

# Spectrochemical Measurements

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

Partial quantities -  $B_{1-2} = B_1 d_2$

Total quantities -  $B = B_0 d$

**TABLE 2-1**  
Radiometric system

Quantity	Symbol(s)	Description	Defining equation <sup>a</sup>	Unit(s)
<b>General</b>				
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 <sup>-3</sup>
Radiant flux or radiant power	$\Phi(P)$	Rate of transfer of radiant energy	$\Phi = \frac{\partial Q}{\partial t}$	W
<b>Source</b>				
Radiant intensity	$I$	Radiant power per unit solid angle from a point source	$I = \frac{\partial \Phi}{\partial \Omega}$	W sr <sup>-1</sup>
(Radiant) emittance or (radiant) exitance	$M$	Radiant power per unit area	$M = \frac{\partial \Phi}{\partial A}$	W cm <sup>-2</sup>
(Radiant) emissivity	$J$	Radiant power per unit solid angle per unit volume	$J = \frac{\partial^2 \Phi}{\partial \Omega \partial V}$	W sr <sup>-1</sup> cm <sup>-3</sup>
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 <sup>-1</sup> cm <sup>-2</sup>
<b>Receiver</b>				
Irradiance	$E$	Radiant power per unit area	$E = \frac{\partial \Phi}{\partial A}$	W cm <sup>-2</sup>
(Radiant) exposure	$H$	Integrated irradiance	$H = \int_0^t E dt$	J cm <sup>-2</sup>

Important quantities:

### Radiant flux ( )

rate of energy transfer

$$\text{J}\cdot\text{s}^{-1} = \text{W}$$

### Radiant intensity (I)

radiant flux from a point source per unit solid angle ( /4 ) - applies to source

$$\text{J}\cdot\text{s}^{-1}\cdot\text{sr}^{-1}$$

### Radiance (B)

radiant intensity (I) per projected area\* ( /4 ) - applies to source

\*depends on angle between detector and radiation propagation direction (see Fig 2-3)

$$\text{J}\cdot\text{s}^{-1}\cdot\text{sr}^{-1}\cdot\text{cm}^{-2}$$

### Irradiance (E)

radiant flux ( ) onto/from a surface per unit area ( / ) - applies to source or detector

$$(\text{J}\cdot\text{s}^{-1}\cdot\text{cm}^{-2})$$

### (radiant) Exposure (H)

time-integrated irradiance ( (t)/ ·dt)

$$\text{J}\cdot\text{cm}^{-2}$$

### Fluence

often used but meaning is imprecise

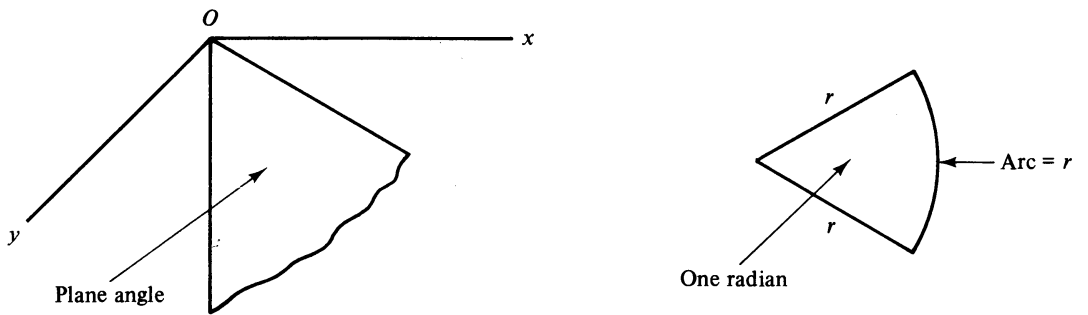
Geometric factors:

