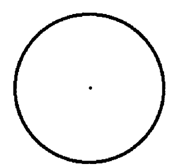
Chapter 66 NUCLEAR CHEMISTRY, Part 1

Now we start a very different path.

Way back in Section 2.1, we set up the basics for the atom and the basics for our primary focus since then.

> “ Chemical units begin with atoms. Every atom is made of "subatomic particles", which include protons, neutrons and electrons. (Some of these can be broken down further and there are other subatomic particles, but we won't go there.) Matter is composed of protons, neutrons and electrons but <u>it is the different numbers of these which give us different atoms</u>. Here are nine basics for atoms which you need for right now. Know these.
>
> 1. Protons (symbol, p^+) have a 1+ charge.
> 2. Electrons (symbol, e^-) have a 1− charge.
> 3. Neutrons (symbol, n^0) have no charge.
> 4. The size of one single proton or one single neutron or one single electron is incomprehensibly tiny.
> 5. At the center of the atom lie all of the atom's protons and neutrons. Together, these make up the nucleus. Since all protons and neutrons are incomprehensibly tiny, the nucleus is also incomprehensibly tiny. Too small to even worry about for our purposes.
> 6. Protons and neutrons have very similar masses. They're not quite exactly the same, but close enough: a neutron is 1.0014 times heavier than a proton. Compared to one proton or one neutron, one electron has very little mass. In fact, the mass of a neutron or proton is about 1800-times the mass of an electron. An electron's mass is at most 0.05% of a whole atom's mass. (Values for the masses are in Section 2.3.)
> 7. IMPORTANT RESULT FOR MASS: The mass of an atom is almost entirely (99.95% or more) in the nucleus with the protons and neutrons.
> 8. The electrons are widely spread out in a volume surrounding the nucleus. This volume is actually very large (by many thousands of times) when compared to the size of the nucleus. Although this volume is large compared to the nucleus, "large" to an atom is still very small compared to anything we can normally see.
> 9. IMPORTANT RESULT FOR SIZE: The size of the atom is almost entirely determined (~99.99%) by the volume in space which is occupied by the electrons.
>
> Your basic picture of an atom is shown at right. OK, the drawing is flat and that's not right: atoms are really three-dimensional, so an atom is more like a ball and not like a circle. The tiny dot in the middle represents the nucleus. The big circle represents the volume occupied by the electrons. Notice that I keep saying "volume occupied by the electrons", but it's not so simple. There's a lot more to that and we will get into that beginning in Chapter 20. For now we'll stick with the simple picture.
>
> 
>
> Everything about an atom is infinitesimally tiny. The masses of individual atoms start at 0.000000000000000000000002 grams. The sizes of atoms are on the order of 0.0000000001 meters. These are incredibly small numbers. ”

Then,

> “ For the most part, CHEMISTRY INVOLVES ELECTRONS. Not protons. Not neutrons. (Unless you're nuking things.) ELECTRONS DO CHEMISTRY! This will be a recurring theme throughout the entire course. This makes electrons a primary focus in our coverage... ”

Ever since then, it has indeed been mostly about electrons. But now we change that. Now we consider nuclear aspects.

66.1 Some preliminaries

The chemistry of the nucleus is vastly different from the more usual chemistry due to electrons. The approach is also somewhat different. Although there will be a few parallels to make, I want to highlight some of the differences and bring in some new terminology at this time.

A nuclear process involves a change among the protons and neutrons within the nucleus, either in their numbers or in the way they are arranged. An individual proton or an individual neutron can convert into something else or one can be formed from something else. These conversions are possible because protons and neutrons are themselves composed of even smaller particles, called quarks. As noted and quoted above from Chapter 2, there are yet other subatomic particles; these add quite a bit of flavor and color to the overall picture but those details are more in the domain of nuclear physics. We will not be dealing with the many quirks of the many quarks, nor of the antiquirks of the antiquarks, although we will deal with a few things as we go.

By the way, although protons and neutrons are composed of smaller particles, electrons are not. They are fundamental particles and not further divisible.

Recall that the number of protons in the nucleus is the atomic number, *Z*, and this gives element identity (Section 2.2). Since we will now be changing the number of protons, we will also change *Z* and we will also change the identity of the element involved. This is totally different from all chemistry which we have covered to date; nothing we have done so far has changed an element's identity. Furthermore, we may also be changing the number of neutrons in the nucleus of an atom. Recall that the sum of the numbers of protons and neutrons is the mass number, *A*, and that gives isotope identity for a given element (Section 2.2).

It might be useful to look over Sections 2.1 and 2.2 as a refresher. Section 2.3 will also be important for u later.

Besides *Z* and *A*, we now add *N*. *N* is the number of neutrons in a nucleus. All of these are very important characteristics of a nucleus; they are related by the mass number relationship.

$$A = Z + N$$

We use these symbols quite a bit, so you need to get them down.

IMPORTANT POINT: Nuclear processes will depend on a specific isotope. Different isotopes of the same element will give different outcomes. This is very different from the usual chemical reactions whereby different isotopes usually don't matter for a particular element.

Here's a new term: "nucleon". A nucleon is a nuclear particle, either a proton or a neutron. We can now say that mass number, *A*, is the sum of the nucleons which are present. Here's another new term: "nuclide". A nuclide is an atom whose nucleus has a specific number of protons and a specific number of neutrons, and which is in a specific energy state. Later in the Chapter we'll cover some of the energy state business, but we don't really need it right now. Until we do, a nuclide has a specific number of protons and a specific number of neutrons in its nucleus. The term isotope is somewhat related, but isotopes are specifically atoms of the same element with a different *N* (and therefore a different *A*). Here's an example of the distinction between nuclides and isotopes. Of the following four,

$$^{14}N \qquad ^{16}O \qquad ^{17}O \qquad ^{19}F$$

we can say that each is a different nuclide, while ^{16}O and ^{17}O are different isotopes. By the way, notice the notation from Section 2.2 which incorporates the mass number as a prior superscript. Also noted back then was an alternate version which included the atomic number as a prior subscript, such as $^{14}_{7}N$. Since nuclear processes depend on a specific isotope for a specific element, we will use both of these notations a lot!

A change in the number of protons or of neutrons in a nucleus can occur either as a result of a nuclear decay or a nuclear reaction.

Nuclear decay arises from within an unstable nuclide as a natural consequence of its own make-up. These nuclides can undergo a nuclear change on their own.

