Lecture 5. **Radiation and energy.**

Objectives:

1. The most important aspects of the quantum theory: atom, subatomic particles, atomic number, mass number, atomic mass, isotopes, simplified atomic diagrams, atomic orbitals, electron transitions.
2. Electromagnetic radiation as a traveling wave and as a photon of energy.
3. Spectrum of electromagnetic radiation.
4. Absorption of radiation by gases.

Readings: Turco: p. 38-39, 48-61, 507-508; Brimblecombe: p. 7-10

1. The most important aspects of the quantum theory.

Chemistry is the study of ***atoms***-how these basic units combine, and how substances made of ***atoms*** are changed into other substances.

According to atomic theory, all matter, whether solid, liquid, or gas, is composed of particles called **atoms.**

The simplest view of the atom is that it consists of a tiny ***nucleus*** and ***electrons*** that move about the nucleus.

Electron is a subatomic particle, which carries a negative charge.

- The chemistry of an atom arises from its electrons. Therefore the relatively crude nuclear model will do.

The **nucleus** is assumed to contain **protons**, which have a positive charge equal in magnitude to the electron's negative charge, and **neutrons**, which have virtually the same mass as a proton but no charge.

Atoms have no net charge: the number of electrons must equal the number of protons.

Atomic number is the number of protons in an atom nucleus. Since every atom has the same number of electrons as protons, the ***atomic number*** also equals the number of electrons.

atomic number = number of protons = number of electrons

- The ***atomic number*** is the most important identification of an atom because the properties that enable us to distinguish one type of atom from another are related to the ***atomic number***. It is the atom's signature.

Atomic mass (weight) : The modern system of atomic masses, instituted in 1961, is based on ^{12}C (carbon twelve) as the standard. In this system ^{12}C is assigned a mass of exactly 12 *atomic mass units* (amu), and the mass of all other atoms are given relative to this standard.

Table. Summary of subatomic particles

Particle	Symbol	Charge	Mass (g)	Mass (amu)	Approximate mass (amu)
electron	**e**	**1-**	**$9.111x10^{-28}$**	**$5.486x10^{-4}$**	**0**
proton	**p**	**1+**	**$1.673x10^{-24}$**	**1.007**	**1**
neutron	**n**	**0**	**$1.675x10^{-24}$**	**1.008**	**1**

Element is a large collection of atoms that have the same atomic number (the same proton number. For instance, the element gold consists of many atoms each with atomic number 79.

- Atom is the smallest part of an element that still has the chemical properties of that element.

NOTE: Most elements occur in nature as mixtures of ***isotopes***, thus atomic masses are usually average values.

