# SECTION 1: INTRODUCTION

Chemistry is the science of atoms – their electronic structure, reactivity and the shapes, sizes and functionality of the compounds they form. Atomic properties are summarized in the form of the Periodic Table, which Mendeleev conceived based on chemical intuition, but which now finds exposition in terms of quantum theory.

But, what is the fundamental property of an atom that distinguishes it from other elements? And where did these atomic building blocks come from? The unique character of each element is determined by its atomic nucleus, the product of nucleosynthesis during stellar evolution. Fig 1-1 shows the relative abundances of the
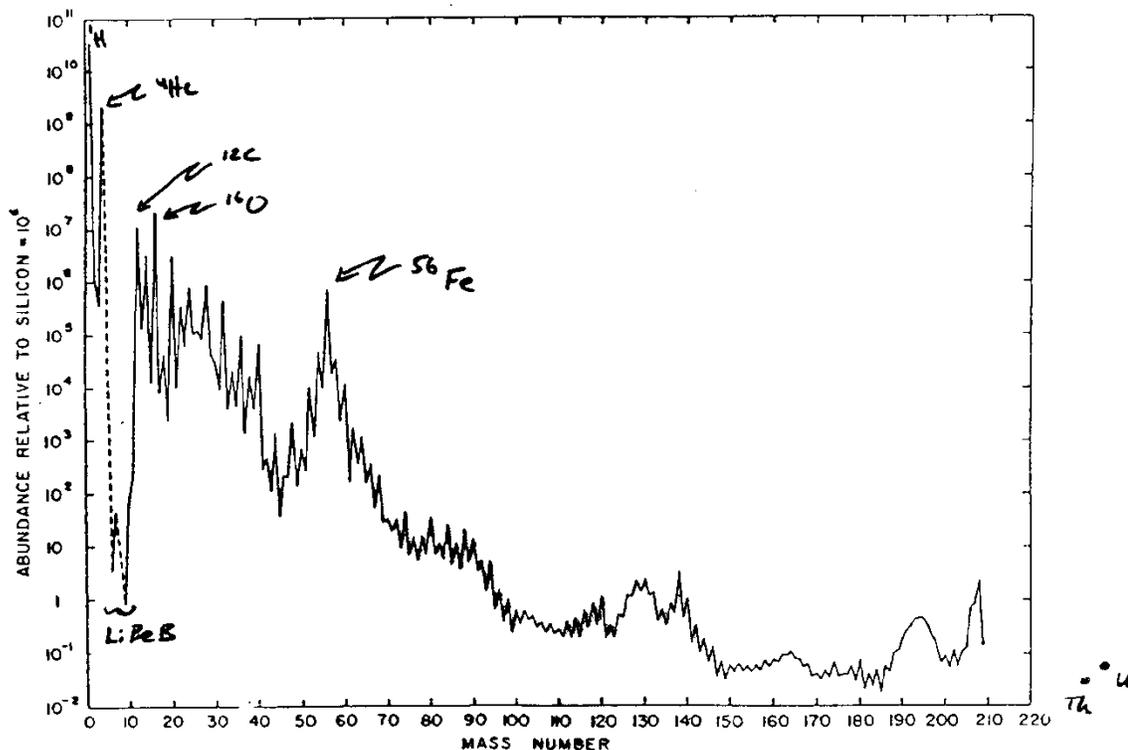
Fig. 1-1 Solar system abundances as a function of mass

elements in our solar system. One observes that the lightest elements are most abundant (our Sun is mostly hydrogen and helium) and as the elements become heavier, the abundances decrease. However, there is considerable structure in this plot, e.g. peaks and valleys and odd-even effects. All of these features can be traced to nuclear structure and reactions, which will be made more apparent as this course progresses.

In this course several relevant questions will be addressed. We know that at the heart of every atom there is a dense, positively-charged nucleus.

- How did our current picture of the atom and its nucleus emerge?
- What is the nature of radioactivity?
- What is the structure of the nucleus?
- How do nuclei react with one another?

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- Where did the nuclei come from?
- What are the biological effects of radiation?
- What are the pros and cons of nuclear power?

These are some of the subjects that will be covered in this course.

Nuclear Chemistry today is active as a basic science, an analytical tool and the basis for numerous applications in the field of medicine (e.g. MRI and PET scans, radiation therapy, etc.). Fig. 1-2 illustrates the use of radioactive ^{14}C to investigate atmospheric chemistry.

