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## PHOTOCHEMISTRY: Light chemistry.

GEOCHEMICALLY: Electron-transfer reactions driven by Solar energy.

- The most important photochemical processes on earth are PHOTOSYNTHETIC REACTIONS. But, that being the domain of biochemists, we will stick to

### ABIOTIC PHOTOCHEMICAL REACTIONS

## GENERAL CONCEPTS:

**Photon**: A quantum particle that has no mass, (no rest mass, to be exact) and which carries the energy embodied by electromagnetic radiation

The ENERGY CONTENT of a photon is a linear function of the FREQUENCY ( $\nu$ ) of the wave function that describes the light. (Recall the wave-particle duality of radiation, with a nod to Prof. de Broglie and friends.)

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$$\text{Photon Energy} = h\nu$$

$h$  = Planck Constant

(also known as the "Max Factor")

$\nu$  = frequency, with units =  $\text{sec}^{-1}$

(can also use the more familiar  
cycles/sec = hertz; abbreviate  
this frequency as  $f = 2\pi\nu$ )

If we express frequency as  $\nu$  (units =  $\text{s}^{-1}$ )  
then the relationship between wavelength ( $\lambda$ )  
and frequency is

$$\nu = \frac{c}{\lambda}$$

$c$  = speed of light =  $3.0 \times 10^8 \text{ m s}^{-1}$

E.g. GREEN LIGHT,  $\lambda \approx 500 \text{ nm}$

$$\nu = \frac{3 \times 10^8 \text{ m s}^{-1}}{500 \times 10^{-9} \text{ m}} = 6 \times 10^{14} \text{ s}^{-1}$$

$$f = 2\pi\nu = 1.8 \times 10^{15} \text{ Hz} \quad (1.8 \text{ PHz})$$

③

Hence, we can compute the energy of a photon of green light:

⇒  $h = 6.6 \times 10^{-34} \text{ J}\cdot\text{s}$  (use with  $\nu$ )

⇒  $\hbar = 1.05 \times 10^{-34} \text{ J}\cdot\text{s} = \frac{h}{2\pi}$  (use with  $f$ )

Photon Energy =  $(6.6 \times 10^{-34} \text{ J}\cdot\text{s})(6 \times 10^{14} \text{ s}^{-1}) = 4 \times 10^{-19} \text{ J}$

Which does not seem like much, but this is for only a single photon. Noonday sunlight in mid-latitudes in July has a photon flux (visible range) of approximately  $1500 \mu\text{Einstein}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$  ( $\mu\text{E}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ )

An "Einstein" is one mole of photons

Noon Sun =  $1500 \mu\text{mole-photon}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$

Energy Flux (if entirely due to green light, which is not a bad approx. since green light is sort of an "average" wavelength) is then:

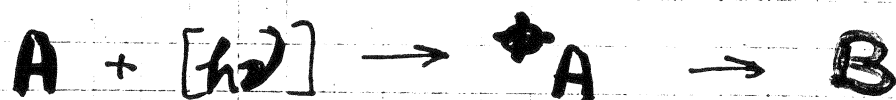
Energy-Flux =  $(1500 \frac{\mu\text{mole-photon}}{\text{m}^2\cdot\text{s}})(6.02 \times 10^{17} \frac{\text{photons}}{\mu\text{mole}})(4 \times 10^{-19} \text{ J})$

$\approx 360 \text{ J}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$

(sounds about right if we recall ESE ~~530~~ 530)

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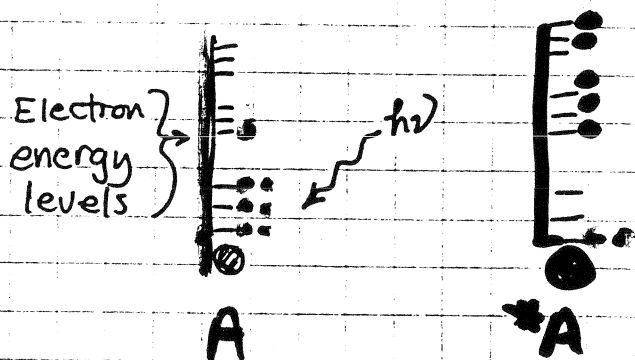
## GENERAL PHOTOCHEMICAL REACTION:



${}^*A$  = Electronically excited state of A

B = reaction product(s)

E.g.



← Energy of photon transferred to some electrons, which drives them up to excited energy levels.

