UNIT-I (SEM- I)

Atoms are the basic particles of the chemical elements. An atom consists of a nucleus of protons and generally neutrons, surrounded by an electromagnetically bound swarm of electrons. The chemical elements are distinguished from each other by the number of protons that are in their atoms. For example, any atom that contains 11 protons is sodium, and any atom that contains 29 protons is copper. Atoms with the same number of protons but a different number of neutrons are called isotopes of the same element.

Atoms are extremely small, typically around 100 picometers across. A human hair is about a million carbon atoms wide. Atoms are smaller than the shortest wavelength of visible light, which means humans cannot see atoms with conventional microscopes. They are so small that accurately predicting their behavior using classical physics is not possible due to quantum effects.

More than 99.94% of an atom's mass is in the nucleus. Protons have a positive electric charge and neutrons have no charge, so the nucleus is positively charged. The electrons are negatively charged, and this opposing charge is what binds them to the nucleus. If the numbers of protons and electrons are equal, as they normally are, then the atom is electrically neutral as a whole. If an atom has more electrons than protons, then it has an overall negative charge, and is called a negative ion (or anion). Conversely, if it has more protons than electrons, it has a positive charge, and is called a positive ion (or cation).

The electrons of an atom are attracted to the protons in an atomic nucleus by the electromagnetic force. The protons and neutrons in the nucleus are attracted to each other by the nuclear force. This force is usually stronger than the electromagnetic force that repels the positively charged protons from one another. Under certain circumstances, the repelling electromagnetic force becomes stronger than the nuclear force. In this case, the nucleus splits and leaves behind different elements. This is a form of nuclear decay.

Atoms can attach to one or more other atoms by chemical bonds to form chemical compounds such as molecules or crystals. The ability of atoms to attach and detach from each other is responsible for most of the physical changes observed in nature. Chemistry is the science that studies these changes.

History of atomic theory

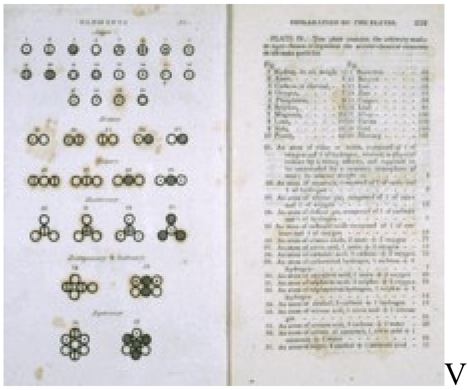
Main article: History of atomic theory

In philosophy

Main article: Atomism

The basic idea that matter is made up of tiny indivisible particles is an old idea that appeared in many ancient cultures. The word *atom* is derived from the ancient Greek word *atomos*,[a] which means "uncuttable". But this ancient idea was based in philosophical reasoning rather than scientific reasoning. Modern atomic theory is not based on these old concepts.[1][2] In the early 19th century, the scientist John Dalton (1766–1844) found evidence that matter really is composed of discrete units, and so applied the word *atom* to those units.[3]

Dalton's law of multiple proportions



Various atoms and molecules from *A New System of Chemical Philosophy* (John Dalton 1808).

In the early 1800s, John Dalton compiled experimental data gathered by him and other scientists and discovered a pattern now known as the "law of multiple proportions". He noticed that in any group of chemical compounds which all contain two particular chemical elements, the amount of Element A per measure of Element B will differ across these compounds by ratios of small whole numbers. This pattern suggested that each element combines with other elements in multiples of a basic unit of weight, with each element having a unit of unique weight. Dalton decided to call these units "atoms".[4]

For example, there are two types of tin oxide: one is a grey powder that is 88.1% tin and 11.9% oxygen, and the other is a white powder that is 78.7% tin and 21.3% oxygen. Adjusting these figures, in the grey powder there is about 13.5 g of oxygen for every 100 g of tin, and in the white powder there is about 27 g of oxygen for every 100 g of tin. 13.5 and 27 form a ratio of 1:2. Dalton concluded that in the grey oxide there is one atom of oxygen for every atom of tin, and in the white oxide there are two atoms of oxygen for every atom of tin (SnO and SnO_2).[5][6]