NEWS OF THE WEEK

ATMOSPHERIC CHEMISTRY

FINDING HYDROXYL

Radioactive carbon monoxide is used to trace key atmospheric "cleanser"

EXPANDING ITS ROLE BEyond dating ancient objects, carbon-14 is proving be a powerful tracer of the hydroxyl radical, a difficult-to-measure but all-important atmospheric cleanser that oxidizes greenhouse gases such as methane and pollutants such as carbon monoxide.

Until now, scientists have inferred atmospheric levels of the radical, which has a lifetime of one second, largely by measuring concentrations of methyl chloroform, a man-made molecule that reacts almost exclusively with OH. Nobel Laureate F. Sherwood Rowland, chemistry professor at the University of California, Irvine, introduced the method in the early 1980s. But methyl chloroform, an ozone-depleting compound, has been banned, and its concentrations in the atmosphere are dwindling.

The new study by Martin R. Manning, a director of the United Nations Intergovernmental Panel on Climate Change support unit at the National Oceanic & Atmospheric Administration in Boulder, Colo., and colleagues makes use of ^{14}CO, a rare atmospheric gas also oxidized by OH. Like methyl chloroform, CO levels presumably decrease when there's more OH around.

CO lasts only a few months before it's oxidized, compared with the over-five-year lifetime of methyl chloroform. That means that with CO, researchers can observe short-term fluctuations in OH, such as those caused by major atmospheric events like the eruption of Mount Pinatubo in 1991. But unlike ^{12}CO, which has innumerable sources and sinks, both natural and man-made, ^{14}CO has the benefit of being largely produced during a cascade of reactions initiated by cosmic rays.

Manning's group collected an enormous trove of ^{14}CO measurements, spanning 13 years, from the Southern Hemisphere, in Baring Head, New Zealand, and in Antarctica (*Nature* 2005, *436*, 1001). Overall, they find, there's been no large rise or drop in atmospheric OH.

The researchers can infer fluctuations in OH levels lasting a period of a few months, however. The Pinatubo eruption, as well as a rash of forest fires in Indonesia in 1997, led to OH declines as large as 20%, they report. Their findings are similar to OH levels inferred from methyl chloroform measurements reported by atmospheric chemistry professor Ronald G. Prinn at Massachusetts Institute of Technology and colleagues (*Geophys. Res. Lett.* 2005, *32*, 07809).

"This is a very interesting measurement" that Manning's group has produced, Rowland says.

"^{14}CO should become the principal diagnostic tool for monitoring the oxidative capacity of the atmosphere," say Patrick Jöckel and Carl A. M. Brenninkmeijer of Max Planck Institute for Chemistry in Mainz, Germany, in a commentary accompanying the *Nature* report. "This tracer is a cosmic dowry for atmospheric chemists."
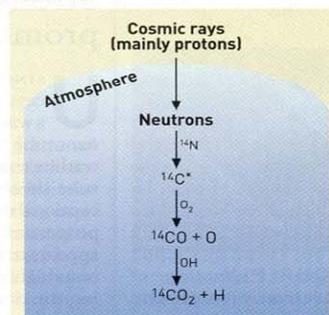
Manning says a confluence of technological and modeling advances made the work possible—most notably, the capability to accurately determine how much ^{14}CO is produced in the atmosphere. Protons in cosmic rays hitting Earth's atmosphere produce neutrons, which react with ^{14}N nuclei to produce excited ^{14}C, which quickly reacts with O_2 to form ^{14}CO. Complicating matters is the 11-year cycle of solar activity that affects cosmic radiation. The amounts of ^{14}CO produced are also extremely small—only about 10 atoms per cm^3—requiring sensitive detector technology.

Jos Lelieveld, director of the atmospheric chemistry department at Max Planck Institute for Chemistry, who also calls the work "very interesting," and Rowland both note that further measurements and modeling will be needed to nail down the inherent complexity and uncertainty of atmospheric OH.—ELIZABETH WILSON

SCENIC SCIENCE
Manning's group makes ^{14}CO measurements at the atmospheric observation station at Baring Head in New Zealand.

