CHAPTER 2 THEORETICAL

2.1 Glasses [17, 18]

2.1.1 Definitions of Glass

The origin of the word glass is the Late Latin term glaesum, which refers to a lustrous and transparent or translucent body. Glassy substances are also called *vitreous*, originating from the word vitrum, again denoting a clear, transparent body. Although glass became a popular commodity in the growth of civilization, perhaps because of its transparency, luster (or shine), and durability, the understanding of glass no longer requires any of these characteristics to distinguish it current from other substances. Glass can be inorganic (non-carbon-based) as well as organic (carbon-based), and fusion is not the only method to make a glass. Thus, the old American Society for Testing and Materials (ASTM) definition that glass is an inorganic product of fusion which has been cooled to a rigid condition without crystallizing is not appropriate.

Unlike a crystal, glass may not be represented by a simple chemical formula. There are no restrictions with regard to the relative numbers of chemically different atoms other than the fact that the valences and/or coordination requirements may need to be satisfied. Unlike a crystal, glass does not have a sharp melting point when heated. The seemingly rigid solid gradually softens and flows at higher temperatures. At ambient temperatures, however, the *viscosity* of glass may be sufficiently high that measurable flow does not occur over millennia—certainly not over practical time scales in typical laboratory experiments. It is doubtful that glass windows in building structures of the Middle Ages have flowed to become thicker at the bottom. Chunks of glass do not have habit planes, nor does glass have identifiable cleavage planes. In the absence of externally applied mechanical, electrical, thermal, magnetic, and gravitational fields, *the properties of glass are essentially isotropic like those of a typical liquid.*

The isotropic of physical properties makes glasses resemble liquids. It follows that the atomic arrangements in glass must display the long-range order typical of liquids. In order not to be overly restrictive, we are left to define glass as a solid with liquid like structure, a *non-crystalline solids or simply as an amorphous solids,* with the understanding that the amorphous characteristic here is intended to describe atomic disorder as evidenced by an X-ray diffraction (XRD) analysis; it excludes substances such as “amorphous” powders that may simply be “micro-crystals” and that display more or less sharp peaks in XRD analysis. To get a clearer picture of the fundamentals of glass, we devoted to consideration of the volume-temperature relationship (the V-T diagram) of the glass with respect to a liquid and a crystal.

2.1.2 The Volume-Temperature Diagram

Consider a small volume of material at a high temperature in liquid form; its state is given by the point “a” on the *V-T* diagram (Figure 2.1). On cooling the volume gradually decreases along the path “abc.” Point “b” corresponds to T_m, the melting point of the corresponding crystal, which may be defined as the temperature at which the solid and the liquid have the same vapor pressure or have the same Gibbs free energy. At this temperature, an infinitely small amount of crystals is in thermodynamic equilibrium with the liquid. However, for a perceptible level of crystallization, some finite amount of undercooling of the liquid to a point “c” below T_m is required. Crystallization occurs if, and only if, (i) there are a sufficiently large number of nuclei present in the mass, ad (ii) a large enough crystal growth rates exists. The location of the point “c” below T_m varies depending upon when the thermodynamic driving force created by the undercooling causes a particular group of atoms to transform from the liquid state to the crystal state, and upon the velocity at which the atoms from the liquid can be transported to the crystal-liquid interface. For these reasons, we have shown a wide, shaded region with varying probability representing the crystallization path. Volume shrinkage generally accompanies the crystallization. Upon further cooling the crystals so formed shrink along the crystal line to the point “e”

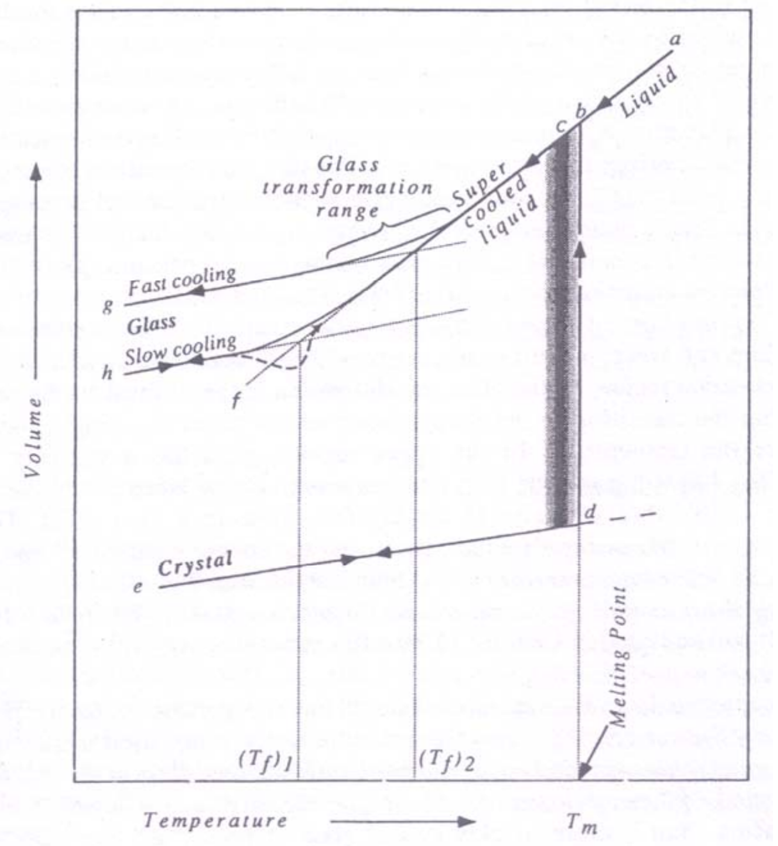


Figure 2.1 The volume-temperature diagram.

If crystallization does not occur below T_m (mostly because the cooling rate is high), the liquid mass moves into the supercooled liquid state along the line “bcf”, which is an extrapolation of the line “abc”. No discontinuities in the *V-T* are observed. The volume, however, shrinks continuously, i.e., the structure of the liquid rearranges itself into a lower volume along the line “vcf” required by the lower energy corresponding to a lowered temperature. As cooling continues, the molecules become less and less mobile, i.e., the viscosity of the system rapidly increases. At sufficiently low temperatures, the molecular groups cannot rearrange themselves fast enough to reach the volume characteristic of that temperature. The state line then starts a smooth departure from “bcf” and soon become a near-straight line (often roughly parallel to “de”), ending at point “g”, when cooled fast, or at “h”, when cooled slowly. The material in the near-straight, low-temperature part of the curve behaves essentially as a solid. *This is the glassy state.*

The smooth curve between the onset of departure from the supercooled liquid line and the completion to a seemingly rigid condition is termed the glass transition region, or the glass transformation range. It must be emphasized that the transition to the glassy state does not occur at a single, sharp value of the temperature. In the upper regions, glass has a viscosity of ~10^8 Pa·s (=10^9 poise) or less, whereas in the glassy state the viscosity of exceeds ~10^{15} Pa·s or more to quality for appearance as a solid. The intersection of the extrapolated glass line and the supercooled liquid line is termed the fictive temperature (T_f). One may imagine that T_f is the temperature at which the structure of the supercooled liquid is instantly frozen into the glass

The departure from the supercooled liquid line is the dependent upon the rate of cooling. Slower cooling allows the structure to rearrange itself to stay on “bcf” somewhat longer, and hence the more slowly cooled glass at “h” would be expected to have a lower volume (higher density) and a lower fictive temperature than a more quickly cooled glass at point “g”. For now, it suffices to suggest that the volume of the corresponding crystal is expected to be less than that of the most slowly cooled glass.

When the glass at “h” is reheated, the state smoothly moves through the transition region along the dashed curve to the supercooled liquid state “fcb” and ultimately to the liquid state. The *V-T* curve *NEVER retraces its path in the transition region*. Other than the gradually increasing fluidity and, perhaps, a color change due to radiative emission, in general there are no changes in the physical appearance of glass with the reheating.

If the crystals at “e” are heated, the state will move along crystal line up to “d” (= the melting temperature, T_m) past the shaded region, melt at T_m to reach point “b”, and subsequently follow the liquid path “ba”. One may question whether it is possible to superheat a crystal or not. Melting produces atomic disorder in a substance and proceeds from the surface inwards. Hence, crystals may be superheated to temperatures beyond T_m if the heat is provided internally or if melting produces a very high-viscosity liquid phase such that atoms within the interior of the crystal do not have “room or time to disorder”. Ordinarily, the melting of a crystal is mush sharper (on the temperature scale) than the freezing of liquid.

Note that, with regard to the slight separation “b-c” between the crystallization and the melting paths near T_m, the *V-T* diagram presented here differs slightly from those usually presented by other authors.

To understand the structural relationship between the glassy state and other states of matter, we need to understand the pair distribution function and the radial distribution function used commonly to describe the distribution of atoms in amorphous solids.

