

Objective 10

Light and Color

Relate EM radiation properties,

Describe how light is produced with E level diagrams,

Understand quantization.

Elements

Periodic Table
Metals/Non-metals
Molar Mass
Properties

Chemical Reactions

Coefficients and Mole Ratio
Stoichiometry
 ΔH of reaction - Hess' law
Exo/endothermic

Energy
Heat

Or
Light

Formation Reaction
 ΔH_f - Appendix 2

Single Replacement
Reactions
Oxidation-reduction

Combustion
Reaction

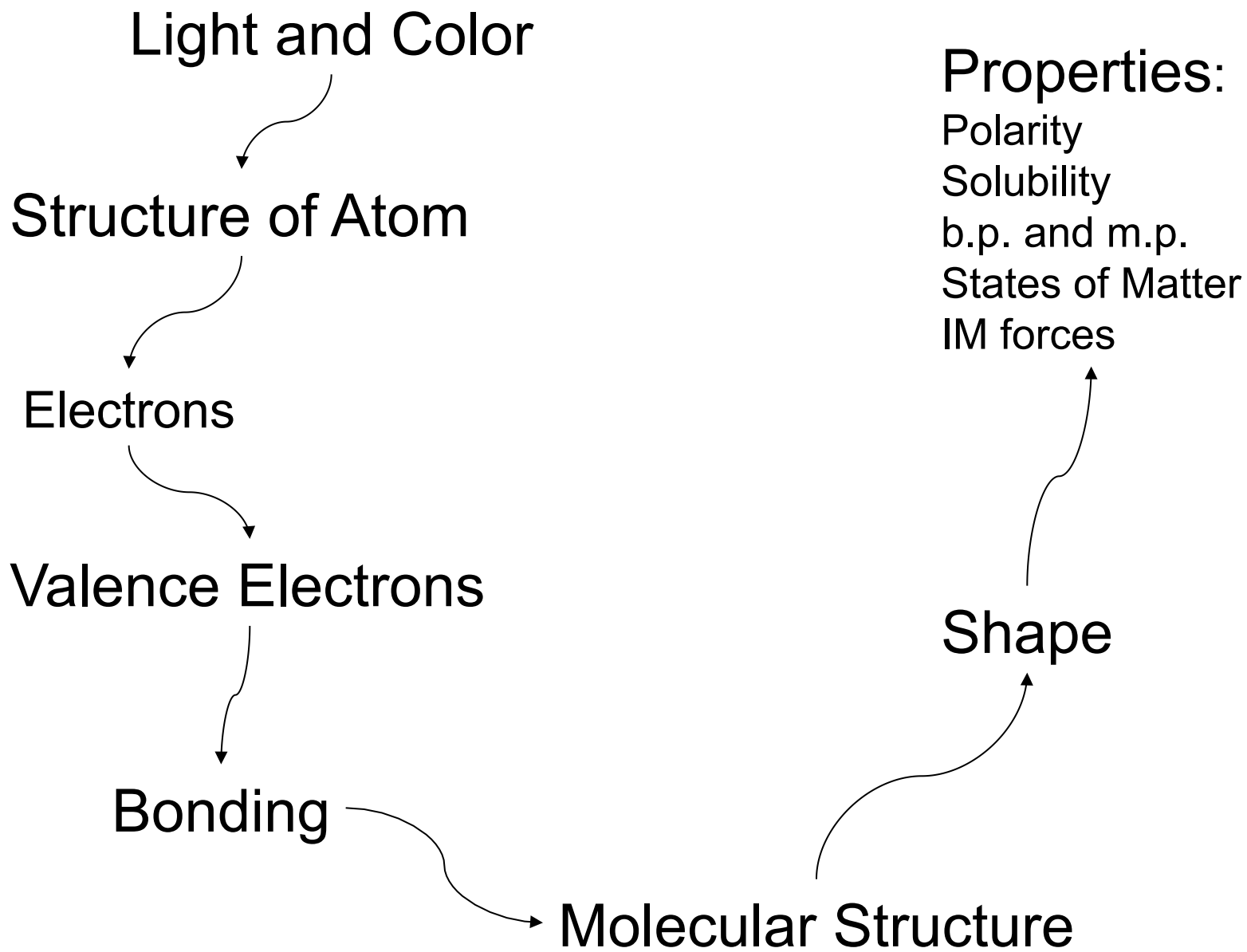
Compounds

Chemical Formula
Subscripts
Molar Mass
Elemental Analysis
% Composition
Properties

Double Replacement
Reactions

Acid-Base
pH

Activity Series



Fiat Lux “Let There Be Light”

Light is Electromagnetic (EM) Radiation

EM radiation has Electric and Magnetic Field components

Transmission of energy by **waves**

Animation: http://dwb4.unl.edu/ChemAnime/atomic_orbits.htm

EM Radiation travels at speed of light ($c = 3.00 \times 10^8$ m/sec)

$$\text{Energy} = E \text{ (in J)} = h\nu = hc/\lambda$$

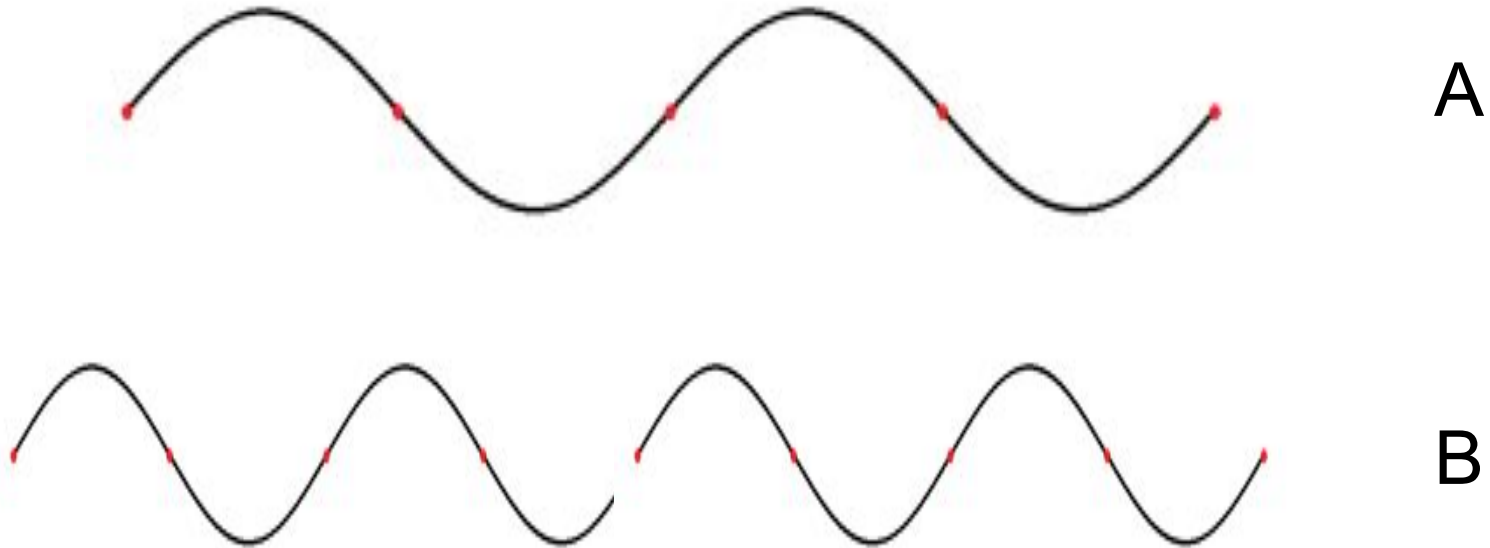
where h = Planck's constant = 6.63×10^{-34} J sec

ν = frequency = c/λ

λ = wavelength

Objective: relate wavelength to frequency to energy

Light is a Wave - quantified by wavelength, frequency, speed, and amplitude.



Which wave has the longer wavelength?

Which wave has the higher frequency?

Which wave has the higher energy?

More wave properties: Reflection, Refraction, Diffraction

Color is Light We Can See - Visible Light

A supermarket scanner uses a He-Ne laser, which emits **656** nm red light.

Objective: Calculate the energy in J of 656 nm red light.

- a. 6.56×10^7
- b. 4.57×10^{14}
- c. 3.03×10^{-19}



<http://www.laserfest.org/lasers/innovations.cfm>

1974: The first barcode scanner used in supermarkets.
(1st public laser)

Color is Light We Can See - Visible Light

Calculate the energy in J of 656 nm red light.

$$\begin{aligned} E \text{ (in J)} &= h\nu = hc/\lambda \\ &= \frac{(6.63 \times 10^{-34} \text{ J sec})(3.00 \times 10^8 \text{ m/sec})}{656 \times 10^{-9} \text{ m}} \\ &= 3.03 \times 10^{-19} \text{ J} \end{aligned}$$

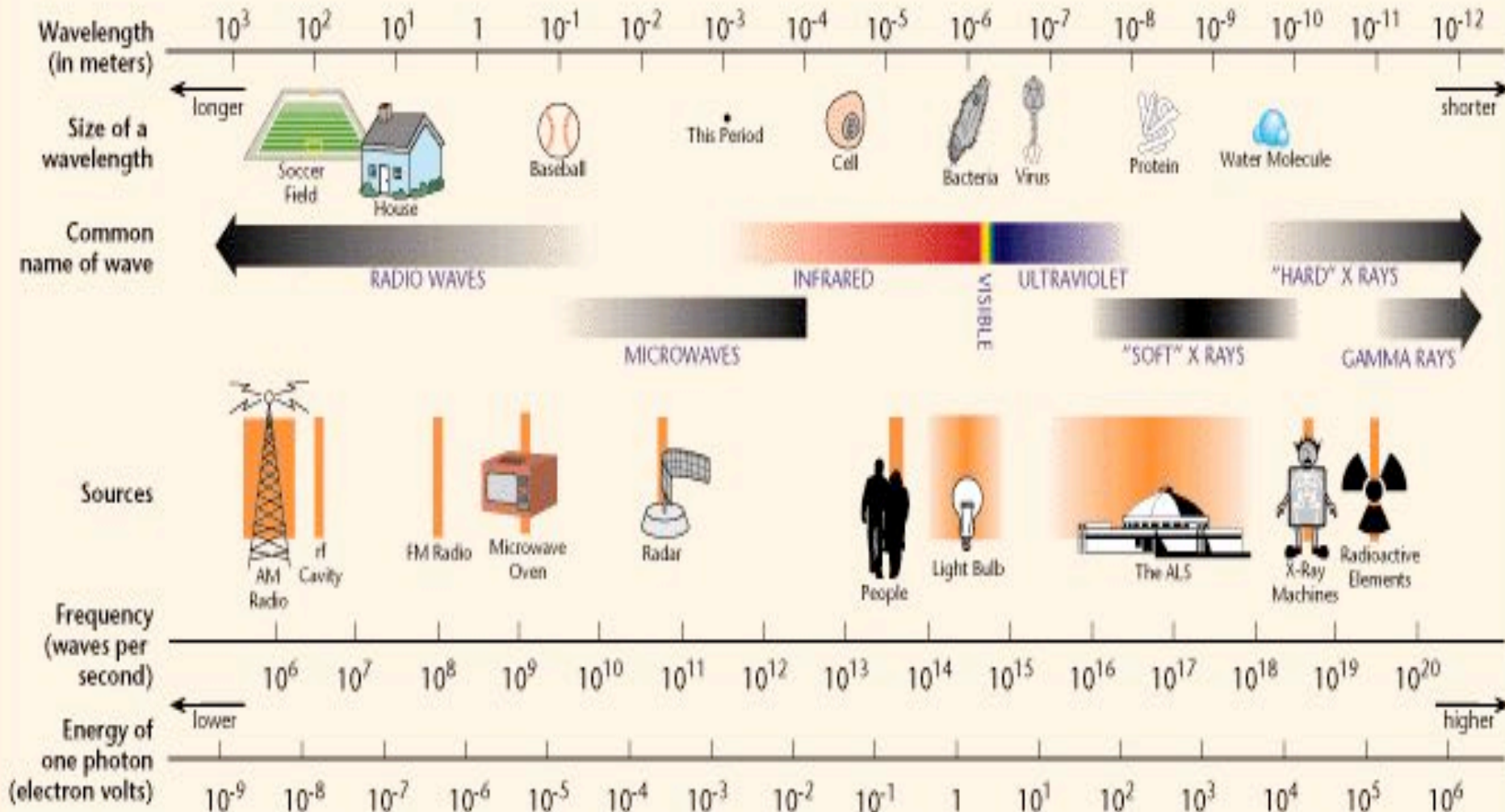


<http://www.laserfest.org/lasers/innovations.cfm>

Visible light is one slice of the Electromagnetic Spectrum

Where does light (EM radiation) come from?

