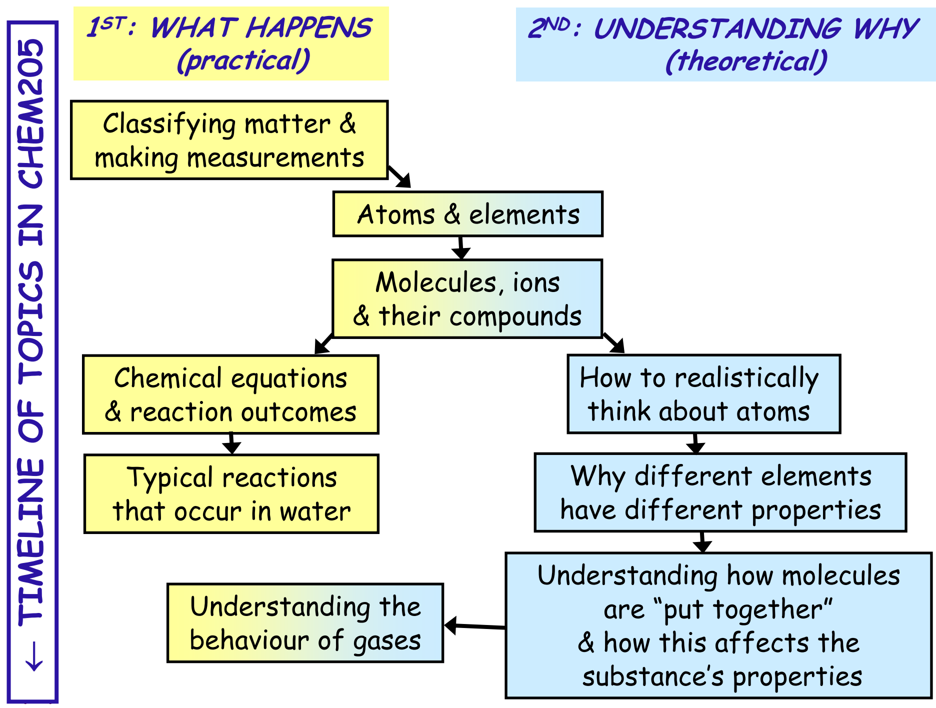
Precipitate *Acid* *Base* *Oxidizing agent* *Reducing agent*

(c) Show by ½-rxn method that the balanced equation is: (a hard one)

$$4Au(s) + 8NaCN(aq) + O_2(g) + 2H_2O(\ell) \rightarrow 4Na[Au(CN)_2](aq) + 4NaOH(aq)$$

(d) If you had 2500 tonnes of gold-bearing rock that is 0.019% gold, how much NaCN (in kg) would you need to add to your extraction solution to extract all the gold from the rock? 240 kg

(e) If gold is currently worth \$650/ounce (1 oz. = 28.35 g), how much would the gold in the rock be worth? \$11 million…



- Why do groups of elements have such similar properties?
- Can we explain this based on the structure of their atoms?
- How ARE atoms structured? (We know what is IN them.)

Chapter 7: Atomic Structure

7.1 Electromagnetic Radiation
7.2 Planck, Einstein, Energy & Photons
7.3 Atomic Line Spectra & Niels Bohr
7.4 Quantum Properties of the Electron
7.5 Quantum Mechanical View of the Atom
7.6 Shapes of Atomic Orbitals
7.7 Atomic Orbitals & Chemistry

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Chapter Goals:

- Describe properties of electromagnetic radiation.
- Understand origin of light from excited atoms & how this relates to atomic structure.
- Describe experimental evidence for wave-particle duality.
- Describe basic ideas of quantum mechanics.
- Define the three quantum numbers (n, ℓ, m_ℓ) and their relation to atomic structure.

