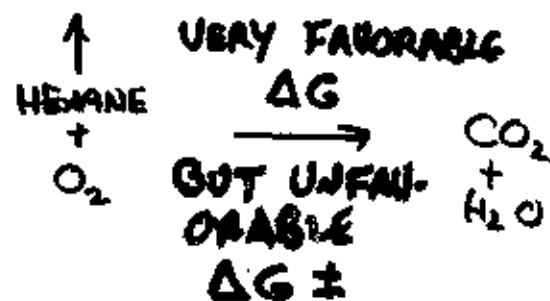
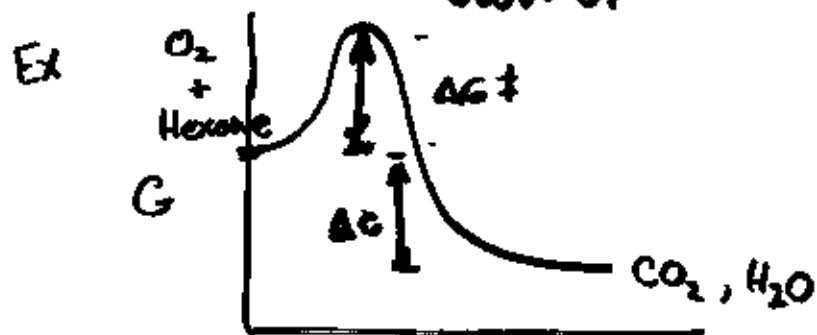


## ABIOTIC TRANSFORMATIONS

WITHOUT Biological CATALYSIS

Chemical breakdown less likely: Activation Energy is a barrier



BUT TWO COMMON ABIOTIC PATHWAYS OVERCOME THIS...

### 1. PHOTOLYSIS

Light photons provide the needed  $\Delta G^\ddagger$  (act. energy)

### 2. HYDROLYSIS:

ENORMOUS concentration of WATER (55.4 mol/L) overcomes the low probability of getting enough  $\Delta G^\ddagger$  (Low prob. x Very High "opportunities")

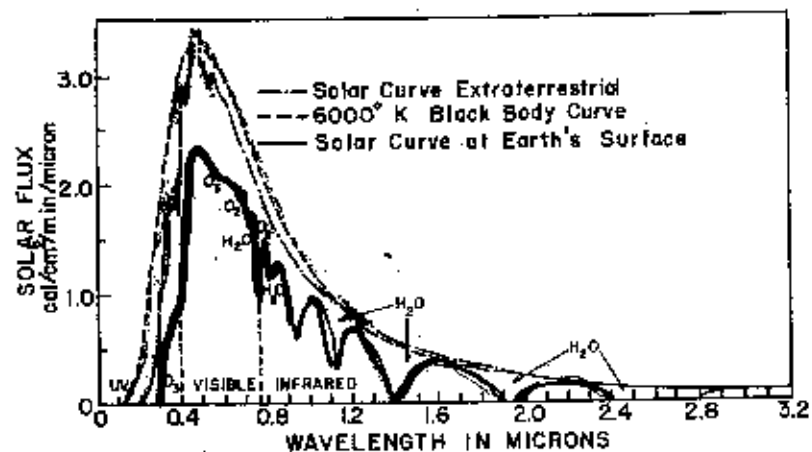
# PLANCK'S LAW

$$E = h\nu$$

$$h = 6.6 \times 10^{-34} \frac{\text{J}}{\text{s}}$$

SHORT  $\lambda \rightarrow$  HIGH FREQ ( $\nu$ )  
 $\rightarrow$  HIGH ENERGY

E.g. BLUE light has  $\sim 2\times$  the energy per photon as red

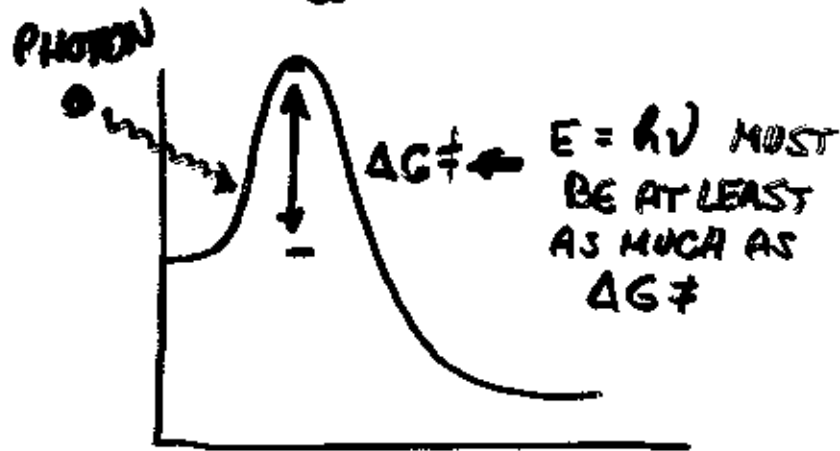


HIGH ENERGY PHOTONS

LOW ENERGY PHOTONS

FREQUENCY:  $\nu = \frac{c}{\lambda} = \frac{3 \times 10^8 \text{ m/s}}{\lambda (\text{m})}$