In multicomponent systems, the temperature T_m is generally identified as the *liquidus temperature*. At temperatures above the liquidus, the system is completely liquid. Growth of one crystalline phase may occur just below the liquidus. As the temperature is lowered further, more crystalline phases may grow. Experimental measurement of the liquidus temperature is often desirable for large-scale glass manufacturing to avoid problems due to *devitrification* in the glass tank delivery system, or in the finished product, where they appear as inclusions often termed stones. A convenient method is described in ASTM C829-81, where grains of glass are placed in a suitable boat and heated inside a gradient furnace for a desired period of time. Liquids temperature is located by visually judging the demarcation between clear glass and the appearance of opacity.

2.2 Glass Formation

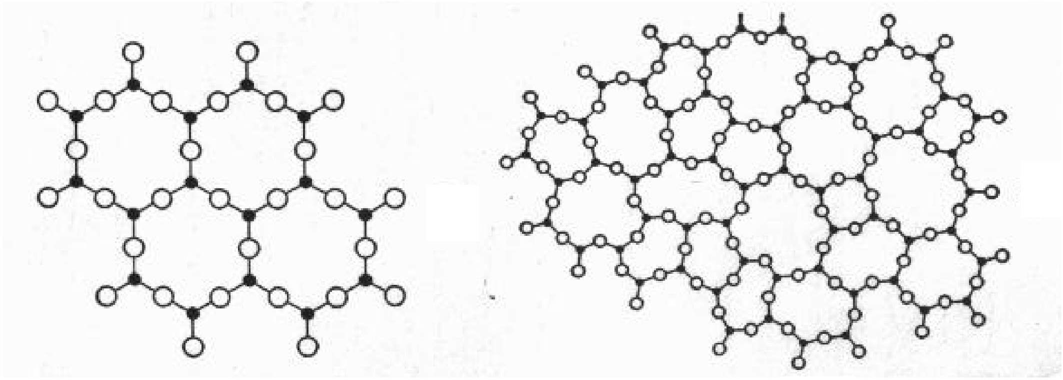
2.2.1 Structural Concepts of Glass Formation

A variety of materials form glass readily by cooling from the molten state. It may be recognized that the glass formation range is quite extensive. Many other materials, on the other hand, form a noncrystalline solid only when special techniques, such as cooling from the vapor state, are used. A prime example of this is a-Si:H (amorphous hydrogenated silicon), used extensively for solar cell applications. It is not clear whether most of these amorphous solids are, in fact, glassy solids with a thermodynamic continuity to a supercooled liquid state.

The question of what characteristics make a substance a ready glass former has been the subject of intense research. Historically, the most prevalent thoughts were advanced by Zachariasen, who suggested four rules for and oxide, A_mO_n, to form a glass readily:

1. The oxygen is linked to no more than two atoms of A.
2. Coordination of the oxygen about A is small, say 3 or 4.
3. Oxygen polyhedra share corners, and not edges or faces.
4. At least three corners are shared.

Application of the above “random network theory” concepts suggests why oxides such as SiO_2, GeO_2 and B_2O_3, where the oxygen formed tetrahedra or triangles, are ready glass formers, and why compounds such as A_2O and AO have to be ruled out. Figure 2.2 shows a two-dimensional representation of the atomic arrangements in an A_2O_3 glass versus its corresponding crystalline form. (The figure may also correspond to AO_2, where A is tetrahedrally bonded to oxygens, the fourth oxygen being out of the plane of the paper.) Whereas the local oxygen coordination is almost the same as that in a corresponding crystalline solid, the intermediate range order described by ring structures clearly differs considerably between the crystalline and the glassy forms. The glass network consists of holes that are larger than those in the crystal. (The aggregate of the holes yields the free volume discussed above.) When a compound such as Na_2O is introduced in silica, the arrangement of atoms in a two-dimensional plane is believed to look somewhat like that in Figure. 2.3. Those oxygens, which connect two silicon tetrahedral at corners, are called bridging oxygens (BOs). Some oxygens are linked to only one silicon; these are called the nonbridging oxygens (NBOs). Since oxygen is a bivalent ion, its connection to only one silicon ion leaves one negative charge, which is satisfied by a univalent positive sodium ion in the interstitial spaces.



(*a*) (*b*)

Figure 2.2 A two-dimensional representation of A_2O_3 : (*a*) crystal and (*b*) glass.

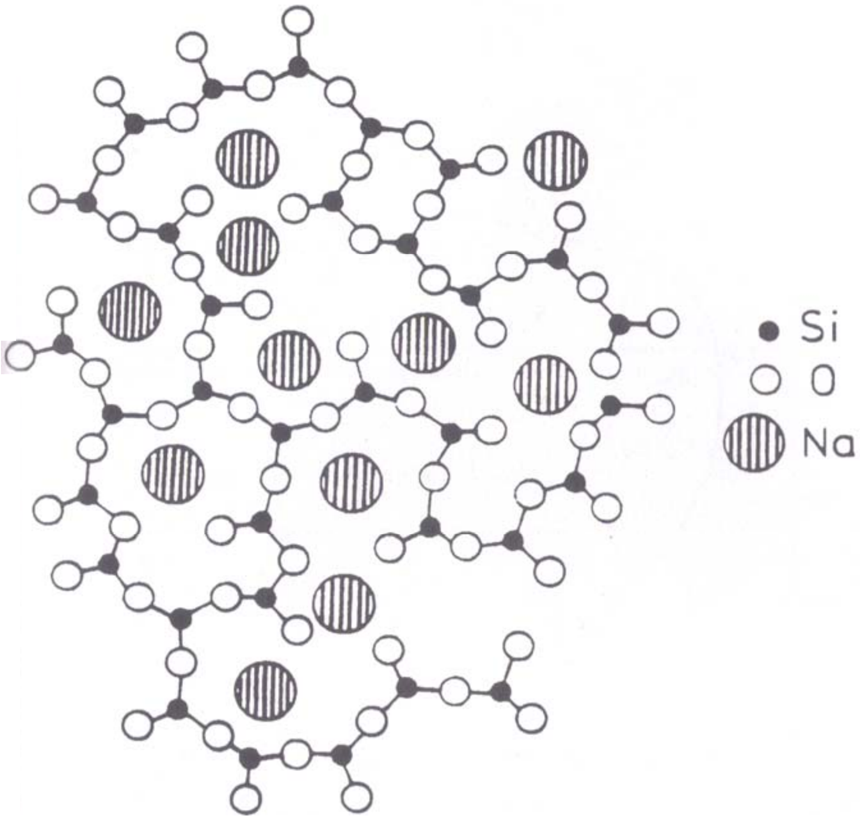


Figure 2.3 A two-dimensional representation of a sodium silicate glass.

Much of the early criticism of Zachariasen was based on the discussion of how random is random and, of course, the observation that elements such as S and Se make good glasses yet they did not fit Zachariasen's criteria. Electron microscopy of several otherwise transparent glasses has shown that glass may not be as random as Zachariasen thought and that some type of phase segregation exsists in many glasses.

On the basis of the calculation of single bond strengths in an oxide AO_x, Sun suggested that oxides such as B_2O_3, SiO_2, GeO_2, P_2O_5, V_2O_5, and As_2O_5 should be classified as *glass network formers* (NWFs), as they ought to be able to form the glass skeleton on their own. Oxides such as Li_2O, Na_2O, K_2O, CaO, BaO, ZnO, CdO, Ga_2O3, In_2O_3, and PbO_2 were classified as *glass network modifiers* (NWMs); the cations of these oxides occupied the interstitial spaces in the network formed by the NWF oxides and, hence, acted as network modifiers only. Oxides such as BeO, $A1_2O_3$, TiO_2, and ZrO_2 were termed *intermediates*; these did not make glass readily on their own, but did make a glass when present in large quantities mixed with the NWF or NWM oxides.

2.2.2 Borosilicate Glasses

Borosilicate glasses are of technological interest because they have many applications. They generally have a lower thermal expansion than soda-lime silica glasses; have good chemical resistance, high dielectric strength and a higher softening temperature than soda-lime silica glasses. For these reasons they are used for laboratory glassware, household cooking ware, industrial piping, bulbs for hot lamps and electronic tubes of high voltage such as X-ray tubes. Beside these applications one must mention the use of barium crown glasses for optical purposes. Furthermore, borosilicate glass plays an important role in the production of what is known as Vycor glass. This glass contains about 96% SiO_2 and is an important substitute for fused silica. Vycor glass can be produced at lower working temperatures than fuse silica, which is of economic interest. It is used, for instance, in projection lamps.