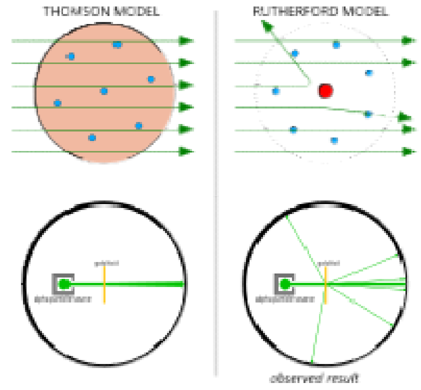
Dalton also analyzed iron oxides. There is one type of iron oxide that is a black powder which is 78.1% iron and 21.9% oxygen; and there is another iron oxide that is a red powder which is 70.4% iron and 29.6% oxygen. Adjusting these figures, in the black powder there is about 28 g of oxygen for every 100 g of iron, and in the red powder there is about 42 g of oxygen for every 100 g of iron. 28 and 42 form a ratio of 2:3. Dalton concluded that in these oxides, for every two atoms of iron, there are two or three atoms of oxygen respectively (Fe_2O_2 and Fe_2O_3).[b][7][8]

As a final example: nitrous oxide is 63.3% nitrogen and 36.7% oxygen, nitric oxide is 44.05% nitrogen and 55.95% oxygen, and nitrogen dioxide is 29.5% nitrogen and 70.5% oxygen. Adjusting these figures, in nitrous oxide there is 80 g of oxygen for every 140 g of nitrogen, in nitric oxide there is about 160 g of oxygen for every 140 g of nitrogen, and in nitrogen dioxide there is 320 g of oxygen for every 140 g of nitrogen. 80, 160, and 320 form a ratio of 1:2:4. The respective formulas for these oxides are N_2O, NO, and NO_2.[9][10]

Discovery of the electron

In 1897, J. J. Thomson discovered that cathode rays are not a form of light but made of negatively charged particles because they can be deflected by electric and magnetic fields.[11] He measured these particles to be at least a thousand times lighter than hydrogen (the lightest atom).[12] He called these new particles *corpuscles* but they were later renamed *electrons* since these are the particles that carry electricity.[13] Thomson also showed that electrons were identical to particles given off by photoelectric and radioactive materials.[14] Thomson explained that an electric current is the passing of electrons from one atom to the next, and when there was no current the electrons embedded themselves in the atoms. This in turn meant that atoms were not indivisible as scientists thought. The atom was composed of electrons whose negative charge was balanced out by some source of positive charge to create an electrically neutral atom. Ions, Thomson explained, must be atoms which have an excess or shortage of electrons.[15]

Discovery of the nucleus



The Rutherford scattering experiments:
Left: All the alpha particles should have passed the atom with negligible deflection.
Right: A small portion of the particles were heavily deflected by the concentrated charge of the nucleus.

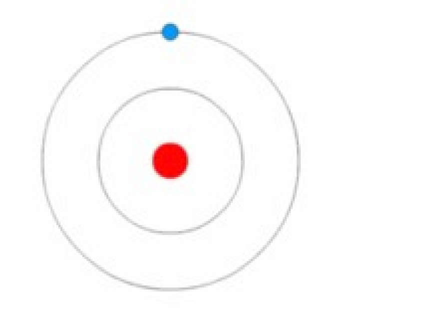
Main article: Rutherford scattering experiments

The electrons in the atom logically had to be balanced out by a commensurate amount of positive charge, but Thomson had no idea where this positive charge came from, so he tentatively proposed that this positive charge was everywhere in the atom, the atom being in the shape of a sphere. Following from this, he imagined the balance of electrostatic forces would distribute the electrons throughout the sphere in a more or less even manner.[16] Thomson's model is popularly known as the plum pudding model, though neither Thomson nor his colleagues used this analogy.[17] Thomson's model was incomplete, it was unable to predict any other properties of the elements such as emission spectra and valencies. It was soon rendered obsolete by the discovery of the atomic nucleus.

Between 1908 and 1913, Ernest Rutherford and his colleagues Hans Geiger and Ernest Marsden performed a series of experiments in which they bombarded thin foils of metal with a beam of alpha particles. They did this to measure the scattering patterns of the alpha particles. They spotted a small number of alpha particles being deflected by angles greater than 90°. This shouldn't have been possible according to the Thomson model of the atom, whose charges were too diffuse to produce a sufficiently strong electric field. The deflections should have all been negligible. Rutherford proposed that the positive charge of the atom along with most of the atom's mass is concentrated in a tiny nucleus at the center of the atom. Only such an intense concentration of positive charge, anchored by its high mass and separated from the negative charge, could produce an electric field that could deflect the alpha particles so strongly.[18]

Bohr model

Main article: Bohr model



The Bohr model of the atom, with an electron making instantaneous "quantum leaps" from one orbit to another with gain or loss of energy. This model of electrons in orbits is obsolete.