A nuclear reaction involves a nuclide reacting with some other reactant which originates from outside that atom; in other words, something else is shot into the nucleus from outside the atom. The other reactant can be another nuclide, a particle, or even a very high energy (gamma, γ) photon.

Gamma? Remember? Section 20.2:

> " ... gamma rays, γ, overlap and extend beyond X-rays, and γ is the strongest, most powerful, and deadliest of all EM radiation. You don't normally run into γ unless you're nuking things (starting in Chapter 66) or you're in outer space. The atmosphere pretty much protects surface-dwellers from the gamma rays which come from the sun or from other extra-terrestrial sources. "

Now, we're nuking things, and some nuclear changes involve γ.

Note the distinction in the above two nuclear processes: decay occurs on its own, completely within a single atom, while a reaction requires something from outside the atom. And note something else: in all prior coverage of chemical reactions, any chemical change was called a reaction. In the field of nuclear chemistry, however, a "decay" is not considered a "reaction", and these are separate categories. That distinction is a bit subtle, but keep it in mind.

As for many prior studies of chemical processes, we will also be discussing energies for nuclear processes. IMPORTANT POINT: Everything about nuclear change involves very large energies, and those energies can easily be millions of times greater than usual chemical energies. Instead of typical chemical reactions involving hundreds or thousands of kJ's, many nuclear processes will involve millions or billions of kJ's, even on a one-mole scale. The energies are simply outrageously high, and we will see more of this later.

The field of nuclear chemistry handles some symbols differently and balances equations differently. Charges for ions are commonly not shown; in fact, chemical identities themselves are commonly not shown. For balancing equations, as we have seen in the past over many Chapters, chemical equations require mass balance and charge balance. Mass balance was the same as atom balance, and you needed equal counts of the same atoms on the left and right sides of the equations. Charge balance was electron balance, and you needed equal numbers of total electrons on the left and right sides of the equations. Nuclear equations also require mass and charge balance, but the prior approaches won't work. We can't just balance atom counts anymore because the atoms themselves can change identity. We can't just balance charges anymore simply by counting electrons, because we may be changing identities of these or other particles which have charge . Instead, mass balance is handled by balancing the total numbers of nucleons on the left and right of the equation. Since the total number of nucleons is given by the mass numbers, A, then we simply balance mass numbers. Charge balance is handled by charge numbers, such as the atomic number, Z, for nuclei. In equations, mass numbers and charge numbers are given as prior superscripts and subscripts. Here's a preliminary example of these various aspects.

$$^{238}_{92}\text{U} \rightarrow {}^{234}_{90}\text{Th} + {}^{4}_{2}\text{He}$$

Mass numbers are given by the superscripts; these must balance to the same total on both sides.

Superscript mass numbers: 238 = 234 + 4

Charge numbers are subscripts; these must also balance.

Subscript charge numbers: 92 = 90 + 2

That's all there is to balance! But what about chemical identities? The chemical identities are not directly indicated. The uranium could be a metal elemental form, or it could be in UO_2 or it could be in UF_6 or it could be in any chemical form whatsoever. Likewise for the thorium: it could be a metal elemental form or it could be in some compound. The He part is a specific form, which I will explain in the next Section; in fact, it is an ion, $^4He^{2+}$. The balanced nuclear equations show the important details of the nuclear process, regardless of chemical identities. Besides, chemical identities don't even matter much! Since the energies of nuclear processes are millions of times greater than chemical energies, then whether the reactant is U(s) or UO_2(s) has a negligible effect on the nuclear change. Nevertheless, chemical identity can still be deduced; for example, if we start with U as metal, then formation of the He^{2+} cation requires formation of a Th anion with 2− chemical charge.

$$\text{U} \rightarrow \text{Th}^{2-} + \text{He}^{2+}$$

But, again, nuclear equations are primarily concerned with the nuclear change, and the prior equation

$$^{238}_{92}\text{U} \rightarrow {}^{234}_{90}\text{Th} + {}^{4}_{2}\text{He}$$

provides the necessary information. It is true that a chemical change can follow the nuclear change due to the energies and charges involved, but that is a separate step. For example, the He^{2+} in this process would come flying out with a very large energy, wreaking havoc in its immediate surroundings; eventually, it will chemically oxidize something to form neutral He. That is not part of the nuclear change and it is not included in the nuclear equation.

Although this example equation only deals with nuclei, other equations may include separate, individual particles such as individual protons, neutrons and electrons. These are represented in equations as follows.

A proton is a single nucleon (mass number = 1) and it carries a 1+ charge (charge number = 1). Informally, we can write this as p^+ but in an equation we write this as $^1_1$p.

A neutron is a single nucleon (mass number = 1) and it carries no charge (charge number = 0). Informally, we can write this as n^0 but in an equation we write this as ${}^{1}_{0}n$.

An electron is NOT a nucleon (mass number = 0) and it carries a 1− charge (charge number = −1). Informally, we can write this as e^- but in an equation we write this as ${}^{0}_{-1}e$.

That's enough for now. We'll do more with balancing equations as we go.

One final point before we get into actual nuclear processes: discussions in nuclear chemistry typically deal with the individual atom scale instead of the mole scale. There is some parallel to our prior discussions of electronic structure (Chapters 20 and 21) which were also on the per-atom scale. Be aware of this scale as we continue.

66.2 Elements of decay

We start with radioactive decay.

An unstable nuclide ("radionuclide") is radioactive; it undergoes a nuclear decay of some sort by emitting some particle or photon, thereby producing a new nuclide. The starting nuclide undergoing decay is called the parent; the product nuclide is called the daughter. Decays, on average, can range from incredibly fast to incredibly slow, depending on the nuclide and the type of decay. The fast and slow aspects will lead into kinetics. Radioactive decay follows first order kinetics (as introduced in Chapter 49), and half-lives (Section 49.3), $t_{1/2}$, are a very important parameter. Although we had worked with time units of s, min and h back in Chapter 49, the kinetics of decay can get into billions of years; we will still work with units of s, min and h, but we'll also be adding d (day) and y (year). Half-lives themselves range from μs to 10^{20} y, and some even outside this. I'll show some half-lives shortly below with various examples of the various decay types, just to illustrate some of the values. We'll get more into kinetics in the next Chapter.