2.3 Optical Properties

2.3.1 Introduction [19]

If one were to list the major technological developments that have added to the comforts of living, glass as an aid to failing vision, glass windows to bring daylight into housing structures while providing protection from the harsh elements of nature, glass in the light bulb to provide a similar function after dark, and glass fibers for enhanced communication capabilities would perhaps rank very high.

For the glass window and the glass bulb to function, the optical transmission property is important. The correction for the failing vision and glass fiber communication are based upon the refractive, optical dispersion and transmission properties of glass. Beside there are many more technological advances where the optical properties of glass play a vital role.

Before we begin, we should note that, in the visible (VIS) region, light rays are generally referred to by their wavelength (λ) stated in nanometers (SI units) or angstroms. In the infrared (IR) region, the wave number ($=1/\lambda$) with units cm^{-1} is used. In the ultraviolet (UV) region, sometimes the energy E(eV) of the photons is used.

When light travels through a medium, a part of it is reflected from the front surface, part is absorbed, and the balance is transmitted.

The reflectance R at normal incidence for light waves traveling from one dielectric medium to another is given by:

$$R = \left[\frac{n_1 - n_2}{n_1 + n_2} \right]^2 \tag{2.1}$$

where the refractive index, n, is the ratio of the velocities of light in vacuum to that in the medium; it is unitless.

When light waves travel from one medium of refractive index n_l into another medium of refractive index n_2 the incident and refracted rays remain in the same plane and the angles of incidence i and refraction r (angles between the ray and the surface normal) are related through Snell's law:

$$\frac{\sin r}{\sin i} = \frac{n_1}{n_2} \tag{2.2}$$

when $n_l > n_2$, $r = 90^0$ at the critical angle of incidence θ_c (called Brewster's angle). Upon $i > \theta_c$, the incident ray is total internally reflected. The bending of light ray as they pass from one medium to another is the key to the design of lenses in eyeglasses, microscopes, telescopes, and cameras.

The absorption coefficient (α) is defined by Beer-Lambert's law for intensity I transmitted through a distance z in a medium:

$$I = I_0 \exp[-\alpha z] \tag{2.3}$$

where I_0 is the incident intensity. The units of α are cm^{-1}. (Note: this unit has yet to be replaced by m^{-1}.) Occasionally, the Beer-Lambert law is written as:

$$I = I_0 10^{-\alpha z} \tag{2.4}$$

we may think of the absorption as due to a solution of the absorbing species in the medium, in which case it is useful to define a molar extinction coefficient δ as:

$$\alpha = \delta c \tag{2.5}$$

where c is the concentration (mol L^{-1}) of the absorbing centers. δ is expressed as $L \cdot mol^{-1} \cdot cm^{-1}$.The absorbance A and the optical density D are given by:

$$A = -\ell n[\frac{I}{I_0}] \tag{2.6}$$

$$D = -\ell og[\frac{I}{I_0}] \tag{2.7}$$

one other important criterion in the design of optical components to be considered is the correction for chromatic aberration resulting from the dispersion of light, i.e., the variation of n with wavelength λ. A way from an absorption peak, n may be expressed by Cauchy's dispersion formula:

$$n = A' + \frac{B'}{\lambda^2} + \frac{C'}{\lambda^4} + \ldots \tag{2.8}$$

where A′ , B′ and C ′are constants. It may be noted that, according to this relation, the refractive index decreases with increasing wavelength. While this is true for the most part, the relation breaks down in the region where the material strongly absorbs light rays.

Useful parameters in the correction for chromatic aberration are the Abbe number v_d, and the partial dispersion. The Abbe number is defined by:

$$v_d = (n_d - 1)(n_F - n_C) \tag{2.9}$$

where the F-line is the blue λ = 486.1327 nm line from the hydrogen spectrum, the C-line is the red λ = 656.2725 nm line, also from the hydrogen spectrum, and the is the yellow λ = 587.5618 nm line from the He spectrum. The partial dispersion for any two wavelengths x and y is given by:

$$p_{x,y} = \left(\frac{n_x - n_y}{n_F - n_C} \right) \tag{2.10}$$

2.4 Density and Molar Volume

2.4.1 Definitions

Density of a substance is defined as the mass per unit volume, and is an intensive property. Appropriate units are g/cm^3 or g/cc (in cgs system) and kg.m^{-3} in the SI system. The dependence of density upon temperature is through the volume thermal expansion coefficient.

Since glasses may, in general, be regarded as solution, a more useful property is the molar volumes V, defined as the volume of one gram mole of glass, and then proceed to define partial molar volumes of the various structural units constituting the glass. The partial volume v_i of a species i in a solution defined by [19]:

$$v_i = \left(\frac{\partial v}{\partial n_i} \right)_{nj,} T, P \qquad (2.11)$$

and hence, $V = n_i v_i + n_j v_j$

In essence, the total molar volume is treated as an property in terms of the partial molar volumes of individual species or structural groups. The partial molar volume information can be extracted from the density data of glasses where the constituents have been systematically varied. If a Na^+ is replaced by K^+ in the glass and occupies the same interstice (without changing its size), it is clear that, although the glass density would increase because of the higher atomic weight of K^+ , the partial molar volume of the alkali ion would not change. Any increase in the molar volume would be an increase in the partial molar volume of K^+ relative to Na^+. This is likely to have some relation to the relative ionic sizes of the two ions. One may readily note that, although the measurement of density changes in a family of glasses may provide only the trends, the extraction of the partial molar volumes from the density data provides further insight into structure while canceling out the effect of atomic masses.

2.4.2 Methods of Measurement

Density is measured most commonly by weighing a suitably selected piece of glass in air and dividing this weight by the buoyancy (the reduction in weight) when the sample is suspended in water. According to Archimedes' principle, the buoyancy equals the weight of the displaced fluid, which, for water, equals the volume. Thus, if w_a is the weight of the specimen in air, and w_b in water, then the buoyancy is w_a - w_b and the density [19]:

$$\rho = \frac{w_a}{w_a - w_b} \qquad (2.12)$$

occasionally, the glass may be affected by water immersion, in which case a suitable inert liquid such as kerosene may be selected. The specimen volume in this case is given by $(w_a - w_b)/\rho_m$ where ρ_m is the density of the immersion medium. A kit supplied by scientific balance manufacturers can utilized to obtain density measurements accurate to 0.001 g/cc.

Automatic measurements of density can be carried out using pycnometers that utilize He gas as the displacement fluid. A small sample, of the order of a few milligrams, is all that needed to make the measurement. The accuracy of such instruments is generally about 0.002 g/cc. In a manufacturing environment, a comparative density (easily accurate to 0.0002 g/cc) is more rapidly obtained using a gradient column. The gradient column consists of a vertically held long (often 1 – 1.5 m), glass tube with one end closed. The tube contains a liquid with a linear density gradient. To prepare the density gradient, a heavy liquid such as *sym*-tetrabromoethane (= 2.96 g/cc) or methylene iodide (= 3.32 g/cc) is first poured into the tube, and then a lighter liquid such as isopropyl salicylate (ρ = 1.1 g/cc) is gently poured to float above the heavy liquid. With time, the liquids diffuse into each other, establishing a gradient with the help of gravity. The gradient is calibrated by allowing density standards to gently float in the column at different heights. The density of an unknown glass is obtained by reading its flotation level against a precalibrated scale placed adjacent to the column.

2.5 Type of Radiation Produced by Radioactive Decay

When an atom undergoes radioactive decay, it emits one or more forms of radiation with sufficient energy to ionize the atoms with which it interacts. Ionizing radiation can consist of high speed subatomic particles ejected from the nucleus or electromagnetic radiation (gamma-rays) emitted by either the nucleus or orbital electrons.

2.5.1 Alpha Decay

Certain radionuclides of high atomic mass (Ra-226, U-238, Pu-239) decay by the emission of alpha particles. These alpha particles are tightly bound units of two neutrons and two protons each (He-4 nucleus) and have a positive charge. Emission of an alpha particle from the nucleus results in a decrease of two units of atomic number (Z) and four units of mass number (A). Alpha particles are emitted with discrete energies characteristic of the particular transformation from which they originate. All alpha particles from a particular radionuclide transformation will have identical energies.

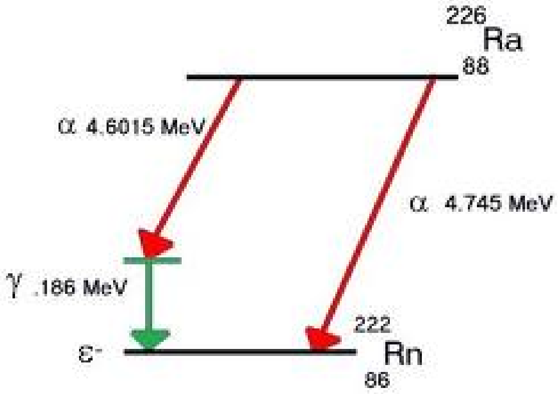


Figure 2.4 Alpha decay.