Often, radiometric quantities include a solid angle or projected area

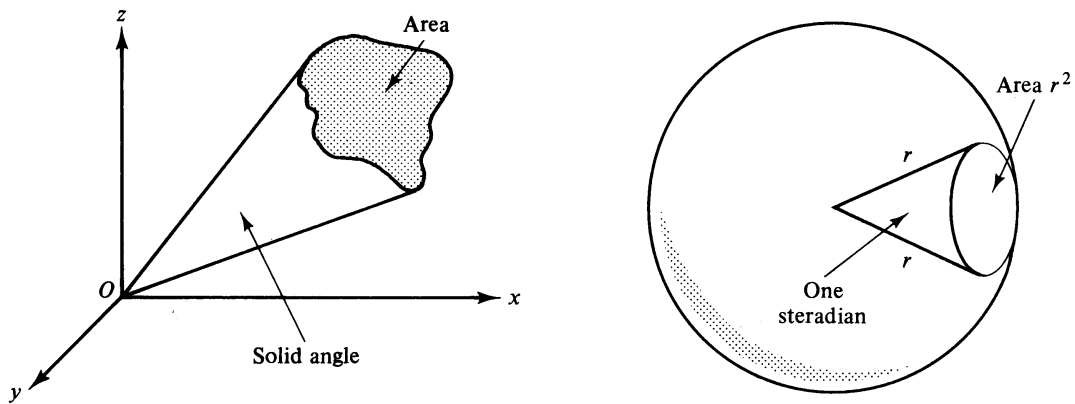
**Solid angle** - 1 steradian (sr) is the part of the surface area of a sphere of radius  $r$ , having an area of  $r^2$

$$A_{\text{sphere}} = 4 \pi r^2$$

$$\# \text{ steradians in sphere} = \frac{4 \pi r^2}{r^2} = 4 \pi = 12.57$$



(a)



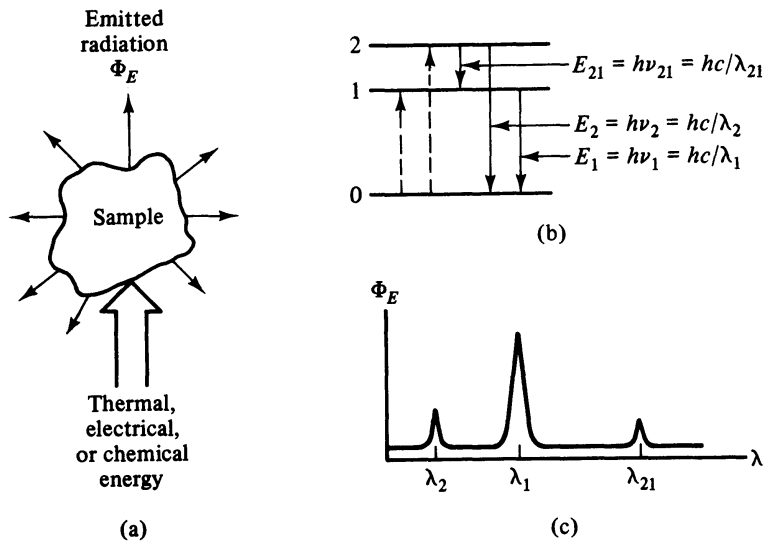
(b)

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

$$I = \frac{\text{flux}}{\text{solid angle}}$$

How are these quantities related to spectrochemical techniques?

Emission Spectroscopy:



- Emission refers to **thermally** excited atoms or molecules
  - flame, ICP, electrical discharge (plasma)

Interested in number of atoms per unit volume element observed:

$$\text{emission} = A_{ji} h \nu_{ij} n_j V$$

observation volume

# atoms in excited state j

energy per transition

Einstein coefficient (transition probability j → i)

$n_j$  can be defined if in **thermal equilibrium** by Boltzmann expression

$$\begin{aligned} \text{emission} &= A_{ij} h_{ij} n_j V \\ &= A_{ij} h_{ij} n_{\text{total}} \underbrace{\frac{g_j e^{-E_j/kT}}{\sum_{i=0} g_i e^{-E_i/kT}}}_{\text{fraction of total in state } j} V \end{aligned}$$