THE ELECTROMAGNETIC SPECTRUM



<http://www.lbl.gov/MicroWorlds/ALSTool/EMSpec/EMSpec2.html>

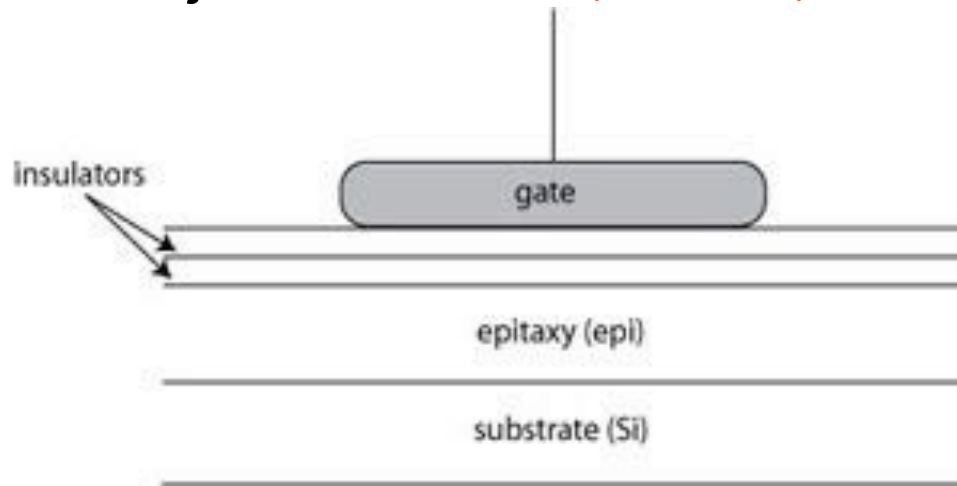
Our Body is a Good Detector of EM Radiation



http://www.eslsmartboard.com/vocabulary_lessons/face_and_body/human_body/

EM Radiation Detectors:

Charge Coupled Device (CCD) – UV, Vis, and IR photon hits doped Si and ejects electron (PE effect) → electrical signal



http://www.specinst.com/What_Is_A_CCD.html

Photomultiplier tube, film, CMOS

Photo-conductive cells, e.g., CdS

Photovoltaic cells, e.g., Se

X-rays – photographic film (Ag), semiconductors (Si (Li), CdTe)

Scientists, such as astronomers, like to talk about redshifts and blueshifts.

If the universe is *expanding*, as astronomers believe, would you observe a redshift and blueshift?



<http://scienceblogs.com/startswithabang/2011/12/02/dark-energy-accelerated-expans/>

The Radiation Type Has a Different Effect on Matter

Microwaves Cause Molecules to **Rotate** (spin)

IR Causes Bonds to **Vibrate**

Visible and **UV** Causes Bonds to **Break!**



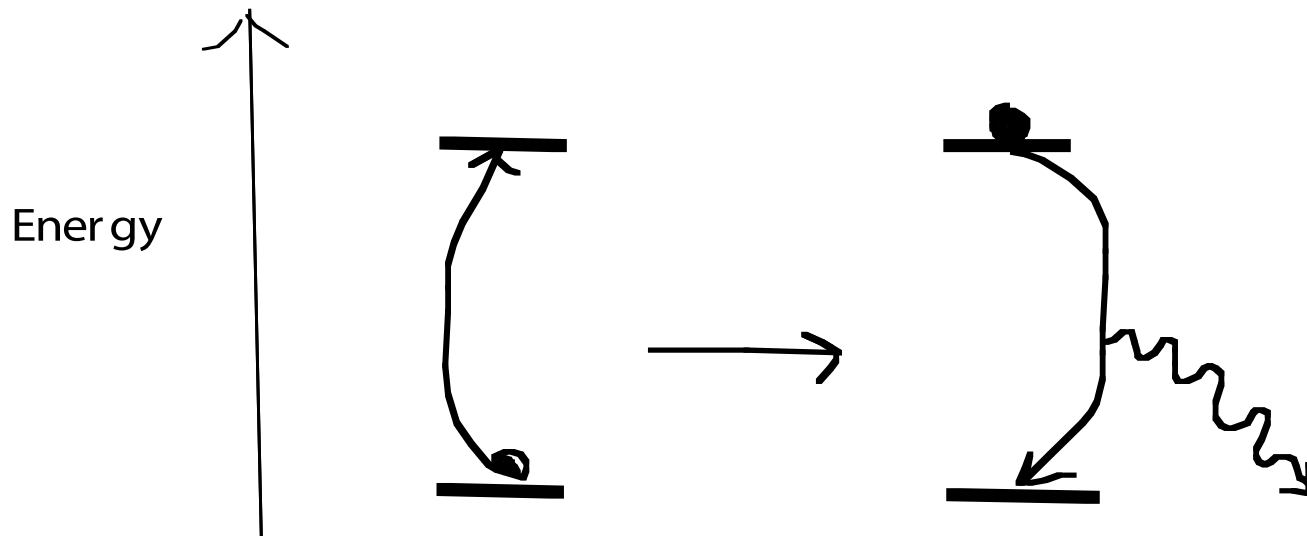
Water boils when placed in a microwave oven but will ice melt in a microwave?

http://www.123rf.com/photo_8416291_hand-drawn-illustration-of-a-microwave-oven-on-white-background.html

Objective: Describe How Light Is Produced

When a _____ absorbs the right amount of E , an _____ undergoes a transition from a _____ energy state to a _____ energy state (excited state).

Light is Produced when an _____ undergoes a transition from a _____ energy state to a _____ energy state.



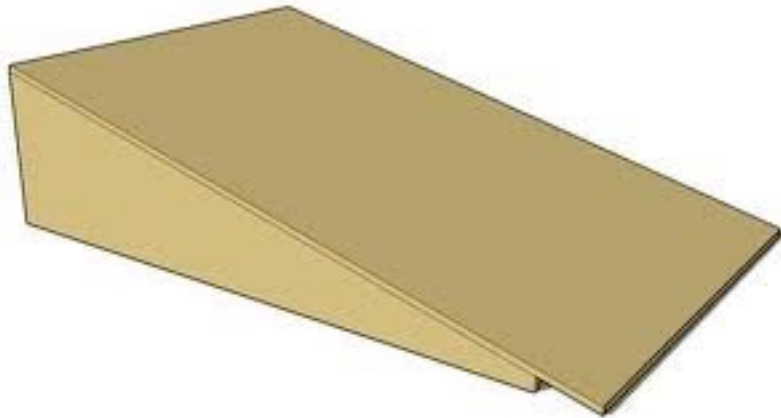
What does “***energy of an electron is quantized***” mean?

What is a Quantum? What is Quantized?

Egg



Baseball



Ramp



Stairs

Lab 8: How is light produced in a Ne gas discharge tube?

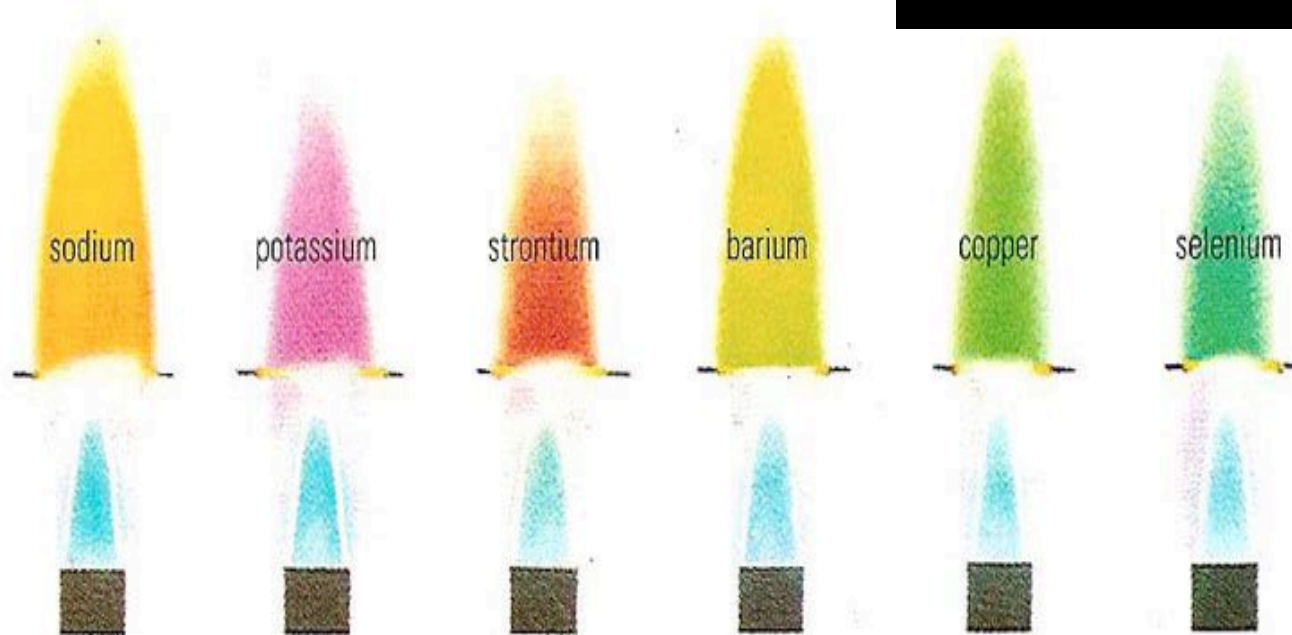


http://www.m2c3.com/chemistry/VLI/M1_Topic2/M1_Topic2_print.html

Why do *different* substances emit *different* colors or wavelengths of light?

Fireworks

<http://www.conciergepreferred.com/navy-pier-fireworks/4679-fourth-of-july-fireworks-at-navy-pier-2012.html>



Flame Tests

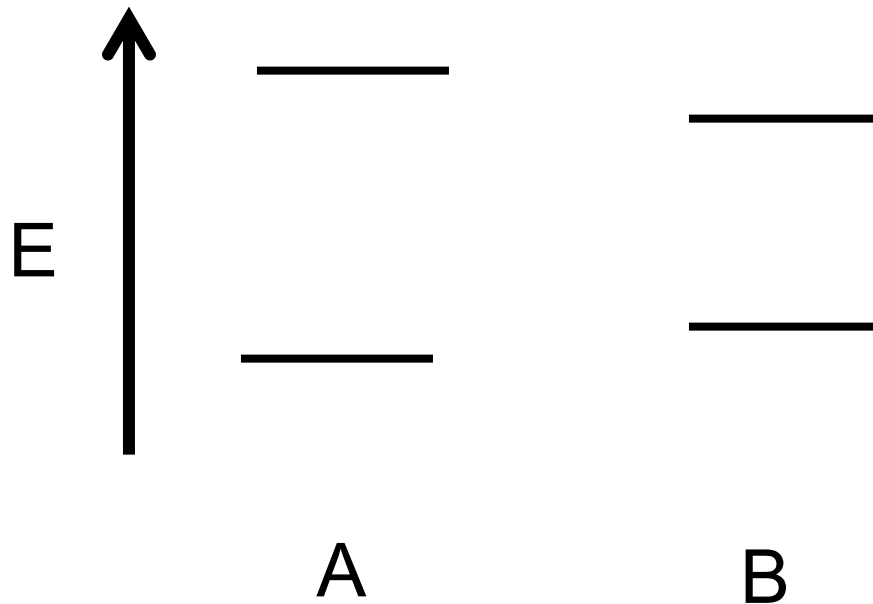
http://www.daviddarling.info/encyclopedia/F/flame_test.html

Why do **different** substances emit **different** colors or wavelengths of light?



Fireworks

<http://www.conciergepreferred.com/navy-pier-fireworks/4679-fourth-of-july-fireworks-at-navy-pier-2012.html>



Which E level diagram, A or B, represents green?

Which E level diagram, A or B, represents red?
Give reasons.

Lab 8. Color (and Light) Is Quantified By _____
The λ 's of Light Emitted by a Substance is Measured in
an *Emission Spectrum*
An Emission Spectrum is Used to Identify Substances
(like a fingerprint)

Astronomers use emission spectra to identify a star's composition.



Emission spectrum of sun

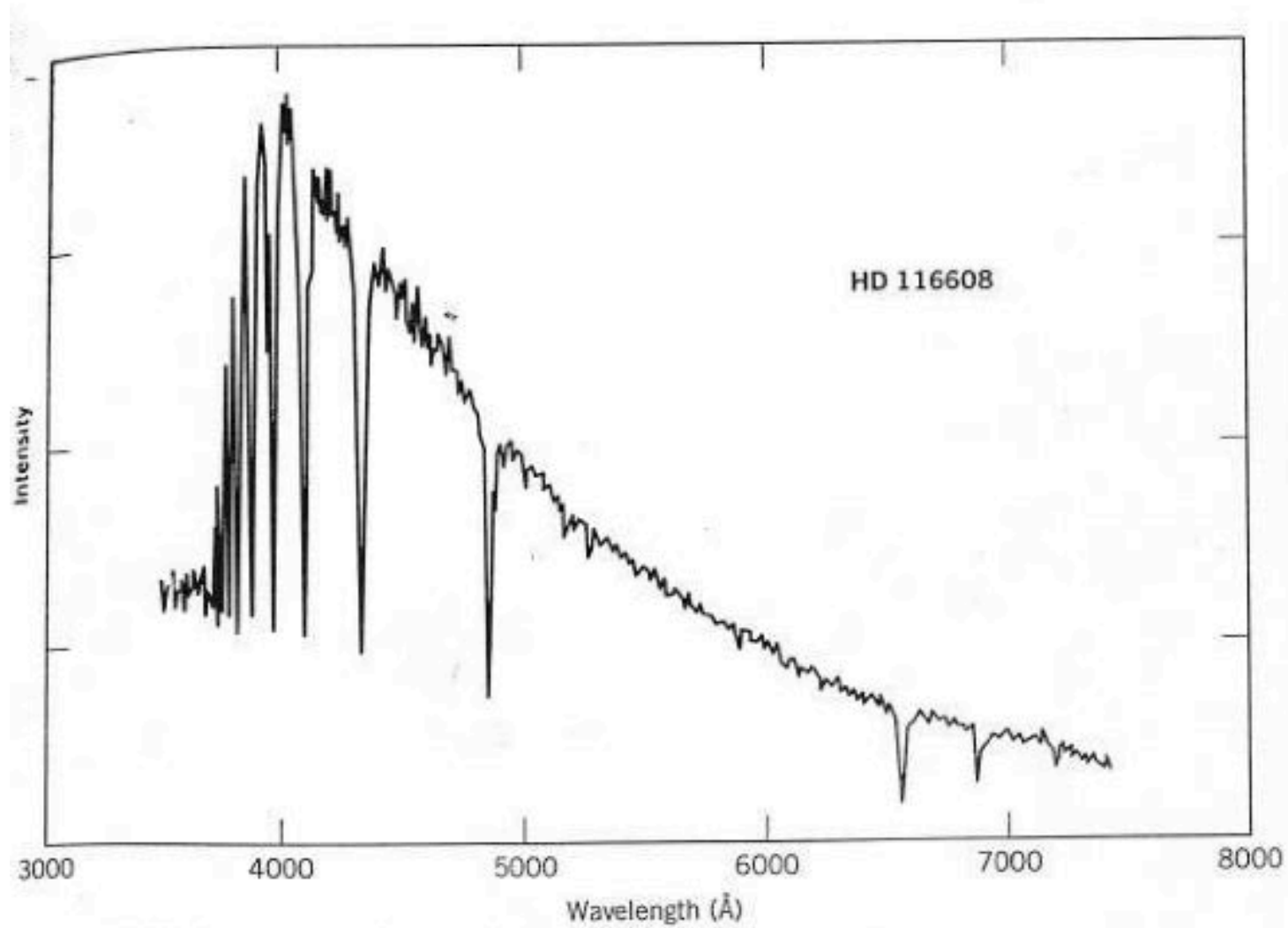


H emission spectrum

http://coolcosmos.ipac.caltech.edu/cosmic_classroom/ir_tutorial/spec.html

A spectrometer is used to measure an emission spectrum.
How does a spectrometer work?