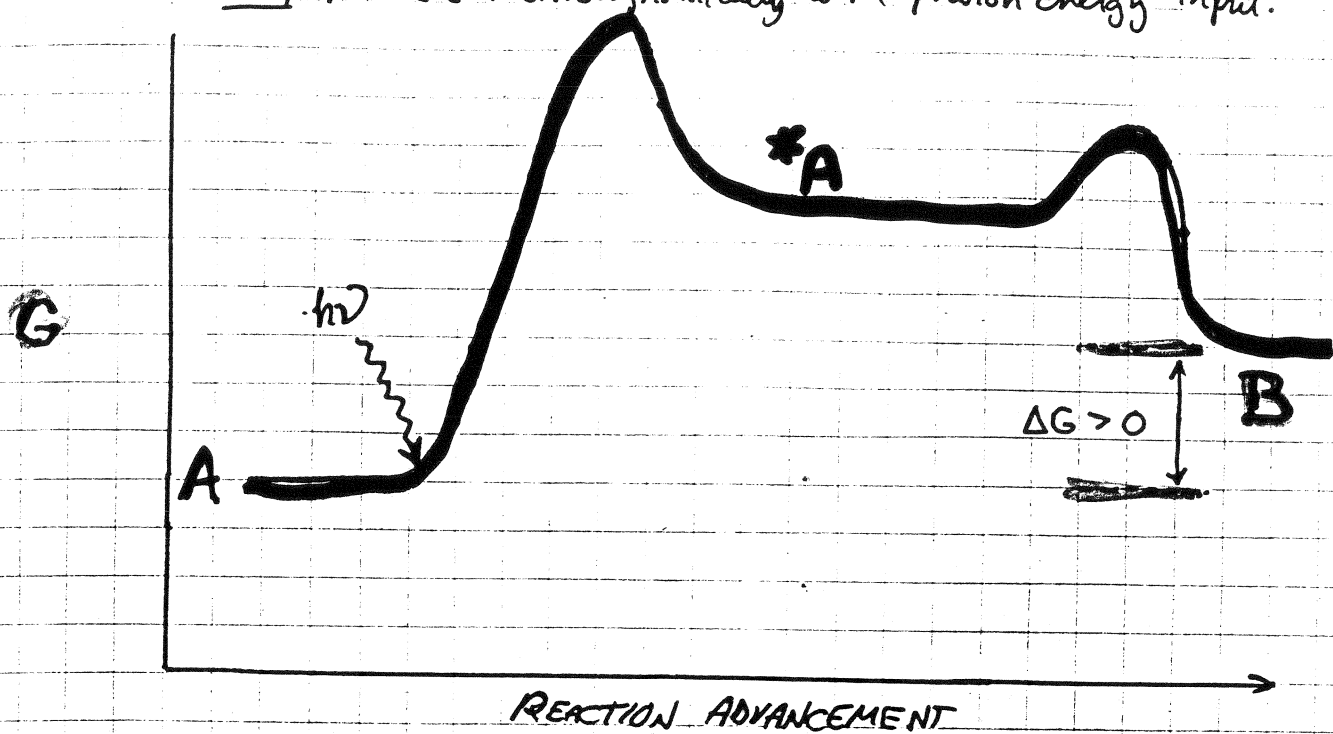
Reaction may be either "photocatalysis" or simply photo-energetically driven.

PHOTO-ENERGETIC: Overall  $\Delta G$  unfavorable, rxn energy provided by photon

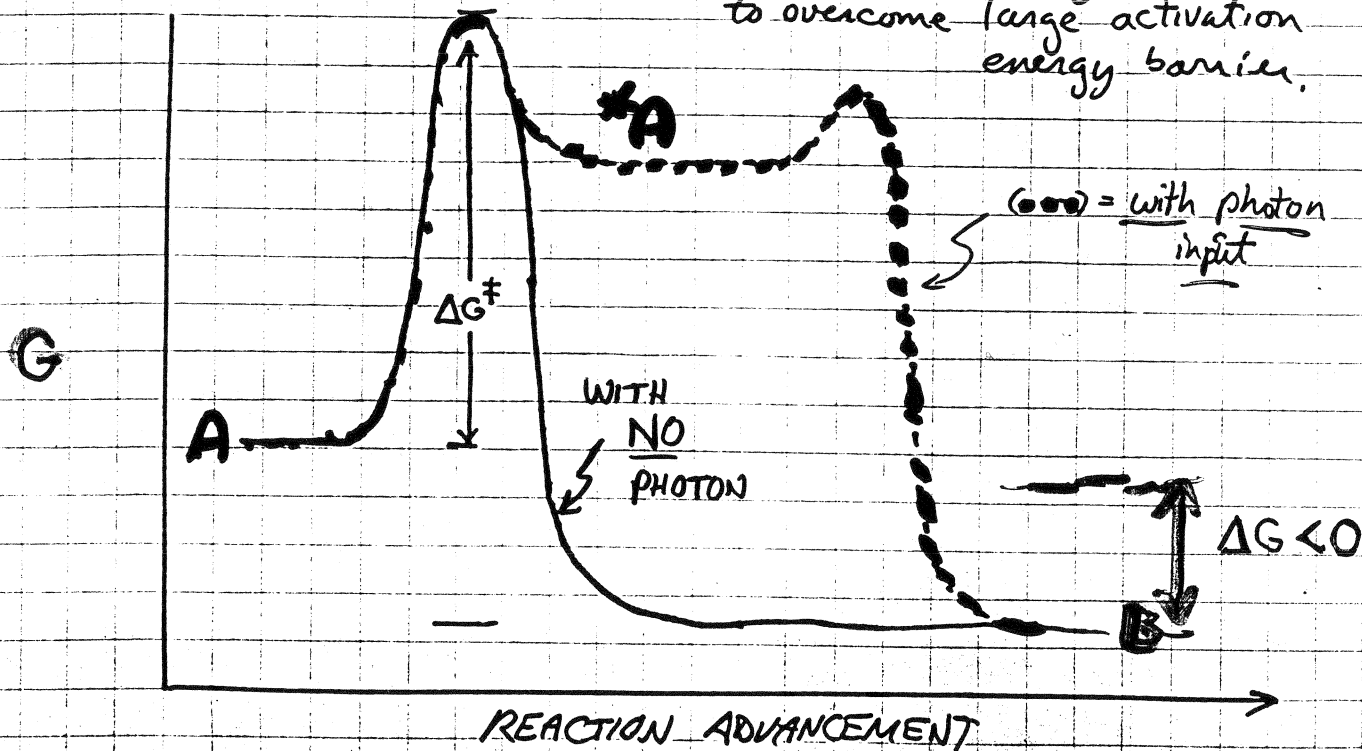
PHOTO-CATALYSIS: Overall  $\Delta G$  favorable; photon provides the activation energy ( $\Delta G^\ddagger$ )