Before we begin, we must accept a strange fact:
Small things & big things play by different rules

<u>1900 – 1930's…</u>

Revolution in physics:

- behaviour of light & atoms **cannot** be explained by Newton's classical laws of physics
  - ⇨ needed to create a "new physics"

Classical mechanics	**Quantum mechanics**
the PHYSICS of the MACROSCOPIC world	the PHYSICS of very small things (electrons, light…)

Start by thinking about the nature of light…

7.1 Electromagnetic radiation *(= light)*

Light = RADIANT ENERGY

- Behaves as a wave
- Travels at "speed of light"

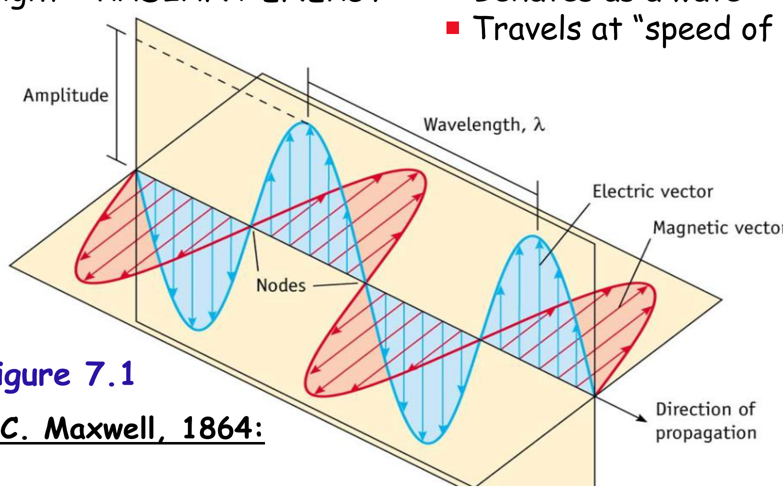


Figure 7.1

<u>J.C. Maxwell, 1864:</u>

Radiation = oscillating perpendicular electric & magnetic fields…
…emanated from vibrating charges in the "source"

See CD-ROM screen 7.3

Primary characteristics of light waves

Wavelength (λ) **"LAMBDA"**: distance between 2 consecutive peaks or troughs in a wave.

Frequency (ν) **"NU"**: number of waves per second that pass a given point in space.

Speed **(c)**: constant for all λ's: 2.9979×10^8 m/s (in vacuum)

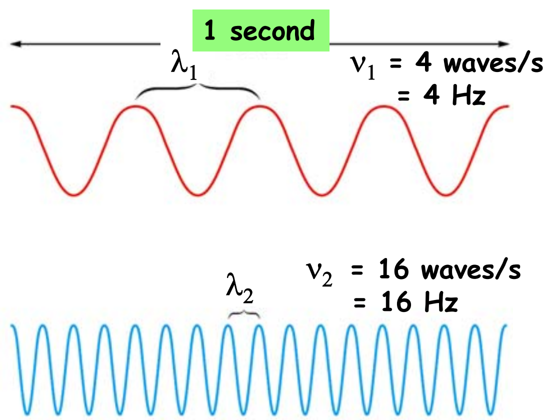
$$c = \lambda \nu$$

c = speed of light (ms^{-1})
λ = wavelength (m)
ν = frequency (s^{-1} Hertz)

Zumdahl's Figure 7.1:

$\lambda_1 > \lambda_2$
$\nu_1 < \nu_2$

shorter wavelength
CORRESPONDS TO
higher frequency



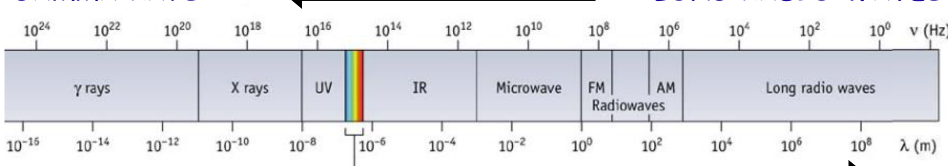
Light is commonly classified by wavelength

Fig7.3

Highest energy
GAMMA RAYS

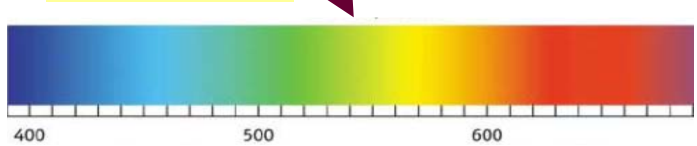
Increasing energy

Lowest energy
LONG RADIO WAVES



Increasing wavelength

Visible Spectrum:
~ 400-700 nm



higher energy
higher frequency
shorter wavelength

lower energy
lower frequency
longer wavelength

Example: The red light emitted by the lasers used to read CDs has a wavelength of 685 nm. What is the frequency of this light?