A nuclide is considered stable if it has never been experimentally proven to undergo a radioactive decay of any type. There are 254 stable nuclides, and all are found naturally on Earth. It is believed that some of the "stable" nuclides should be radioactive, but their decays have simply escaped observation. This is not necessarily a simple measurement to make, especially for really slow decays and/or decays which occur with very low energies. Every now and then, as methods get better, they do prove a "stable" nuclide does undergo decay. Once a nuclide is caught in the act of decaying, then that nuclide gets kicked off the stable list.

Most elements have one or more isotopes which are stable, and all elements have several or many isotopes which are unstable. Most unstable isotopes, by far, are not found naturally on Earth, but humans have made these by some nuclear process. All stable nuclides have a measurable natural abundance on Earth (although some are very small). Here are some examples and illustrations of stable/unstable and natural/unnatural isotopes for several elements.

Hydrogen has three natural isotopes.

	${}^{1}H$	${}^{2}H$	${}^{3}H$
Z	1	1	1
N	0	1	2
name	protium	deuterium	tritium

${}^{1}H$ and ${}^{2}H$ are stable; ${}^{3}H$ is unstable and radioactive. Notice in the chart a peculiarity for hydrogen: it's the only element with names for its natural isotopes. Although tritium is naturally present on Earth, it is only in scant, trace amounts and it does not have a significant natural percent abundance. When needed for human applications, it is made using nuclear reactions. In addition to the above isotopes, there are also the unnatural isotopes ${}^{4}H$, ${}^{5}H$, ${}^{6}H$ and ${}^{7}H$; they are all radioactive.

Carbon also has three natural isotopes.

	${}^{12}C$	${}^{13}C$	${}^{14}C$
Z	6	6	6
N	6	7	8

${}^{12}C$ and ${}^{13}C$ are stable, while ${}^{14}C$ is radioactive. ${}^{14}C$ is naturally present on Earth but again it does not have a significant percent abundance. There are 12 other isotopes of carbon, none of which are natural and all of which are radioactive.

Fluorine comes in only one isotope naturally, ^{19}F. 100% abundant, fully stable. There are 15 other isotopes known for F, all of which are unnatural and radioactive. Phosphorus is similar, naturally 100% ^{31}P, stable. There are 22 other isotopes of P, all radioactive.

There are no stable isotopes at all for the elements of high atomic number beginning with $Z = 83$, Bi. Bismuth has only one significant, natural isotope, ^{209}Bi, and it is radioactive. There are 31 other isotopes of Bi, all radioactive.

All isotopes of uranium are radioactive. Three do have a significant natural abundance: ^{234}U, ^{235}U and ^{238}U. There are 22 other isotopes, all radioactive.

OK, these are just some illustrations. Later, we'll discuss some of the reasons why some nuclides are stable while others are not, but right now we will get into the most common categories of decay. Historically, these categories were labeled by the first three Greek letters, α, β and γ, although β is further divided into three separate types.

• ALPHA DECAY

An α particle is composed of two protons and two neutrons; it has no electrons. In essence, it is a bare nucleus of ^4He. Since it is a nucleus only with no electrons, the chemical notation would be He^{2+} but, as explained above, the ion charge is typically left out of the nuclear symbol. The following are common ways of representing an alpha particle.

$$\alpha \qquad {}^4_2\alpha \qquad {}^4_2\text{He}$$

Alpha decay involves the emission of an α particle from the nucleus. This is a very common type of radioactive decay for heavy nuclides. In essence, the nucleus spits out a chunk of four nucleons. An example is given by ^{238}U,

$$ {}^{238}_{92}\text{U} \rightarrow {}^{234}_{90}\text{Th} + {}^4_2\alpha \qquad t_{1/2} = 4.47 \times 10^9 \text{ y}$$

which is the same equation as mentioned in the last Section but now using the α symbol. For every α decay, the daughter has two fewer protons and two fewer neutrons than the parent, so *Z* and *N* decrease by two, while *A* decreases by four. Since *Z* decreases by two, you back up two squares in the Periodic Table to find the element which is formed. Here are two other examples; one saves lives

$$ {}^{241}_{95}\text{Am} \rightarrow {}^{237}_{93}\text{Np} + {}^4_2\alpha \qquad t_{1/2} = 432 \text{ y}$$

and another often kills, naturally.

$$ {}^{222}_{86}\text{Rn} \rightarrow {}^{218}_{84}\text{Po} + {}^4_2\alpha \qquad t_{1/2} = 3.82 \text{ d}$$

All of these equations are balanced. The sum of superscripts is the same left and right for each; the sum of subscripts is the same left and right for each. Here, do ^{209}Bi.

$$ {}^{209}_{83}\text{Bi} \rightarrow \underline{\qquad\qquad} + {}^4_2\alpha \qquad t_{1/2} = 1.9 \times 10^{19} \text{ y}$$

What's the missing superscript? 205. What's the missing subscript? 81. Write these in. The subscript is the atomic number, so find the symbol of that element in the Periodic Table and write that in. You're done.

By the way, α decay is overwhelmingly the largest source of He(*g*) on Earth. Although it is produced in the decay as the $^4He^{2+}$ ion, this ion is an extremely powerful oxidant, and it will eventually rip two electrons from just about anything to form neutral He. In the underground of your radioactive Earth, over billions of years and continuing today, the He from α decay has been collecting, trapped in rock, often as a component of natural gas from which it is eventually obtained. Although many people think that the helium in a balloon comes from the air, it doesn't. Helium comes from deep within the ground, initially formed from radioactive decay. There are ppm levels of He in the atmosphere, but that is not a practical source of the element.

• BETA DECAY

Beta decays are characterized as involving an electron or its antiparticle, but how that happens also involves the transformation of a proton into a neutron or the transformation of a neutron into a proton. This leads to a key distinction between α and β decays. α decay is the ejection of two protons and two neutrons which pre-existed in the nucleus; no protons or neutrons were formed or destroyed in the process. On the other hand, β decay does convert between a proton and a neutron. There are three types of beta decay.