The weighting factor  $g_j$  (**statistical weight**) is the number of degenerate states at each energy  $E_j$

$$g = 2J + 1$$

$J$  is the total angular momentum  $(L+S), (L+S-1) \dots (L-S)$

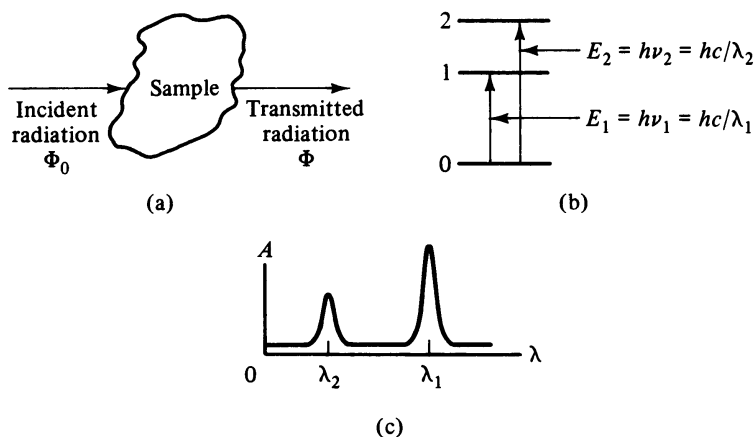
Example:  $g(2s)=2$

$$g(2p_{1/2})=2$$

$$g(2p_{3/2})=4$$

Hence, radiant flux emission can *absolutely* determine the concentration of atoms in detection volume

## Absorption Spectroscopy:



Absorbance  $A$  given by **Beers' Law**; related to the measured quantities  $\Phi_0$  and  $\Phi$  (radiant flux) by

$$A = -\log T = -\log \frac{\Phi}{\Phi_0} = \epsilon b c$$

concentration ( $\text{mol}\cdot\text{L}^{-1}$ )

cell pathlength (cm)

molar absorptivity ( $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ )

$$= \Phi_0 10^{-\epsilon b c}$$

Luminescence measurements:

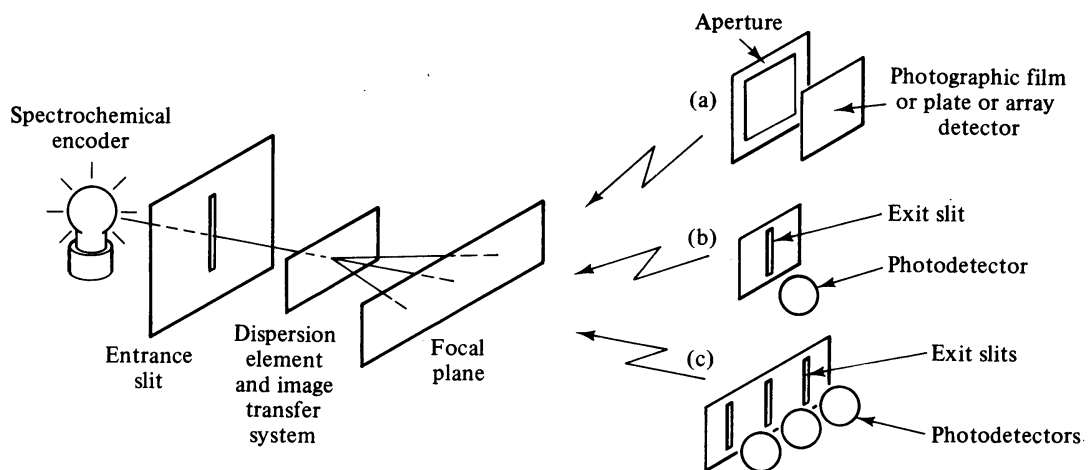
Scattering measurements:

## Optical Instruments:

Many spectrochemical instruments share common components

- a radiation source
- optics to define light paths
- a sample container
- a dispersion element
- detector (transducer)

Specific names are applied to the various instruments:



A **spectroscope** disperses a range of  $\lambda$ 's for visual viewing

A **spectrograph** disperses a range of  $\lambda$ 's onto focal plane for simultaneous measurements by a photographic film or array detector