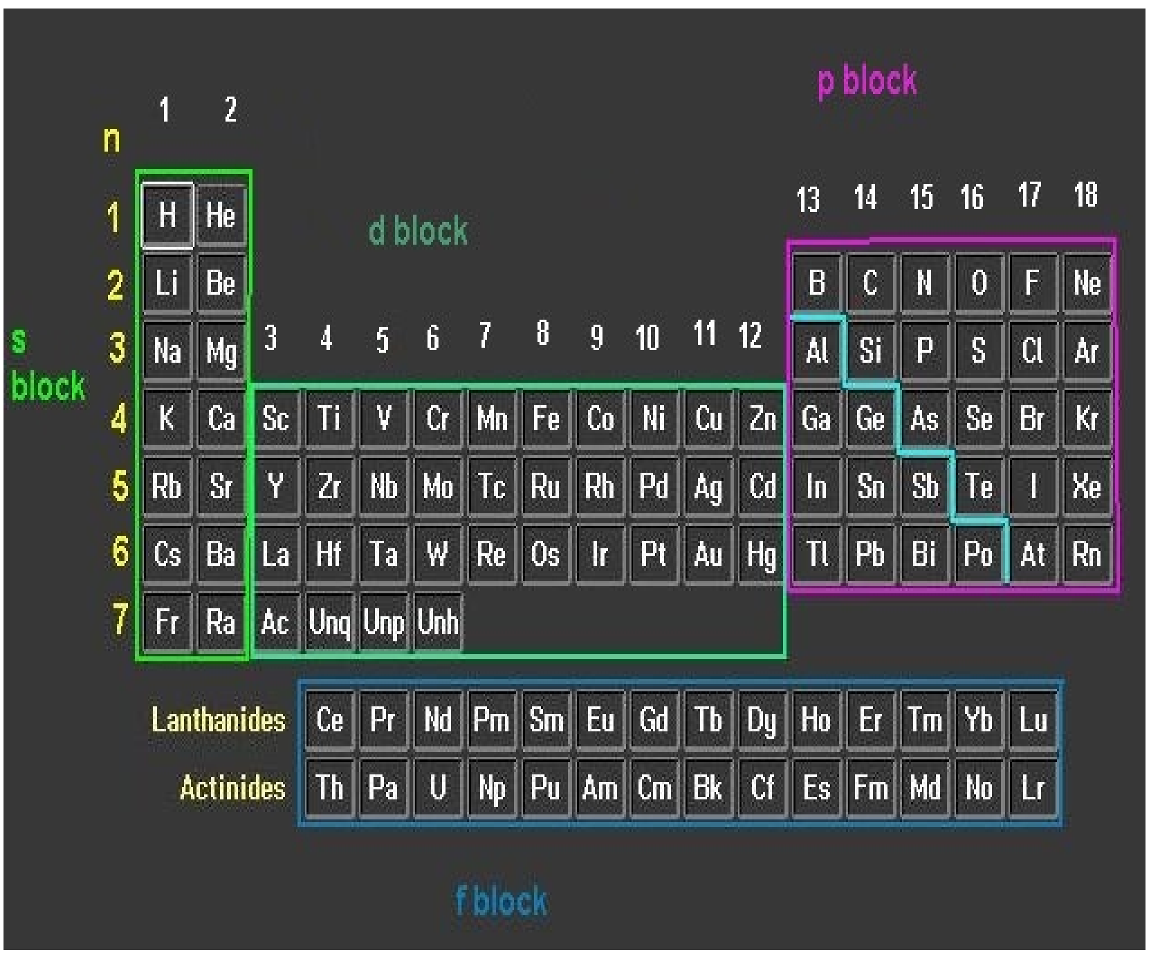
Isotopes are atoms with the same number of protons but different numbers of neutrons.

<u>Mass number</u> of an atom is found by adding the number of ***protons*** and ***neutrons*** in its nucleus, while ignoring the contribution of electrons.

mass number = number of protons + number of neutrons

NOTE: number of neutrons = mass number - atomic number

<u>Periodic table</u> is a system of classifying elements.

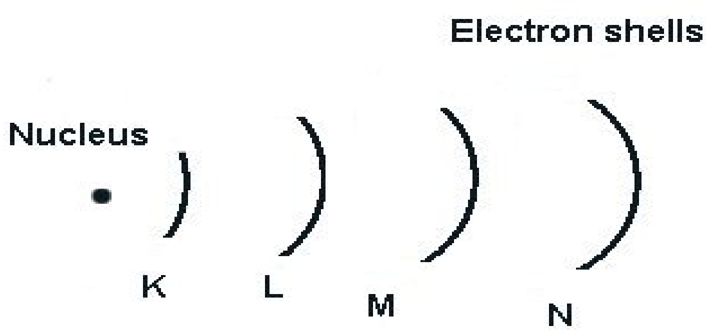


<u>NOTE:</u> that He is moved

<u>Simplified atomic diagrams</u> are used to show the electron arrangement of the atoms. They are unreal in the sense that they are simplified attempts to visualize the mathematical equations that describe the behavior of electrons in atoms**. The electron shell diagram** and **Lewis symbol** are often used simplified diagrams.

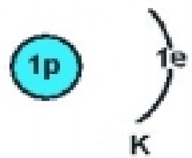
Electron shell diagram assumes that electrons are located in one or more shells outside the nucleus. These shells do not represent exact locations of the electrons, but they provide a convenient way to identify electrons found at certain average distances from the nucleus.

Figure 5.2 Electron shells.



- Each ***shell*** in an atom can hold only a limited number of electrons $2n^2$, where n is the number of the *shell*.

Example: hydrogen atom (*atomic number* = 1, *mass number* = 1)

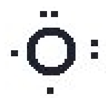


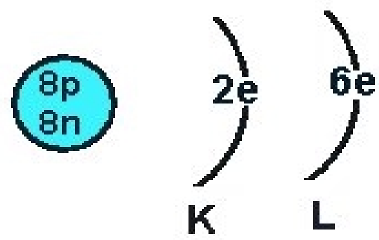
Lewis symbol (electron-dot notation) consists of the symbol for the element along with either dots (**.**) or crosses (**x**) that represent the outer shell electrons.