NATIONAL INSTITUTE OF WATER & ATMOSPHERIC RESEARCH PHOTO

Cosmic rays (mainly protons)

Atmosphere

Neutrons

^{14}N

$^{14}C^*$

| O_2

$^{14}CO + O$

| OH

$^{14}CO_2 + H$

BIRTH OF A TRACER
Cosmic rays initiate a reaction cascade that produces ^{14}CO. Atmospheric OH, which reacts with ^{14}CO, can be tracked by measuring ^{14}CO levels.

Fig. 1-2

This just one simple example of how radioactivity plays a role in multiple sciences.

Nuclear science traces its roots to Henri Becquerel's discovery in 1896 of highly penetrating radiation emitted by uranium salts (see Appendix 1-1). In 1898 Marie and Pierre Curie concluded

that the radiation Becquerel had observed was a property of the uranium atom, independent of the chemical or physical state of the compound. They coined the term 'radioactivity' to describe this phenomenon. Stimulated by these unexpected results, the next decade was one of intense investigation of uranium radioactivity. Previously, it had been believed that elements were not transmutable. However, several new elements were found that turned out to be directly related to uranium decay. These investigations involved painstaking chemical separations procedures, most notable of which was Marie Curie's isolation of 0.1 grams of radium (element 88) from several tons of uranium ore, a remarkable piece of separations chemistry. Much of this early work demanded chemical techniques, which portended a long collaboration between chemists and physicists in the investigation of the atomic nucleus. The term 'Radiochemistry' emerged and served as the forerunner of the broader field of Nuclear Chemistry that evolved in the 1940s.

Once the existence of radioactivity was established, the next step was to identify the particles that were emitted by uranium and its daughter nuclei. Based upon the ability of energetic radiation to ionize air (as measured by an electroscope/electrometer) and the attenuating effects of various metals, J.J. Thomson concluded there were three types of particles, named by Ernest Rutherford as:
- Alpha rays (α) : stopped by a thin sheet of aluminum foil,
- Beta rays (β): requiring 100 times thicker foils to be stopped, and
- Gamma rays (γ): could not be stopped, only attenuated in intensity.

Deflection in electric and magnetic fields permitted determination of the charge and charge/mass ratio, leading to the identification of each type of ray summarized in Fig. 1-3. Details of Thomson's apparatus and the associated physics concepts are described in Appendix 1-2.

Particle	Charge	Mass (rest)	Comment	
β	e= chg. On electron	9.1091×10^{-28}g	Same as electron	
α	-2e	Same as He^{2+}	Same as He^{+2}	
γ	0	0		

Fig. 1-3 Table of particles: $\beta = e$; $\alpha = He^{+2}$; $\gamma =$ energetic photon

Studies of the residues of uranium decay (elements 84-91) revealed that these elements were much more kinetically unstable than their parent. Radioactive decay was observed to follow a first-order decay law; i.e. if N is the number of nuclei and t the time, the following mathematics describe the decay of the system:

$$\frac{dN}{dt} = -\lambda N \qquad \text{from observation; } \lambda \text{ is a constant known as the } \textbf{decay constant.}$$

$$\frac{dN}{N} = -\lambda dt$$

$$\int \frac{dN}{N} = \int -\lambda dt$$

$$\ln(N) = -\lambda t + a \text{ ; a is a constant of integration}$$

When t=0, we have N_0 initial # of nuclei of the radioactive substance. Therefore we get,

$$\ln\left(\frac{N}{N_0}\right) = -\lambda t$$

$$N(t) = N_0 e^{-\lambda t}$$

Let $t_{1/2}$ be the time it takes for N_0 nuclei to decay into $N_0/2$ nuclei.

$$\ln\left(\frac{N_0/2}{N_0}\right) = -\lambda t_{1/2} \qquad \text{so} \qquad \ln(1/2) = -\lambda t_{1/2} \qquad \text{or} \qquad t_{1/2} = \frac{\ln(2)}{\lambda} = \frac{0.69315}{\lambda}$$

Half-lives are a characteristic of a particular decay. For example,
^{40}K undergoes β decay with a half-life of 1.27 x 10^9 years to transform itself into ^{40}Ca

Note: if N is replaced by concentration [ ] and λ by k, the above expressions are identical to the standard notation in chemical kinetics for a first-order reaction.