2.5.2 Beta Decay

A nucleus with an unstable ratio of neutrons to protons may decay through the emission of a high speed electron called a beta particle. This results in a net change of one unit of atomic number (Z). Beta particles have a negative charge and the beta particles emitted by a specific radionuclide will range in energy from near zero up to a maximum value, which is characteristic of the particular transformation.

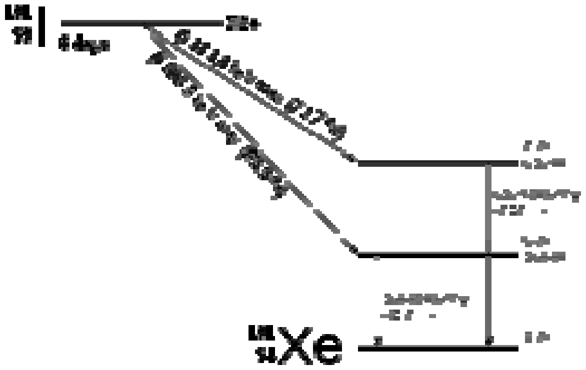


Figure 2.5 Beta decay.

2.5.3 Gamma Decay

A nucleus which is in an excited state may emit one or more photons (packets of electromagnetic radiation) of discrete energies. The emission of gamma rays does not alter the number of protons or neutrons in the nucleus but instead has the effect of moving the nucleus from a higher to a lower energy state (unstable to stable). Gamma ray emission frequently follows beta decay, alpha decay, and other nuclear decay processes.

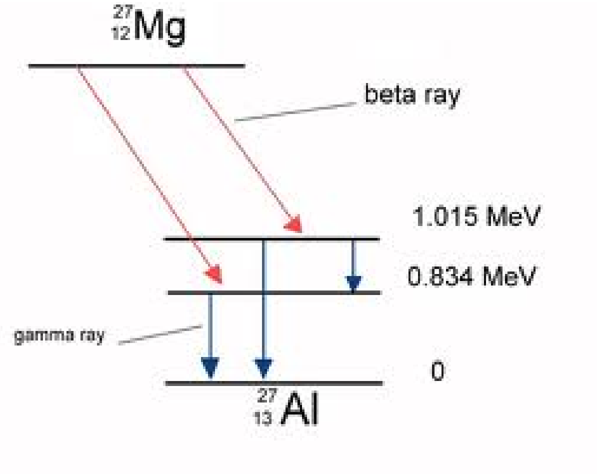


Figure 2.6 Gamma decay.

2.6 Interactions of Gamma and X-Rays with Matter

X-rays and γ rays are electromagnetic radiation. Considered as particles, when they travel with the velocity of light c, their rest mass is zero and so is their charge. A common name for X-rays and γ-rays as particles is photons. The relationship between energy E, frequency v, and wavelength λ is:

$$E = h\nu = h\frac{c}{\lambda} \tag{2.13}$$

where c is electromagnetic velocity in vacuum

There is no clear distinction between X-rays and γ-rays. The term X-rays is applied generally to the photons with E < 1 MeV. Gammas are the photons with E ≥ 1 MeV. In what follows. The terms photon, γ, and X-rays will be used interchangeably.

X-rays are generally produced by atomic transitions such as excitation and ionization. Gamma rays are emitted in nuclear transitions. Photons are also produced as bremsstrahlung, by accelerating or decelerating charged particles. X-rays and γ-rays emitted by atoms and nuclei are monoenergetic. Bremsstrahlung has a continuous energy spectrum.

There is a long list of possible interactions of photons, but only the three most important ones will be discussed here: the photoelectric effect, Compton scattering, and pair production.

2.6.1 The Photoelectric Effect

The photoelectric effect is an interaction between a photon and a bound atomic electron. As a result of the interaction, the photon disappears and one of the atomic electrons is ejected as a free electron, called the photoelectron (Figure2.7). The kinetic energy of the electron (T_e) is [20]:

$$T_e = E_\gamma - BE \tag{2.14}$$

where E_γ = energy of the photon
BE = binding energy of the electron

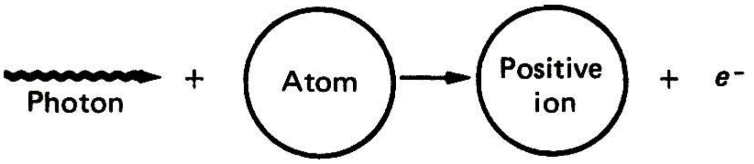


Figure 2.7 The Photoelectric effect [20].

The probability of this interaction occurring is called the photoelectric cross section or photoelectric coefficient. It is important to discuss the dependence of this coefficient on parameters such as gamma rays energy (E_γ), atomic number (Z), and mass number (*A*). The equation giving τ may be written as [20]:

$$\tau\left(m^{-1}\right) = aN\frac{Z^n}{E_\gamma^m}\left[1-\theta(Z)\right] \tag{2.15}$$

where τ = probability for photoelectric effect to occur per unit distance traveled by the photon

a = constant, independent of Z and E_γ

m,n = constants with a value of 3 to 5 (their value depends on E_γ)

N = number of atom/m^3.

The term in parentheses indicates correction terms of the first order in Z. Figure 2.8 shows how the photoelectric coefficient changes as a function of E_γ and Z. As Figure 2.8 and Eq. (2.15) show, the photoelectric effect is more important for high-Z material, i.e., more probable in Pb (Z=82) than in Al (Z=13). It is also more important for E_γ = 10 keV than E_γ = 500 keV (for the same material). Using Eq. (2.15), one can obtain estimates of the photoelectric coefficient of one element in terms of that of another. If one takes the ratio of τ for two elements, the result for photons of the same energy is [20]:

$$\tau_2\left(m^{-1}\right) = \tau_1\frac{\rho_2}{\rho_1}\left(\frac{A_1}{A_2}\right)\left(\frac{Z_2}{Z_1}\right)^n \tag{2.16}$$

where ρ and A are density and atomic weight, respectively, of the two elements, and τ_1 and τ_2 are given in m^{-1}. If τ_1 and τ_2 are given in m^2/kg, Eq. (2.17) takes the form [20]:

$$\tau_2\left(m^2/kg\right) = \tau_1\frac{A_1}{A_2}\left(\frac{Z_2}{Z_1}\right)^n \tag{2.17}$$

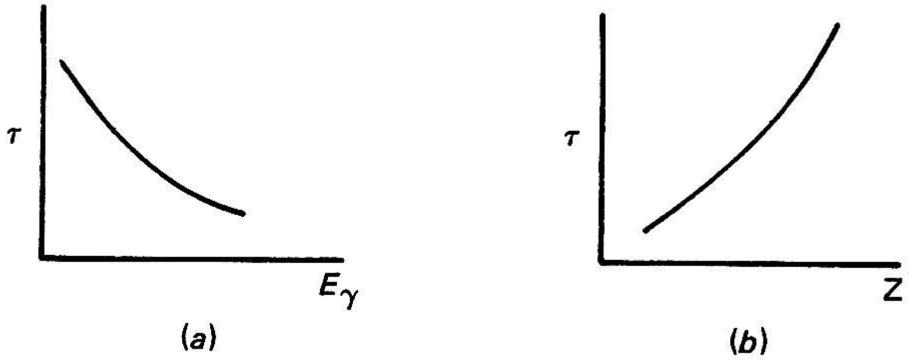


Figure 2.8 Dependence of the photoelectric cross section on (a) photon energy and (b) atomic number of the material [20].

2.6.2 Compton Scattering or Compton Effect

The Compton effect is a collision between a photon and a free electron. Of course, under normal circumstances, all the electrons in a medium are not free but bound. If the energy of the photon, however, is of the order of keV or more, while the binding energy of the electron is of the order of eV, the electron may be considered free.

The photon does not disappear after a Compton scattering. Only its direction of motion and energy change (Figure 2.9). The photon energy is reduced by a certain amount that is given to the electron. Therefore, conservation of energy gives (assuming the electron is stationary before the collision) [20]:

$$T_e = E_\gamma - E_{\gamma'} \tag{2.18}$$

where T_e, E_γ and $E_{\gamma'}$ are kinetic energy of the electron, incident photon energy and scattered photon energy respectively.