1. β^- EMISSION. The β^- part is specifically pronounced as "beta negative" in order to distinguish it from the general category of all betas. (It also goes by the name of "negatron" which avoids any mention of beta. We will stay with beta negative, but you can find negatron in other sources.) The β^- particle is an electron, and one of very high energy. It is NOT one of the orbital electrons in the atom; it originates within the nucleus from the transformation of a neutron into a proton and an electron.

$$^{1}_{0}n \rightarrow {}^{1}_{1}p + {}^{0}_{-1}\beta$$

The proton remains behind in the nucleus. The electron has so much energy that the atom can't hold onto it, so it shoots completely out of the atom, still at high energy. The symbol ${}^{0}_{-1}\beta$ is used in equation format for β^-. Be careful with these symbols. Although it is an electron, it does not take the symbol ${}^{0}_{-1}e$ or e^- in an equation. The symbols ${}^{0}_{-1}e$ and e^- designate an orbital electron (the usual kind in an atom), while the symbols ${}^{0}_{-1}\beta$ or β^- designate an electron produced in and emitted from the nucleus. The latter are of much higher energy than an orbital electron, as a result of the nuclear process.

As an example, tritium undergoes β^- decay.

$$^{3}_{1}H \rightarrow {}^{3}_{2}He + {}^{0}_{-1}\beta \qquad t_{1/2} = 12.3 \text{ y}$$

In every β^- decay, the atomic number increases by one for the daughter, so you advance one square in the Periodic Table to arrive at that element. The mass number does not change. ^{14}C also does β^- decay

$$^{14}_{6}C \rightarrow {}^{14}_{7}N + {}^{0}_{-1}\beta \qquad t_{1/2} = 5.70 \times 10^3 \text{ y}$$

and, because of this reaction, you are constantly disintegrating. Again for balancing purposes, note that the sum of superscripts and the sum of subscripts are the same left and right. You can do ^{131}I.

$$^{131}_{53}I \rightarrow \underline{\qquad\qquad} + {}^{0}_{-1}\beta \qquad t_{1/2} = 8.02 \text{ d}$$

In medical practice, they use ^{131}I to kill peoples' thyroid glands, based on this decay.

2. β^+ EMISSION. β^+ is a positron. A positron is the antiparticle of an electron. An antiparticle is the antimatter of a normal particle. Particles and antiparticles are the same except for possessing opposite signs of some properties. The important one for now is charge: a positron is an electron-like particle but it has a positive charge. Same size, same mass, opposite charge.

β^+ is produced in a nucleus from the transformation of a proton into a neutron.

$$^{1}_{1}p \rightarrow {}^{1}_{0}n + {}^{0}_{1}\beta$$

The positron is emitted from the atom while the neutron stays behind in the nucleus. You don't normally encounter these, but you may have heard of PET scans used in medical diagnostics. PET stands for positron emission tomography; if you ever get a PET scan, they will nuke you by injecting you with a positron emitter. The most widely used nuclide in PET scans is ^{18}F.

$$^{18}_{9}F \rightarrow {}^{18}_{8}O + {}^{0}_{1}\beta \qquad t_{1/2} = 1.83 \text{ h}$$

In every β^+ decay, the atomic number decreases by one for the daughter, so you back up one square in the Periodic Table. The mass number does not change. ^{20}Mg also undergoes positron emission.

$$^{20}_{12}Mg \rightarrow {}^{20}_{11}Na + {}^{0}_{1}\beta \qquad t_{1/2} = 91 \text{ ms}$$

You can do the equation for ^{13}N, a nuclide which is sometimes used in PET scans.

$$^{13}_{7}N \rightarrow \underline{\qquad\qquad} + {}^{0}_{1}\beta \qquad t_{1/2} = 9.96 \text{ min}$$

3. ELECTRON CAPTURE (EC). OK, this one finally involves a normal, everyday chemistry electron. This electron comes from an orbital and, now, it gets absorbed by the nucleus. There, it combines with a proton to transform into a neutron.

$$^{1}_{1}p + {}^{0}_{-1}e \rightarrow {}^{1}_{0}n$$

As noted upstairs, an orbital electron is depicted by 'e' symbolism and not 'β'. The electron is a core electron (not valence), and the most common orbital to lose an electron to this fate is the 1*s* orbital. Recall that the 1*s* orbital is the smallest orbital and the one most concentrated at the nucleus, so they are the most vulnerable to be captured. Electrons from 2*s* and other orbitals are sometimes captured instead, but not as often. An example of EC is given by ^{195}Au.

$$^{195}_{79}Au + {}^{0}_{-1}e \rightarrow {}^{195}_{78}Pt \qquad t_{1/2} = 186 \text{ d}$$

Like positron decay, in every EC, the atomic number of the daughter element decreases by one, so you back up one square in the Periodic Table; also, the mass number does not change. Electron capture is the only type of decay for which two things are shown on the left side of the balanced equation; nevertheless, the nucleus and the electron are still from the same atom. Another example is given by ^{108}Sn.

$$^{108}_{50}\text{Sn} + {}^{0}_{-1}\text{e} \rightarrow {}^{108}_{49}\text{In} \qquad t_{1/2} = 10.3 \text{ min}$$

Your turn: ^{41}Ca.

$$^{41}_{20}\text{Ca} + {}^{0}_{-1}\text{e} \rightarrow \_\_\_\_\_\_ \qquad t_{1/2} = 1.02 \times 10^{5} \text{ y}$$

This ends our discussion of the common types of β decay. To summarize, all types of β decay produce a daughter with the same mass number as the parent. This much is easy to remember. The atomic number <u>increases</u> by one for β^- decay but <u>decreases</u> by one for β^+ decay and EC.

Before going to our final category of decay, I bring in a TECHNICAL POINT as an aside. It applies to all three types of β decay, but not to α decay.

As an illustration of other subatomic particles, I will make brief mention of neutrinos and their antiparticles, the antineutrinos. These are mysterious particles of negligible mass and which interact to an extremely minute extent with normal matter. They do not interact with EM radiation, so they cannot be observed directly by any of the standard tools covering any part of the EM spectrum. They exist in astronomical numbers throughout the Universe. Every β^+ decay and every EC produce one neutrino, and every β^- decay produces one antineutrino. These are also produced in nuclear reactions, including the nuclear reactions of the Sun and other stars. Given the nuclear fury and flurry of the Sun, Earth is constantly bombarded by these particles, to the extent of $\sim 10^{11}$ neutrinos per square centimeter per second. That's 100,000,000,000 PER SECOND passing through one cm^2. They are also passing through you. They are even passing through the entire volume of Earth. Out of the gajillions of such particles striking Earth each year, only several hundred can be detected. They mostly just go right through.

This TECHNICAL POINT is FYI. As I've said, there are other particles out there and some have strange properties, but we're not covering everything.

Resume.