Example: hydrogen atom

$H^{\cdot}$ or H^{x}

Example: oxygen atom in Lewis symbol and shell diagram:





Electron configuration is the arrangement of electrons in an atom.

The quantum theory states:

- The energy of electrons in an atom can have only certain fixed values. The energies of the electrons are said to be **quantized**. Electrons restricted to the same allowed value of energy are said to occupy the same **energy levels**. All energy levels except the first one are divided into **sublevels**. There are **four** different sublevels, labeled **s**, **p**, **d**, and **f**. The s sublevel has the lowest energy, followed by the p sublevel, then the d sublevel, and finally the f sublevel.

NOTE: that shells considered above correspond to the *energy levels*.

- **Heisenberg uncertainty principle**: we can never know the *exact* positions of electrons in an atom at a given instant of time. However, we can predict the **probability** of finding electrons at certain locations which are called **electron orbitals**. Each orbital can hold up to **two** electrons with different **spins**.

Table. Relationship between sublevels, orbitals and electrons.

Sublevel	**Number of orbitals**	**Maximum number of electrons**
s	1	2
p	3	6
d	5	10
f	7	14

Table. Summary of sublevels in atoms of known elements.

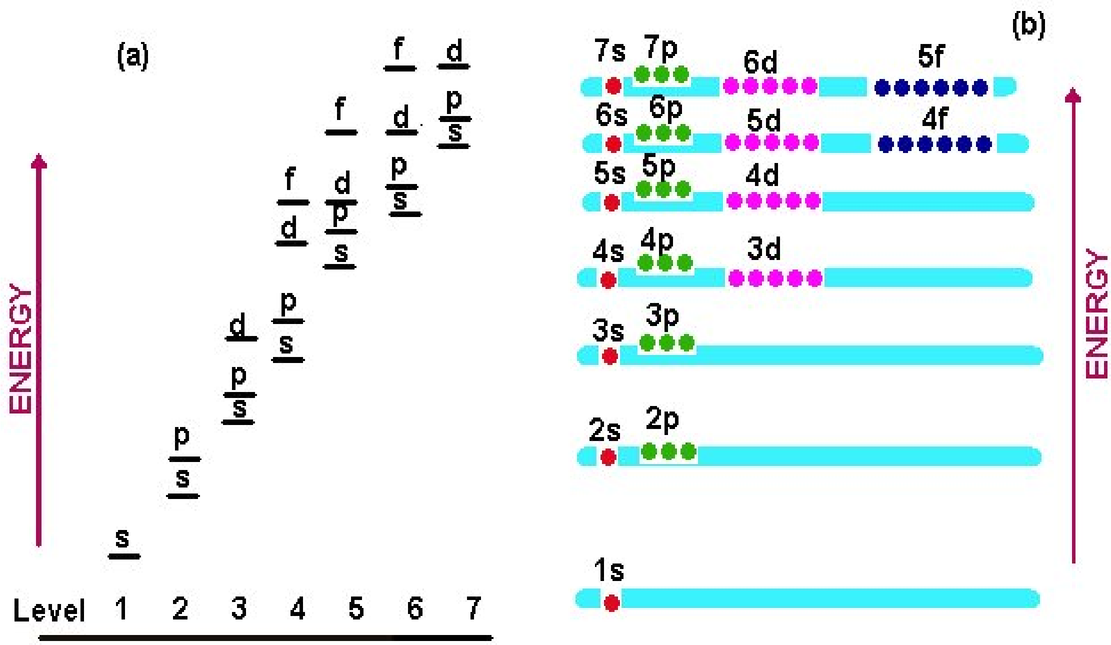
Principal energy level	**Electron sublevels**
1	1s
2	2s, 2p
3	3s, 3p, 3d
4	4s, 4p, 4d, 4f
5	5s, 5p, 5d, 5f
6	6s, 6p, 6d
7	7s, 7p

NOTE: The *periodic table* above shows possible sublevels of elements.

Figure 5.3 Energy level diagrams.