If Eq.(2.18) is used along with the conservation of momentum equations, the energy of the scattered photon as a function of the scattering angle θ can be calculated. The result is [20]:

$$E_{\gamma'} = \frac{E_\gamma}{1+(1-\cos\theta)E_\gamma / mc^2} . \tag{2.19}$$

Using Eq. (2.18) and Eq. (2.19), one obtains the kinetic energy of the electron.

$$T_e = \frac{(1-\cos\theta)E_\gamma / mc^2}{1+(1-\cos\theta)E_\gamma / mc^2} E_\gamma \tag{2.20}$$

A matter of great importance for radiation measurement is the maximum and minimum energy of the photon and the electron after the collision. The minimum energy of the scattered photon is obtained when $\theta = \pi$. This, of course, corresponds to the maximum energy of the electron. From Eq. (2.19):

$$E_{\gamma',\min} = \frac{E_\gamma}{1+2E_\gamma / mc^2} \tag{2.21}$$

and

$$T_{e,\max} = \frac{2E_\gamma / mc^2}{1+2E_\gamma / mc^2} E_\gamma . \tag{2.22}$$

The maximum energy of the scattered photon is obtained for $\theta = 0,$ which essentially means that the collision did not take place. From Eq. (2.19)

$$E_{\gamma',\max} = E_\gamma \tag{2.23}$$

$$T_{e,\min} = 0 \tag{2.24}$$

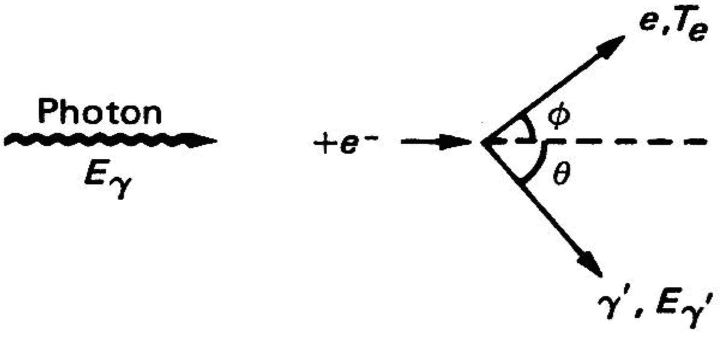


Figure 2.9 The Compton effect [20].

The conclusion to be drawn from Eq. (2.21) is that the minimum energy of the scattered photon is greater than zero. Therefore, in Compton scattering, it is impossible for all the energy of the incident photon to be given to the electron. The energy given to the electron will be dissipated in the material within a distance equal to the range of the electron. The scattered photon may escape.

The probability that Compton scattering will occur is called the Compton coefficient or the Compton cross section. It is a complicated function of the photon energy, but it may be written in the form [61]:

$$\pi(m^{-1}) = NZf(E_\gamma) \tag{2.25}$$

where $\pi =$ probability for Compton interaction to occur per unit distance $f(E_\gamma) =$ a function of E_γ. If one writes the atom density N explicitly, Eq.(2.25) takes the form:

$$\pi \sim \rho \frac{N_A}{A} Zf(E_\gamma) \sim \rho \left(\frac{N_A}{A} \right) \frac{A}{2} f(E_\gamma) \sim \rho \frac{N_A}{2} f(E_\gamma). \tag{2.26}$$

In deriving Eq. (2.26), use has been made of the fact that for most materials, except hydrogen, $A \approx 2Z$ to $A \approx 2.6Z$. According to Eq. (2.26), the probability for Compton scattering to occur is almost independent of the atomic number of the material. Figure 2.10 shows how π changes as a function of E_γ and Z. If the Compton cross section is known for one element, it can be calculated for any other by using Eq. (2.25) (for photons of the same energy):

$$\pi_2(m^{-1}) = \pi_1 \left(\frac{\rho_2}{\rho_1} \right) \left(\frac{A_1}{A_2} \right) \left(\frac{Z_2}{Z_1} \right) \tag{2.27}$$

where π_1 and π_2 are given in m^{-1}. If π_1 and π_2 are given in m^2/kg, Eq. (2.28) takes the form:

$$\pi_2\left(m^2/kg\right) = \pi_1\left(\frac{A_1}{A_2}\right)\left(\frac{Z_2}{Z_1}\right) \tag{2.28}$$

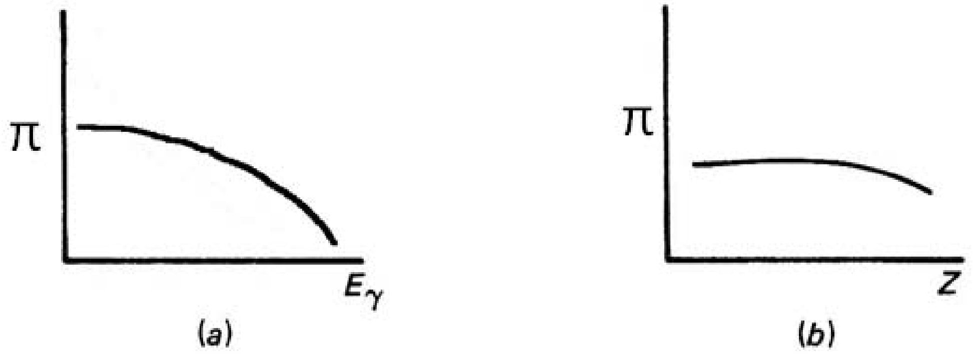


Figure 2.10 Dependence of the Compton cross section on (a) photon energy (b) atomic number of the materials [20].

2.6.3 Pair Production

Pair production is an interaction between a photon and a nucleus. As a result of the interaction, the photon disappears and an electron-positron pair appears (Figure 2.11). Although the nucleus does not undergo any change as a result of this interaction, its presence is necessary for pair production to occur. A γ-rays will not disappear in empty space by producing an electron-positron pair.

Conservation of energy gives the following equation for the kinetic energy of the electron and the positron:

$$T_{e^-} + T_{e^+} = E_\gamma - \left(mc^2\right)e^- - \left(mc^2\right)e^+ = E_\gamma - 1.022 \text{ MeV} \tag{2.29}$$

Pair production may take place in the field of an electron. The probability for that to happen is much smaller and the threshold for the threshold for the gamma energy is $4mc^2$ =2.04 MeV.

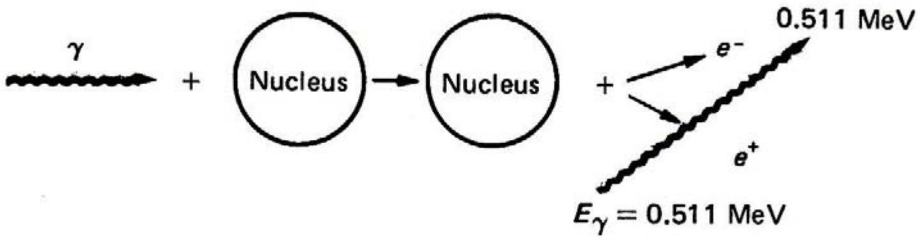


Figure 2.11 Pair production. The gamma disappears and a positron-electron pair is created. Two 0.511 MeV photons are produced when the positron annihilates [20].

The available kinetic energy is equal to the energy of the photon minus 1.022 MeV, which is necessary for the production of the two rest masses. Electron and positron share, for all practical purposes, the available kinetic energy, i.e.:

$$T_{e^-} = T_{e^+} = \frac{1}{2}\left(E_\gamma - 1.022 MeV\right) \tag{2.30}$$

Pair production eliminates the original photon, but two photons are created when the positron annihilates. The annihilation gammas are important in constructing shielding against them as well as for the detection of gammas.

The probability for pair production to occur, called the pair production coefficient or cross section, is a complicated function of E_γ and Z. It may be written in the form:

$$\kappa\left(m^{-1}\right) = NZ^2 f\left(E_\gamma, Z\right) \tag{2.31}$$

where κ is the probability for pair production to occur per unit distance traveled and $f\left(E,Z\right)$ is a function which change slightly with Z and increases with E_γ. Figure 2.12 shows how κ changes with E_γ and Z. It is important to note that κ has a threshold at 1.022 MeV and increases with E_γ and Z. Of the three coefficients (τ and π being the other two), κ is the only one increasing with the energy of the photon.

If the pair production cross section is known for one element, an estimate of its value can be obtained for any other element by using Eq. (2.31) (for photons of the same energy):

$$\kappa_2\left(m^{-1}\right) = \kappa_1\left(\frac{\rho_2}{\rho_1}\right)\left(\frac{A_1}{A_2}\right)\left(\frac{Z_2}{Z_1}\right)^2 \tag{2.32}$$

where κ_1 and κ_2 are given in m^{-1}.