Despite the rapid advances in the understanding of radioactivity in the early 1900s, the structure of the atom remained unclear. Thomson proposed a 'plum pudding' model in which protons and electrons were randomly distributed throughout the volume of the atom (radius ~ 10^{-8} cm). This schematic model is shown in Fig.1-4.

Thomson
model of the
atom

Geiger and Marsden (Phil. Mag. 25, 605 (1913)) scattered α particles off different foils.

Pt "Reflector"

RaC source

ZnS screen

Microscope

See also: http://dbhs.wvusd.k12.ca.us/webdocs/Chem-History/GeigerMarsden-1913/GeigerMarsden-1913.html

Fig. 1-4

To test this hypothesis, in 1909 Hans Geiger and Ernest Marsden performed a scattering experiment in which positively-charged alpha particles from a radioactive source were scattered off thin metallic foils, also shown in Fig. 1-4. About 1 in 8000 alpha particles were surprisingly scattered to very large angles, a result that could
only be explained by assuming the positive charge in the atom was concentrated in a dense, compact object of dimension ~10^{-12} cm in the core of the atom, i.e. the nucleus. Based on Coulomb's Law, Rutherford accounted for the scattering results in terms of Coulomb's Law, as described in Appendix 1-3. Thus, the concept of the nuclear atom, surrounded by a sea of orbiting electrons, began to take hold.

In 1918 Rutherford demonstrated that the transmutation of one element into another could be induced by nuclear reactions as well as by spontaneous decay. Later experiments led him to conclude that there was more to the atom than just protons and electrons; i.e. there appeared to be a neutral particle with mass similar to the proton that was emitted in some reactions. In 1932 James Chadwick identified this particle, the neutron. With this new particle available to induce nuclear reactions, scientists were afforded a new dimension for the study of nuclear reactions. Most spectacular was the discovery of nuclear fission in 1938 by chemist Otto Hahn and physicist Fritz Strassman, an event that subsequently spawned the atomic age and Nuclear Chemistry as a broad-based interdisciplinary science.

In this course we will first focus on the basic aspects of nuclear behavior – radioactive decay, nuclear reactions and nuclear structure, all of which have direct analogies in the chemistry curriculum. The basic notation that will be used to describe nuclei is as follows:

A **nucleus** (or **nuclide**) is any combination of neutrons and protons and is written as

$$^{A}_{Z}X_{N} \quad , \text{where}$$

- **Z** is the **atomic number**, the number of protons in the nucleus of element X,
- **N** is the **neutron number**, the number of neutrons in the nucleus, and
- **A** = Z + N is the **mass number**, the total number of neutrons and protons (or nucleons) in the nucleus.

Note: *the mass number A is a dimensionless integer and is NOT the same as the mass of the nucleus.* Thus the charge on the nucleus is +Z and a neutral atom has Z negative electrons. The upper right-hand space above the element symbol is the atomic charge,

Z protons – number of electrons,

not shown when the value is zero.

The above nomenclature gives rise to the following common definitions:
- Isotopes: nuclei with constant Z ($^{12}C_6$, $^{13}C_7$, $^{14}C_8$),
- Isotones: nuclei with constant N ($^{11}B_6$, $^{12}C_6$, $^{13}N_6$),
- Isobars: nuclei with constant A (^{14}C, ^{14}N, ^{14}O).

In addition, every science has its standard units. In Table 1-2 the most commonly used units and symbols that will often appear in this course.

1. Time: s – seconds

2. Energy: E – electron Volt
   $1\ MeV = 1.6 \times 10^{-6}\ ergs = 3.8 \times 10^{-14}\ cal = 11.6 \times 10^{9}\ °K$

3. Mass: $M – u$ – atomic mass unit
   $1\ u = 1.6705655 \times 10^{-24}\ g$

4. Length: r, d, R
   $$\frac{1\ fm = 10^{-13}\ cm}{Fermi} = \frac{10^{-15}\ m}{femtometer}$$

5. Electric charge – e
   $e = 0, \pm 1, \pm 2...$ integral

6. Angular Momentum – $\hbar$ (AM)
   s – intrinsic spin
   1 = orbital
   I = total $= = \bar{s} + \bar{\ell}$
   $I\hbar = 0,\ 1/2,\ 1,\ 3/2,\ 2...\ n/2$

Table 1-2 Common units in nuclear chemistry

Appendix 1-1 Becquerel's Paper

We are constantly bombarded with radiation from above (Cosmic rays) and below (ores in the earth).