The emission spectrum tells us the composition of this star.



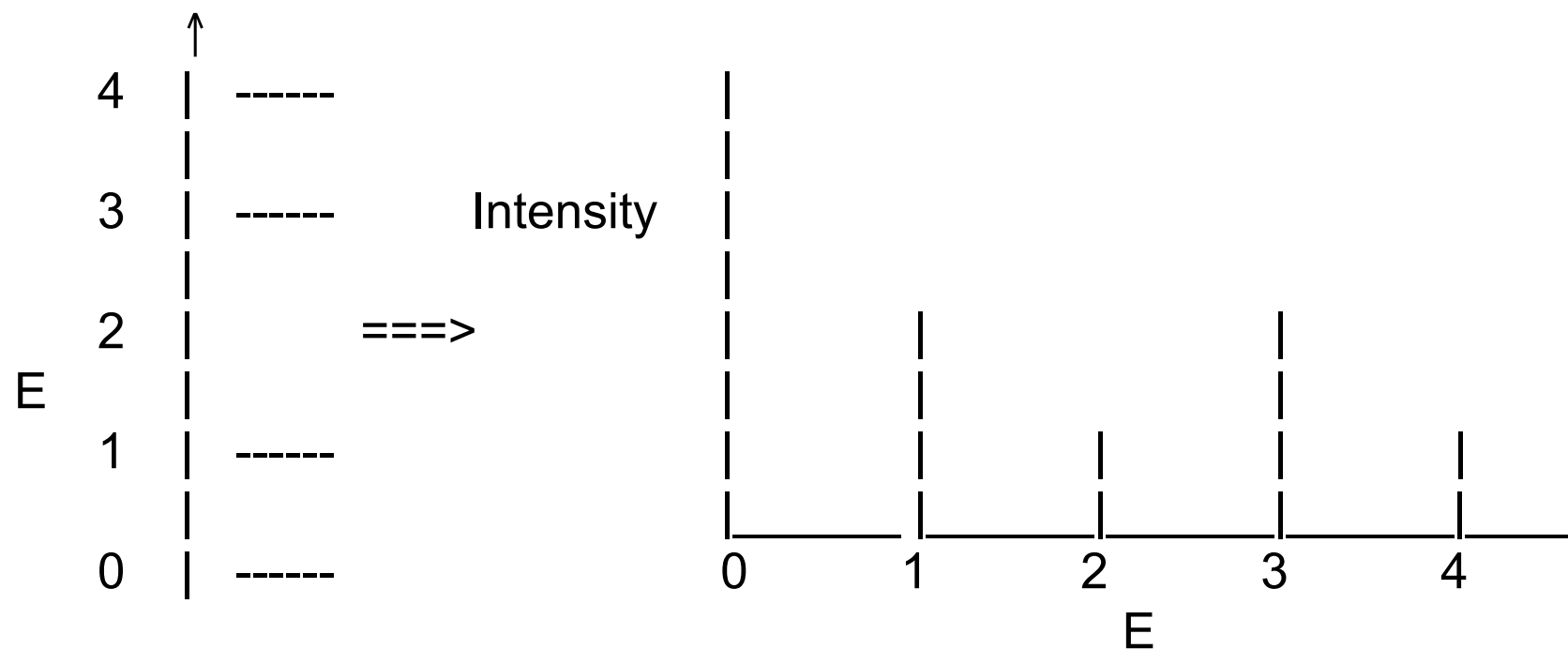
What is the composition of this star?

Objective: relate emission spectrum to electronic structure

An Emission Spectrum tells us about ***Electronic Structure***

(energy states of electrons in an atom or molecule)

Given an energy level diagram, draw an emission spectrum that fits the diagram.

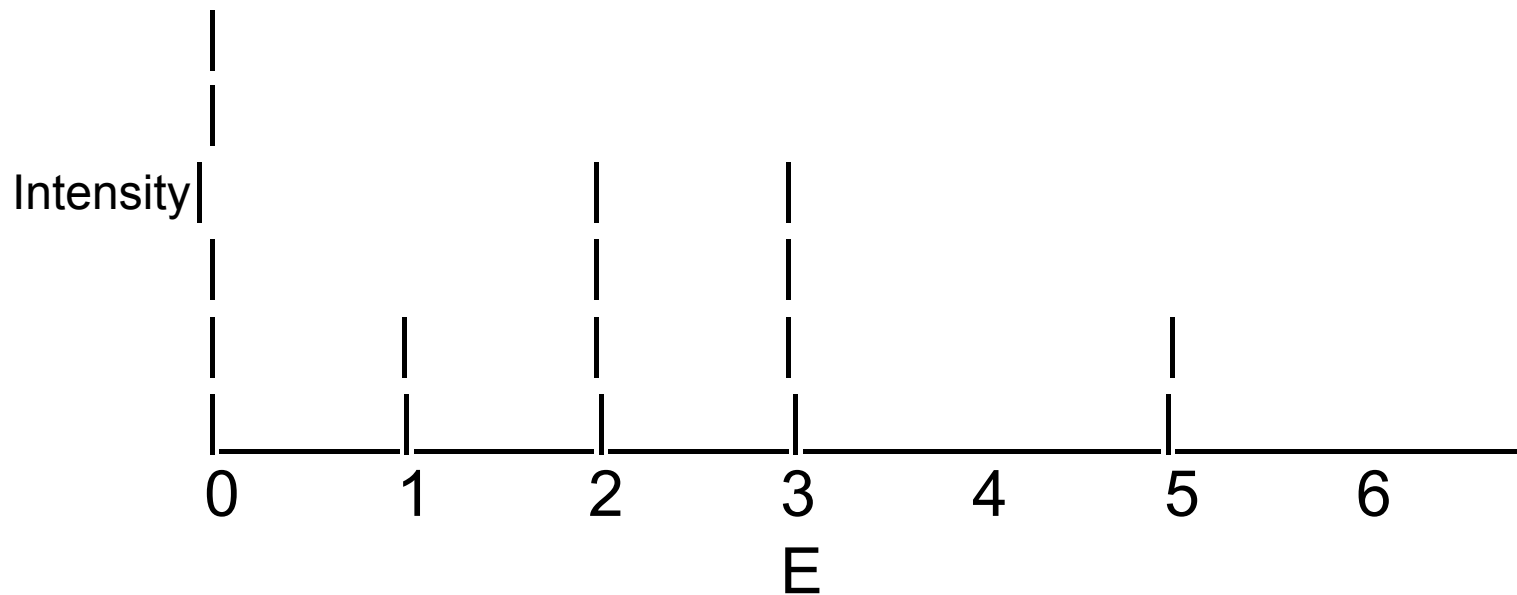


Energy Level Diagram

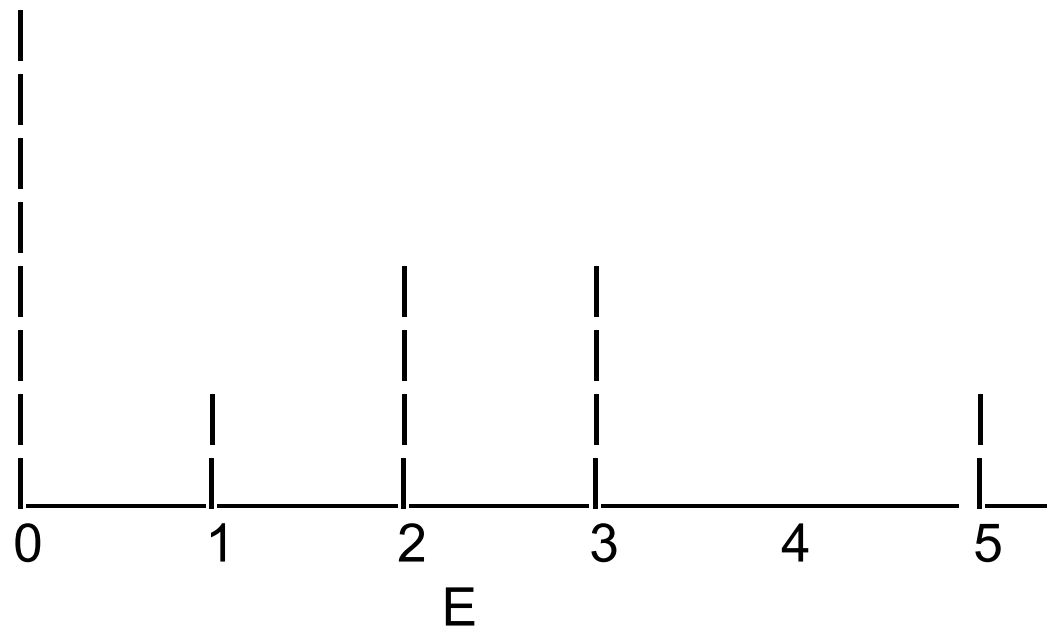
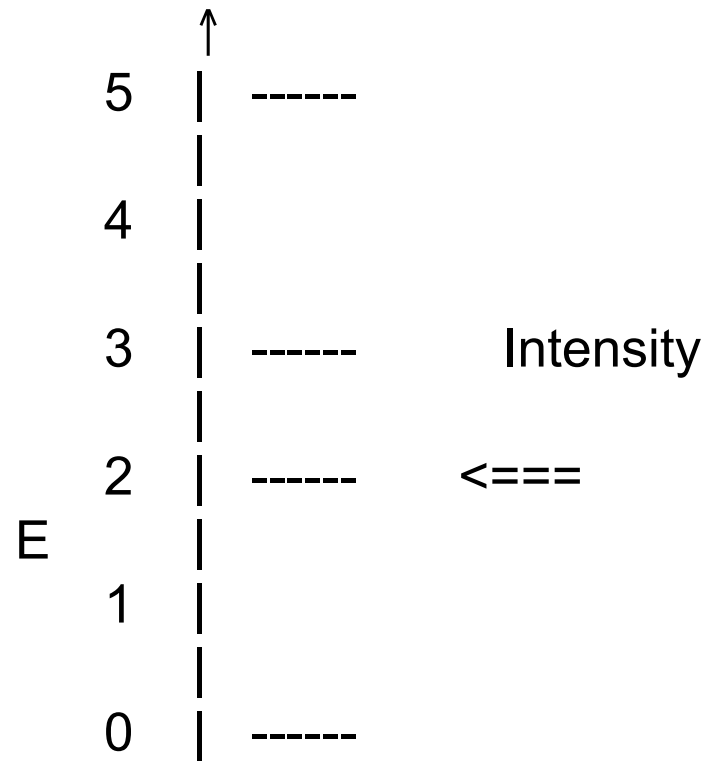
Emission Spectrum

Objective: relate emission spectrum to electronic structure

You measured the emission spectrum of a new substance you have just synthesized. Determine the electronic structure of this substance. In other words, draw an energy level diagram that fits the emission spectrum.



An Emission Spectrum tells us about ***Electronic Structure***
Solution:

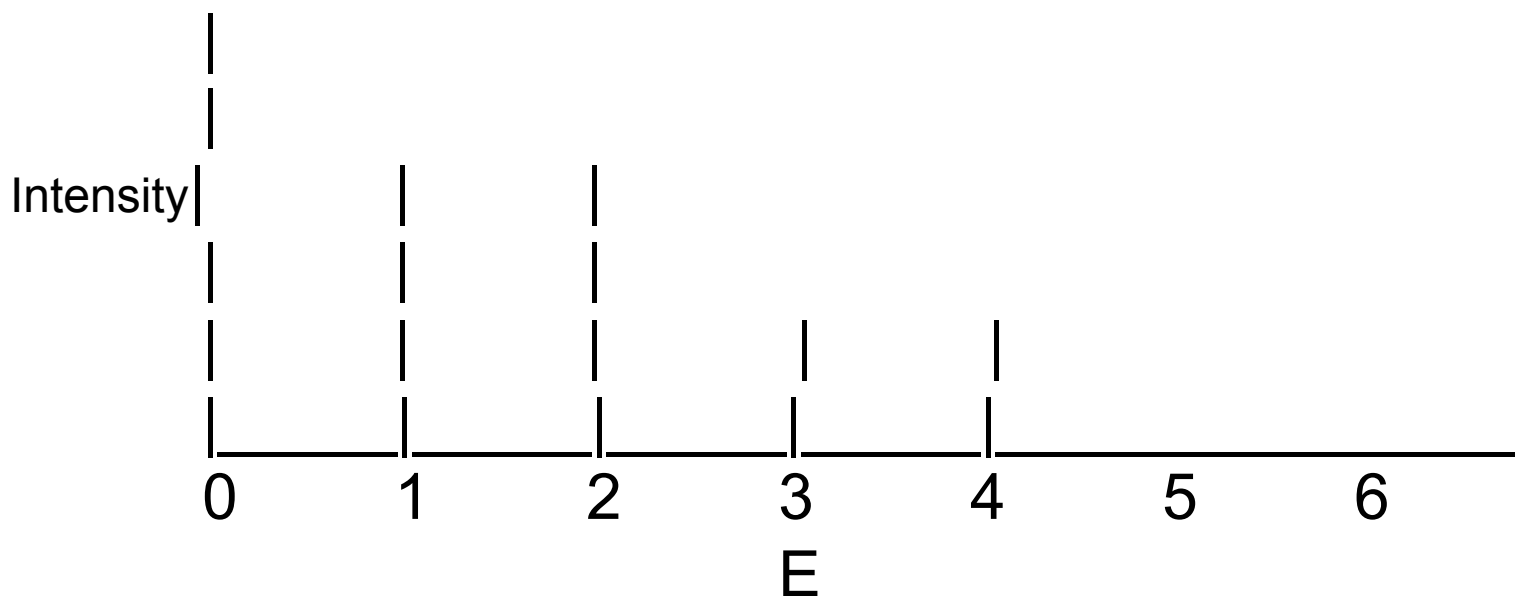


Energy Level Diagram

Emission Spectrum

Objective: relate emission spectrum to electronic structure

You measured the emission spectrum of a new substance you have just synthesized. Determine the electronic structure of this substance. In other words, draw an energy level diagram that fits the emission spectrum. **See Practice Problem 3.**



The ***Emission Spectrum*** of the **H atom** is described by **Bohr's Model**

Postulates:

1. Energy of an electron has specific, not arbitrary, values (energy of an electron is **quantized**)

$$E = -R_H/n^2 \quad \text{where } R_H = \text{Rydberg's constant} = 2.18 \times 10^{-18} \text{ J} \\ \text{and } n = 1, 2, 3, \dots$$

This Equation Can ONLY Be Used for the H atom!!