(15) Ans: $\lambda = 6.85 \times 10^{-7}$ m; $\nu = 4.38 \times 10^{14}$ s^{-1} (= Hz)

7.2 Planck, Einstein, Energy & Photons

The beginning of building a new kind of physics…

Max Planck (1900): "Energy is QUANTIZED"

Matter cannot absorb/emit just any amount of energy…

Energy can only be transferred in multiples of discrete units (packets of energy), called "quanta".

Max Planck
1858-1947
Nobel Prize in Physics 1918

Where did this idea come from?

→ studies of the light emitted by hot objects

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Imagine heating a piece of metal…

As T is increased:

- radiate heat → red light → white light

If measure light emitted:

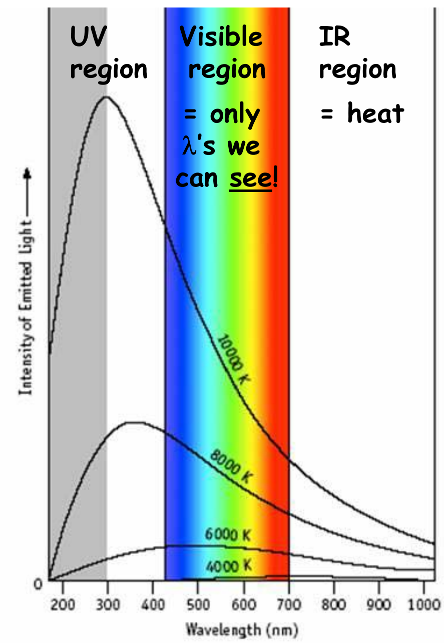
- spectrum of λs emitted…
- as T ↑, spectrum shifts to higher E (shorter λ)

According to classical theory:

- atoms vibrate: E & $\nu \propto T$
- if change from higher to lower E vibration ⇨ excess E emitted as light

- **predicted: intensity ↑ as E ↑**
- **observed: ↓ at highest Es…**
  "the ultraviolet catastrophe"

Figure 7.5



Planck's new ideas tackle this problem…

1.) Quantization of energy 2.) Distribution of vibrations

ONLY CERTAIN VIBRATION ENERGIES ARE ALLOWED
= Vibrational energy is **"QUANTIZED"**

$$E = h\nu$$

- E: Allowed energy for vibrating system (J)
- h: Planck's constant (6.626×10^{-34} J·s)
- ν: Allowed frequency of vibration (s^{-1})

If atom changes vibration energy & emits light:

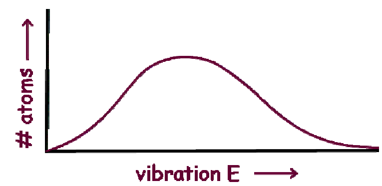
$$\Delta E_{atom} = h\Delta\nu_{atom} = E_{light}$$

Planck's new ideas tackle this problem…

1.) Quantization of energy   2.) Distribution of vibrations

- **In object: predictable distribution of allowed vibrations**
  - → most atoms: intermediate E
  - → smaller #'s: higher & lower E
  - → average E ↑ with ↑ T

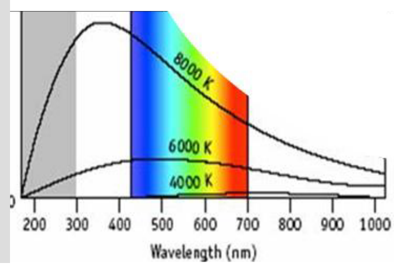
    (curve stretches rightward as T ↑)



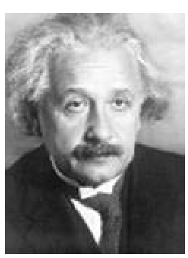
NEW IDEAS SOLVE CATASTROPHE:

Many different vibration energies ($E = h\nu$) are allowed…   SO:

- a collection of atoms emits a spectrum of wavelengths
- with maximum emission intensity at intermediate energies



Einstein's 1st big discovery builds on Planck's



Albert Einstein
1879 – 1955

Nobel Prize in physics 1921
For "services to theoretical physics, especially for the discovery of the law of the photoelectric effect"