ENERGY OF EACH PHOTON:  $E = h\nu$



SO RED LIGHT MAY NOT WORK BUT BLUE LIGHT DOES

# STEPS IN PHOTOLYSIS

- I.**
- Rxn requires certain  $\Delta G \neq 0$
  - Only some photons ( $\nu > \nu_{min}$ ) can drive that rxn ( $h\nu_{min} = \Delta G \neq 0$ )

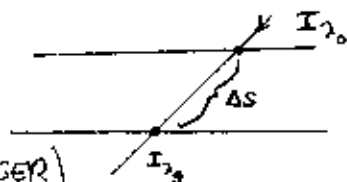
SO THOSE WAVELENGTHS OF LIGHT MUST BE PRESENT

- II.**
- Molecule must be able to absorb that type of photon
  - "Chromophore" must exist
  - IF not, then no photochemistry possible there



**BEER'S LAW**

(LAMBERT-BEER BOUGER LAW)



STRICTLY:  
MONOCHROMATIC LIGHT  
(one, pure wavelength)

BUT CAN BE ADAPTED  
FOR SUNLIGHT  
(many wavelengths)

$$dI_\lambda = -a_\lambda I_\lambda$$

"The amount of change in light intensity is a linear proportion of intensity"

(Imagine you invest in a stock fund that is losing at a negative interest rate of 5%/year)

$$d\$ = -0.05(\$)$$

For general medium:

$$dI_\lambda = \underbrace{(-\rho k_{\lambda} ds)}_{a_\lambda} I_\lambda$$

INTEGRATE over  $s$

$$\frac{I_{\lambda_s}}{I_{\lambda_0}} = \exp\left(-\int_0^s \rho k_{\lambda} ds\right)$$

↑ Allows for variable dens.  
Variable  $k_{\lambda}$  w/  $s$  (e)

$$\frac{I_{\lambda_s}}{I_{\lambda_0}} = e^{-Ks}$$

for a uniform medium  
(or "EFFECTIVELY" UNIFORM)

PRACTICAL APPLICATIONS OF BEER'S LAW:

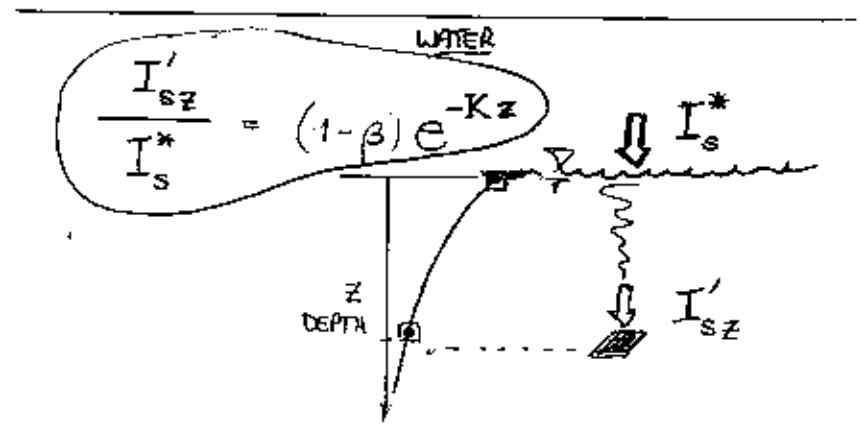
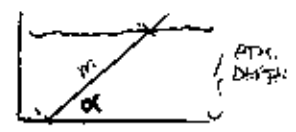
$$\frac{I_c}{I_0} = e^{-n a_1 m}$$