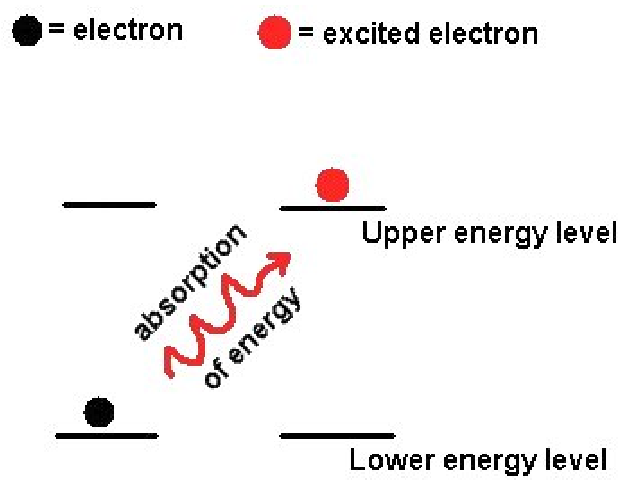
(a) the sublevels are indicated by horizontal lines;

(b) the orbitals within the sublevels are shown as circles.

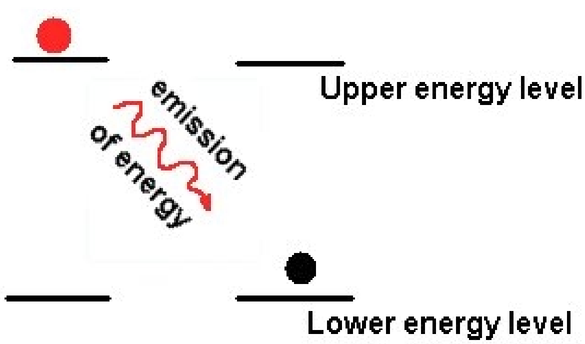


Electron transitions

All the electrons of an atom that is in electronic ground state are in the lowest energy levels possible. If energy is added to an atom, its electron may be made to jump to higher energy levels. The addition of energy is said to excite the electrons and the resulting atom is said to be in an excited state. This process is called absorption of energy by an atom. Because the energy levels of an atom are fixed, only certain definite amounts of energy can be absorbed (which is a difference in energy between two energy levels).



Electrons generally remain *excited* only for short periods. They soon return to a more stable lower energy level, and release their extra energy. This process is called emission.

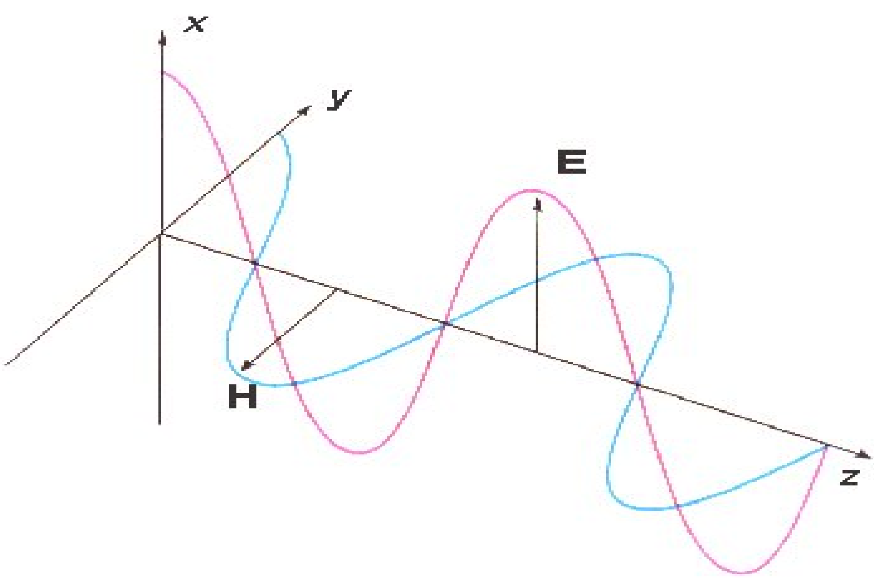


NOTE: both emission and absorption of energy by an atom correspond **to electron transition**, the movement of an electron from one level to another.

2. Electromagnetic radiation is form of transmitted energy**. *Electromagnetic radiation*** is so-named because it has electric and magnetic fields that simultaneously oscillate in planes mutually perpendicular to each other and to the direction of propagation through space.

Examples: the light from the sun; energy used to cook food in microwave oven, the X rays used by dentist, the radiant heat from a fireplace, etc.

Figure 5.4 Electromagnetic radiation has oscillating electric (E) and magnetic (H) fields.