• GAMMA DECAY

As noted and quoted above from Section 20.2, γ photons are the highest energy of the entire EM spectrum. The γ range overlaps a bit with the X-ray range but γ does extend beyond that. A photon of 10 pm wavelength could be a γ photon or an X-ray photon; it's the same photon regardless, but humans distinguish the two types by their origin: a γ photon originates from a nuclear process while an X-ray photon originates from an orbital electron process. The processes of concern here are relaxations. We did quite a bit with electron transitions in Chapters 20 and 21; commonly those involve UV or vis photons. Less commonly, an electron relaxation can emit an X-ray photon, but those cases typically involve an electron relaxing to 1*s* in an atom of high atomic number.

A nuclear relaxation has a lot of parallel to electron relaxations. The nucleus is also subject to the rules of the quantum realm. Although nuclear structure is very different from the arrangement of electrons in orbitals, there are still quantized energy levels for a nucleus and this gives rise to one ground state and many possible excited states. This is the reason the definition of nuclide includes a specific energy level: the ground state and each excited state of a nucleus constitute different nuclides. For atoms, molecules or ions in electron excited states, there are two general outcomes: they could undergo chemical change while in the excited state or they could relax to a lower energy state. Likewise, a nuclide in an excited state can undergo nuclear change (such as α or β decay) or it can relax to a lower energy state. The latter type is our focus here. Since everything about nuclear change involves very large energies, nuclear energy levels are spread out over a huge range. Thus, relaxations involve very high energy, resulting in the emission of a γ photon. Like electronic excited states, nuclear excited states can relax immediately or they can take their time. The ones which do not relax immediately are called metastable and get the symbol m with the mass number. For example, the excited state for ^{99}Tc is designated ^{99m}Tc.

$$^{99m}_{43}\text{Tc} \rightarrow {}^{99}_{43}\text{Tc} + \gamma \qquad t_{1/2} = 6.01 \text{ h}$$

Since γ is a photon, it does not get the mass number and charge number notation. The γ photon for this decay has a wavelength of 8.7 pm. There is no change in the number and type of nucleons here, so there's not much to balance for an equation. By the way, I mentioned PET scans used in medical diagnostics; γ-emitters are also used. In fact, ^{99m}Tc is the leading radioactive isotope used out of all diagnostic procedures in nuclear medicine. If you ever get one of these procedures, you will be nuked by having a compound of technetium injected into you.

For another example of γ decay, consider ^{69m}Zn.

$$^{69m}_{30}\text{Zn} \rightarrow\ ^{69}_{30}\text{Zn} + \gamma \qquad\qquad t_{1/2} = 13.8\text{ h}$$

Gamma emission is actually a common nuclear process, since many of the other decays and many nuclear reactions give products in excited states. These can then relax as a next step, shooting out γ.

This ends the various categories of decay for our coverage. I will also point out that many nuclides can decay by two or more routes, to different extents. For example, ^{177}Pt decays 94% of the time by EC and 6% of the time by α. Furthermore, many nuclides which can undergo β^+ decay can also decay by EC, and vice versa. Both types of decay give the same daughter, so it may not be obvious which is operating if only the parent and daughter are specified. Multiple decay routes are not unusual; be aware that this can happen.

Note in all types of decay above that there are three items in each equation; if given two, you should be able to deduce the third. Typically, you work with balancing the equation and that means you work with mass numbers and charge numbers. Don't forget that values for *Z* are connected to element symbols in the Periodic Table. You also need to remember the following designations.

$$^{4}_{2}\alpha \qquad ^{0}_{-1}\beta \qquad ^{0}_{1}\beta \qquad ^{0}_{-1}\text{e} \qquad \gamma$$

Of these, $^{0}_{-1}$e is the only one that goes on the left side of the equation. Here are some samples.

. . . .

Example

A. Write a balanced equation for electron capture by ^{177}Pt.
B. Write a balanced equation for alpha decay by ^{177}Pt.
C. Write a balanced equation for gamma decay by ^{79m}Br.
D. What nuclide undergoes positron emission to produce ^{11}B?
E. What process produces ^{110}Cd from ^{110}Ag?

. . . .

For each case, you work with the superscripts and the subscripts.

A. For EC, you need $^{0}_{-1}$e; it goes on the left side of the equation, along with the ^{177}Pt. From the Periodic Table, the atomic number of Pt is 78.

$$^{177}_{78}\text{Pt} +\ ^{0}_{-1}\text{e} \rightarrow$$

What's the sum of superscripts? 177. What's the sum of subscripts? 77.

$$^{177}_{78}\text{Pt} +\ ^{0}_{-1}\text{e} \rightarrow\ ^{177}_{77}$$

Now, who's #77? From the Periodic Table, it's Ir.

$$^{177}_{78}\text{Pt} +\ ^{0}_{-1}\text{e} \rightarrow\ ^{177}_{77}\text{Ir}$$

Done.

B. For α decay, use $^{4}_{2}\alpha$; it goes on the right side of the equation. ^{177}Pt is by itself on the left.

$$^{177}_{78}\text{Pt} \rightarrow\ ^{4}_{2}\alpha +$$

Fix the sums for your supers and subs, left and right.

$$^{177}_{78}\text{Pt} \rightarrow\ ^{4}_{2}\alpha +\ ^{173}_{76}$$

Who's #76?

$$^{177}_{78}\text{Pt} \rightarrow\ ^{4}_{2}\alpha +\ ^{173}_{76}\text{Os}$$

Next.

C. γ decays are easy to write.

$$^{79m}_{35}Br \rightarrow ^{79}_{35}Br + \gamma$$

That's all there is to do.

D. You want $^{0}_{1}\beta$ on the right side, along with the product ^{11}B.

$$\rightarrow ^{0}_{1}\beta + ^{11}_{5}B$$

Set the supers and subs equal, left and right.

$$^{11}_{6} \rightarrow ^{0}_{1}\beta + ^{11}_{5}B$$

Who's #6?

$$^{11}_{6}C \rightarrow ^{0}_{1}\beta + ^{11}_{5}B$$

^{11}C is your answer.

E. Now you're looking for the type of decay. Set up the given information.

$$^{110}_{47}Ag \rightarrow ^{110}_{48}Cd$$

Right away, it's not γ decay because γ does not change element identity. The superscripts are already equal on both sides, so you'll need a zero superscript on the missing item. That eliminates α and we're down to one of the betas, either $^{0}_{-1}e$ on the left or $^{0}_{-1}\beta$ or $^{0}_{1}\beta$ on the right. The only one which balances the subscripts is $^{0}_{-1}\beta$.

$$^{110}_{47}Ag \rightarrow ^{110}_{48}Cd + ^{0}_{-1}\beta$$

Thus, the process is beta negative decay.