2. Electrons can undergo transitions from one energy state to another:

Lower E state --> Higher E state absorption

Higher E state --> Lower E state emission

(2 others)

What is E of the n = 1 electron energy state in H?

What wavelength is emitted in the n = 2 to n = 1 transition?

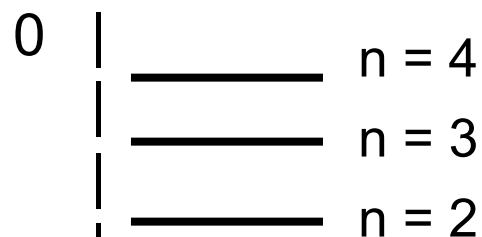
Hydrogen Emission Spectrum

http://coolcosmos.ipac.caltech.edu/cosmic_classroom/ir_tutorial/spec.html



Lab 8. Identify the electron states that produces each color.

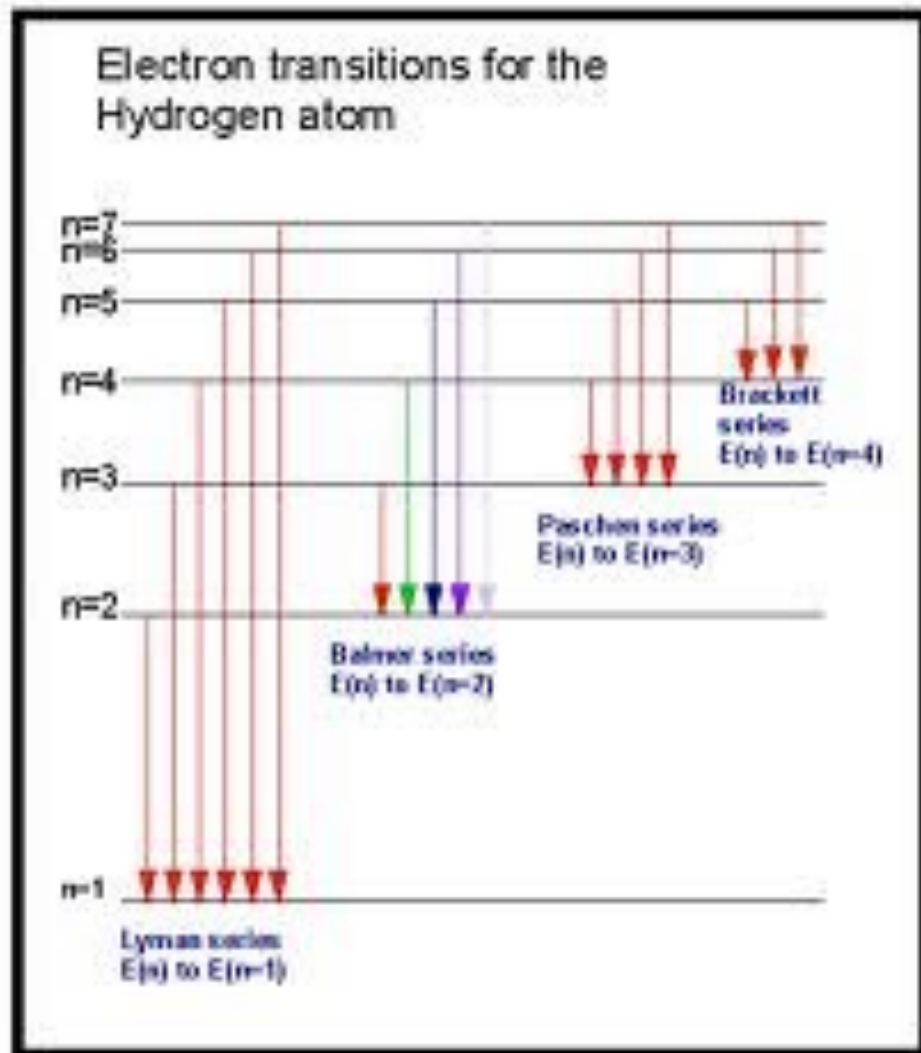
E, $\times 10^{-18}$ J



Observed Wavelength, nm	Observed Color	$\frac{1}{\lambda R}$	n_f	n_i	$(\frac{1}{n_f^2} - \frac{1}{n_i^2})$	$\Delta E, J$



E, J



$$E = -R_H/9$$

$$E = -R_H/4$$

$$E = -R_H$$

http://www.files.chem.vt.edu/RVGS/ACT/notes/notes-electronic_structure.html

Light is Used In Many Different Ways and Applications

Fluorescent lights <http://home.howstuffworks.com/fluorescent-lamp.htm>

Lasers

Supermarket scanners - He/Ne laser

TV <http://electronics.howstuffworks.com/tv.htm>

Electron gun inside TV

<http://electronics.howstuffworks.com/question694.htm>

LCD <http://electronics.howstuffworks.com/lcd2.htm>

LED – see 2014 Nobel Prize in Physics

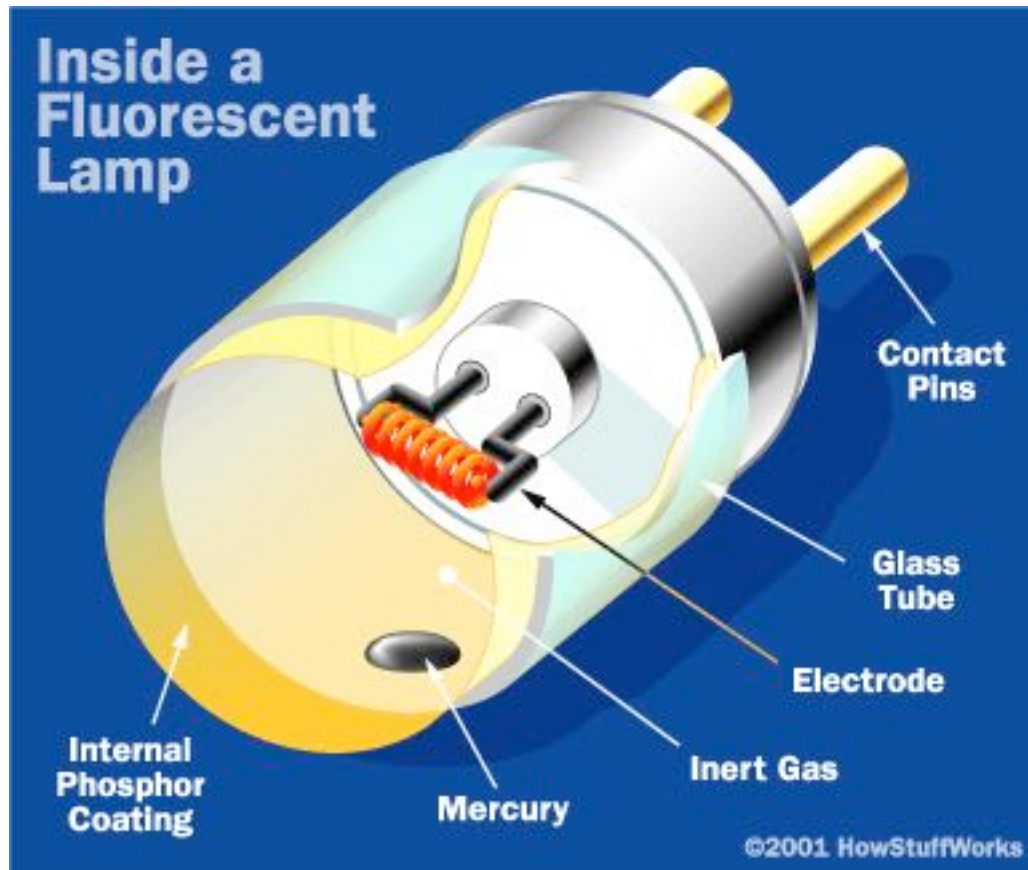
Reactant in Chemical Reactions - Photochemistry

Cameras - analog and digital

Information transfer (radio, cell phones, fiber optics)

How Fluorescent Lamps Work

(<http://home.howstuffworks.com/fluorescent-lamp1.htm>)



$\text{Hg (l)} \rightarrow \text{Hg (g)}$

Hg emits UV.

UV excites phosphor.
Phosphor emits white light.

What excites Hg?

Why do ***different*** substances emit ***different*** colors or wavelengths of light?

Mercury (Hg) Is Used In Fluorescent Lights

which is the reason fluorescent lights should not be thrown out with the garbage.

The 546.1 nm line is used to calibrate light detectors and diffraction gratings.

Calculate the frequency and energy in J/photon and kJ/mole.

What Is A *Photon*?

Light as a Reactant in a Chemical Reaction

Dentistry:

Blue light for curing composite resins



<http://laserpointerforums.com/f38/blue-ray-whitens-teeth-47683.html>



<http://science.howstuffworks.com/zoology/question554.htm>

Light as a Product in a Chemical Reaction

Fireflies

Light sticks



<http://onlyhdwallpapers.com/tag/lightsabers/>

Supply Energy to Produce Light

<http://iet.jrc.ec.europa.eu/energyefficiency/residential-lighting/european-cfl-quality-charter>



Supply Light to Produce Energy

<http://www.gizmag.com/low-grade-silicon-solar-cell-efficiency/27426/>

Lab 8: **Glowing** pickle??

What makes the pickle glow this color??



<http://www.fotosearch.com/illustration/pickle.html>

<https://portal.magnet.fsu.edu/lists/announcements/dispform.aspx?id=162>

Lasers are used in supermarket scanners, medical and industrial uses.

How does a laser work? See <http://science.howstuffworks.com/laser.htm>

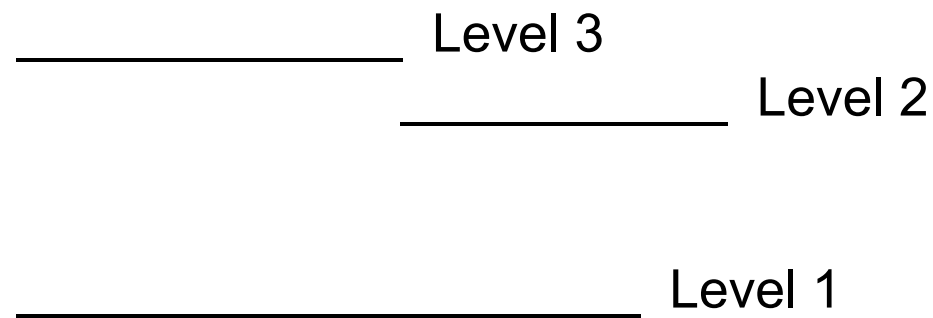
Laser Properties:

1. Directionality (tight beam, strong and focused). Compare to flashlight.
2. High spectral brightness
3. Monochromaticity (spectral purity) – narrow bandwidths. Some lasers have bandwidths < 1 MHz (or 10^{-4} cm^{-1})
4. Coherence (light waves of similar frequency and well defined phase relationships)
5. Short pulses – some lasers have pulse widths $< 10^{-13}$ sec

3 Elements of a Laser:

1. Active medium
2. Energy pump source (to create population inversion)
3. Resonant cavity to contain light

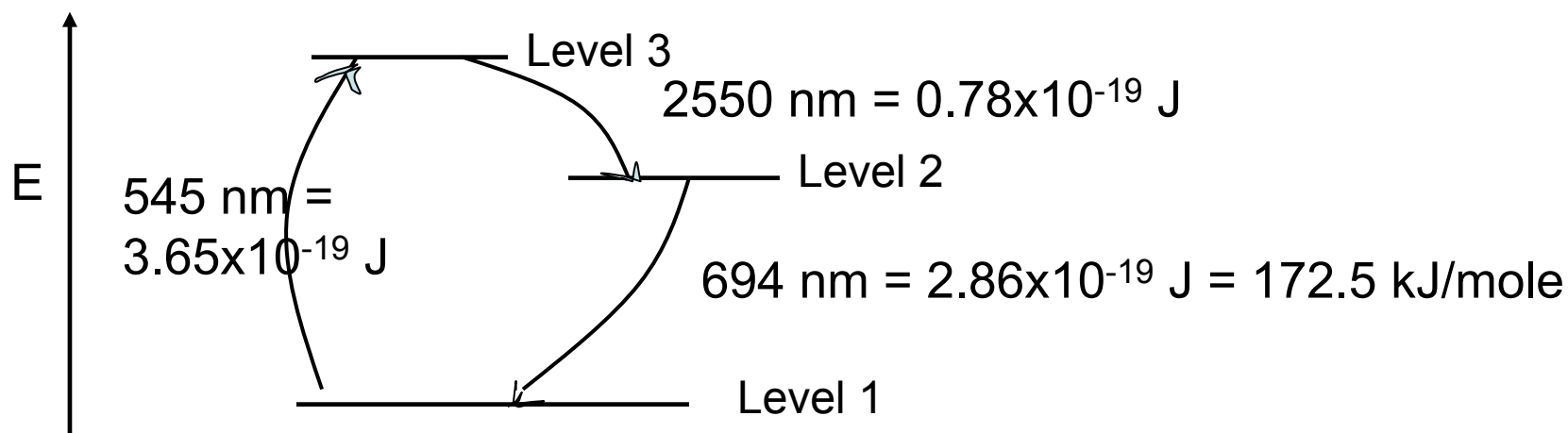
The gemstone ruby is alumina (Al_2O_3) doped with Cr^{3+} . The color of a ruby is due to electron transitions of Cr^{3+} in alumina. These electron transitions can be used in a ruby laser. Three transitions occur: one transition corresponds to a wavelength of 545 nm, another transition corresponds to a wavelength of 694 nm, and a third transition corresponds to a wavelength of 2550 nm. See **Practice Problem 5**.



