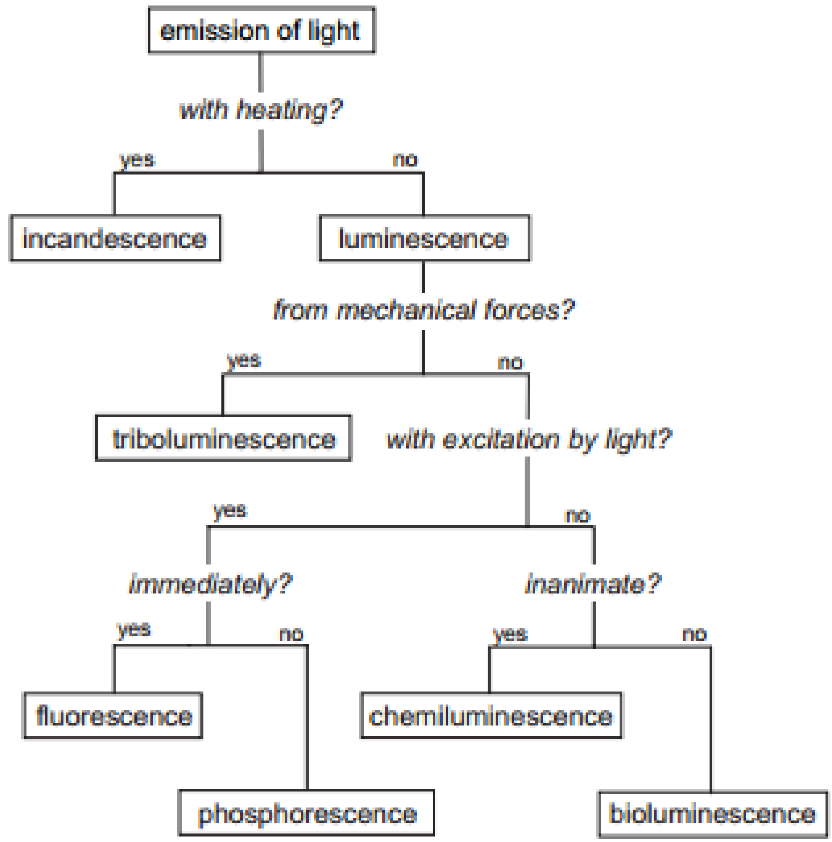
Physical Science in 21st Century (PS-21)

Chemiluminescence – Transferring Chemical Energy to Light Energy

PS-21 October 4, 2013

Manners in which atoms or molecules absorb energy and release light

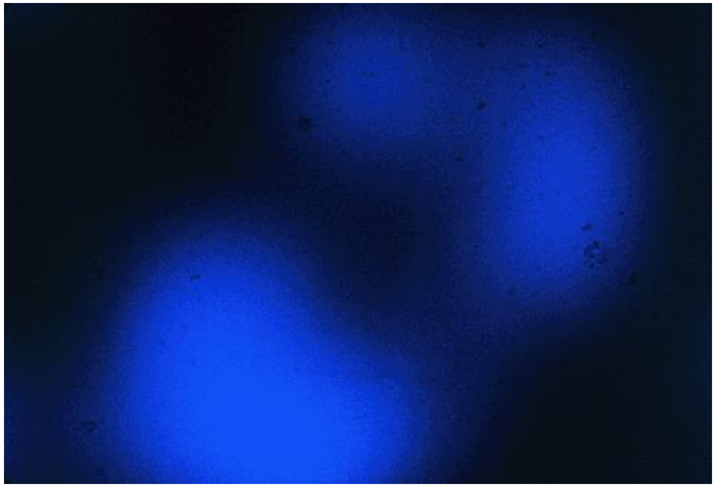


Incandescence

- Incandescent processes are caused by heating a material until it glows
- Example -Tungsten light bulb
- Electric current flowing through tungsten filament heats until its glows

Triboluminescence

- Excitation energy is mechanical energy
- Break a wintergreen (methyl salicylate) Lifesaver with a hammer, pair of pliers, or in the moth of a volunteer in a dark room



Bioluminescence

- Production of chemiluminescence by living organisms
- Best known example is firefly
- In a biochemical reaction in the body of the insect, light is produced by the action of an enzyme on its substrate, luciferin

Chemiluminescence

- Chemiluminescence occurs when an energy-releasing reaction produces a molecule in an electronically excited state and that molecule, as it returns to the ground state, releases its energy as a photon of light

