Photophysics Basic

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- **Expressions of Intensity:**

- **Quantities based on radiometric system (not photometric**
- **system)**

- **Basic unit is joule and other SI units**
  (sometimes non-Si units for convenience)

- **Often definitions include area, volume or solid angle**
- **Spectral quantities –** B_λ
- **Partial quantities –** $B_{\lambda_1-\lambda_2} = \int_{\lambda_1}^{\lambda_2} B_\lambda d\lambda$
- **Total quantities -** $B = \int_0^\infty B_\lambda d\lambda$

Photochemical Technique: Radiometric system

TABLE 2-1
Radiometric system

Quantity	Symbol(s)	Description	Defining equation[a]	Unit(s)
General				
Radiant energy	Q	Energy in the form of radiation		J (ergs)
(Radiant) energy density	U	Radiant energy per unit volume	$U = \frac{\partial Q}{\partial V}$	$J\ cm^{-3}$
Radiant flux or radiant power	$\Phi(P)$	Rate of transfer of radiant energy	$\Phi = \frac{\partial Q}{\partial t}$	W
Source				
Radiant intensity	I	Radiant power per unit solid angle from a point source	$I = \frac{\partial \Phi}{\partial \Omega}$	$W\ sr^{-1}$
(Radiant) emittance or (radiant) exitance	M	Radiant power per unit area	$M = \frac{\partial \Phi}{\partial A}$	$W\ cm^{-2}$
(Radiant) emissivity	J	Radiant power per unit solid angle per unit volume	$J = \frac{\partial^2 \Phi}{\partial \Omega\, \partial V}$	$W\ sr^{-1}\ cm^{-3}$
Radiance	$B(L)$	Radiant power per unit solid angle per unit projected area	$B = \frac{\partial^2 \Phi}{\partial \Omega\, \partial A_p} = \frac{\partial^2 \Phi}{\partial \Omega\, \partial A \cos\theta}$	$W\ sr^{-1}\ cm^{-2}$
Receiver				
Irradiance	E	Radiant power per unit area	$E = \frac{\partial \Phi}{\partial A}$	$W\ cm^{-2}$
(Radiant) exposure	H	Integrated irradiance	$H = \int_0^t E\, dt$	$J\ cm^{-2}$

- **Radiant flux (F) : rate of energy transfer : $J \cdot s^{-1} = W$**
- **Radiant intensity (I) : radiant flux from a point source per unit solid angle ($\Phi/4\pi$) -applies to source**

  $J \cdot s^{-1} \cdot sr^{-1}$
- **Radiance (B) :radiant intensity (I) per projected area* ($\Phi/4\pi A$) - applies to source**
- ***depends on angle between detector and radiation propagation direction ; $J \cdot s^{-1} \cdot sr^{-1} \cdot cm^{-2}$**
- **Irradiance (E) : radiant flux (F) onto/from a surface per unit area (Φ/A) - applies to source or detector :**

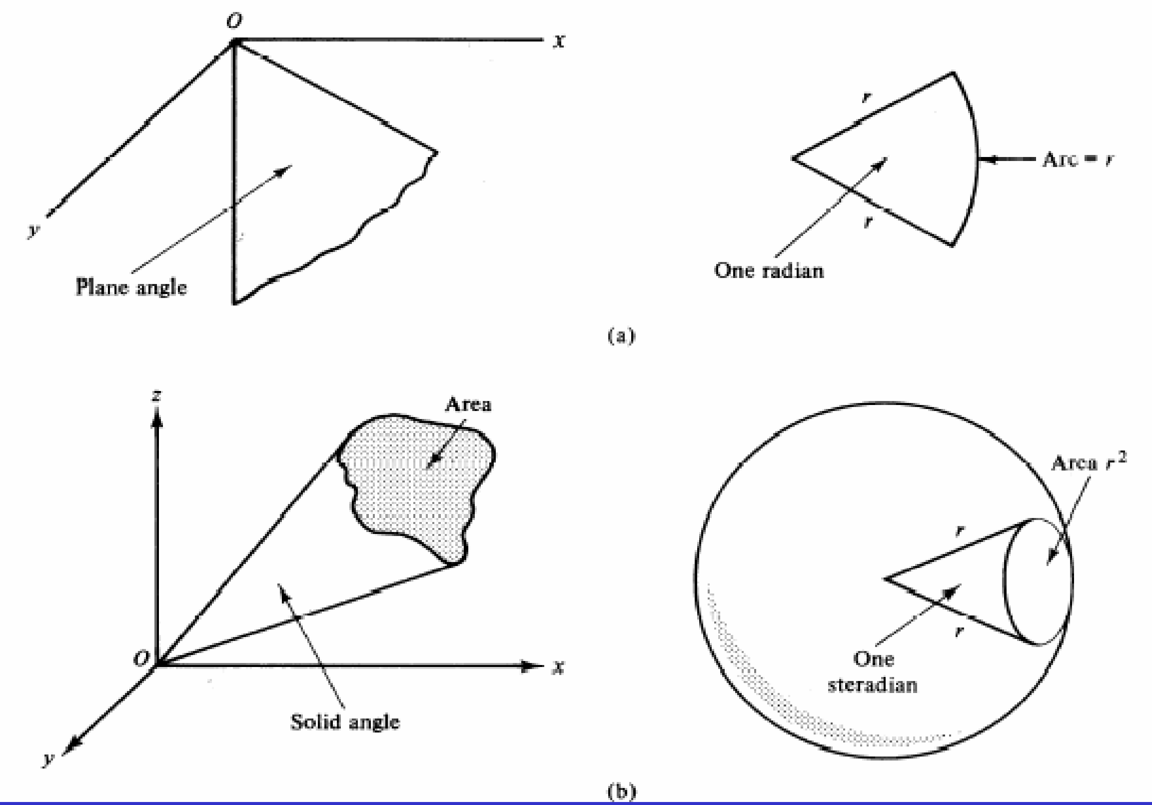
  $J \cdot s^{-1} \cdot cm^{-2}$
- **(radiant) Exposure (H)**
- **time-integrated irradiance ($\Phi(t)/A \cdot dt$) : $J \cdot cm^{-2}$**