- a. Rubies are red. Which transition gives ruby its color? Be specific with the initial and final energy levels. Give reasons.
- b. In a laser,
- (i) a flash tube excites (pumps) electrons in Cr^{3+} from Level 1 to Level 3. Which wavelength corresponds to this transition?
- (ii) Electrons from Level 3 undergo a transition to Level 2 to release heat and create a population inversion (high number of excited state electrons). Which wavelength corresponds to this transition?
- Confirm that ΔE for the Level 1 to Level 3 transition equals the sum of ΔE for the Level 3 to Level 2 transition and ΔE for the Level 2 to Level 1 transition.

Solution: The color of a ruby is due to electron transitions of Cr^{3+} in alumina. Three transitions occur:

λ , nm	Color	ΔE , J	ΔE , kJ/mole	Transition
545	green	3.65×10^{-19}	219.7	1 \rightarrow 3
694	red	2.87×10^{-19}	172.5	2 \rightarrow 1
2550	IR	0.78×10^{-19}	47.0	3 \rightarrow 2



$$\Delta E_{1 \rightarrow 3} = \Delta E_{3 \rightarrow 2} + \Delta E_{2 \rightarrow 1}$$

$$3.65 \times 10^{-19} \text{ J} = 0.78 \times 10^{-19} \text{ J} + 2.87 \times 10^{-19} \text{ J}$$

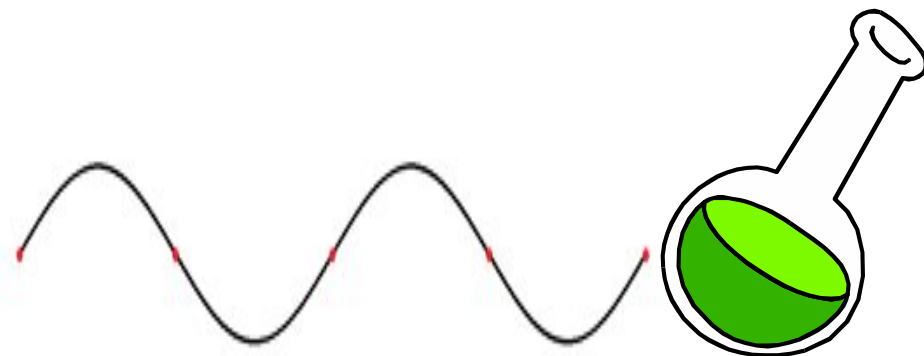
Transition Metals Give Gemstones Their Color

Gemstone	Color	Formula
Ruby	Red	Cr^{3+} in Al_2O_3
Emerald	Green	Cr^{3+} in beryllium aluminum silicate
Sapphire	Blue	Fe^{3+} and Ti^{4+} in Al_2O_3
Garnet	Red	Fe^{2+} in $\text{Mg}_3\text{Al}_2(\text{SiO}_4)_3$
Peridot	Yellow-green	Fe^{2+} in Mg_2SiO_4
Turquoise	Blue-green	Cu^{2+} in $\text{CuAl}_6(\text{PO}_4)_4(\text{OH})_8 \cdot 4\text{H}_2\text{O}$
Diamond	Colorless, pale blue or yellow	N atoms trapped in crystal

Reference: <http://scifun.chem.wisc.edu/chemweek/PDF/Gemstones.pdf>

Spectroscopy Is The Interaction of Light With Matter

What happens when light comes in contact with a substance?



Light is **reflected** off of substance.

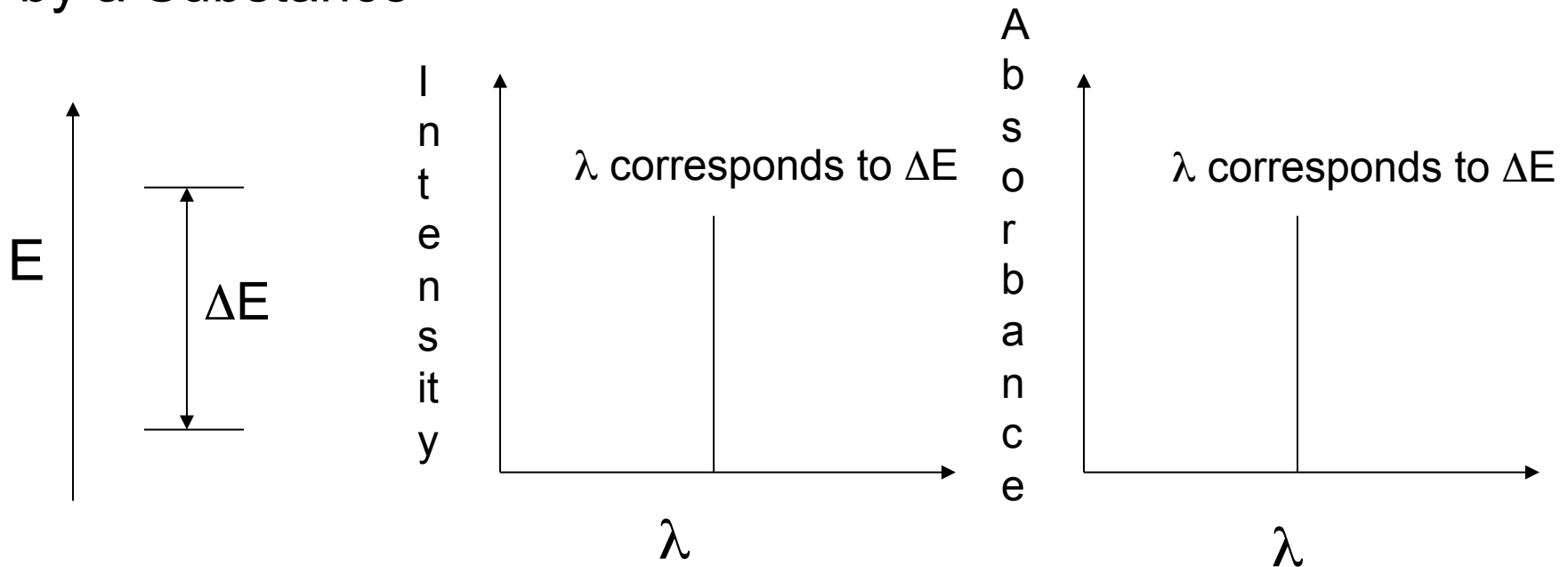
Light is **transmitted** through substance.

Light is **absorbed** by the substance.

Light is **absorbed** by the substance, then **emitted** by substance.

An **Emission** Spectrum Measures the λ 's of Light **Emitted** by a Substance

An **Absorption** Spectrum Measures the λ 's of Light **Absorbed** by a Substance



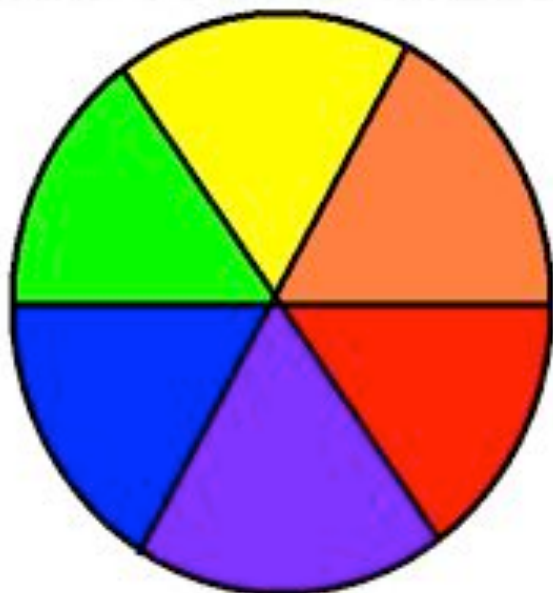
E Level Diagram
Shows the energy of electron energy states

Emission Spectrum
 λ 's emitted is color you see

Absorption Spectrum
 λ 's absorbed is not color you see ==>
complementary color is color you see
Color Wheel

Objective: relate absorbed color to observed (complementary) color

BASIC COLOR WHEEL



<http://trehautecouture.blogspot.com/2012/06/how-to-mix-colors-in-your-wardrobe.html>

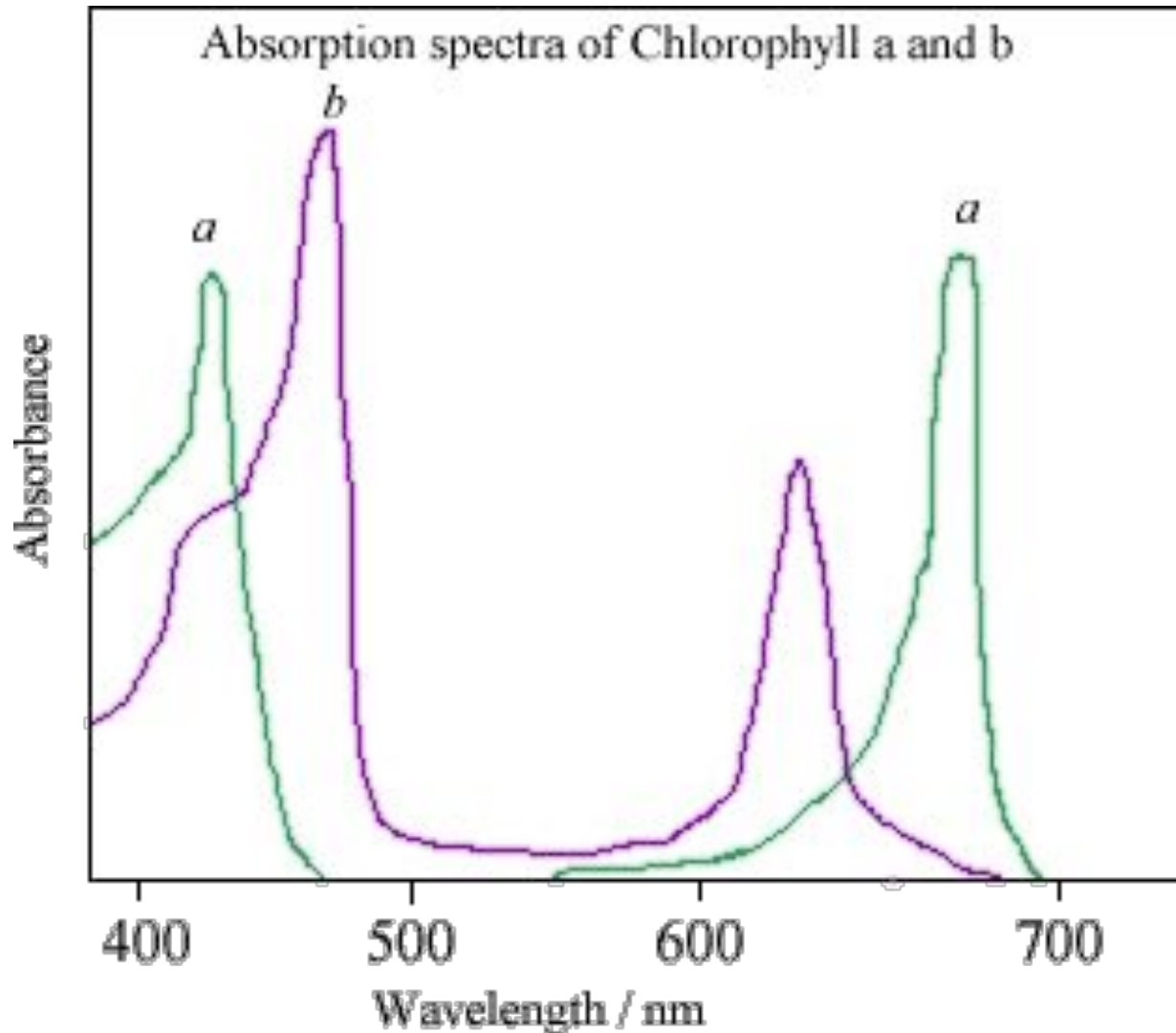
If a substance absorbs red, it appears _____.



<http://technorati.com/lifestyle/green/article/levis-jeans-reduces-carbon-footprint/>

If a substance appears blue, it absorbs _____.

Chlorophyll is the Green pigment in plants
What color is absorbed by chlorophyll? See Practice Problem
6.