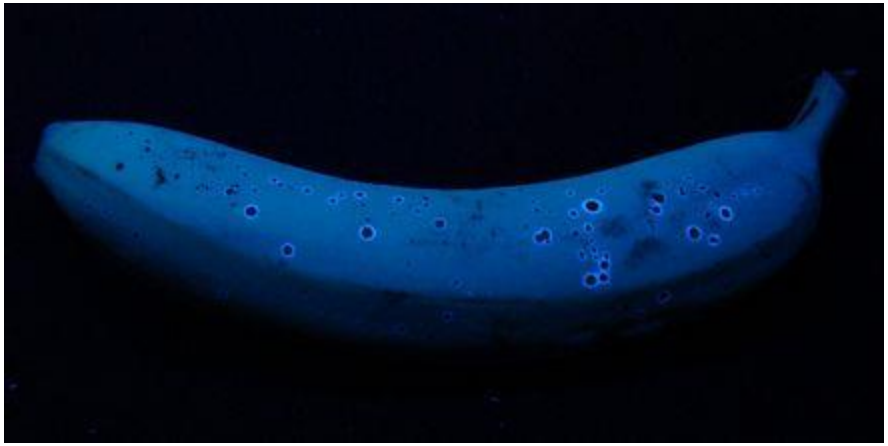
Lightning

- Lightning is an example of gas phase chemiluminescence.
- When an electrical discharge occurs in the atmosphere, gas molecules (O_2, N_2, etc.) are excited from the ground state to higher energy states.
- Additionally, N, O, and other atoms are produced.
- The recombination of these atoms into molecules, as well as the return of excited molecules to the ground state, releases energy in the form of light.

Distinct from Fluorescence or Phosphorescence

- Both of these require absorption of light to produce the excited molecule
- Fluorescent species have lifetimes of only 10^{-9} to 10^{-6} seconds and thus essentially only emit light while being radiated.
- Phosphorescent species have lifetimes of 10^{-3} seconds to several minutes and can “appear” to emit light without being irradiated (although irradiation had to occur at an earlier time)

Banana under daylight (top) and under UVA (bottom). Degradation product of chlorophyll supposedly responsible.

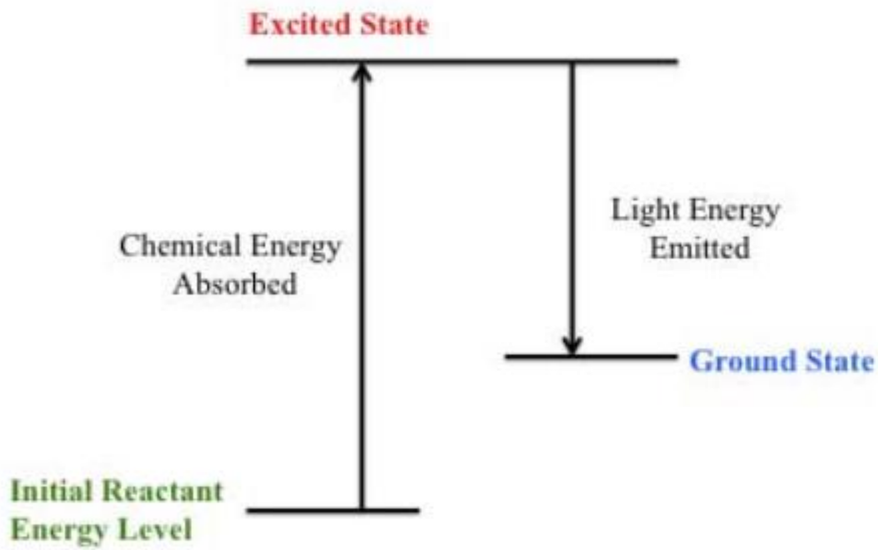


Energy Conversion

- An energy conversion is a change from one form of energy to another (or others).
- Chemiluminescence obeys law of conservation of energy – energy cannot be created nor destroyed; i.e., the total energy in a closed system is always the same
- Conversion of chemical energy → light energy

Chemiluminescence

$$A + B \longrightarrow C + D^{*} \longrightarrow D + \text{light}$$



Requirements for Chemiluminescence

1) Reaction must generate enough energy to create an electronically excited state – i.e., enough energy to promote an electron to a higher energy orbital
2) Reaction must produce a species that is capable of forming an electronically excited state

3) The reaction must follow a mechanism that favors the production of the excited state over direct formation of the ground state

4) The reaction mixture must contain a molecules that deactivates from the electronically excited state by the emission of a photon

5) The rate of production of the excited state must be sufficiently greater than the rate of quenching for the luminescence to be observable