A problem in classical mechanics is that an accelerating charged particle radiates electromagnetic radiation, causing the particle to lose kinetic energy. Circular motion counts as acceleration, which means that an electron orbiting a central charge should spiral down into the nucleus as it loses speed. In 1913, the physicist Niels Bohr proposed a new model in which the electrons of an atom were assumed to orbit the nucleus but could only do so in a finite set of orbits, and could jump between these orbits only in discrete changes of energy corresponding to absorption or radiation of a photon.[19] This quantization was used to explain why the electrons' orbits are stable and why elements absorb and emit electromagnetic radiation in discrete spectra.[20] Bohr's model could only predict the emission spectra of hydrogen, not atoms with more than one electron.

Discovery of protons and neutrons

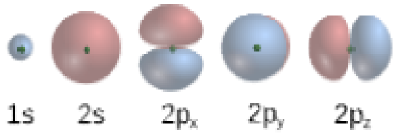
Main articles: Atomic nucleus and Discovery of the neutron

Back in 1815, William Prout observed that the atomic weights of many elements were multiples of hydrogen's atomic weight, which is in fact true for all of them if one takes isotopes into account. In 1898, J. J. Thomson found that the positive charge of a hydrogen ion is equal to the negative charge of an electron.[21] In 1913, Henry Moseley discovered that the frequencies of X-ray emissions from an excited atom were a mathematical function of its atomic number and hydrogen's nuclear charge. In 1917 Rutherford bombarded nitrogen gas with alpha particles and detected hydrogen ions being emitted from the gas, and concluded that they were produced by alpha particles hitting and splitting the nitrogen atoms.[22]

These observations led Rutherford to conclude that the hydrogen nucleus is a singular particle with a positive charge equal to the electron's negative charge.[23] He named this particle "proton" in 1920.[24] An element's atomic number, which is defined as the element's position on the periodic table, is also the number of protons it has in its nucleus. The atomic weight of each element is higher than its proton number, so Rutherford hypothesized that the surplus weight was carried by unknown particles with no electric charge and a mass equal to that of the proton.

In 1928, Walter Bothe observed that beryllium emitted a highly penetrating, electrically neutral radiation when bombarded with alpha particles. It was later discovered that this radiation could knock hydrogen atoms out of paraffin wax. Initially it was thought to be high-energy gamma radiation, since gamma radiation had a similar effect on electrons in metals, but James Chadwick found that the ionization effect was too strong for it to be due to electromagnetic radiation, so long as energy and momentum were conserved in the interaction. In 1932, Chadwick exposed various elements, such as hydrogen and nitrogen, to the mysterious "beryllium radiation", and by measuring the energies of the recoiling charged particles, he deduced that the radiation was actually composed of electrically neutral particles which could not be massless like the gamma ray, but instead were required to have a mass similar to that of a proton. Chadwick now claimed these particles as Rutherford's neutrons.[25]

The current consensus model



The modern model of atomic orbitals draws zones where an electron is most likely to be found at any moment.

In 1925, Werner Heisenberg published the first consistent mathematical formulation of quantum mechanics (matrix mechanics).[26] One year earlier, Louis de Broglie had proposed that all particles behave like waves to some extent,[27] and in 1926 Erwin Schroedinger used this idea to develop the Schroedinger equation, which describes electrons as three-dimensional waveforms rather than points in space.[28] A consequence of using waveforms to describe particles is that it is mathematically impossible to obtain precise values for both the position and momentum of a particle at a given point in time. This became known as the uncertainty principle, formulated by Werner Heisenberg in 1927.[26] In this concept, for a given accuracy in measuring a position one could only obtain a range of probable values for momentum, and vice versa.[29] Thus, the planetary model of the atom was discarded in favor of one that described atomic orbital zones around the nucleus where a given electron is most likely to be found.[30][31] This model was able to explain observations of atomic behavior that previous models could not, such as certain structural and spectral patterns of atoms larger than hydrogen.

Structure

Subatomic particles

Main article: Subatomic particle

Though the word *atom* originally denoted a particle that cannot be cut into smaller particles, in modern scientific usage the atom is composed of various subatomic particles. The constituent particles of an atom are the electron, the proton and the neutron.

The electron is the least massive of these particles by four orders of magnitude at 9.11×10^{-31} kg, with a negative electrical charge and a size that is too small to be measured using available techniques.[32] It was the lightest particle with a positive rest mass measured, until the discovery of neutrino mass. Under ordinary conditions, electrons are bound to the positively charged nucleus by the attraction created from opposite electric charges. If an atom has more or fewer electrons than its atomic number, then it becomes respectively negatively or positively charged as a whole; a charged atom is called an ion. Electrons have been known since the late 19th century, mostly thanks to J.J. Thomson; see history of subatomic physics for details.