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I. Reaction is ONLY possible thermodynamically with photon energy input.



II. Reaction is thermodynamically possible, but photon energy needed to overcome large activation energy barrier.



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We can pull these two concepts together:

1. Photons provide a relatively intense source of energy to the molecules that absorb them.
2. The photo-excitation of molecules can allow reactions that otherwise could not proceed for energetic reasons.

How much energy can a molecule absorb?

Assume complete absorption of green (500 nm)

light:

Avogadro's No.

$$E_{\lambda} = N(h\nu) = \frac{Nhc}{\lambda}$$

$$E_{\lambda} = \frac{(6.02 \times 10^{23})(6.6 \times 10^{-34} \text{ J}\cdot\text{s})(3.0 \times 10^8 \text{ m}\cdot\text{s}^{-1})}{\lambda}$$

$$E_{\lambda} = \frac{0.12}{\lambda} \text{ Joules/mol}$$

To put this in convenient units of  $\lambda = \text{nm}$ ,  $E_{\lambda} = \text{kJ or kcal}$

$$E_{\lambda} = \frac{120,000}{\lambda_{\text{nm}}} \text{ kJ mol}^{-1}$$
$$E_{\lambda} = \frac{28,000}{\lambda_{\text{nm}}} \text{ kcal mol}^{-1}$$

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$\lambda$	$E_{\lambda}, \text{kcal mol}^{-1}$	$E_{\lambda}, \text{KJ} \cdot \text{mol}^{-1}$
<u>250 nm (ultraviolet)</u>	110	480
<u>400 nm (blue)</u>	70	300
<u>500 nm (green)</u>	55	240
<u>800 nm (red)</u>	35	150

Ultraviolet light provides the most energy, and the available energy decreases toward the red and infrared.

Energies of UV  $\rightarrow$  visible photons are about the same general category as covalent bond energies. Hence UV-vis light is ideal for stimulating chemical reactions. (It is no coincidence that plants and eyes respond primarily to the 'visible' range of radiation: these wavelengths have enough energy to drive the chemical reactions of photosynthesis and vision, but are not "too energetic" [like UV light] to be safely controlled by the organism.)

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Note that the other source of activation energy (or endothermic reaction energy) is the thermal energy of molecular collisions.

How does  $55 \text{ kcal mol}^{-1}$  for green light compare to thermal energy in a compound at room temperature? The Boltzmann distribution tells us how many atoms have a thermal energy  $\gg$  at a certain temperature

$$\frac{n_i}{n_0} = \exp[-(E_i - E_0)/RT]$$

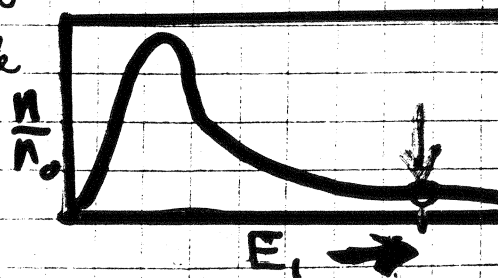
$n_i$  = # of molecules with energy  $E_i$

$E_0$  = energy of standard state

$R$  = gas constant

$T$  = temp. (K)