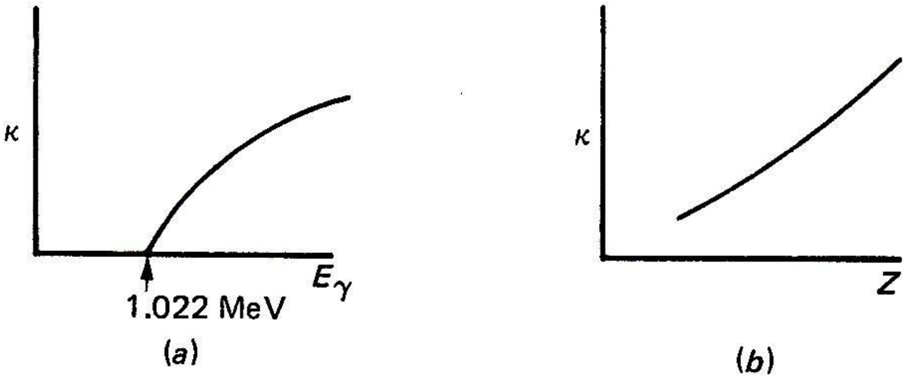


Figure 2.12 Dependence of the pair-production cross section on (a) photon energy and (b) atomic number of the material [20].

2.6.4 Total Attenuation Coefficient

When a photon travels through matter, it may interact through any of the three major interactions discussed earlier. (For pair production, E_γ>1.022 MeV.) There are other interactions, but they are not mentioned here because they are not important in the detection of gammas.

Figure 2.13 shows the relative importance of the three interactions as E_γ and Z change. Consider a photon with E = 0.1 MeV. If this particle travels in carbon (Z=6), the Compton effect is the predominant mechanism by which this photon interacts. If the same photon travels in iodine (Z=53), the photoelectric interaction prevails. For a γ of 1MeV, the Compton effect predominates regardless of Z. If a photon of 10 MeV travels in carbon, it will interact mostly through Compton scattering. The same photon moving in iodine will interact, mainly, through pair production.

The total probability for interaction μ, called the total *linear* attenuation coefficient, is equal to the sum of the three probabilities:

$$\mu = \tau + \pi + \kappa \tag{2.33}$$

physically, μ is the probability of interaction per unit distance.

There are tables that give μ for all the elements, for many photon energies. Most of the tables provide μ in units of m^2/kg. (or cm^2/g), because in these units the density of the material does not have to be specified. If μ is given in m^2/kg (or cm^2/g),

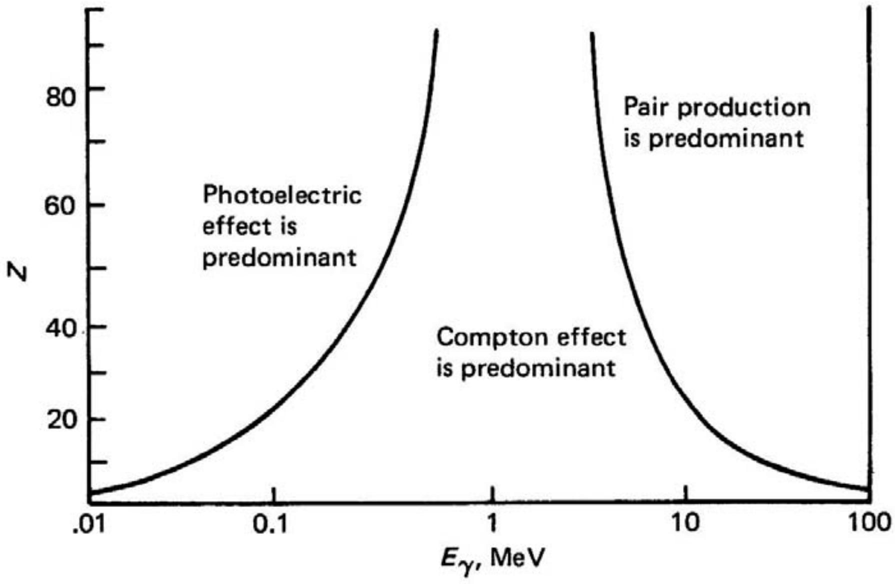


Figure 2.13 The relative importance of the three major gamma interactions [20].

it is called the total mass attenuation coefficient. The relationship between linear and mass attenuation coefficients is:

$$\mu_m = \frac{\mu}{\rho} \tag{2.34}$$

Figure 2.14 shows the individual coefficients as well as the total mass attenuation coefficient for lead, as a function of photon energy. The total mass attenuation coefficient shows a minimum because as E increases, τ decreases, k increases, and σ does not change appreciably. However, the minimum of μ does not fall at the same energy for all elements. For lead, μ is minimized at $E_\gamma \sim 3.5$ MeV; for aluminum, the minimum is at 20 MeV; and for NaI, the minimum is at 5 MeV.

If a parallel beam of monoenergetic γ rays goes through a material of thickness x, the fraction of the beam that traverses the medium without any interaction is equal to $e^{-\mu x}$ (Figure 2.15). The probability that a photon will go through thickness x without an interaction is:

$$\frac{I_0 e^{-\mu x}}{I_0} = e^{-\mu x} \tag{2.35}$$

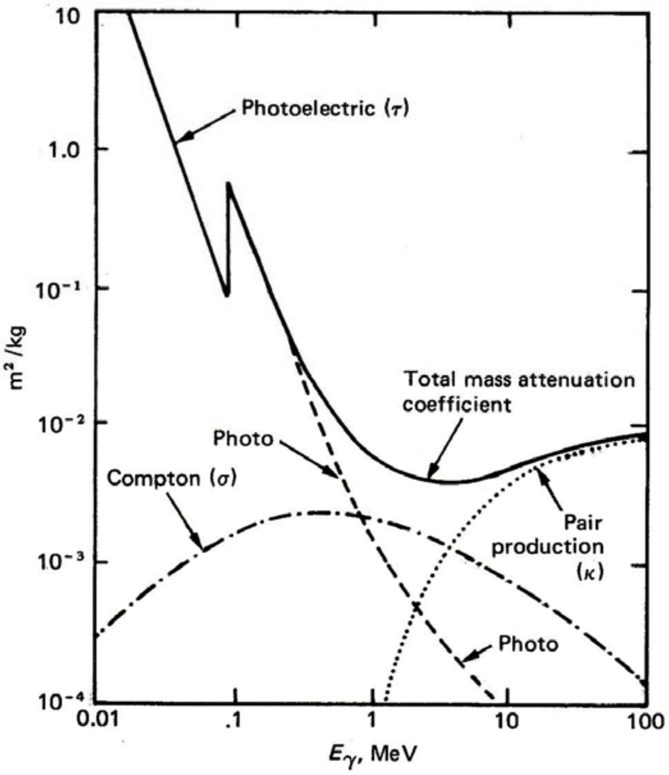


Figure 2.14 Mass attenuation coefficients for lead (Z=82, $\rho = 11.35 \times 10^3$ kg/m^3) [20].

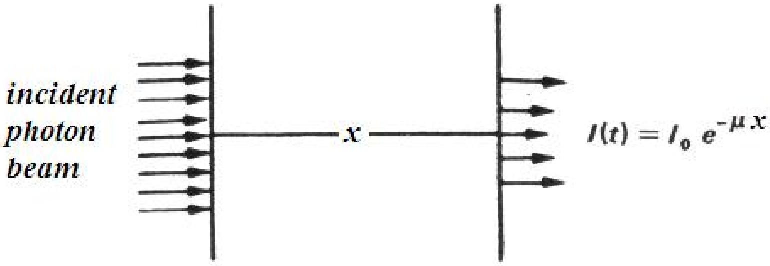


Figure 2.15 The intensity of the transmitted beam (only particles that did not interact) decreases exponentially with material thickness [20].

The average distance between two successive interactions, called the mean free path (*MFP*), is given by:

$$MFP = \frac{\int_0^\infty x e^{-\mu x} dx}{\int_0^\infty e^{-\mu x} dx} = \frac{1}{\mu} \tag{2.36}$$

thus, the mean free path is simply is simply the inverse of the total linear attenuation coefficient. If $\mu = 10\ \mathrm{m}^{-1}$ for a certain γ ray traveling in a certain medium, then the distance between two successive interactions of this gamma in that medium is
$MFP = 1/\mu = 1/10\,m = 0.10m.$

The total mass attenuation coefficient for a compound or a mixture is calculated by: [20]

$$(\mu_m)_c = \sum_{i=1}^{n} w_i (\mu_m)_i \tag{2.37}$$

where $(\mu_m)_c$ = total *mass* attenuation coefficient for a compound or a mixture
w_i = weight fraction of ith element in the compound
$(\mu_m)_i$ = total *mass* attenuation coefficient of i^th^ element

The thickness of any given material where 50% of the incident energy has been attenuated is known as the half-value layer (HVL). The HVL is expressed in units of distance (mm or cm). Like the attenuation coefficient, it is photon energy dependant. Increasing the penetrating energy of a stream of photons will result in an increase in a material's HVL.

The HVL is inversely proportional to the attenuation coefficient. If an incident energy of 1 and a transmitted energy is 0.5 is plugged into the equation introduced on the preceding page, it can be seen that the HVL multiplied by m must equal 0.693.