66.3 Generations of daughters

Oftentimes, the daughter of an α or β decay is also radioactive. Eventually, it, too, will do its nuke thing. Perhaps that next product might also be radioactive and undergo another α or β step. These steps can go on and on, but eventually the sequence will hit a step which gives a stable product. The sequence of multiple decay steps is called a decay series or a radioactive series or a decay chain or something like that. Hitting a stable product breaks the chain and stops the series for those atoms. Notice that γ decay does not count as a step in a decay series; each step considered for a chain involves a change in Z, element identity.

Although numerous decay chains are known, the most important ones are the natural ones on Earth which were operating when Earth was formed 4.5 billion years ago and which still continue today. There are only three of these left to a reasonable extent, and these start from ^{232}Th, ^{235}U and ^{238}U. We will focus on the ^{238}U chain for illustration.

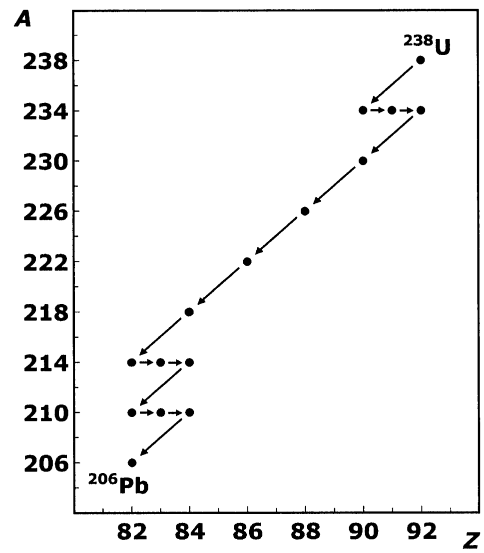
There are 14 steps in the ^{238}U series, eventually ending in ^{206}Pb as the ultimate daughter, which is a stable nuclide. The full equations are given below, with half-lives included. (The parent/daughter terminology is retained for individual steps in a chain. For example, ^{234}Th is the daughter in Step 1 but it is the parent in Step 2.) Although some nuclides along the way can decay by two routes, we will only consider the dominant (>99%) steps.

1.	$^{238}_{92}U \rightarrow ^{234}_{90}Th + ^{4}_{2}\alpha$	4.47×10^{9} y
2.	$^{234}_{90}Th \rightarrow ^{234}_{91}Pa + ^{0}_{-1}\beta$	24.1 d
3.	$^{234}_{91}Pa \rightarrow ^{234}_{92}U + ^{0}_{-1}\beta$	6.70 h
4.	$^{234}_{92}U \rightarrow ^{230}_{90}Th + ^{4}_{2}\alpha$	2.46×10^{5} y
5.	$^{230}_{90}Th \rightarrow ^{226}_{88}Ra + ^{4}_{2}\alpha$	7.54×10^{4} y
6.	$^{226}_{88}Ra \rightarrow ^{222}_{86}Rn + ^{4}_{2}\alpha$	1,600 y
7.	$^{222}_{86}Rn \rightarrow ^{218}_{84}Po + ^{4}_{2}\alpha$	3.82 d
8.	$^{218}_{84}Po \rightarrow ^{214}_{82}Pb + ^{4}_{2}\alpha$	3.10 min
9.	$^{214}_{82}Pb \rightarrow ^{214}_{83}Bi + ^{0}_{-1}\beta$	26.8 min
10.	$^{214}_{83}Bi \rightarrow ^{214}_{84}Po + ^{0}_{-1}\beta$	19.9 min
11.	$^{214}_{84}Po \rightarrow ^{210}_{82}Pb + ^{4}_{2}\alpha$	164 μs

12. $^{210}_{82}Pb \rightarrow ^{210}_{83}Bi + ^{0}_{-1}\beta$ 22.2 y

13. $^{210}_{83}Bi \rightarrow ^{210}_{84}Po + ^{0}_{-1}\beta$ 5.01 d

14. $^{210}_{84}Po \rightarrow ^{206}_{82}Pb + ^{4}_{2}\alpha$ 138 d



A graph is shown at right; mass number (*A*) is the vertical axis and atomic number (*Z*) is the horizontal axis. The mix of α and β^- decays provides a zigzag path for the steps; each diagonal arrow is for α while each short horizontal arrow is for β^-. All of these steps have been operating throughout the history of Earth. The half-life of ^{238}U is about the same as the age of the Earth; therefore, half of all ^{238}U originally present on Earth is still with us, still decaying. This ^{238}U is present in a variety of minerals scattered all over the planet. Some geographic locations will have higher or lower amounts of ^{238}U in the soil and rock than other locations. Regardless, all of these radioactive steps keep going on. Naturally. And as long as everything stays far enough underground, the radioactivity also stays underground. But there's one problem, and that's ^{222}Rn from Step 6.

Radon is a noble gas, in Group 18. The neutral atom has the very favorable noble gas configuration. Once a neutral atom of Rn is formed, it will not react chemically with surrounding rock and soil. It stays monatomic, gas phase. Since it does not bond to anything, it will migrate through the ground. The half-life of 3.82 days is long enough for the radon to get around to some extent. It could reach ground level and escape to the open air. Or, it can reach someone's basement foundation underground, and it can migrate into that basement through cracks. Now, that home has radioactive Rn. If you breathe in Rn and breathe out Rn, then no harm is done. Rn has no chemical hazard whatsoever because it doesn't react chemically. But if you breathe in Rn and it happens to decay (Step 7) while in your lungs, then you just took an α hit, and α packs the most wallop of any of the decay types, as to be seen in Section 68.3. Furthermore, it's not Rn anymore, it's Po. Polonium <u>is</u> chemically reactive; it will react with and bind to surrounding tissue. You are now subject to several more α decays and also β^- decays from subsequent steps. Even if the Rn decays outside of your lungs but in your home's air, then the Po which is formed will react with air molecules and/or bind to some dust particle floating by. You could later inhale that and be subject to further decays. Otherwise, the dust particle might just end up trapped in your furnace/AC filter. Should you be concerned by all this Rn? It depends.