$n_0$  = total # of molecules



For room temperature ( $\sim 298 \text{ K}$ )

$$n_i/n_0 \approx e^{-50/0.58} \approx 10^{-38}$$

I.e. a mole fraction of  $10^{-38}$  or a molar

concentration of  $\sim 10^{-15}$  molecules/mole

I.e. THIS MANY MOLECULES HAVE THE THERMAL ENERGY =  $55 \text{ kcal/mol}$



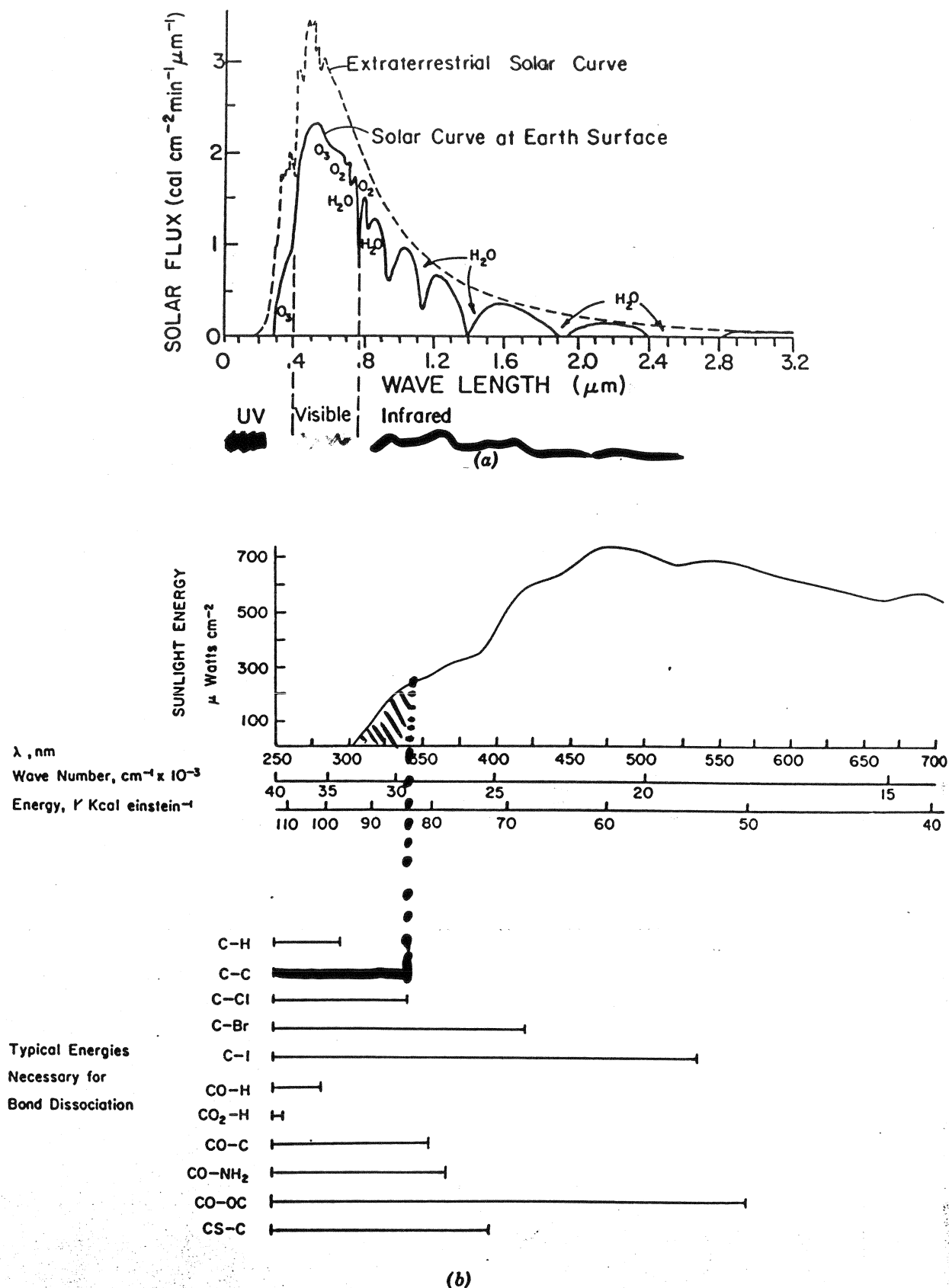


Figure 7.8 (a) Solar spectrum at the earth's surface. From Gates, 1962.<sup>16</sup> (b) Comparison of the uv-visible solar flux with typical bond-breaking energies. From Zika, 1981.<sup>14</sup>

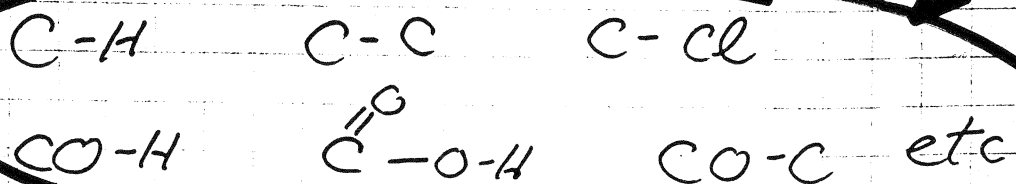
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CONCLUSION: Photons can easily drive reactions that thermal energy could never possibly drive.