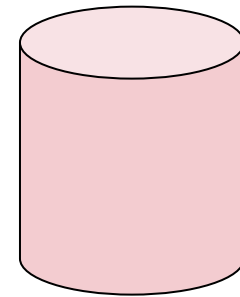
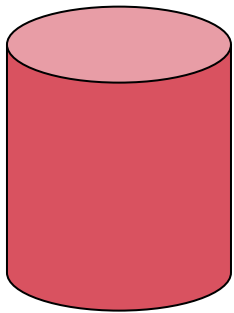


<http://www.webexhibits.org/causesofcolor/7A.html>

**A Substance *Absorbs* a Specific Wavelength of Light
The Amount of Light Absorbed by the Substance
(chromophore) is Proportional to Concentration**

Beer's law: $A \propto C$

where A = Absorbance
and C = concentration



Which solution absorbs more light? What color is absorbed?
Which solution is less concentrated?

Beer's law is used to determine the concentration of a substance in a solution.

E.g., breath analyzer

<http://luxfashiontrends.com/ysl-sunglasses-spring-summer-collection-for-you.html>



Sunglasses are designed:

- to protect your eyes from glare (polarized)
- UV light (DNA damage)
- to make you look cool.

Some sunglasses claim “**100% UV protection**” but ...
“*Sunglasses Carry Shady UV-Protection Claims, Study Reveals*”

(<http://www.livescience.com/6524-sunglasses-carry-shady-uv-protection-claims-study-reveals.html>)

Lab 8: How would you test sunglasses?

Bring A Pair Of Sunglasses To Lab!

Sunscreens Are Chemicals That Absorb UV Light

Sun Protection Factor (SPF) tells you how much UV light is absorbed:

$$\text{SPF} = \frac{1}{T} = \frac{1}{1 - A}$$

where T = transmittance (light of specific λ transmitted through sample)
and A = Absorbance (light of specific λ absorbed by sample)

SPF	A
15	0.933
20	0.95
30	0.967
50	0.98

Is it worth getting an SPF over 30?

Lab 8. Absorption Spectra applications

Measure the Absorption Spectra of 2 food colors.

Mix 2 food colors to get a new color.

Measure the Absorption Spectrum.

Did a chemical reaction occur?

Bring A Colored Food To Lab.

Extract the color from the food.

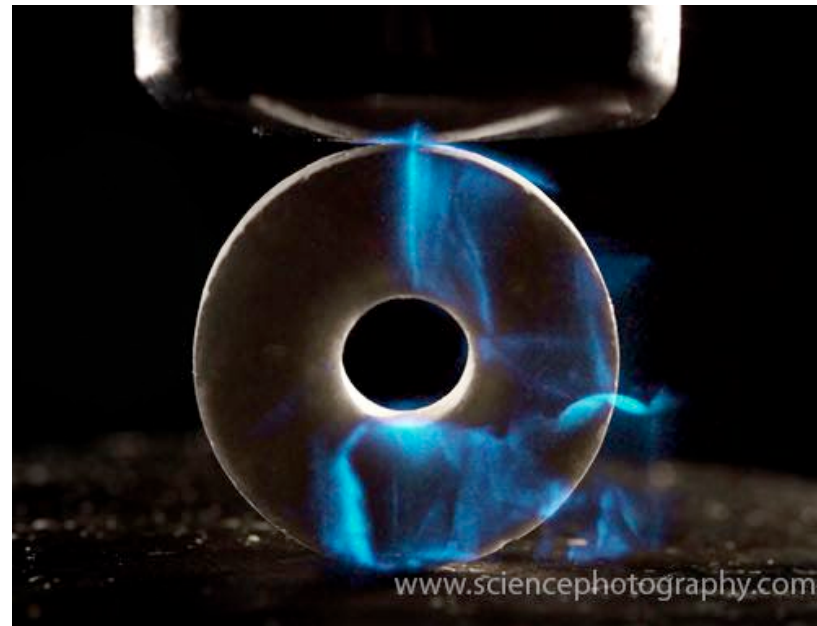
Measure the Absorption Spectrum.

Is the color from the food a food coloring?

Wint-O-Green Lifesavers: See Practice Problem 7.



<http://familyembellishments.blogspot.com/2011/06/wintergreen-lifesavers-spark-great.html>



<http://scienceblogs.com/photosynthesis/2009/09/23/luminescent-candy/>

Light and Color

Where does light come from?

How is light produced?

Why do different substances have different color?

How is light studied?

What does the study of light tell us?

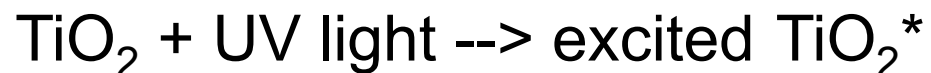
TiO₂ is a White Pigment used in Paint and Food coloring



Nano-sized TiO₂ added to concrete keeps concrete white

<http://cen.acs.org/articles/89/i24/Building-Small.html>

Self-cleaning property:



TiO₂^{*} works as a catalyst for oxidizing organic grime and “eats” smog (NO_x, SO_x, carbon monoxide, aromatics, ammonia, and aldehydes)

Add TiO₂ to surfaces to reduce air pollution.

Application: Far IR is used in chemical analysis and
1 Terahertz (THz) = 10^{12} Hz)

Development of instrumentation for THz spectroscopy.

Detects small amounts of C-4 explosives hidden in sealed envelopes (590 cm^{-1}). C-4 cannot be detected by X-rays or metal detectors.



Imaging in medical, security, and other applications that capitalize on the light's ability to penetrate plastics, paper, and textiles

Burning of Fossil Fuels ==> Global Warming

2007: World oil demand = 85 million barrels/day

US oil demand = 20 million barrels/day,
approx 10 million barrels/day for gasoline,
141 billion gallons gas/year

California = 16 billion gallons gas/year

Gasoline is a mixture of hydrocarbons.

One gallon of burned octane produces 8250 g of CO₂.

CO₂ absorbs IR radiation ==> IR = heat

The amount of IR radiation (heat) absorbed by CO₂ is proportional to the CO₂ concentration. (*Beer's law: $A \propto C$*)

Atmospheric [CO₂] = 380 ppm

References:

Greenhouse gases explained

http://tonto.eia.doe.gov/energyexplained/index.cfm?page=environment_about_ghg

CO₂ absorption spectrum

<http://www.iitap.iastate.edu/gccourse/forcing/images/image7.gif>

Solar radiation in and earth's thermal radiation out

http://www.te-software.co.nz/blog/augie_auer.htm

Global warming potential table http://unfccc.int/ghg_data/items/3825.php

CO₂ and T data http://www.geocraft.com/WVFossils/temp_vs_CO2.html

CO₂ and T data last 800,000 years

<http://en.wikipedia.org/wiki/File:Co2-temperature-plot.svg>

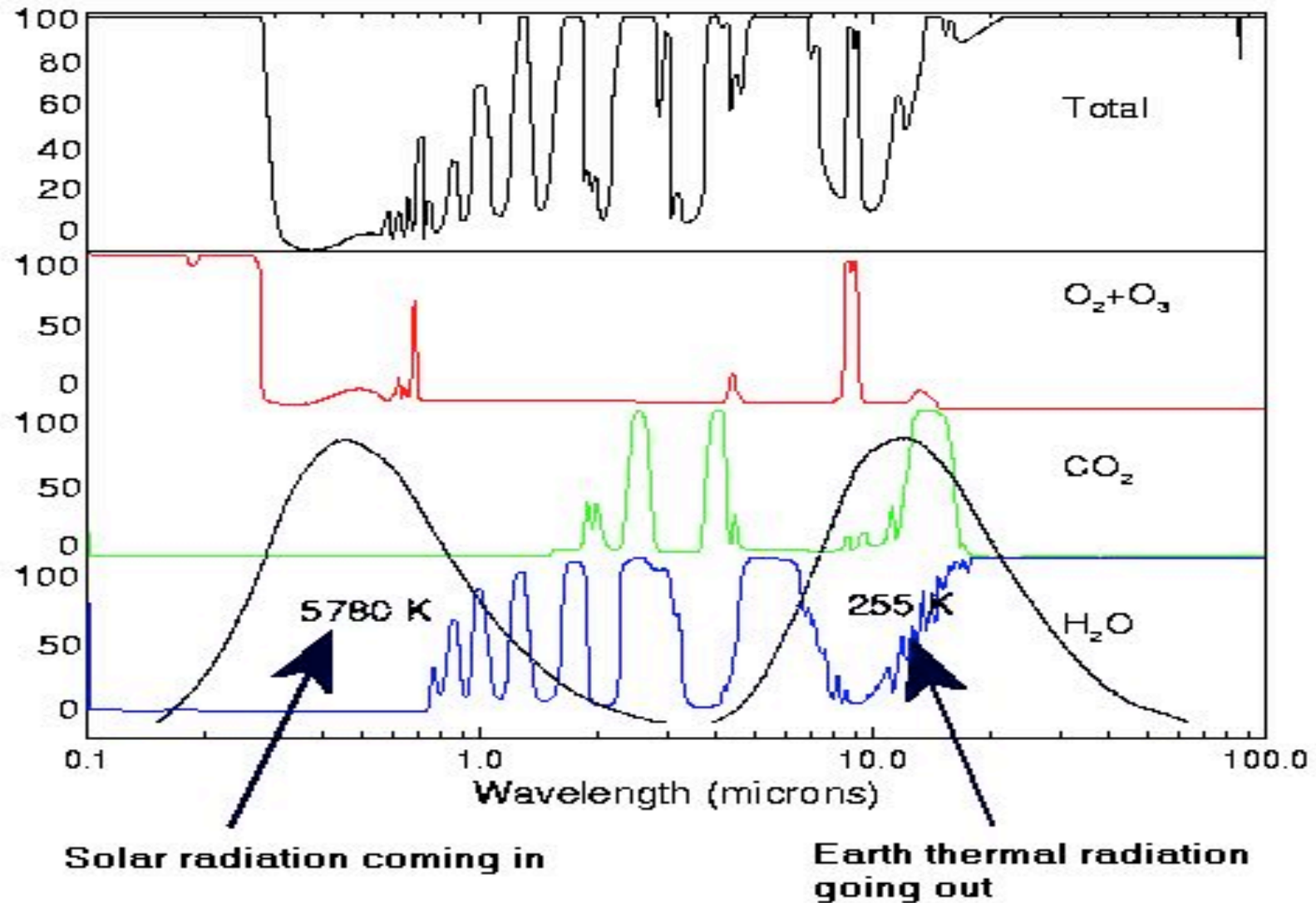
Cold facts on global warming <http://brneurosci.org/co2.html>

Global warming: a chilling perspective

http://www.geocraft.com/WVFossils/ice_ages.html#anchor2117056

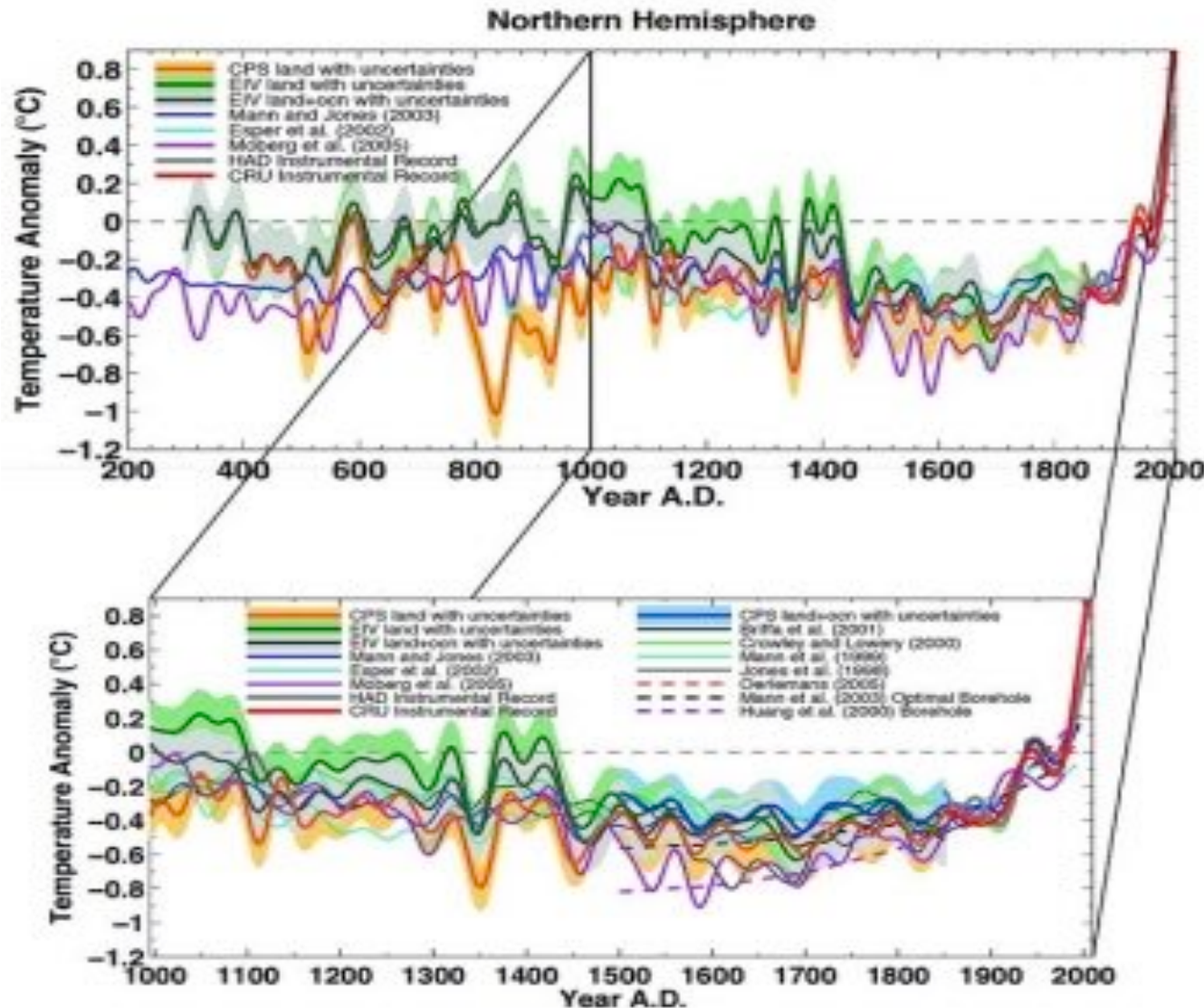
Iowa State global change course <http://www.iitap.iastate.edu/gccourse/units01.html>