On average, there are ~10^7 atoms of ^{222}Rn per m^3 in the air in a home in the United States. That's an extremely minute amount compared to the ~10^{28} molecules of air itself in that volume. But that amount of ^{222}Rn gives 48 decays per second. That comes to 4.1 million decays per day per m^3 in the air you breathe. That's ~9,000 decays per day inside an average adult lung. Some homes will have lower amounts of ^{222}Rn, some homes will higher amounts, and some homes will have much, much higher amounts. It depends on your geographic location, your soil structure, your home construction, and other factors. Natural Rn is actually a serious environmental issue in some areas. Notably, ^{222}Rn exposure is the second leading cause of lung cancer, second only to smoking. Fortunately, homes can be tested for Rn levels, and remediation methods are known, if needed.

OK, enough of the chain gang. So far, we've talked quite a bit about decay but not the reasons for it. The reasons for decay tie into why any particular nuclide is stable or radioactive. We now turn to some of these aspects.

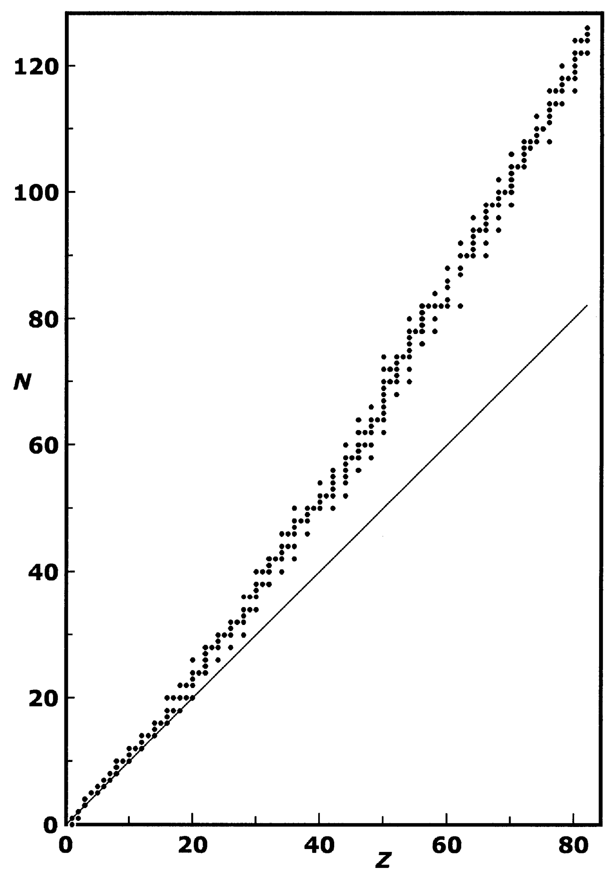
66.4 Nuclear structure and (in)stability

There are over 3,000 nuclides known, most of which, by far, are radioactive. Only 254 are stable. Why so few out of so many?

A nucleus is a mysterious place, and certainly not one which is completely understood. The quantum realm of the nucleus is far more complicated than the realm of electrons in orbitals. In a nucleus, you now have two different kinds of nucleons, one with a charge and one without, all in proximity, and shoved into some ridiculously tiny volume. The size of the nucleus is several fm in radius. The 'f' is for femto, which is the next smaller SI prefix after pico; f = 10^{-15}. One fm = 10^{-15} m and that is really small, even on the atomic scale. By comparison, sizes of unbonded atoms run up to 350 pm in radius; the size of an average atom is in the ballpark of 50,000 times the size of its nucleus. And again, protons and neutrons are themselves composed of quarks which are smaller still; three quarks make up every nucleon. So just what IS going on inside a nucleus?

There is one very obvious problem with this arrangement: every nucleus, except for those of the hydrogen isotopes, contains multiple protons whose positive charges are repelling each other and trying to blow each other out of the nucleus. Opposing that, however, are attractive forces which exist between all nucleons. This attractive force has nothing to do with +/− charge, and it instead relates to something called the "strong force", which is the strongest of all fundamental forces of Nature. The strong force holds quarks together within each nucleon, and "strong" is extremely strong. Not only does it hold the quarks together within a nucleon, but there is also a residual strength which extends beyond any one nucleon. That residual force is attractive to other nucleons, and this holds neighboring nucleons together inside a nucleus. This attraction acts between a proton and a neutron, between two neutrons, and even between two protons. That residual strong force can be ~100 times greater than the charge repulsion between protons, so this is enough to overcome the charge repulsion. BUT THERE'S A CATCH! The residual strong force can only operate between nucleons at extremely, extremely short range. On the other hand, charge repulsion operates over a longer range. Thus, the strong attraction operates between close neighbors within the nucleus but the total charge repulsion can be felt collectively over the whole nucleus. Overall then, there arises some balance of opposing forces. With the right balance, the nucleus is stable; otherwise, the nucleus is radioactive or even nonexistent.

This much is a large part of nuclear stability, but there are a number of other factors also. There is motion within a nucleus among the protons and neutrons. A nucleus has a shape; some are spherical but others are distorted from spherical. The protons and neutrons have their own, separate configurations, and there is a fill sequence for each. There are core and valence protons, and there are core and valence neutrons. Also for each, some configurations are better than others. There is a parallel here to electron configurations: for electrons, noble gas configurations are best, corresponding to 2, 10, 18, 36, 54 and 86 electrons. Protons and neutrons also have preferred numbers in a nucleus, and these are called magic numbers; the magic numbers for each type of nucleon are 2, 8, 20, 28, 50, 82 and 126. Nuclei which have one of these numbers for their protons or for their neutrons are more favored; it's even better if both the protons and the neutrons come in one of these numbers, and those cases are called doubly magic. For example, all oxygen isotopes have a magic number of protons, while ^{16}O is doubly magic. Also as in electron configurations, spin is an issue and so also is pairing. Even numbers allow for pairing; odd numbers do not. An even number of protons is good; an even number of neutrons is good; odd numbers are not so good. Notice that all of the magic numbers are even. These numbers only work for the separate proton and neutron count; odd or even for the sum (A) doesn't matter.



Again, there are yet other factors, but this is a sampling for illustration purposes.