Therefore, the HVL and m are related as follows:

$$HVL = \frac{0.693}{\mu} \tag{2.38}$$

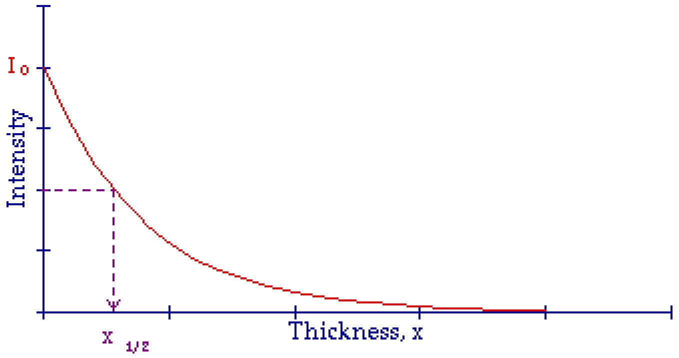


Figure 2.16 The half value layer.

Table 2.1 Approximate HVL for various materials when radiation is from a gamma source**.**

Source	Half –value layer, mm (inch)				
	Concrete	Steel	Lead	Tungsten	Uranium
Iridium-192	44.5 (1.75)	12.7 (0.5)	4.8 (0.19)	3.3 (0.13)	2.8 (0.11)
Cobalt-60	60.5 (2.38)	21.6 (0.85)	12.5 (0.49)	7.9 (0.31)	6.9 (0.27)

2.6.5 Effective Atomic Numbers

In this section we summarize theoretical relations used in the present work. A parallel beam of monoenergetic gamma-ray photons is attenuated in matter according to the Lambert-Beer law :

$$\mathrm{I} = \mathrm{I}_0 \exp(-\mu_m \rho x) \qquad (2.39)$$

where I_0 and I are incident and transmitted intensities of gamma radiation respectively, μ_m is the mass attenuation coefficient for absorber, x is the thickness of absorber, ρ is the density of absorber. Theoretical values of the mass attenuation coefficients of mixture or compound have been calculated by WinXCom, based on the mixture rule from Eq. (2.37).

This mixture rule is valid when the effects of molecular binding, chemical and crystalline environment are negligible. The values of mass attenuation coefficients can be used to determine the total atomic cross-section ($\sigma_{t,a}$) by the following relation:

$$\sigma_{t,a} = \frac{(\mu_m)_{alloy}}{N_A \sum_i^n (w_i / A_i)} \qquad (2.40)$$

where N_A is Avogadro’s number, A_i is atomic weight of the constituent element of mixture . Also the total electronic cross-section ($\sigma_{t,el}$) for the element is expressed by the following formula[33]:

$$\sigma_{t,el} = \frac{1}{N_A} \sum_i^n \frac{f_i A_i}{Z_i} (\mu_m)_i \qquad (2.41)$$

where f_i is the number of atoms of the element i relative to the total number of atoms of all elements in mixture, Z_i is the atomic number of the i^{th} element in alloy. By using the mass attenuation coefficient of mixture, the effective atomic number (Z_{eff}) were determined from Eq. (2.40) and Eq. (2.41):

$$Z_{eff} = \frac{\sigma_{t,a}}{\sigma_{t,el}} \tag{2.42}$$

2.7 X-ray Fluorescence Analysis

X-ray is a type of electromagnetic waves such as visible light ray, but the key difference is its extremely short wavelength, measuring from 100 A^o to 0.1 A^o. And compared to normal electromagnetic waves, x-ray easily passes through material and it becomes stronger as the material's atomic number decreases. X-ray fluorescence analysis is a method that used the characteristic x-ray (fluorescent x-ray) that is generated when x-ray is irradiated on a substance. The fluorescence x-ray is the excess energy irradiated as electromagnetic field, which is generated when the irradiated x-ray forces the constituent atom's inner-shell electrons. The generation of fluorescent x-ray is shown in Figure 2.17. These rays possess energy characteristic to each element, and qualitative analysis using Mosley's equation and quantitative analysis using the energy's x-ray intensity (number of photons) are possible.

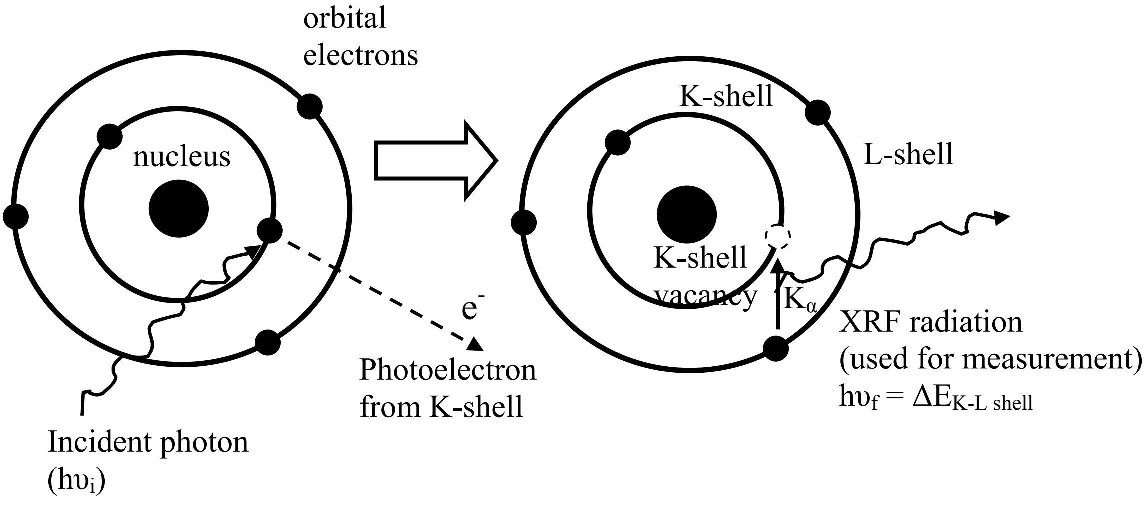


Figure 2.17 X-ray generation.

X-ray fluorescence analysis can be considered as spectrochemical analysis of an x-ray region. It has the same characteristics as atomic absorption spectrometry and optical emission spectrometry which conduct measurement by putting the sample into solution. For example, in flameless atomic absorption spectrometry (FLAAS), elements in the sample are atomized in 2000 to 3000C flame and in ICP atomic emission spectrometry (ICP-AES), sample is excited in 6000 to 9000C plasma flame. X-ray fluorescence likewise excites the sample using x-ray to obtain information.

2.7.1 Device structure

X-ray fluorescence analysis devices can be largely categorized into wavelength-dispersive x-ray spectroscopy (WDX) and energy-dispersive x-ray spectroscopy (EDX).

(Shown in Figure 2.18) WDX disperses the fluorescent x-ray generated in the sample using dispersion crystal and measures it using a goniometer, resulting in a large size. On the other hand, the detector in EDX has a superior energy resolution and requires no dispersion system, which enables downsizing of the device.

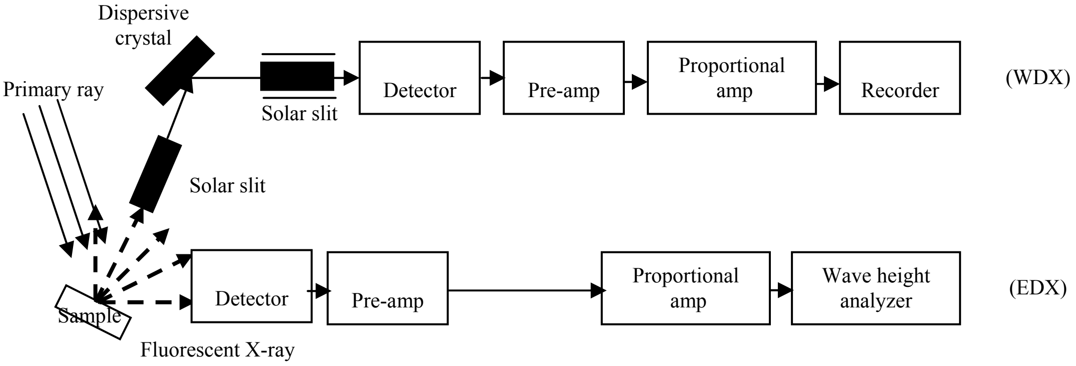


Figure 2.18 WDX and EDX types.

2.7.2 X-Ray Generation

X-ray is generated when the x-ray tube (Figure 2.19) accelerates the electrons at high voltage and bombards them against the metal anode (anti-cathode). There are two types of x-ray tubes, side window type and end window type, and both are designed to irradiate intense x-ray on the sample surface as evenly as possible. Beryllium foil is commonly used for the window for retrieving the incident x-ray. For the anti-cathode, (sometimes referred as 7gtarget7h) tungsten, rhodium, molybdenum and chrome are used. These anti-cathodes are chosen based on the analysis sample. X-ray tubes with anti-cathode similar to analysis element are essentially not used.