However: many wavelengths of light have photons too weak to drive some bond-dissociation reactions

SUNLIGHT ENERGY IS DISTRIBUTED  
NON-UNIFORMLY AS A SPECTRUM

Most energy is found in the GREEN → RED region, which is weaker than necessary to dissociate common bonds such as:



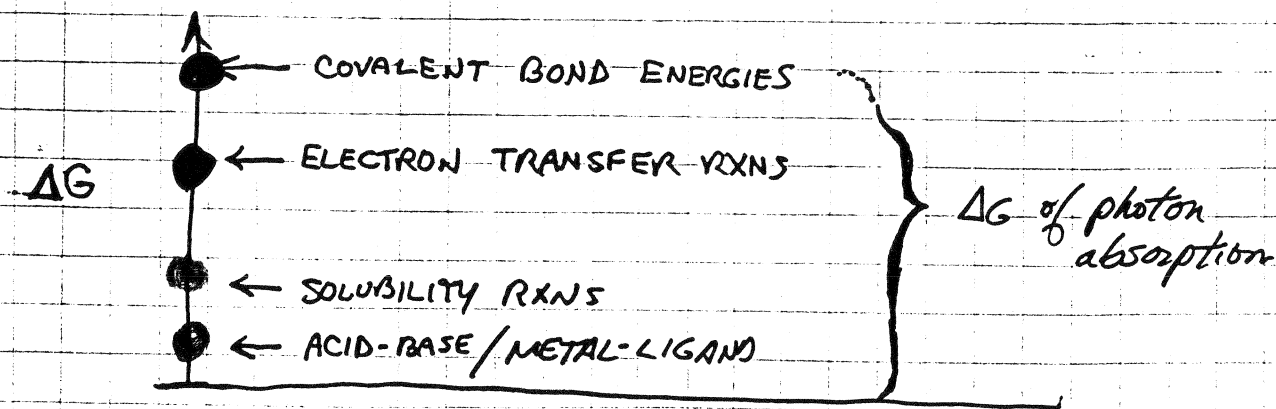
But, a small amount of the solar spectrum overlaps most of these bond energies.

[see next Figure] 15.20

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- Bond-breaking reactions very important in upper stratosphere ( $O_3$  production, etc.)
- B-B rxns somewhat important in troposphere (photochemical smog, etc.)
- Not very important on land or in surface waters.

⇒ But photons have sufficient energy to drive REDOX REACTIONS in which electrons are transferred but covalent bonds are not necessarily broken