- Electromagnetic radiation has the dual nature:

  its exhibits wave properties and particulate properties.

Wave nature of radiation:

Radiation can be thought of as a *traveling wave*.

Waves are characterized by ***wavelength*** *(*symbolized by the Greek letter lambda, λ),

frequency (symbolized by the Greek letter nu, ν), *and speed*.

Wavelength is the distance between two consecutive peaks or troughs in a wave.

Frequency is defined as the number of waves (*cycles*) per second that pass a given point in space.

Since all types of *electromagnetic radiation* travel at the speed of light, short-wavelength radiation must have a high frequency.

- The speed of light in a vacuum: $c = 3.00\text{x}10^8$ m/s

$$\lambda\,\nu = c$$

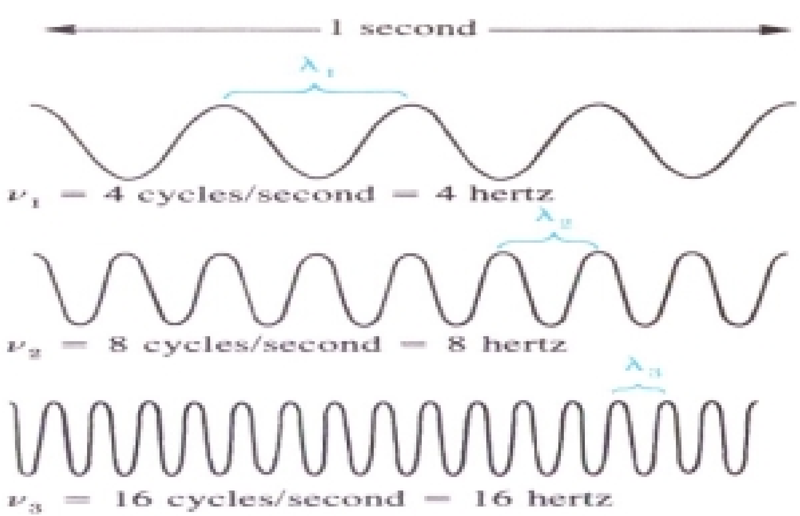
SI system: wavelength units: unit length,

Angstrom (A) : $1\ A = 1\text{x}10^{-10}$ m;

Nanometer (nm): $1\ nm = 1\text{x}10^{-9}$ m;

Micrometer (µm): $1\ \mu m = 1\text{x}10^{-6}$ m;

frequency units: unit cycles per second 1/s (or s^{-1}) is called hertz (abbreviated Hz)



Particulate nature of radiation:

Radiation can be also described in terms of particles of energy, called **photons**.

The energy of each photon is given by the expression:

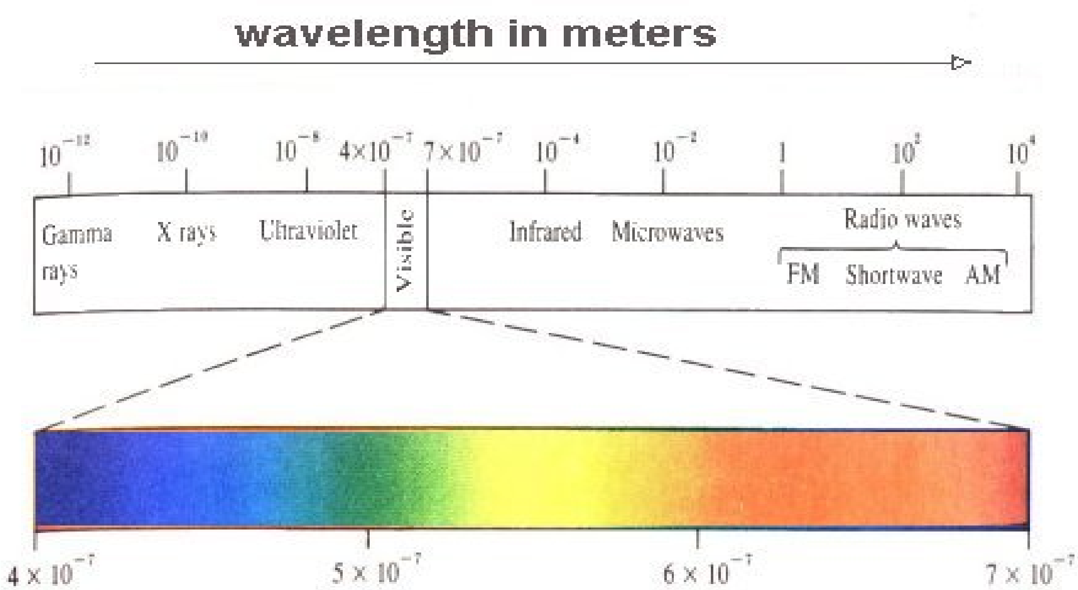
$$E_{photon} = h\nu = hc/\lambda \qquad [1],$$

where h is Plank's constant (h = 6.626x10^{-34} J s), ν is the frequency of the radiation, and λ is the **wavelength** of the radiation.