Absorption Spectra of Atmospheric Gases and Solar/Earth Radiation

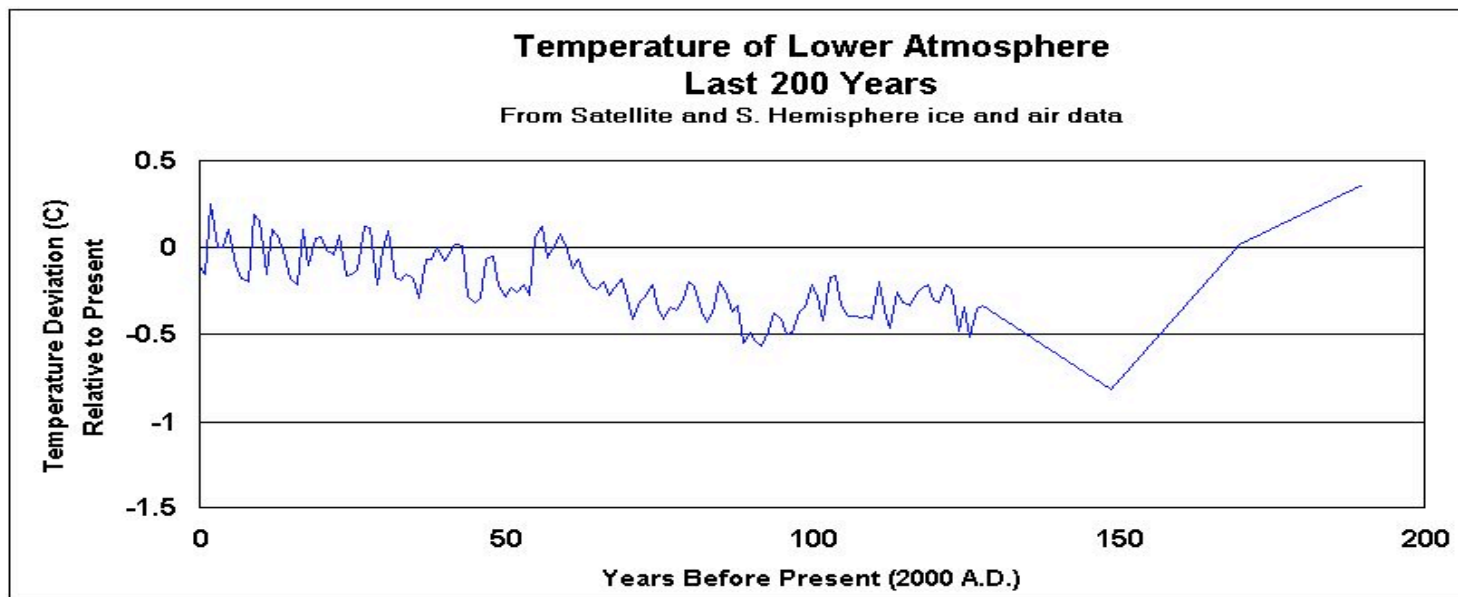
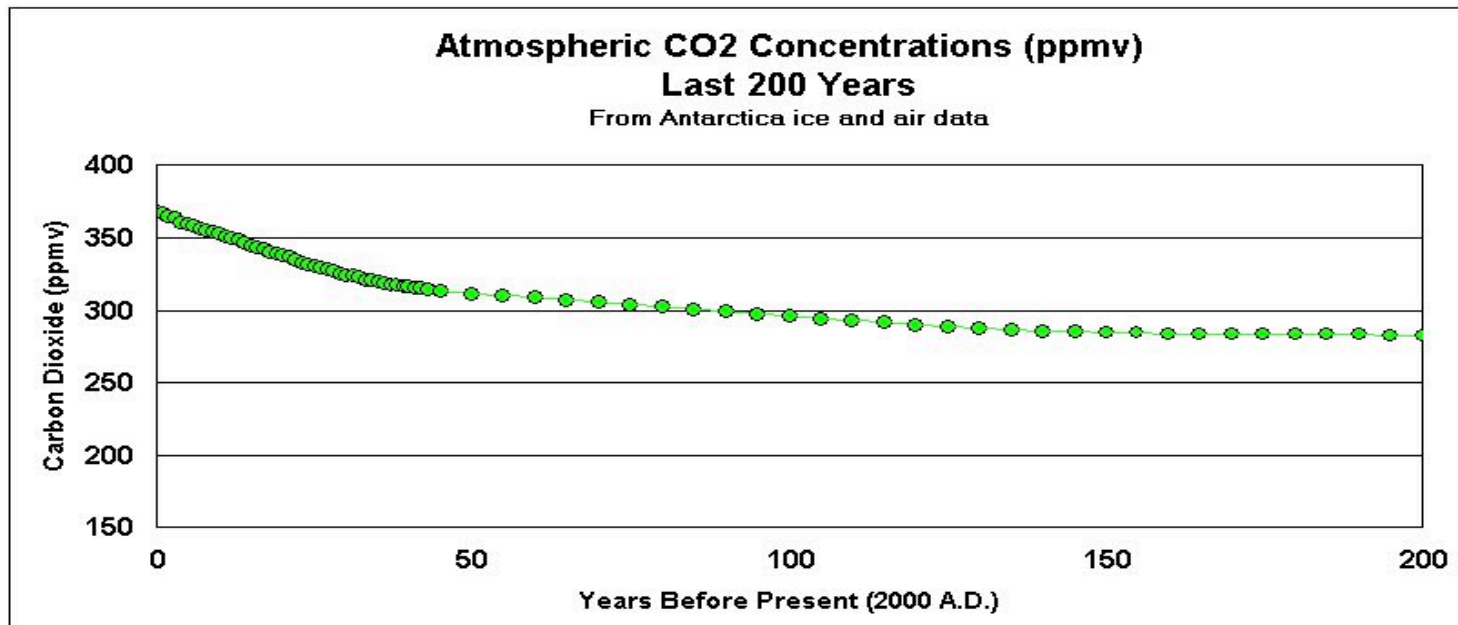


<http://cen.acs.org/articles/90/i50/Michael-Manns-Hockey-Stick.html>

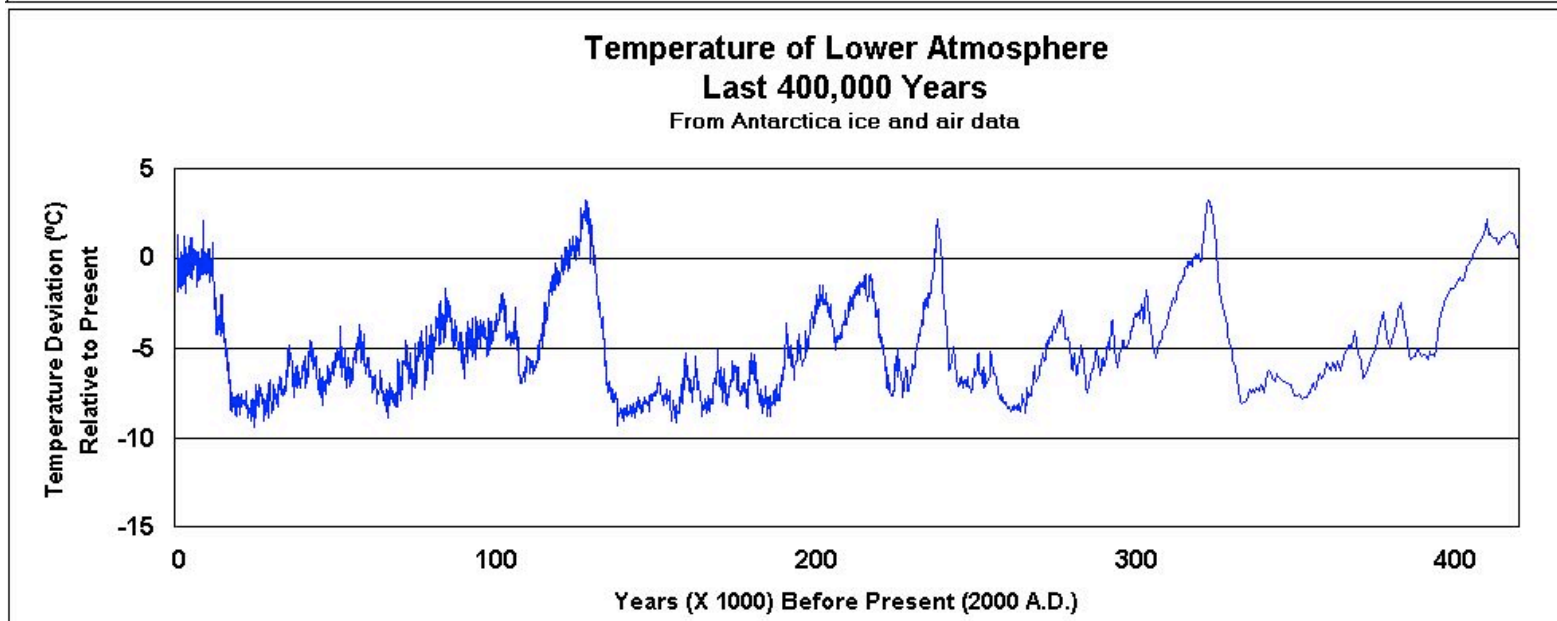
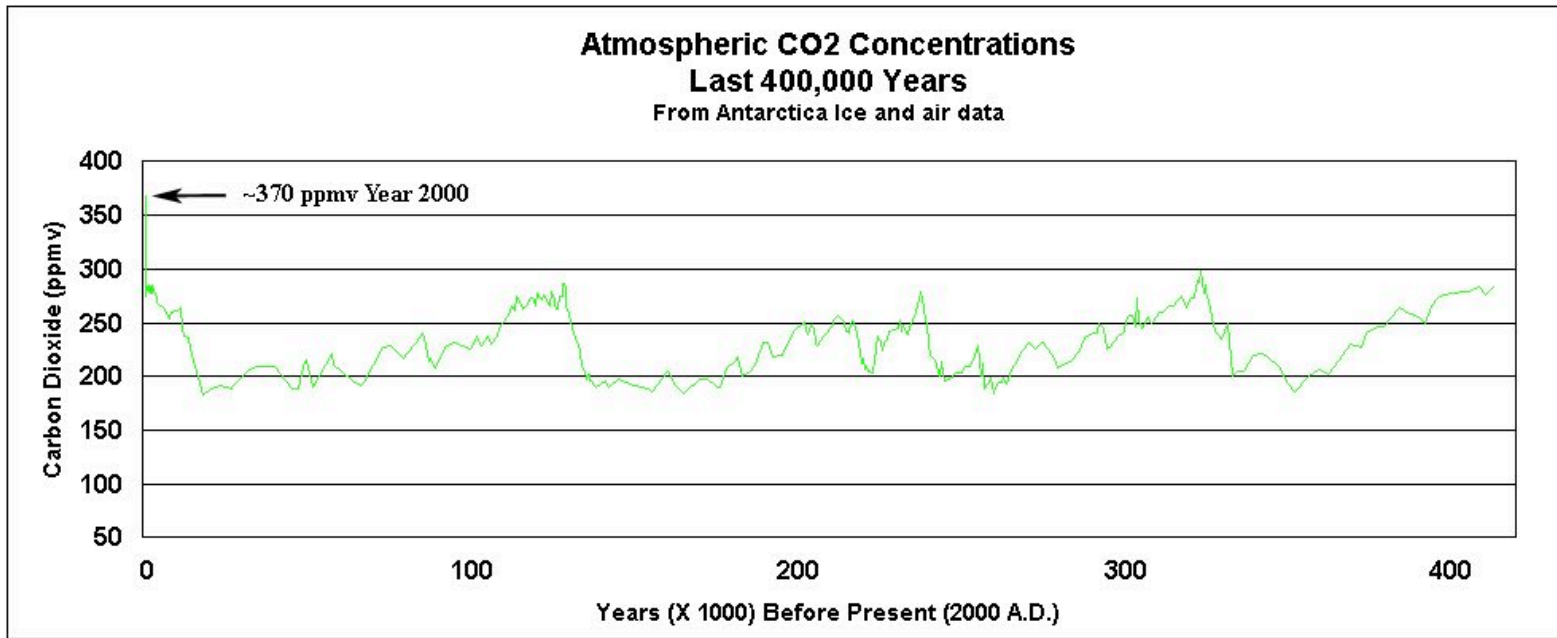
12/10/12, CEN, p. 52 Book Review: “The Hockey Stick And The Climate Wars: Dispatches From The Front Lines”, by Michael E. Mann