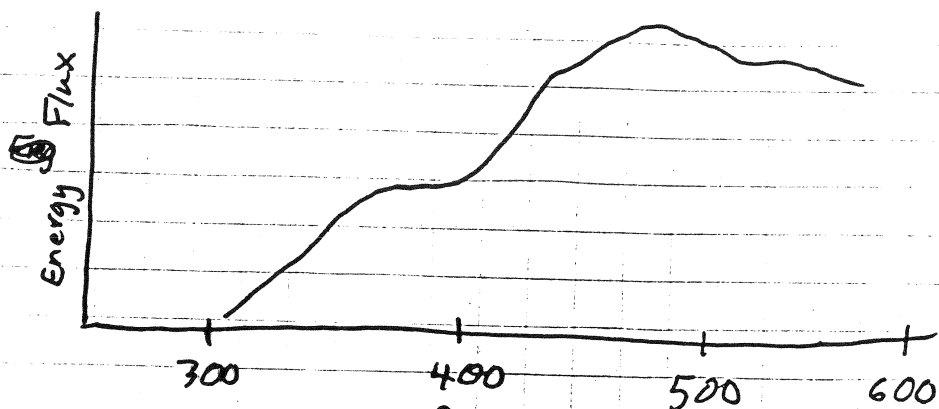
PHOTOREDOX IS RATHER IMPORTANT ON EARTH

- Photosynthesis
- Aquatic abiotic processes

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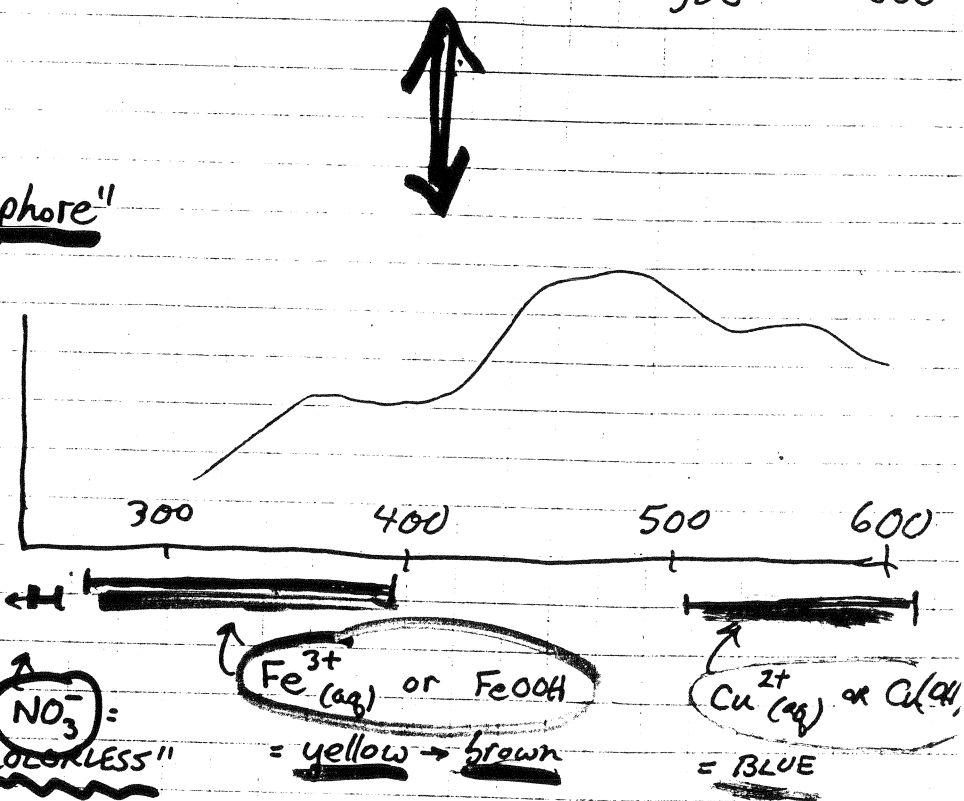
BEFORE we get into that, however, let's review some of the steps that must occur before a rxn can proceed

I. Input Energy Spectrum:



II. Molecule must have a "Chromophore" at one of these wave lengths

⇒ MUST ABSORB LIGHT

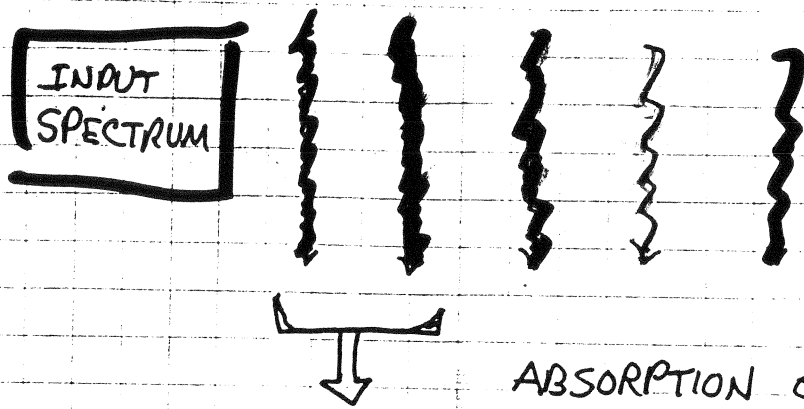


CONCLUSION:

$\text{NO}_3^-$  : No reactions in ordinary sunlight

$\text{Fe}^{III}$   
 $\text{Cu}^{II}$  } : Absorb visible light → Photoreactions are possible

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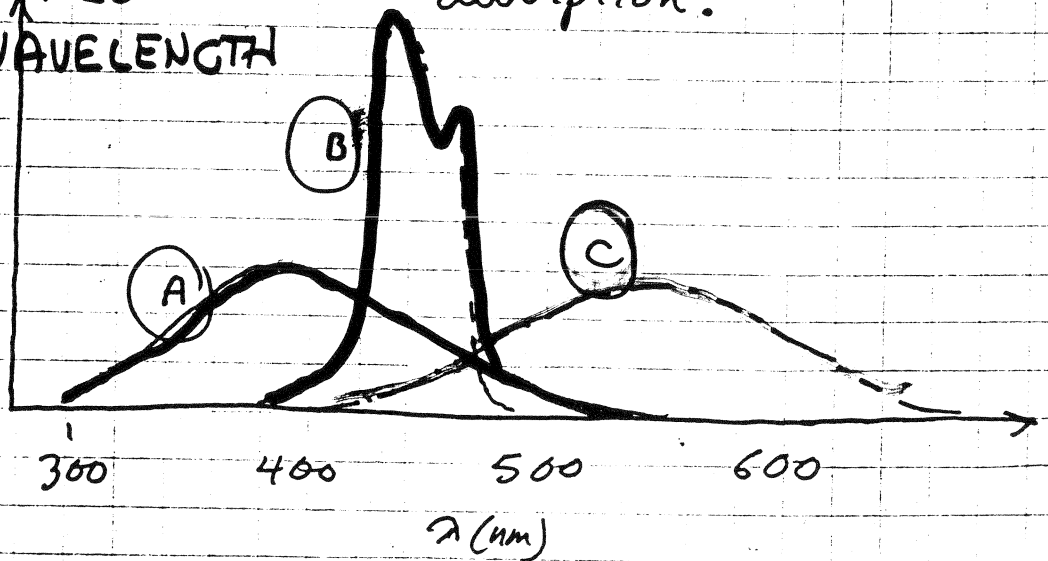
ABSORPTION OF SPECIFIC BAND OF FREQUENCIES (WAVELENGTHS)

a. What range?

b. With what intensity of absorption?