- Equation [1] relates energy of each photon of the radiation to the electromagnetic wave characteristics (ν and λ).

3. Spectrum of electromagnetic radiation.

The various types of electromagnetic radiation differ in their energy, wavelength, and frequency.



Radio wave. This long wavelength, low energy radiation is emitted and received by large antennas. It includes the AM, FM, TV, and shortwave frequencies.

Microwave. This form of radiation is used in microwave ovens. It causes water molecules in food to rotate and vibrate, generating heat. Microwave radiation is also used in communications.

Infrared. Infrared, or IR radiation is produced by warm objects and is felt as heat. An electric heater, for example, emits infrared radiation.

Visible. The only type of electromagnetic radiation that we can see is called visible radiation. It contains the colors of the visible spectrum: red, orange, yellow, green, blue, and violet.

Ultraviolet. Known as UV radiation, ultraviolet radiation has more energy than visible radiation. It is the form of radiation from sun that causes sunburn.

X ray. This high energy radiation can penetrate the body, and it is partially absorbed by the denser parts of the body such as bones or teeth.

Gamma ray. Gamma rays are produced by nuclear reactions. They are extremely high energy.

Table: Relationships between radiation components (from Turco 1997).

Name of spectral region	**Wavelength region, μm**	**Spectral equivalence**
Solar	0.1 - 5	Ultraviolet + Visible + Near infared = Shortwave
Terrestrial	5 - 100	Far infrared = Longwave
Infrared	0.7 - 100	Near infrared + Far infrared
Ultraviolet	0.1 - 0.4	Near ultraviolet + Far ultraviolet = UV-A + UV-B + UV-C + Far ultraviolet
Shortwave	0.1 - 5	Solar = Near infrared + Visible + Ultraviolet
Longwave	5 - 100	Terrestrial = Far infrared
Visible	0.4 - 0.7	Shortwave - Near infrared - Ultraviolet
Near infrared	0.7 - 5	Solar - Visible - Ultraviolet = Infrared - Far infrared
Far infrared	5 - 100	Terrestrial = Longwave = Infrared - Near infrared
Thermal	5 - 100	Terrestrial = Longwave = Far infrared

NOTE: more discussion on solar and terrestrial radiation will be given in Lectures 31-32.

Blackbody radiation:

All objects can emit, absorb, and reflect electromagnetic radiation.

A body which only emits radiation is called **blackbody**.

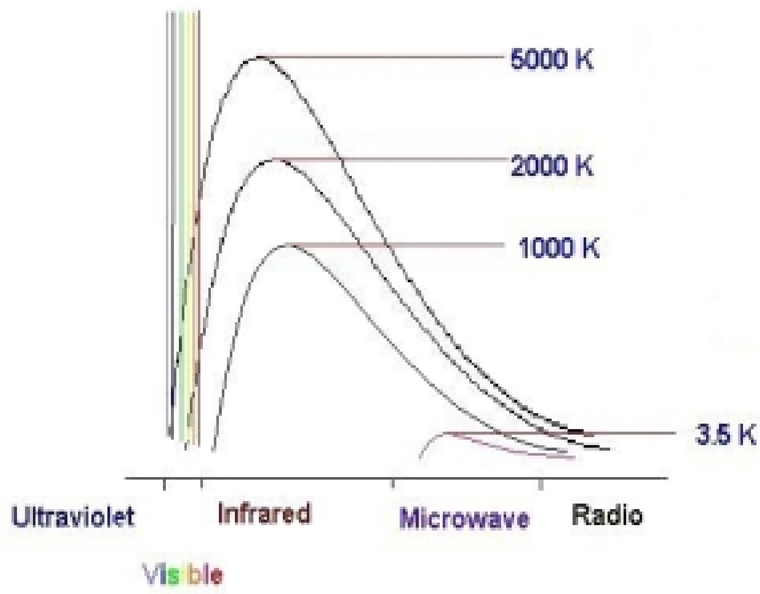
The **Stefan-Boltzmann law** states that the total power (energy per unit time) emitted by a *blackbody*, per unit surface area of the *blackbody*, varies as the fourth power of the temperature.

$$F_b = \sigma_b T^4 \qquad [2]$$

where σ_b is the *Stefan-Boltzmann constant* ($\sigma_b = 5.671 \times 10^{-8}$ W m^{-2} K^{-4}),

F_b is energy flux [W m^{-2}], and T is blackbody temperature [K].