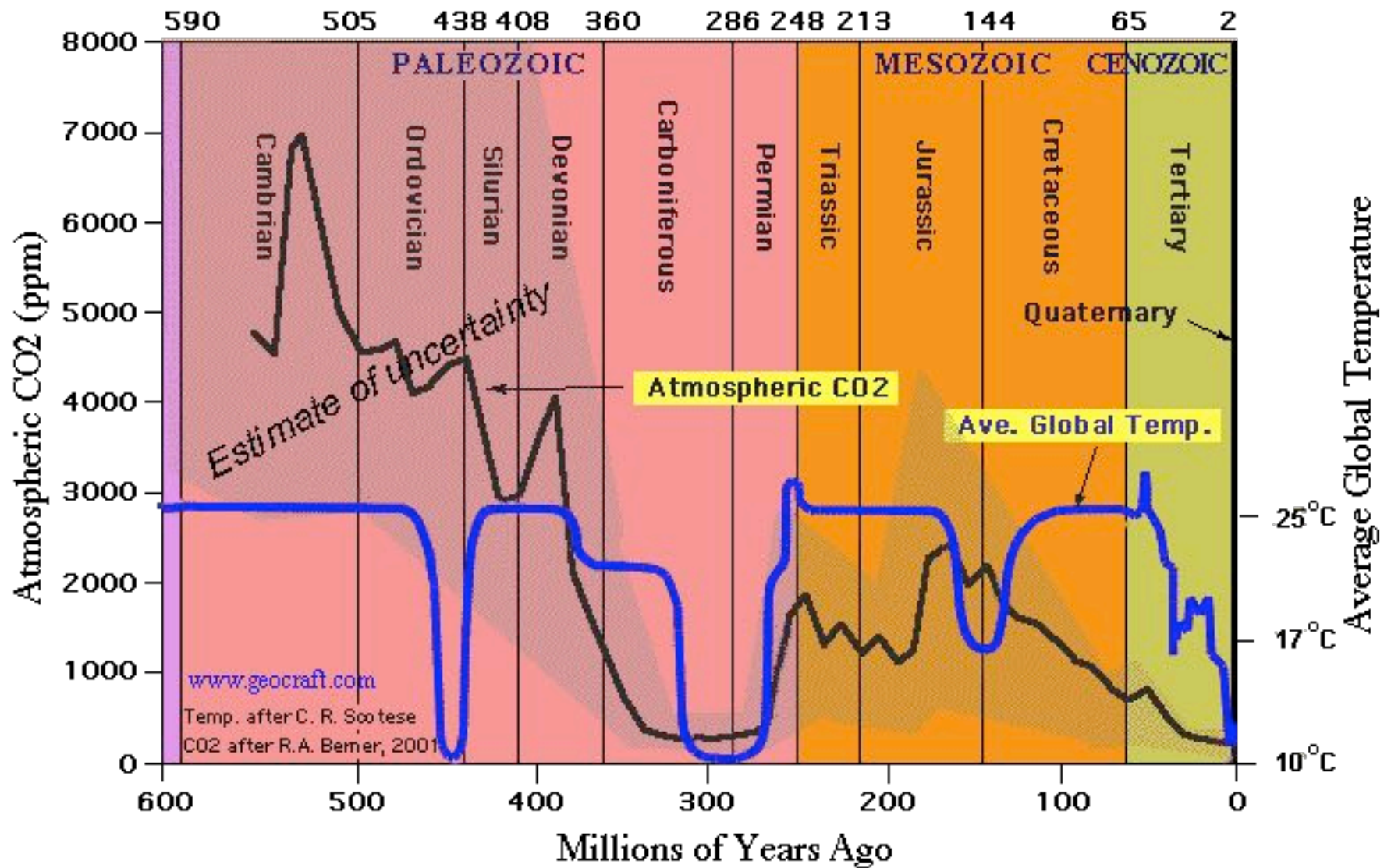
More than a dozen independent temperature reconstructions affirm the conclusion that Earth's temperature has risen sharply in the past century.



http://www.geocraft.com/WVFossils/last_200_yrs.html



http://www.geocraft.com/WVFossils/last_400k_yrs.html



http://www.geocraft.com/WVFossils/Carboniferous_climate.html#anchor147264

Carbon Cycle: Life on earth is carbon-based
Plants absorb CO₂ and emit oxygen as a waste product.
Humans and animals breathe oxygen and emit CO₂ as a waste product.

All sources: Approx. **200 billion tons** of carbon from CO₂ that enter earth's atmosphere each year (½ from oceans, ½ from volcanoes and decaying plants)

Human activity: **6 billion tons** of carbon from CO₂.

CO₂ that goes into the atmosphere is recycled by terrestrial plant life and earth's oceans

CO₂ concentration: **380 parts per million** (ppm) = less than 4/100ths of 1% of all gases present. Compare to former geologic times.

Is CO₂ is an essential ingredient.

Is CO₂ is a nutrient or a pollutant?

Is plant growth stimulated by more CO₂?

http://www.geocraft.com/WVFossils/ice_ages.html

Australian sheep and cattle to be vaccinated to reduce CH₄ emissions.



WWW.SPUDCOMICS.COM

© 2009 LONNIE EASTERLING

<http://spudcomics.com/tag/farting-sheep/>

Sheep and cattle in Australia produce 14% of Australia's total greenhouse emissions (measured in CO₂ equivalents).

Vaccine will reduce CH₄ emissions by 20% in these animals (approx. 300,000 metric tons of CO₂).

CH₄ ≈ 21 x more potent than CO₂ as a greenhouse gas.

(Chemical and Engineering News, 6/18/01, p. 104)

CEN, 7/29/19, “Minimizing methane from cattle”

<https://cen.acs.org/business/food-ingredients/DSM-seeks-approval-additive-minimizing/97/i30>

A cow releases 70-120 kg of methane annually, mostly by burping. Cow’s digestive system has microbes that produce methane.



Livestock accounts for 15% of global greenhouse emissions of which more than ½ from cattle.

3-nitrooxypropanol is a cattle feed additive that can reduce methane emissions by 30%. DSM Co. (Europe) has applied to European regulators to see this additive.



3-nitrooxypropanol

1.3 billion cows in the world (2011)



U.S. Livestock produces 139.8 units of TgCO_2 equivalent
(teragram carbon dioxide equivalent)

≈ 20% of all human methane production and second only to natural gas systems

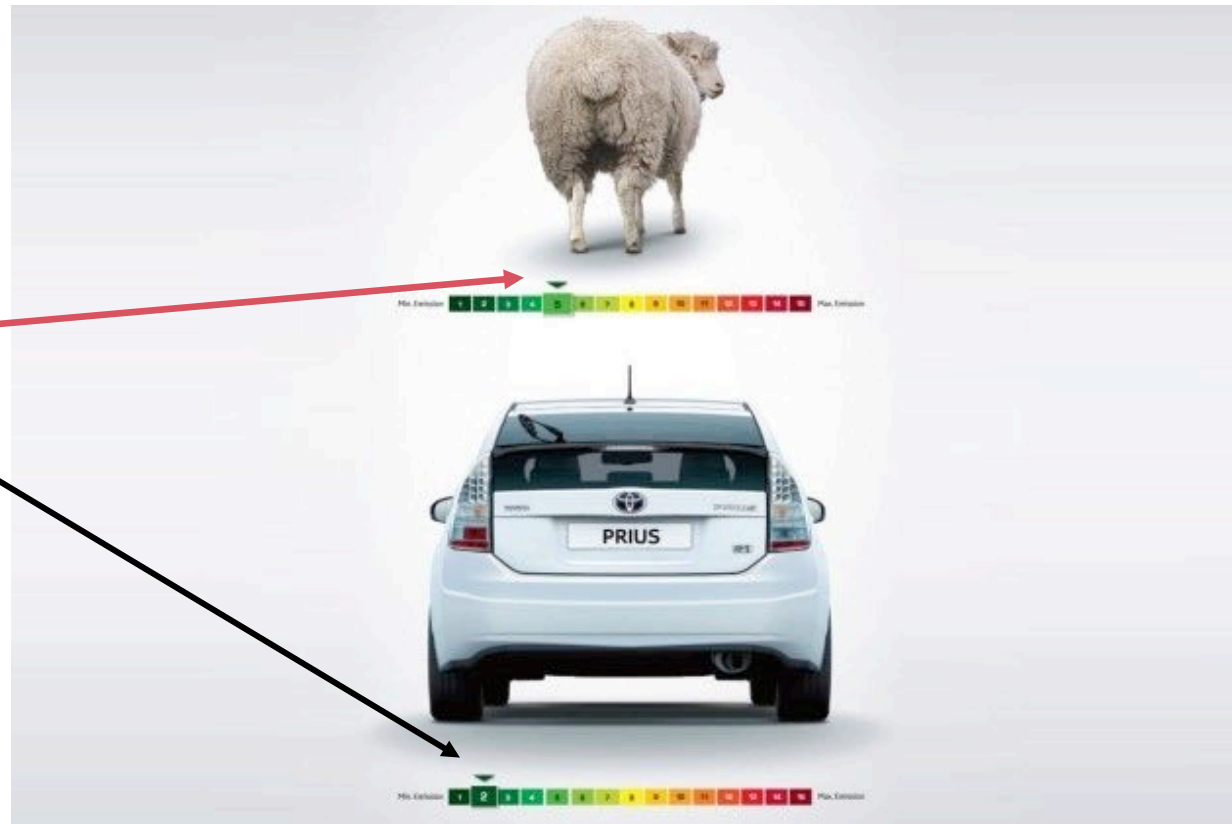
U.S. produces 5,637.9 units of TgCO_2 equivalent per year by burning fossil fuels

<http://bigkingken.wordpress.com/2011/07/05/finally-a-post-on-cow-farts/>

Toyota: Prius exhaust less harmful than sheep emissions

<http://www.autoblog.com/2011/01/04/toyota-prius-exhaust-less-harmful-than-sheep-emissions/>

See scale



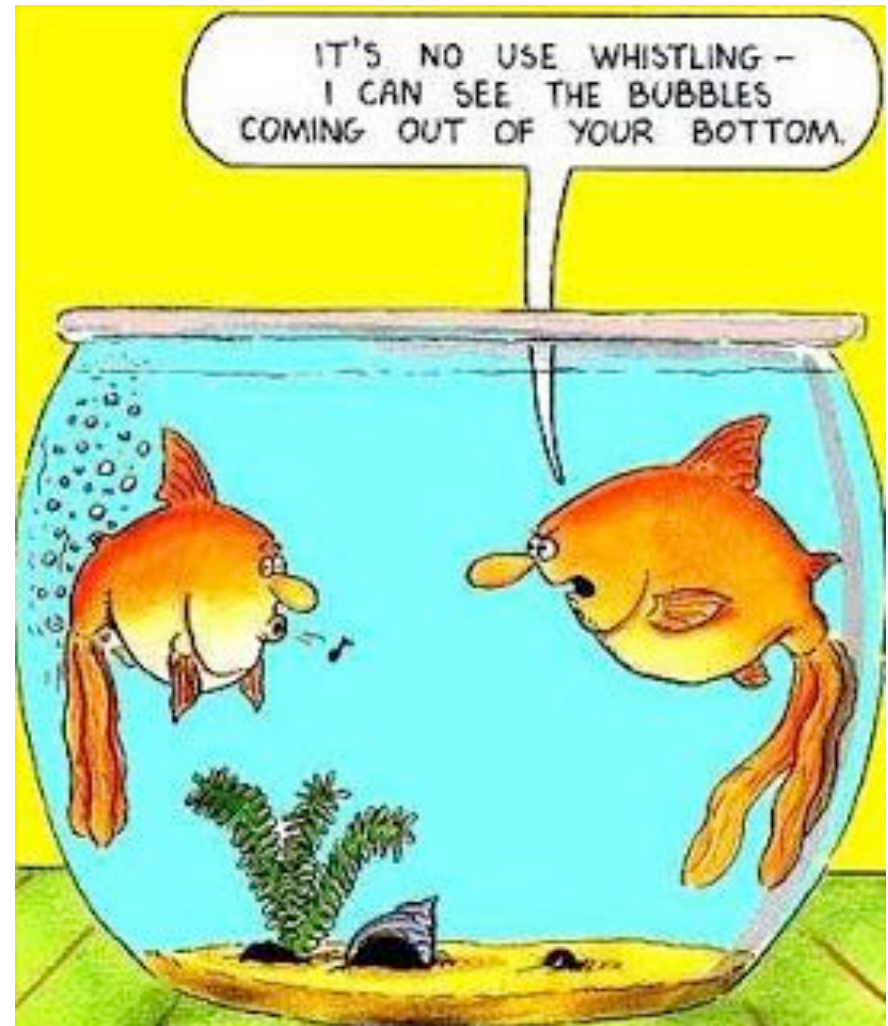
Question: Does one sheep emit more global warming CH_4 than one Prius emit global warming CO_2 ?

Seen in SF



<http://www.freerepublic.com/focus/f-news/1864014/posts>

<http://dotsondds.blogspot.com/2011/02/when-in-malawi-do-not-fart.html>





Search for greenhouse gas emitters by facility, type of factory, amount and type of greenhouse gas, facility location, plant name

<http://ghgdata.epa.gov/ghgp/main.do>

HEATED EXCHANGE

HCFCs and HFCs remain in the atmosphere longer than CFCs

GAS	GLOBAL WARMING POTENTIAL ^a	LIFETIME (YEARS)
CO ₂	1	100+
Chlorofluorocarbons (CFCs)		
CFC-12	10,200 +/- 3,750	100.0
CFC-114	9,880 +/- 3,460	300.0
CFC-113	6,030 +/- 2,110	85.0
CFC-11	4,680 +/- 1,640	45.0
Hydrochlorofluorocarbons (HCFCs)		
HCFC-142b	2,270 +/- 800	17.9
HCFC-22	1,780 +/- 620	12.0
HCFC-124	599 +/- 210	5.8
HCFC-123	76 +/- 27	1.3
Hydrofluorocarbons (HFCs)		
HFC-23	14,310 +/- 5,000	270.0
HFC-125	3,450 +/- 1,210	29.0
HFC-134a	1,410 +/- 490	14.0
HFC-245fa	1,020 +/- 360	7.6
HFC-152a	122 +/- 43	1.4

^a Referenced to CO₂. Global warming potential is a measure of relative ability to affect the global climate.

SOURCES: Intergovernmental Panel on Climate Change and Economic Assessment Panel

CEN, October 3, 2005, pp. 23-24
Hot Times Ahead For Refrigerants
As worry over refrigerants' threat to the ozone layer recedes, concern over global warming rise.

Energy for refrigeration = 1/6 of global energy usage

http://www.nytimes.com/2014/07/27/magazine/what-do-chinese-dumplings-have-to-do-with-global-warming.html?_r=0