Sensitizers

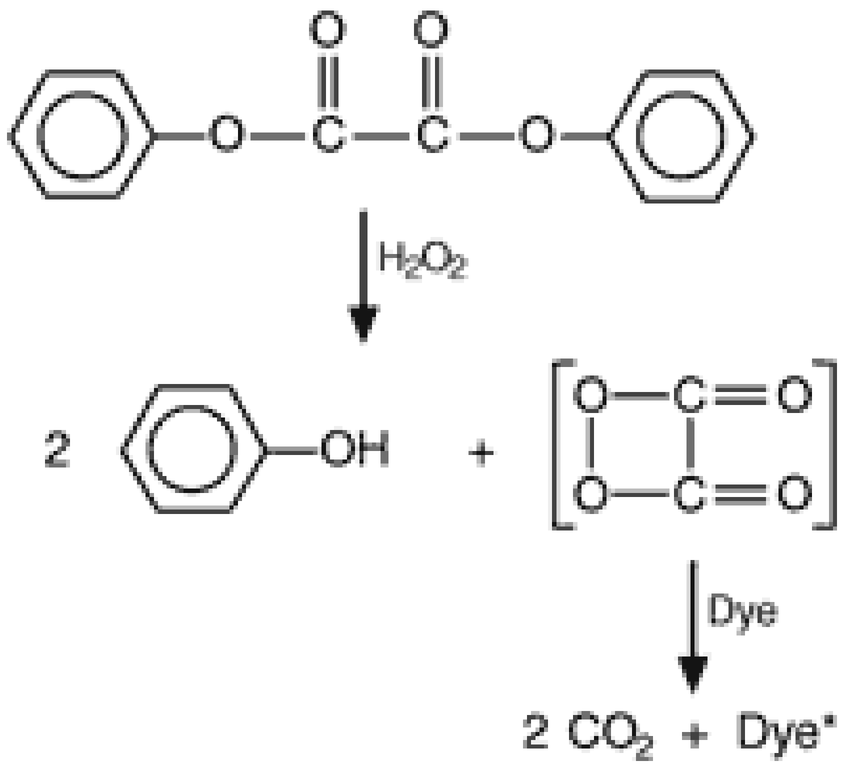
- Luminescence may also arise from acceptor molecules that receive excitation energy from the directly produced excited state species
- The acceptor then subsequently releases the energy as photons of a particular energy – sensitized chemiluminescence
- Acceptors are called sensitizers

Sensitizers

Sensitizer	Color	Intensity	~ Duration
Rhodamine 6G	orange	very bright	30 seconds
Rubrene	yellow	very bright	2 minutes
9,10-diphenulanthracene	blue	very bright	3 minutes
Fluorescein	yellow	dim	5 seconds

Light Sticks – C&E News 1999

- “in the early 1960s, Edwin A. Chandross, a young chemist at Bell Labs in Murray Hill, N.J., was searching for a general way to explain chemiluminescence. Peroxides, with their potential to liberate large amounts of energy during some chemical reactions, seemed to be likely participants.”
- “After a number of experiments, he found to his great excitement that oxalyl chloride mixed with hydrogen peroxide and a fluorescent dye produced chemical light. The efficiency was only about 0.1%, but it was the foundation from which sprang modern chemiluminescence. Chandross, unaware of the powerful potential of his discovery, never patented it.”
- “At about the same time, chemist Michael M. Rauhut was manager of exploratory research at American Cyanamid in Stamford, Conn. He and his colleagues corresponded with Chandross about his oxalyl chloride chemistry, then went to work on the reaction--studying it and looking for avenues that would produce chemical light intense enough to be of practical use.”
- “Rauhut and his colleague Laszlo J. Bollyky developed a series of oxalate esters. Ultimately, Rauhut designed a phenyl oxalate ester that, when mixed with hydrogen peroxide and a dye, gave a [high] quantum yield…--not as efficient as a firefly, but still brilliantly useful. They dubbed it Cyalume, and it became the trademark name for American Cyanamid's chemical light products.”


H2O2
2
OH
+
Dye
2 CO2 + Dye*

- "It was a great project," Rauhut, who is now retired, recalls fondly. "There were a lot of surprises."
- The mechanism that he and other researchers have proposed for the process still stands as the best candidate: The oxalate ester and H_2O_2 react with the help of a salicylate catalyst to form a peroxyacid ester and phenol. The peroxyacid ester decomposes to form more phenol, and most important, a highly energetic intermediate, presumed to be a four-membered ring dimer of CO_2. As the cyclic dimer decomposes into two CO_2 molecules, it gives up its energy to a waiting dye molecule, which then fluoresces.
- The group went searching for fluorescing dyes to make different colors. For example, the common green in most light sticks comes from 9,10-bis(phenylethynyl)anthracene, and 9,10-diphenylanthracene gives blue. "We invented a beautiful yellow," Rauhut remembers.
- American Cyanamid eventually sold its chemical light division in 1993 to Springfield, Mass.-based Omniglow, a manufacturer of chemiluminescent products.
- E. Earl Cranor, head of Omniglow's R&D, continues to develop new commercial uses for chemical light. His latest project is a light stick that works at below-freezing temperatures. He's also always seeking greater efficiencies and better colors. Reds and blues are typically the most difficult to produce, Cranor says. Purple, made from a combination of three dyes, is the most intractable color of all. "Green and yellow," he notes, "are a piece of cake."

Rates of Luminescence - Temperature

- Rates of luminescence reactions, lie those of all reactions, are sensitive to temperature
- To demonstrate, place snapped glow sticks on counter ,in ice, and in boiling hot water (do not let touch sides of container and melt). After about a minute, remove sticks from ice and hot water. Hold all three side-by-side for comparison.
- This is why can place glow stick in freezer to prolong its luminescence

Sources

Stole from the following:

1) "What's this stuff? Light Sticks" C&E News 77 (1999) 65.
2) B. Z. Shakhashiri, Chemical Demonstrations: A Handbook for Teachers of chemistry, Vol. 1, The University of Wisconsin Press, Madison, WI, 1983.
3) P. B. O'Hara, C. Engelson, W. St. Peter, J. Chem. Ed. 82 (2005) 49-52.
4) http://pages.towson.edu/ladon/wg/candywww.htm