A **monochromator** uses entrance slit, exit slit and a dispersion element to separate  $\lambda$ 's in space. If multiple exit slits are used the term **polychromator** is used

A **photometer** measures intensity but has no provision for scanning. Wavelengths can be selected by use of filters

A **spectrometer** includes means of manually or automatically scanning wavelength

A **spectrophotometer** has provision for scanning measurements using two beams of light (useful for ratioing incident and transmitted light)

An **interferometer** is a non-dispersive device that relies on interference to obtain spectral information

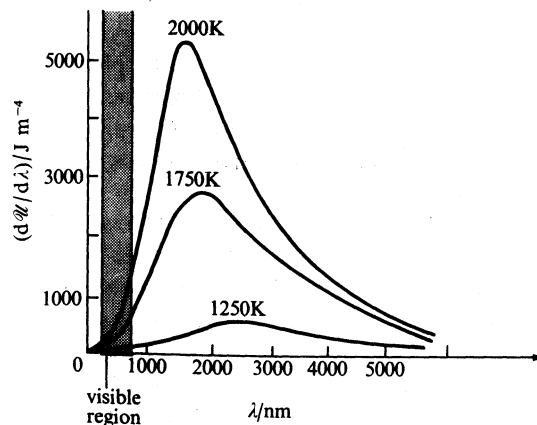
A **detector** is any device whose output is proportional to the intensity of light falling on it. A transducer (more specific) uses electrical signals

# Components of Measurement Instruments

## Radiation Sources:

Many radiation sources are based on black body radiation:

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



Two obvious points:

- total **amount** of energy radiated increases rapidly with T

$$U = a T^4 \quad \text{Stefan's Law}$$

Radiant energy density ( $J\cdot cm^{-3}$ )

- **position** of the maximum spectral radiance ( $\lambda_{max}$ ) blue shifts with increasing T

$$\lambda_{max} = \frac{c_2}{4.965 T}$$

where  $c_2 = 1.438 \times 10^7 \text{ nm}\cdot\text{K}$

Energy density  $U$  ( $\text{J}\cdot\text{cm}^{-3}$ ) is difficult to measure, usually work in radiance ( $B$ ) ( $\text{J}\cdot\text{s}^{-1}\cdot\text{sr}^{-1}\cdot\text{cm}^{-2}$ )

$$B = \frac{U}{4} \quad B = \frac{B}{2} c$$

Planck deduced black body equation after consideration of thermodynamics of system with discrete energy levels (multiples of  $h$  - the beginning of quantum mechanics)

$$B = \frac{2h^3}{c^2} \frac{1}{e^{h/kT} - 1}$$

or in terms of wavelength

$$B = \frac{2h^3 c^2}{5} \frac{1}{e^{hc/kT} - 1}$$

$$= \frac{c_1}{e^{c_2/T} - 1}$$

Planck's radiation law

where  $c_1=2\cdot h\cdot c^2$  ( $1.19\times 10^{16} \text{ W}\cdot\text{nm}^4\cdot\text{cm}^{-2}\cdot\text{sr}^{-1}$ ) and  $c_2=(h\cdot c)/k$  (same as above,  $1.438\times 10^7 \text{ nm}\cdot\text{K}$ )

## Einstein coefficients:

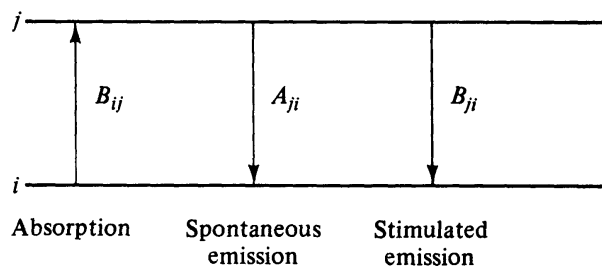
Three Einstein coefficients:

$B_{ij}$  - describes probability of *absorption* from level  $i \rightarrow j$

$B_{ji}$  - describes probability of *stimulated* emission from level  $j \rightarrow i$