$I_0 = I$  at outer limit ATM  
 $I_c =$  cloudless  $I$  at surf. of earth

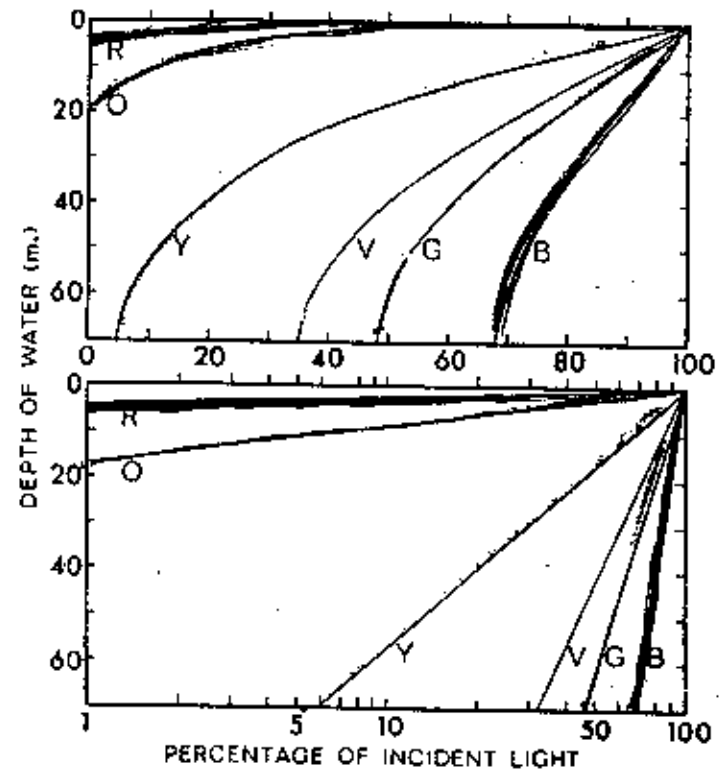
AIR  $a_1 =$  molecular scattering coefficient of pure air ( $O_2/N_2/Ar/CO_2$ )

$n = \frac{a_1}{a_1} =$  "TURBIDITY FACTOR"  
 ~ 2.0 = Clear mth. air  
 ~ 5 = smoggy air

$m =$  relative thickness of air mass = cosecant  $\alpha$   
 ( $\alpha =$  SOLAR ANGLE)

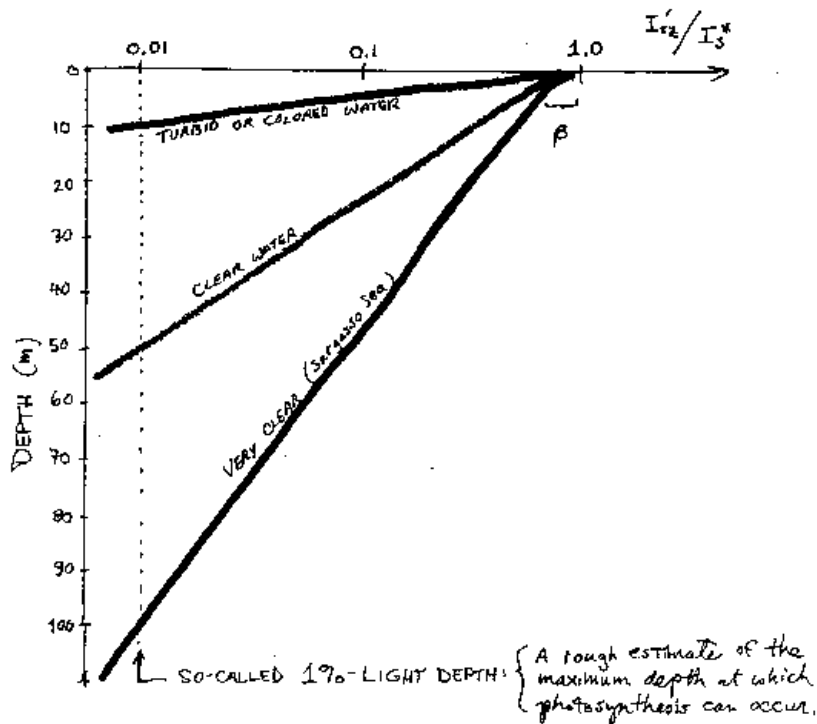


$$\frac{I_{sz}'}{I_s^*} = (1 - \beta) e^{-Kz}$$



ABSORPTION OF LIGHT BY WATER: Logarithmic Presentation

The exponential equation given by Beer's Law can be linearized by taking the natural log of both sides, or, by plotting light intensity on semi-log scaling.



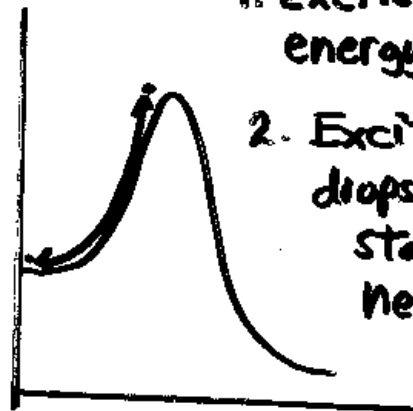
Any-  
why  
... [ - Photons present  
- Chromophore absorbs them ]

III. Absorbed energy must go into breaking down molecule

But that not only place energy can go...