In order to have two or more protons in one nucleus, there must be neutrons. The graph at right shows the number of neutrons versus the number of protons for all stable nuclei, shown by the dots. The diagonal line is for equal numbers, $N = Z$. ^{1}H is the only nuclide with no neutrons, but it doesn't need any because it has only one proton. For two or more protons, in all cases except one, every stable nucleus has at least one neutron for every proton. The one exception here is ^{3}He, which has only one neutron with its two protons. All other cases of stable nuclides have a neutron-to-proton ratio (N/Z) of one or more. This ratio can equal one for light elements but it increases for heavier elements. Thus, as the number of protons increases in a nucleus, an equal number of neutrons is no longer sufficient for stability. The dots show that outcome: as Z increases, a relatively greater number of neutrons is needed to be stable. By the time you hit 20 protons, it's already difficult to keep equal numbers of neutrons and protons, but ^{40}Ca (Z = 20) makes it with its double magic. (It's the last dot on the diagonal line.) Ironically, although neutrons can stabilize a nucleus, too many are bad news. This can even be seen in the hydrogen isotopes: ^{1}H and ^{2}H are stable but all the other isotopes are radioactive. Thus, there is some optimal number of neutrons for some given Z. The highest N/Z ratio for any stable nuclide is 1.55 for ^{204}Hg.

There comes a point when no amount of neutrons is enough. That point is Z = 83, bismuth. As noted previously, there are no stable isotopes for Bi, and there are no stable isotopes for anything of higher Z. Stability, and the dots in the graph, end at Pb, Z = 82 (magic number), whose dominant natural isotope is ^{208}Pb (doubly magic). But there are also two unstable quirks to be aware of before Z = 82. These are Tc (Z = 43), in the middle of the *d*-block of the Periodic Table, and promethium, Pm (Z = 61), down in the *f*-block; these have no stable isotopes whatsoever. (If you look closely, you can see there are no dots in the graph for Z = 43 or 61.) Why are these two such oddballs? There is no single, overwhelming factor which renders all isotopes of Tc and of Pm radioactive; instead, this outcome derives from the balance of several small contributions. Sometimes, that's all it takes.

Thus and overall, there are 80 elements with at least one stable isotope. Most elements have two or more stable isotopes, and tin (Z = 50, magic number) is the winner with ten stable isotopes. The overwhelming majority of stable nuclides have an even number of protons or an even number of neutrons or even numbers for both. Both is best, by far. Out of 254 stable nuclides,

147 have an even number of protons and an even number of neutrons;
54 have an even number of protons and an odd number of neutrons;
48 are vice versa with an odd number of protons and an even number of neutrons;
and, finally, only five nuclides are doubly odd: ^{2}H, ^{6}Li, ^{10}B, ^{14}N and ^{180m}Ta.

^{180m}Ta has the unique characteristic of being the only metastable nuclide which is considered stable. Ground state ^{180}Ta <u>is</u> radioactive, with a half-life of 8.15 h, but ^{180m}Ta has never been observed to decay. Someday this may be experimentally observed, and then ^{180m}Ta will get kicked off the stable list. But it hasn't happened yet.

While all of the above 254 are stable and are found naturally on Earth to a significant extent, there are only 34 radioactive nuclides which have a measurable and significant natural abundance on Earth. Examples include ^{40}K (0.0117%); ^{209}Bi (100%); ^{232}Th (100%); and all three natural U isotopes (^{234}U, 0.0054%; ^{235}U, 0.720%; ^{238}U, 99.27%). All of these have a reasonable abundance because they are very slow to decay. Beyond these, there are yet thousands of other radionuclides. In the graph above, these would be found above or below the stable dots, or out to the right, past Z = 82. Whether it is above, below or past the dots can give a clue as to how that radionuclide might decay.

For a radionuclide above the stable dots, the N/Z ratio is too large. Many of these decay by β^- emission, which decreases N by one and increases Z by one; thus, the N/Z ratio decreases.

Radionuclides below the stable dots in the graph have too small of an N/Z ratio. Many of these decay by β^+ emission and/or by EC, both of which increase N and decrease Z by one each; the N/Z ratio increases.

For heavier and heavier nuclei with more and more total nucleons, especially beyond Z = 82, α emission becomes the most important decay route, since that loses two of each nucleon at once (and it also increases the N/Z ratio when $N > Z$). Actually, other decay modes are known which spit out bigger chunks of nucleons than α, but α is by far the most common. (α, by itself, is also doubly magic.) In extreme cases, the parent nucleus will undergo fission, splitting up completely; we'll come back to this later in Chapter 69.

These are general clues for decays. There will be exceptions and, besides, many radionuclides have multiple decay routes.

These are some of the factors behind stability, radioactivity and types of decay. We will discuss some quantitative aspects of stability in Chapter 69. For now, however, we get quantitative with rates of decay. So far, I've made numerous mention of slow versus fast decays, and I've listed half-lives in the range of 164 μs to 10^{19}y. It's time to get more into the kinetics.

Problems

1. True or false.
   a. An atom of arsenic with 43 neutrons has a total of 76 nucleons.
   b. Positron emission produces a daughter with one less proton than the parent.
   c. All isotopes of astatine (At) are radioactive.
   d. All nuclei have at least one neutron for every proton.
   e. ^{38}Ar is doubly magic.

2. True or false.
   a. Deuterium is radioactive.
   b. Beta negative decay produces a daughter with one less proton than the parent.
   c. Too many neutrons can make a nucleus unstable.
   d. The ultimate daughter of a radioactive decay series is stable.
   e. Nuclei with an even atomic number and an even mass number are least favored for stability.

3. Write a balanced equation for each of the following.
   a. positron emission by ^{26}Si
   b. alpha emission by ^{212}Po
   c. electron capture by ^{67}Ga
   d. beta negative emission by ^{35}S
   e. gamma emission of ^{93m}Ru

4. a. What nuclide is produced in the α decay of ^{221}Ra?
   b. What nuclide is produced by EC in ^{119}Sb?
   c. What nuclide undergoes β^- decay to produce ^{209}Bi?
   d. What nuclide undergoes β^+ decay to produce ^{25}Mg?

5. Which type of decay applies to each of the following?
   a. decay of ^{62}Fe to ^{62}Co
   b. decay of ^{152}Tm to ^{148}Ho
   c. decay of ^{119}Xe to ^{119}I

6. Consider the radioactive decay series for ^{232}Th.
   a. The first four steps of the series involve α, β^-, β^-, α, in that order. What are the daughter nuclides of the first and the fourth step?
   b. The entire series involves a total of six α decays and four β^- decays. What is the ultimate daughter? (The order does not matter for this.)