Figure 5.1 Blackbody radiation for T equals 3.5 K, 1000K, 2000K, and 5000K.



NOTE: The shape and position of blackbody radiation spectrum depend on temperature. In general, the lower the temperature is, the greater the wavelength of the peak intensity of the radiation will be. For an object at T = 5000K, the intensity peaks about 0.58 microns, similar to sunlight.

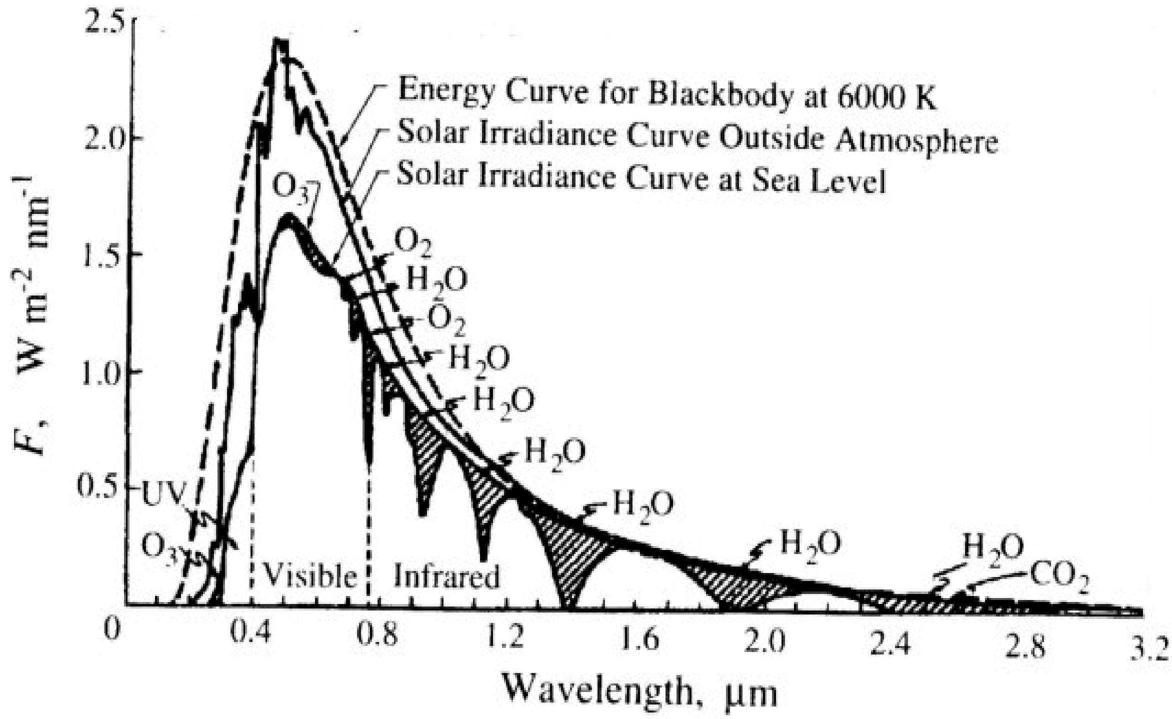
The **Wien's displacement law** states that the wavelength at which the blackbody emission spectrum is most intense varies inversely with the blackbody's temperature. The constant of proportionality is Wien's constant (about 2900 K μm):

$$\lambda_p = 2900 / T$$

where λ_p is the wavelength (in micrometers, μm) at which the peak emission intensity occurs, and T is the temperature of the blackbody (in degrees Kelvin, K).

Solar radiation is emitted by sun. It is the main source of energy in the atmosphere. Solar radiation spectrum is closed to blackbody radiation with T of about 5777K.