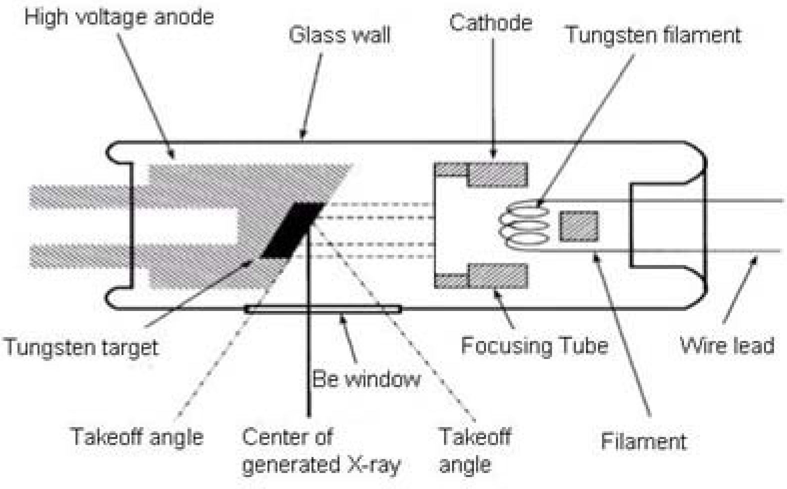


Figure 2.19 X-ray tube bulb.

2.7.3 Detector

Figure 2.20 shows the basic structure of a Si (Li) device. Si(Li) device featuresa p-i-n+structure diode. Diode can only pass electric current in one direction (rectification mechanism). When voltage is applied against the current (reverse bias) and light enters in this state, the electrons in the forbidden band are excited into conductive band and only the current for the excited electron travel. For x-ray detection, each current pulse corresponding to an incident x-ray photon is measured one by one. The instantaneous current value of a single pulse is relative to the incident x-ray energy, so x-ray energy can be found by measuring the wave height of the current pulse. Si(Li) semiconductor detector is a diode with Li spread over high-purity single Si crystal, diameter 3 to 6mm and thickness 3 to 5 mm, cooled with field-effect transistor and liquid nitrogen and maintained in vacuum. When semiconductor detector was first developed, damage caused by application of high voltage that resulted from shortage of liquid nitrogen and consequent temperature rise, was reported. With current devices, the surface temperature of the detector is monitored and when it rises above a certain temperature, protection circuit shuts off the high voltage to the detector, eliminating damage to the detector from accidentally applying high voltage. At low frequency of use, it can be used about 30 minutes after supplying it with liquid nitrogen.

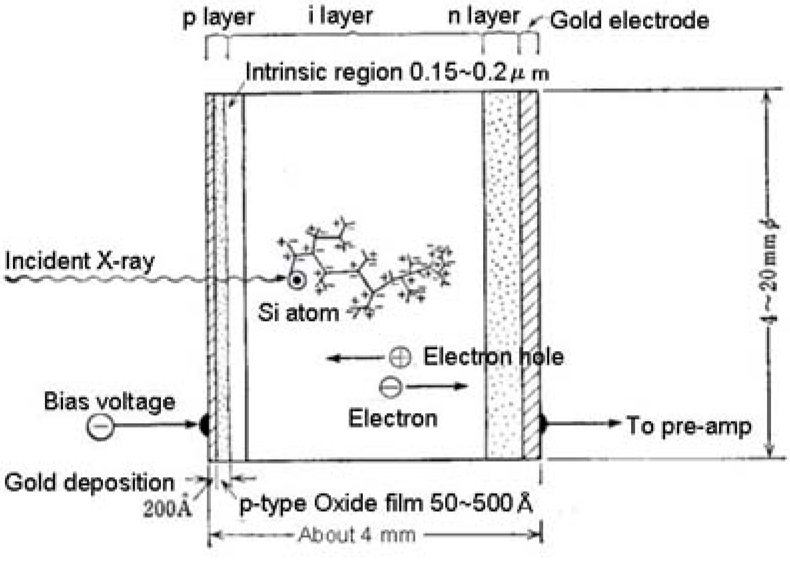


Figure 2.20 Si(Li) device structure.

2.7.4 Sample Chamber & Measurement Atmosphere

There are two types of sample chambers, top-surface irradiation type that irradiate x-rays from above, and bottom-surface irradiation type that irradiate from below. There are not many differences between the two types in detection concentration, but for sample observation and measurements conducted while moving the stage, the top-surface irradiation is better. In most devices, atmosphere in sample chambers can be decompressed. This is because x-rays are absorbed and lose intensity in atmosphere. For light element measurements, setting the measurement atmosphere is vital.

2.7.5 Qualitative Analysis

In defining x-ray fluorescence analysis, the wavelength of the characteristic x-ray or the regularity of the energy and atomic number are used. Most devices are equipped with the automatic identification (definition) feature but it is important to note various interfering spectrums. Depending on the element types contained in the sample, energy position of characteristic x-rays may be close to each other or spectrums may overlap. Figure 2.21 shows an example with As and Pb spectrums.

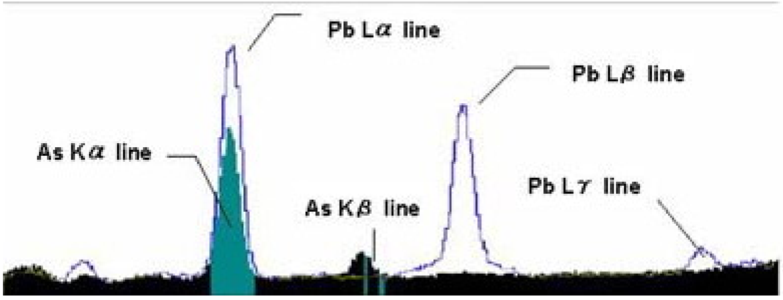


Figure 2.21 As and Pb Spectrum.

As shown above, if Pb is contained in the sample, the energy position of As's Kα line overlap with Pb's Lα line, and would lead to identifying As by mistake. There are multiple characteristic X-rays of an element, such as Kα line, Kβ line, Lα line, Lβ line etc. In cases such as this, confirmation with a KLM marker shown in Figure 2.22 is necessary. A KLM marker compares the intensity and theoretical energy positions of multiple characteristic x-rays. Figure 2.22 shows an example with the KLM marker of Pb displayed on the spectrum.

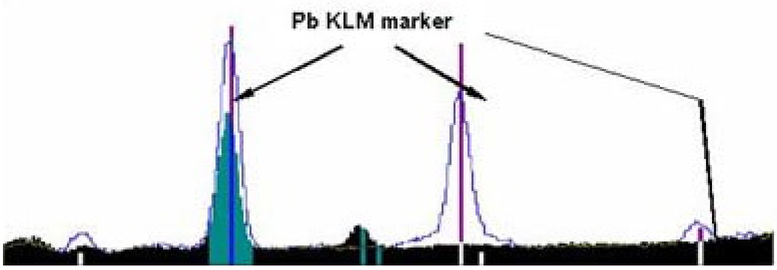


Figure 2.22 Pb KLM marker.

The x-ray intensity of Pb is shown and if the sample contains Pb, a peak would be present at each energy position at about the same interval as the KLM marker. If peaks are not present at Pb energy positions other than Pb Lα line, it can be judged that Pb does not exist in the sample. Likewise, if peaks do not exist on the As Kα line as well as the Kβ line, the sample does not contain As. As above, by displaying the KLM marker and observing the intensity comparison of multiple characteristic x-rays, qualitative analysis can be performed accurately.

2.7.6 Quantitative Analysis

The following is an overview of conducting quantitative analysis using fluorescent x-ray. When a sample that contains element A is irradiated primary x-ray, fluorescent x-ray of element A is generated, but the intensity of this fluorescent x-ray is dependent on the amount of element A in the sample. The more element A contained in the sample, the higher the intensity of the fluorescent x-ray that is generated. Taking this into account, if the fluorescent x-ray intensity and concentration of an element contained in a sample is known, then we can go in reverse and find how much element A contained in another sample by its fluorescent x-ray intensity. When conducting quantitative analysis with fluorescent x-ray, there are two basic methods. The first is to create a standard curve. This method involves measuring several samples with a known element concentration, and finding the relationship between the intensity of the measured element's fluorescent x-ray and the concentration. By referring this relationship, element concentration of unknown sample is obtained only with information on its fluorescent x-ray intensity. The other method is known as the fundamental parameter method of theoretical calculation, or the FP method. With this method, if the type and properties of all elements that compose a sample are known, then the intensity of each fluorescent x-ray can be derived theoretically. By utilizing this method, the composition of unknown sample can be extrapolated by its fluorescent x-ray intensity of each element.