MOLECULES MUST HAVE AN "ANTENNA" TUNED TO CORRECT WAVELENGTH

SPECIFIC (MOLAR) ABSORPTIVITY  $\epsilon_{\lambda}$



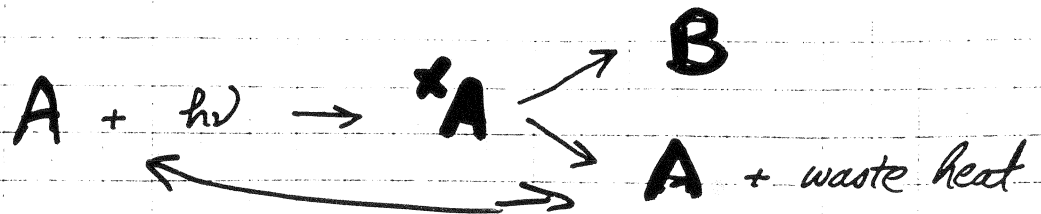
**A:** Absorbs weakly, but over a wide range of fairly energetic wavelengths

**B:** Absorbs only in a narrow range but absorbs strongly (is "deeply colored")

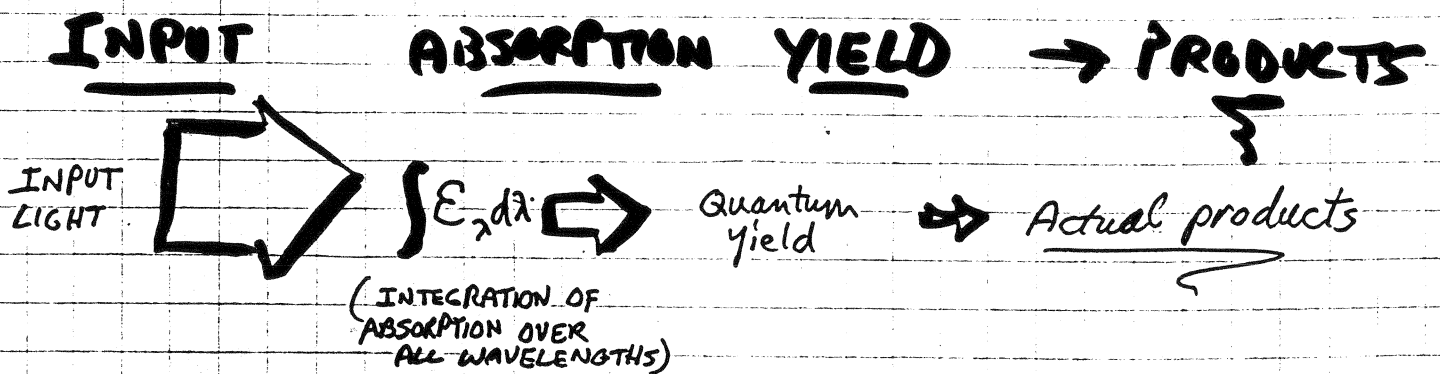
**C:** Looks like "A" but its capture zone is over a range of weak photons

TOTAL E CAPTURED:  $A \approx B \gg C$

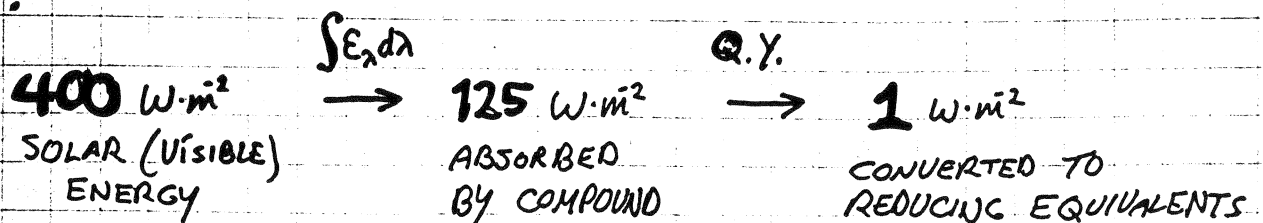
FINALLY, once you capture photons, you must use them to promote rxn:



I.e.: **Never get 100% "quantum yield"** on the second step  ${}^*A \rightarrow B$ . Some (or most) of  ${}^*A$  just drops back to  $A$ -state and gives up its extra energy as heat.