1. Excited molecule dissipate energy as vibrations (heat)

2. Excited state drops back to ground state & emits a new photon (lower energy, longer wavelength)  
(FLUORESCENCE)



- Can also "lock" in to a new excited state that only slowly drops down (releasing photon)

PHOSPHORESCENCE

OR MAY REALLY GET A RXN

• DIRECT PHOTODEGRADATION

Photon  $\rightarrow$  Excited Mol.  $\rightarrow$  Lysis

• INDIRECT PHOTODEGRADATION

Photon  $\rightarrow$  Excited Mol. #1

$\downarrow$  PASSES ENERGY

Mol #2  $\rightarrow$  Excited Mol #2

$\downarrow$  LYSIS

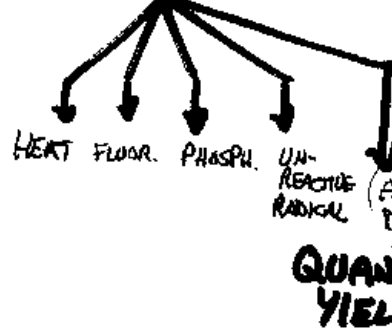
MOL #1  
DROPS BACK  
TO GROUND STATE

PHOTON  
CONC.  
(light intensity)

1 EINSTEIN  
= 1 mole of photons

$\downarrow$   
MOLAR  
ABSORPTION  
 $\times$  CONC.

Fraction of Einsteins  
actually absorbed  
by molecules

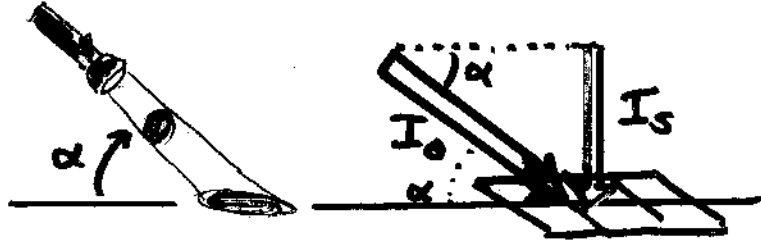


Fraction of  
absorbed photon  
that  
lead to  
degrad'n

PARAMETERS:  $h\nu$ , molar absorptivity, Quantum Yield

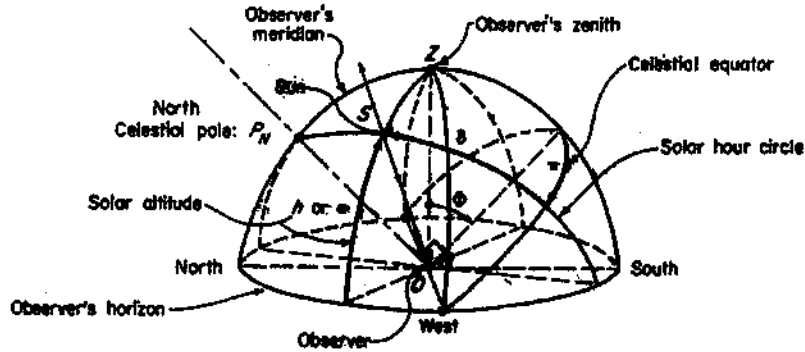
VARIABLES: Light intensity, conc. of chromophore  
(conc. of "Co. compound")

# SOLAR ANGLE



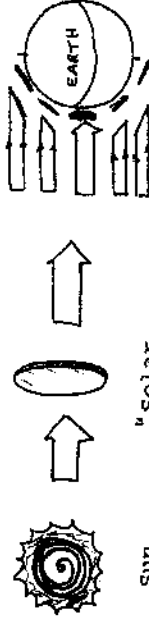
$$\sin \alpha = I_s / I_0$$

$$I_s = I_0 \sin \alpha$$



Great circles on the celestial sphere. (By permission from V. M. Blanco and S. W. McCusky, "Basic Physics of the Solar System," Addison-Wesley Publishing Company, Inc., Reading, Mass., 1961.)

The spherical shape of the earth is very important:



At higher latitudes, light is spread over greater area; hence, less intense.

"Solar constant"

$$W_0 \approx 2.0 \text{ langley's/min} \approx 1,400 \text{ cal/cm}^2/\text{min}$$

$$\text{"Insolation"} = I_0$$

$$I_0 = W_0 \sin \alpha$$

$$= W_0 \cos \phi$$

$$\alpha = [90^\circ - (\text{latitude})]$$

$\alpha$  = solar angle (See Eagle'son's chapter)

for noon at the equinox



Most intense per unit area of surface



Less intense per unit area of surface



SOLAR ANGLE

$$\sin \alpha = \sin \delta \sin \Phi + \cos \delta \cos \Phi \cos \tau$$

$\delta$  = DECLINATION

$\Phi$  = LOCAL LATITUDE

$\tau$  = HOUR ANGLE