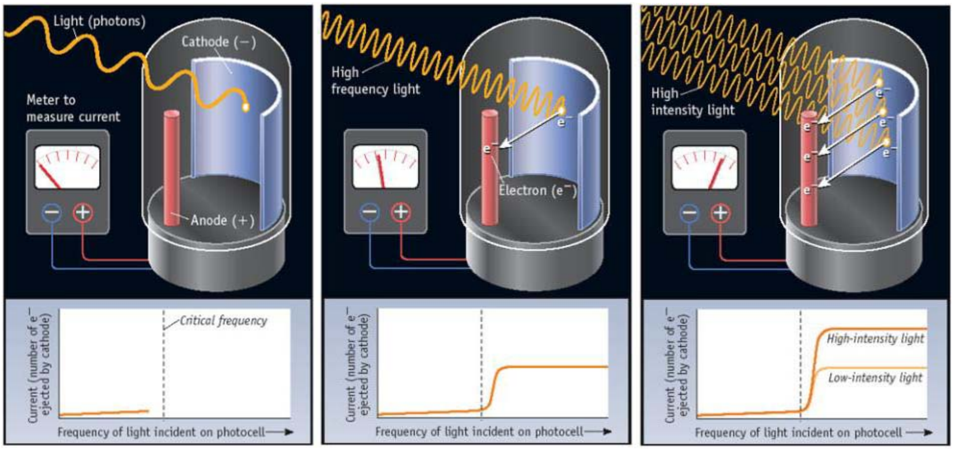
The Photoelectric effect:

If light strikes the surface of a metal
⇨ electrons can be ejected from the metal!

But why?

Einstein's 1st big discovery: the photoelectric effect

Photoionization: seen using a photocell Fig.7.6



- Shine $h\nu$ onto large electrode
- Below threshold E: metal absorbs $h\nu$ ⇨ nothing happens

- Above threshold E: 1 $h\nu$ ⇨ 1e⁻ ejected
- e⁻ travels to anode & gets recaptured ⇨ current flows…

- Higher intensity light ⇨ more e⁻s ejected ⇨ higher current

EINSTEIN'S EXPLANATION of photoelectric effect:

1. Certain quantity of energy required to rip an e⁻ off a metal atom ⇨ only get current if exceed E threshold

2. New idea: Light travels in **energy packets** = **photons**
   - Higher intensity light ⇨ more photons hit metal
     ⇨ more e⁻s ejected
     ⇨ more current…
   - **Energy of each photon is proportional to frequency**:

Higher frequency of light ⇨ higher photon energy

$$\Delta E = h\nu = \frac{hc}{\lambda}$$

Lower photon energy ⇨ Longer wavelength of light

ΔE = energy (in J) change of system absorbing/emitting light = **E**, the energy of the photon!

h = Planck's constant, 6.626×10^{-34} J·s
ν = frequency, in s^{-1}
λ = wavelength, in m

Related example: a photoredox reaction
Photogray lenses in eye glasses incorporate small amounts of AgCl into the glass of the lens. The following reaction occurs in the presence of light, causing the lenses to darken:

$$AgCl(s) \rightarrow Ag(s) + \tfrac{1}{2}\,Cl_2(g)$$

This reaction requires 3.10×10^{2} kJ of energy per mole of AgCl. Assuming all this energy is supplied by light, what is the maximum wavelength of light that can cause this reaction?

- Photo-induced redox rxn: $Cl^{-} + h\nu \rightarrow Cl + e^{-}$, which Ag^{+} picks up…
- *Assume: 1 mole AgCl requires 1 mole of photons*
- *1st: find energy each photon must have…*

$$3.10\times10^{2}\ \text{kJ} \times \frac{1000\ \text{J}}{1\ \text{kJ}} \times \frac{1\ \text{mole}}{6.022\times10^{23}\ \text{photons}}$$

$$= 5.148\times10^{-19}\ \text{J/photon}$$

- *Next: find wavelength of a photon of this energy: where $E = hc/\lambda$*

⇨ $\lambda = hc/E$

$$= \frac{(6.626\times10^{-34}\ \text{J}\cdot\text{s})(2.9979\times10^{8}\ \text{m}\cdot\text{s}^{-1})}{5.148\times10^{-19}\ \text{J}}$$

$$= 3.85\times10^{-7}\ \text{m}$$

$\lambda = 385$ nm

Only light with $\lambda \leq 385$ nm (higher E/photon) can eject e^{-} from Cl^{-} & ∴ darken the lens.

ASSIGNED READINGS

- **BEFORE NEXT CLASS:**

Work on Ch.5 exercises
Practice solution stoichiometry problems…

Read Ch.7 up to section 7.2
Practice frequency↔wavelength↔E conversions

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