E.g. in purely energetic terms might get something like:



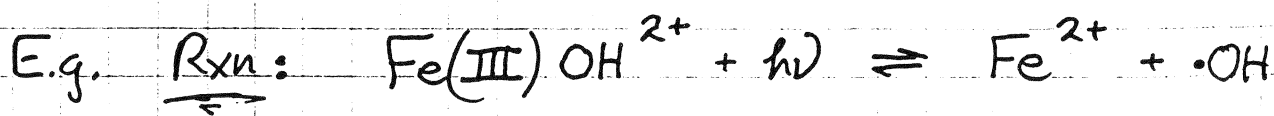
## (15) QUANTUM YIELD

In chemical terms, convenient to express quantum yield as something ~~like~~ like

$$\frac{[\text{moles of product}]}{[\text{Einstein (mole) of light absorbed}]}$$

OR, an overall quantum yield

$$\frac{[\text{moles of product}]}{[\text{Einstein of light in certain range}]}$$



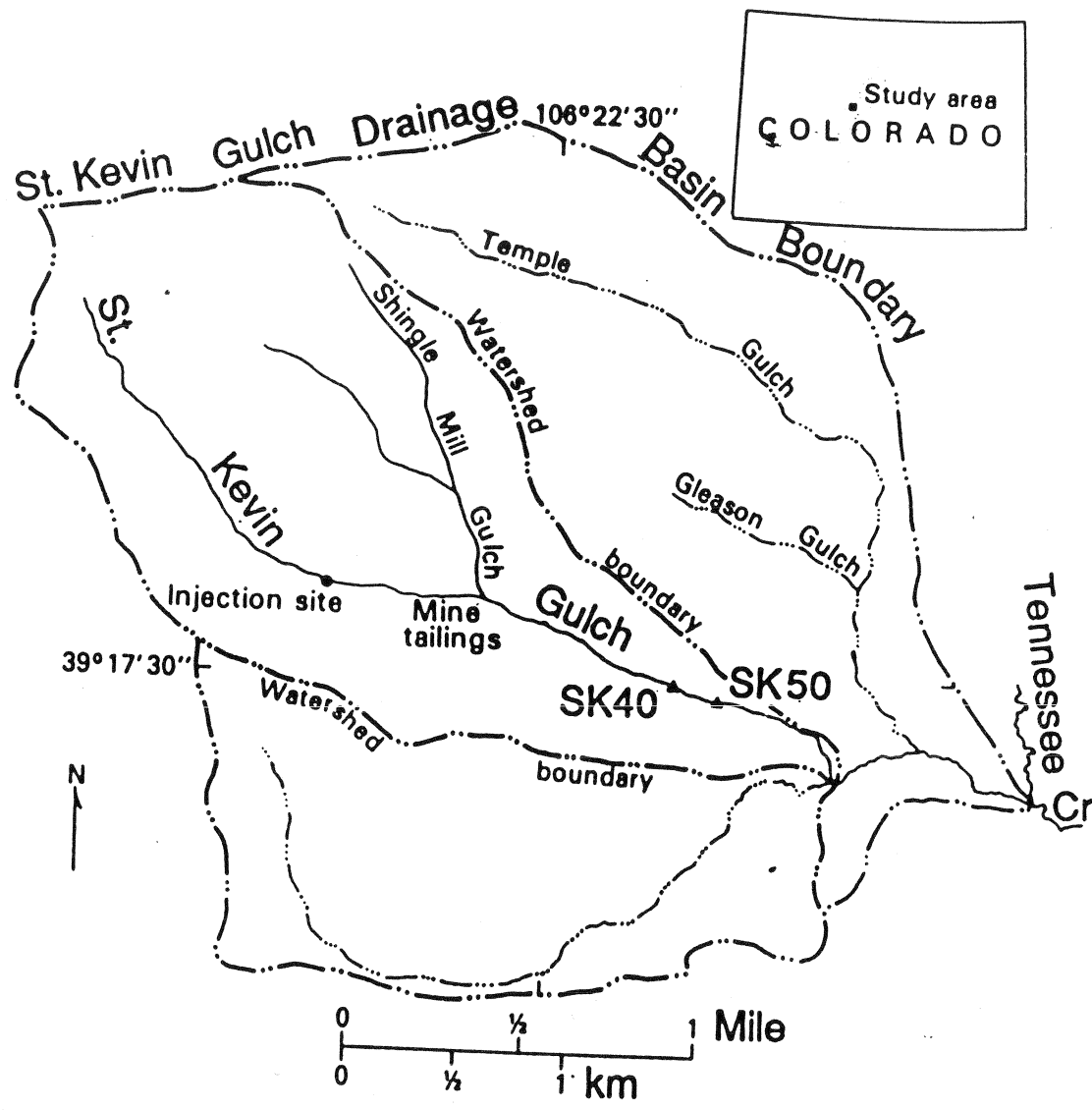
Reduction of  $\text{Fe(III)}_{\text{(aq)}}$  to  $\text{Fe(II)}_{\text{(aq)}}$

Reaction absorbs light primarily in range

$$\lambda = 250 - 425 \text{ nm}$$

QUANTUM YIELD:  $\sim 10^{-2} \text{ mol} \cdot (E_{250-425 \text{ nm}})^{-1}$

$\therefore$  For every mole of photons absorbed by  $\text{FeOH}^{2+}$  in the range 250-425 nm, 0.01 mole of  $\text{Fe}^{2+}$  (and 0.01 mole  $\cdot\text{OH}$  radical) is produced.



**Fig. 1.** Map of St. Kevin Gulch. The catchment area at SK50 is 3.9 km<sup>2</sup>.