Figure 5.2 Solar spectral irradiance at the top of the atmosphere and sea level



Radiation is altered in a number of important ways:

Scattering is a process which conserves the total amount of energy but the direction in which the radiation propagates may be altered.

Absorption is a process that removes energy from the electromagnetic radiation field, and converts it to another form.

Extinction (or attenuation) is the sum of scattering and absorption, so it represents total effect of medium on radiation passing the medium.

Scattering coefficient, $\varepsilon_s(\lambda)$, is a parameter that quantifies the scattering process.

Absorption coefficient, $\varepsilon_a(\lambda)$, is a parameter that quantifies the absorption process.

Extinction coefficient, $\varepsilon_e(\lambda)$, is a of scattering coefficient and absorption coefficient.

$$\varepsilon_e(\lambda) = \varepsilon_s(\lambda) + \varepsilon_a(\lambda)$$

4. Absorption of radiation by gases

4. Absorption of radiation by gases is one of the most important aspects of both global meteorology and atmospheric chemistry.

- Atmospheric gases can both scatter and absorb radiation. The scattering and absorption properties of gases in the atmosphere are determined by their atomic structure.

NOTE: radiative effects of aerosols and clouds will be discussed in Lectures 25-26; atmospheric chemistry initiated by absorption of light by molecules will be discussed in Lectures 7. More discussion on gases absorption in the atmosphere will be given in Lecture 31.

Rayleigh scattering is scattering of solar radiation by air molecules (primarily by O_2 and N_2 because they are most abundant gases in the atmosphere).

For instance, for Rayleigh scattering the scattering coefficient (at sea level) is

$$\varepsilon_s(\lambda) = n_a \, \sigma_s(\lambda)$$

where n_a is the number concentration of air molecules (units: molec. cm^{-3}) at the given altitude, and σ_s is the ***scattering cross section*** of a typical air molecule.

NOTE: both $\sigma_s(\lambda)$ and $\varepsilon_s(\lambda)$ depend on wavelength, λ.

Scattering cross section can be expressed as an effective area that an individual molecule (or particle) presents as a scattering target to the photons of the radiation.

The major absorbing gases in the atmosphere: O_2, O_3, $H_2$0, and CO_2.

NOTE: these gases are minor constituents of the atmosphere (trace gases).

Absorption cross section , $\sigma_a(\lambda)$, is effective cross section of a gas molecule that absorbs radiation at a given wavelength, is obtained experimentally. The larger the cross section, the greater the absorption.

Absorption coefficient for individual species with concentration **n** is determined as

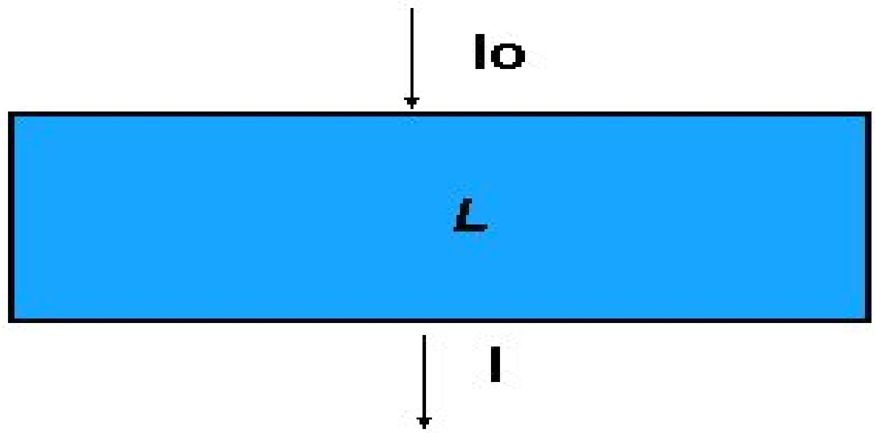
$$\varepsilon_a(\lambda) = n \; \sigma_a(\lambda)$$

- Both scattering cross section and absorption cross section can be expressed in units area/per unit mass (e.g., m^2/kg), then the molecule mass concentration is used to determine the scattering and absorption coefficients.

Beer-Lambert law: states that incident radiance at a given altitude is attenuated exponentially as it travels through air with a given extinction coefficient:

$$I = I_0 \exp(-\varepsilon_e l)$$

where I_0 is incident radiance, I is outgoing irradiance, l is pathlength.



- The dimensionless product $\tau = \varepsilon_e l$ is called the optical depth.