Let's begin with Henri Becquerel. About 1880 he prepared potassium uranyl sulfate: $K_2UO_2(SO_4)_2.2H_2O$
and experimented with it. He was exploring the phenomenon of *fluoresence*.

On Feb. 24, 1896 Henri Becquerel reported his first results. After exposure to bright sunlight, the crystals emitted a radiation that blackened a photographic plate after going through black paper, glass, and other substances. Subsequently he found the effect had nothing to do with the sunlight. Other uranous salts, solutions containing uranium, and even what was believed to be uranium metal all exhibited the same behavior. ["*Chance favors the prepared mind.*"- Louis Pasteur]

On the invisible rays emitted by phosphorescent bodies.
[read before the French Academy of Science 2 March 1896 (*Comptes Rendus* **122**, 501 (1896)) translated by Carmen Giunta]

In the previous session, I summarized the experiments which I had been led to make in order to detect the invisible rays emitted by certain phosphorescent bodies, rays which pass through various bodies that are opaque to light.

I was able to extend these observations, and although I intend to continue and to elaborate upon the study of these phenomena, their outcome leads me to announce as early as today the first results I obtained.

The experiments which I shall report were done with the rays emitted by crystalline crusts of the double sulfate of uranyl and potassium $[SO_4(UO)K+H_2O]$, a substance whose phosphorescence is very vivid and persists for less than 1/100th of a second. The characteristics of the luminous rays emitted by this material have been studied previously by my father, and in the meantime I have had occasion to point out some interesting peculiarities which these luminous rays manifest.

One can confirm very simply that the rays emitted by this substance, when it is exposed to sunlight or to diffuse daylight, pass through not only sheets of black paper but also various metals, for example a plate of aluminum and a thin sheet of copper. In particular, I performed the following experiment:

A Lumière plate with a silver bromide emulsion was enclosed in an opaque case of black cloth, bounded on one side by a plate of aluminum; if one exposed the case to full sunlight, even for a whole day, the photographic plate would not become clouded; but, if one came to attach a crust of the uranium salt to the exterior of the aluminum plate, which one could do, for example, by fastening it with strips of paper, one would recognize, after developing the photographic plate in the usual way, that the silhouette of the crystalline crust appears in black on the sensitive plate and that the silver salt facing the phosphorescent crust had been reduced. If the layer of aluminum is a bit thick, then the intensity of the effect is less than that through two sheets of black paper.

If one places between the crust of the uranium salt and the layer of aluminum or black paper a screen formed of a sheet of copper about 0.10 mm thick, in the form of a cross for example, then one sees in the image the silhouette of that cross, a bit fainter yet with a darkness indicative nonetheless that the rays passed through the sheet of copper. In another experiment, a thinner sheet of copper (0.04 mm) attenuated the active rays much less.

Phosphorescence induced no longer by the direct rays of the sun, but by solar radiation reflected in a metallic mirror of a heliostat, then refracted by a prism and a quartz lens, gave rise to the same phenomena.

I will insist particularly upon the following fact, which seems to me quite important and beyond the phenomena which one could expect to observe: The same crystalline crusts, arranged the same way with respect to the photographic plates, in the same conditions and through the same screens, but sheltered from the excitation of incident rays and kept in darkness, still produce the same photographic images. Here is how I was led to make this observation: among the preceding experiments, some had been prepared on Wednesday the 26th and Thursday the 27th of February, and since the sun was out only intermittently on these days, I kept the apparatuses prepared and returned the cases to the darkness of a bureau drawer, leaving in place the crusts of the uranium salt. Since the sun did not come out in the following days, I developed the photographic plates on the 1st of March, expecting to find the images very weak. Instead the silhouettes appeared with great intensity. I immediately thought that the action had to continue in darkness, and I arranged the following experiment

At the bottom of a box of opaque cardboard I placed a photographic plate; then, on the sensitive side I put a crust of the uranium salt, a convex crust which only touched the bromide emulsion at a few points; then, alongside, I placed on the same plate another crust of the same salt but separated from the bromide emulsion by a thin pane of glass; this operation was carried out in the darkroom, then the box was shut, then enclosed in another cardboard box, and finally put in a drawer.