- **Often, radiometric quantities include a solid angle or projected area**
- **Solid angle - 1 steradian (sr) is the part of the surface area of a sphere of radius r, having an area of r^2**

  $$A_{sphere} = 4\times\pi\times r^2$$
- **# steradians in sphere = $(4\times\pi\times r^2) / r^2 = 4\times\pi = 12.57$**

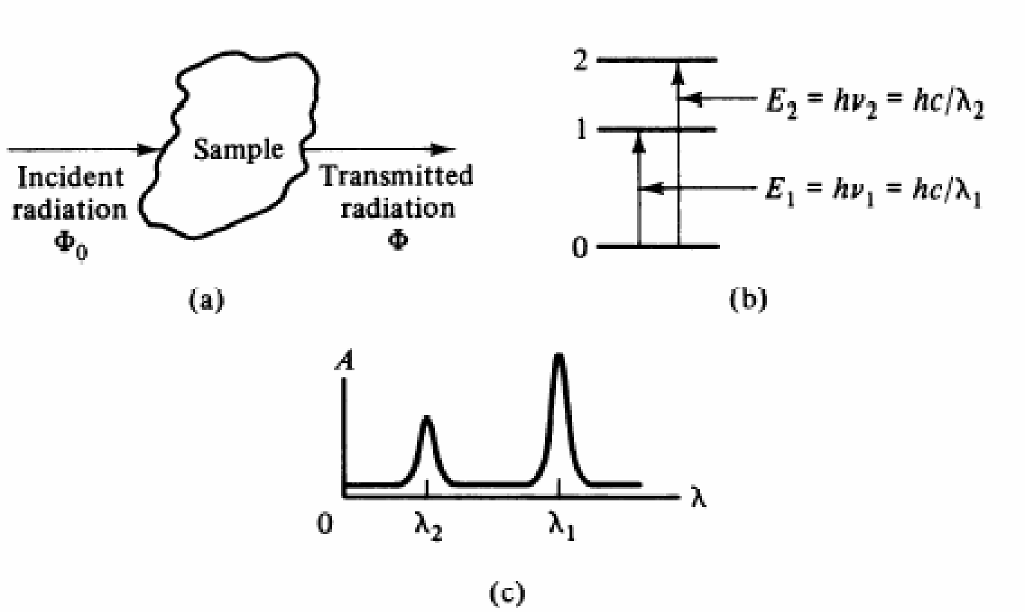
For example, intensity is the radiant flux per unit solid angle

$I = \Phi / 4\pi$



Photochemical Technique: Absorption Spectroscopy

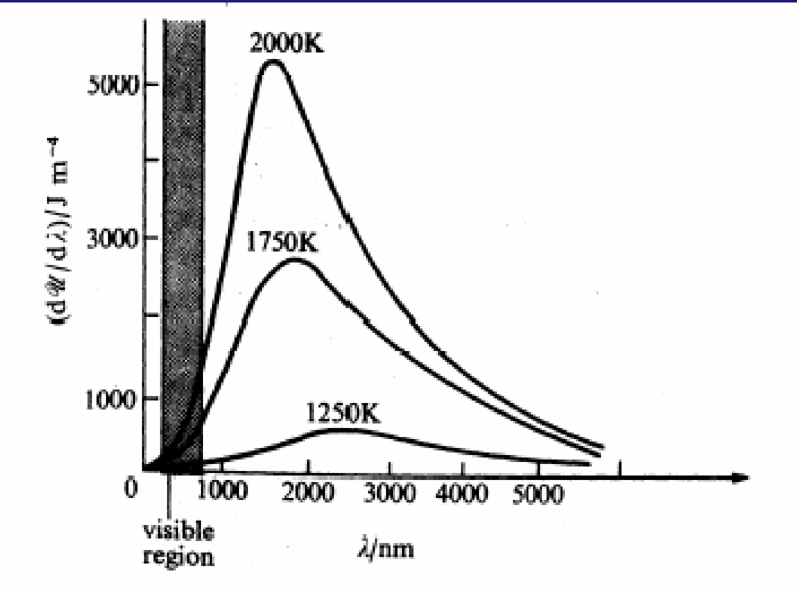
- **Absorbance A given by Beers' Law; related to the measured quantities Φ_0 and Φ (radiant flux) by**



- **$A = -\log T = -\log(\Phi / \Phi_0) = \varepsilon \times b \times c$**
- **c: concentration (mol·L-1)**
- **b: cell pathlength (cm)**
- **ε :molar absorptivity (L·mol-1·cm-1)**
- **$\Phi = \Phi_0 \times 10^{-\varepsilon \times b \times c}$**

Many radiation sources are based on black body radiation:

- • perfect absorber of radiation at all λ's if in thermal equilibrium, must also be perfect radiation emitter



- Two obvious points:
- • total amount of energy radiated increases rapidly with T
- $U = a \times T^4$ <= Stefan's Law
- Radiant energy density ($J \cdot cm^{-3}$)
- • position of the maximum spectral radiance (λmax) blue shifts with increasing T
- $\lambda_{max} = c_2 / 4.965 \times T$
- where c_2 = 1.438x107 nm·K