Note: These two are simply time-reversed processes

$A_{ji}$  - describes probability of *spontaneous* emission from level  $j \rightarrow i$



The **rate** of absorption per unit volume ( $s^{-1} \cdot cm^{-3}$ ) depends on:

(i) number of **atoms in initial state**  $i$ ,  $n_i$

(ii) **probability** of **absorption** from state  $i$  to another state  $j$ ,  $B_{ij}$

(iii) the spectral **energy density of incident radiation**,  $U$

$$-\frac{dn_i}{dt} = B_{ij} U n_i$$

absorption removes  
population from state  $i$ ,  
so  $n_i$  decreases

Similarly, rate of *stimulated* emission is

$$-\frac{dn_j}{dt} = B_{ji} U n_j$$

The rate of absorption and stimulated emission are the same **if** there is an equal population in both states

$$B_{ji} g_j = B_{ij} g_i$$

$g$  is the degeneracy  
(statistical weight)

Rate of spontaneous emission doesn't include a  $U$  term

$$-\frac{dn_j}{dt} = A_{ji} n_j$$

If black body is in thermal equilibrium with surroundings, rate of absorption and emission must be equal:

$$\underbrace{B_{ij} U n_i}_{\text{absorption}} = \underbrace{A_{ji} n_j}_{\text{spontaneous emission}} + \underbrace{B_{ji} U n_j}_{\text{stimulated emission}}$$

$$U = \frac{A_{ji} n_j}{B_{ji} n_i - B_{ij} B_{ij}}$$

$$= \frac{A_{ji} n_j}{B_{ji} (n_i - B_{ij})}$$

$$= \frac{A_{ji} n_j}{B_{ji} (n_i - (g_i / g_j) n_j)}$$

substituting  $B_{ji} g_j = B_{ij} g_i$

At equilibrium, Boltzmann equation can be used to find  $n_j$  from  $n_i$

$$U = \frac{A_{ji} n_j}{B_{ji} (n_i - (g_i / g_j) n_j)}$$

substituting  $n_j = n_i \exp(-h_{ij} / kT)$

$$\begin{aligned} U &= \frac{A_{ji} n_j}{B_{ji} (n_i - (g_i / g_j) n_i \exp(-h_{ij} / kT))} \\ &= \frac{A_{ji}}{B_{ji}} \frac{g_i / g_j}{e^{h_{ij}/kT} - 1} \end{aligned}$$

This looks similar in form to Planck's radiation law

$$B = \frac{2h^3}{c^2} \frac{1}{e^{h/kT} - 1}$$

and gives us the rate of spontaneous emission and absorption

$$A_{ji} = \frac{8 h^3}{g_j c^3} \frac{g_i}{B_{ij}} \quad \text{remembering } B = \frac{U c}{4}$$

$$B_{ji} g_j = B_{ij} g_i$$

Real black body systems:

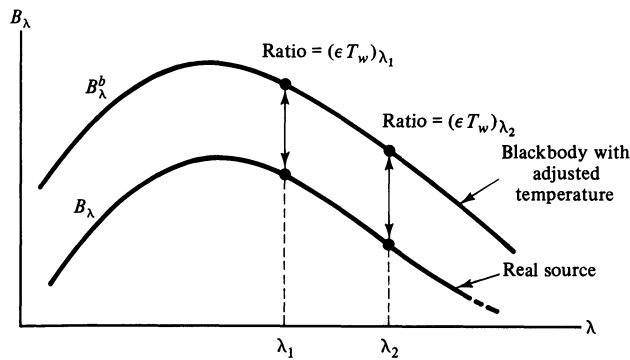
In practice, observe something called a **gray body** defined by

$$B = B^{\text{black body}} (\epsilon) T(\lambda)$$

reflective losses

emissivity (0 ≤ 1)

Gray body produces an apparent temperature (color temperature) where  $\lambda_{\text{max}}$  of the measured and black body curves match:



Tables of  $B_\lambda$  versus  $\lambda$  are available for many materials