I did the same with the case closed by a plate of aluminum in which I put a photographic plate and then on the outside a crust of the uranium salt. The whole was enclosed in an opaque box, and then in a drawer. After five hours, I developed the plates, and the silhouettes of the crystalline crusts appeared in black as in the previous experiments and as if they had been rendered phosphorescent by light. For the crust placed directly on the emulsion, there was scarcely a difference in effect between the points of contact and the parts of the crust which remained about a millimeter away from the emulsion; the difference can be attributed to the different distance from the source of the active rays. The effect from the crust placed on a pane of glass was very slightly attenuated, but the shape of the crust was very well reproduced. Finally, through the sheet of aluminum, the effect was considerably weaker, but nonetheless very clear.

It is important to observe that it appears this phenomenon must not be attributed to the luminous radiation emitted by phosphorescence, since at the end of 1/100th of a second this radiation becomes so weak that it is hardly perceptible any more.

One hypothesis which presents itself to the mind naturally enough would be to suppose that these rays, whose effects have a great similarity to the effects produced by the rays studied by M. Lenard and M. Röntgen, are invisible rays emitted by phosphorescence and persisting infinitely longer than the duration of the luminous rays emitted by these bodies. However, the present experiments, without being contrary to this hypothesis, do not warrant this conclusion. I hope that the experiments which I am pursuing at the moment will be able to bring some clarification to this new class of phenomena.

1898: Pierre and Marie Curie concluded that the uranium rays were an atomic phenomenon (due to the element uranium) and not its chemical or physical state. They introduced the term "radioactivity".

Appendix 1-2 Thompson's Apparatus for Distinguishing α, β and γ rays
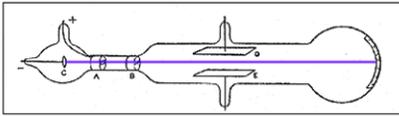
Schematic drawing of Thomson's apparatus in the second experiment. Rays from the cathode (C) pass through a slit in the anode (A) and through a slit in a grounded metal plug (B). An electrical voltage is established between aluminum plates (D and E), and a scale pasted on the outside of the end of the tube measures the deflection of the rays.

Cathode rays (electrons) could be bent by placing a voltage between the plates labeled D and E generating an electric field.

$$\vec{E} = \frac{V}{\vec{d}}$$

where V is the voltage and is the distance between the plates

Alternatively, the electrons can be deflected by a magnetic field. Key to making the experiments work was evacuating the gas in the tube as much as possible.

Appendix 1-3 Rutherford Scattering

Coulomb's Law, Rutherford scattering, and the model of the atom

Coulomb's Law :

$$V(r) = \frac{q_1 q_2}{r}$$

The potential energy, V, between two charges is proportional to the product of their charges (q_1 and q_2 respectively) and inversely proportional to the distance between them (r). Notice that opposite charges repel and opposite charges attract..

Notice the similarity and difference between Coulomb's Law and the equation for gravitational potential

$$V(r) = -G\frac{m_1 m_2}{r}$$

Force is the negative of the derivative of the potential with respect to position (r).

$$F = -\frac{dV}{dr}$$

Therefore the Coulomb interaction between two charges q1 and q2 is:

$$F(r) = \frac{q_1 q_2}{r^2}$$; notice that a positive force is repulsive and a negative force is attractive!

About 1 in 8000 incident alphas was scattered to a large angle and observed on the screen.

Conclusion: The experiments indicated that **the nucleus is a densely charged object**, otherwise these large deflections would not be possible.

$$n(\phi) = n_0 \frac{Nt}{16r^2}\left(\frac{Ze.Z_\alpha e}{\frac{1}{2}M_\alpha V_\alpha^2}\right)\frac{1}{\sin^4(\frac{\phi}{2})}$$

$n(\phi)$ = number of alpha particles falling on a unit area at a distance r from the scattering point to the scattering angle ϕ.
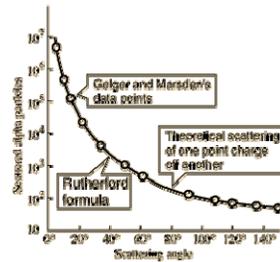n_0 = number of incident alpha particles
t = thickness of the scatterer
N = number of nuclei per unit volume scatterer
M_α = mass of the alpha particle
V_α = initial velocity of the alpha particle
$Z_\alpha e$ = charge of the alpha particle
Ze = charge of the scatterer

What's happening physically?