Protons have a positive charge and a mass of 1.6726×10^{-27} kg. The number of protons in an atom is called its atomic number. Ernest Rutherford (1919) observed that nitrogen under alpha-particle bombardment ejects what appeared to be hydrogen nuclei. By 1920 he had accepted that the hydrogen nucleus is a distinct particle within the atom and named it proton.

Neutrons have no electrical charge and have a mass of 1.6749×10^{-27} kg.[33][34] Neutrons are the heaviest of the three constituent particles, but their mass can be reduced by the nuclear binding energy. Neutrons and protons (collectively known as nucleons) have comparable dimensions—

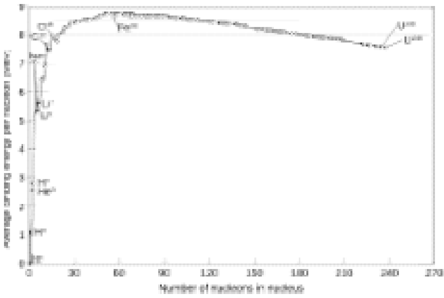
on the order of 2.5×10^{-15} m—although the 'surface' of these particles is not sharply defined.[35] The neutron was discovered in 1932 by the English physicist James Chadwick.

In the Standard Model of physics, electrons are truly elementary particles with no internal structure, whereas protons and neutrons are composite particles composed of elementary particles called quarks. There are two types of quarks in atoms, each having a fractional electric charge. Protons are composed of two up quarks (each with charge +2/3) and one down quark (with a charge of −1/3). Neutrons consist of one up quark and two down quarks. This distinction accounts for the difference in mass and charge between the two particles.[36][37]

The quarks are held together by the strong interaction (or strong force), which is mediated by gluons. The protons and neutrons, in turn, are held to each other in the nucleus by the nuclear force, which is a residuum of the strong force that has somewhat different range-properties (see the article on the nuclear force for more). The gluon is a member of the family of gauge bosons, which are elementary particles that mediate physical forces.[36][37]

Nucleus

Main article: Atomic nucleus



The binding energy needed for a nucleon to escape the nucleus, for various isotopes

All the bound protons and neutrons in an atom make up a tiny atomic nucleus, and are collectively called nucleons. The radius of a nucleus is approximately equal to femtometres, where is the total number of nucleons.[38] This is much smaller than the radius of the atom, which is on the order of 10^5 fm. The nucleons are bound together by a short-ranged attractive potential called the residual strong force. At distances smaller than 2.5 fm this force is much more powerful than the electrostatic force that causes positively charged protons to repel each other.[39]

Atoms of the same element have the same number of protons, called the atomic number. Within a single element, the number of neutrons may vary, determining the isotope of that element. The total number of protons and neutrons determine the nuclide. The number of neutrons relative to the protons determines the stability of the nucleus, with certain isotopes undergoing radioactive decay.[40]

The proton, the electron, and the neutron are classified as fermions. Fermions obey the Pauli exclusion principle which prohibits *identical* fermions, such as multiple protons, from occupying the same quantum state at the same time. Thus, every proton in the nucleus must occupy a quantum state different from all other protons, and the same applies to all neutrons of the nucleus and to all electrons of the electron cloud.[41]

A nucleus that has a different number of protons than neutrons can potentially drop to a lower energy state through a radioactive decay that causes the number of protons and neutrons to more closely match. As a result, atoms with matching numbers of protons and neutrons are more stable against decay, but with increasing atomic number, the mutual repulsion of the protons requires an increasing proportion of neutrons to maintain the stability of the nucleus.[41]

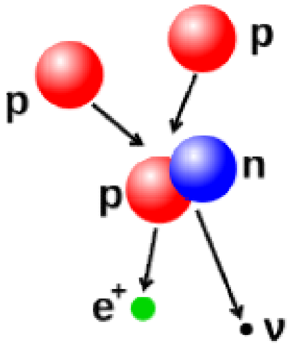


Illustration of a nuclear fusion process that forms a deuterium nucleus, consisting of a proton and a neutron, from two protons. A positron (e^+)—an antimatter electron—is emitted along with an electron neutrino.

The number of protons and neutrons in the atomic nucleus can be modified, although this can require very high energies because of the strong force. Nuclear fusion occurs when multiple atomic particles join to form a heavier nucleus, such as through the energetic collision of two nuclei. For example, at the core of the Sun protons require energies of 3 to 10 keV to overcome their mutual repulsion—the coulomb barrier—and fuse together into a single nucleus.[42] Nuclear fission is the opposite process, causing a nucleus to split into two smaller nuclei—usually through radioactive decay. The nucleus can also be modified through bombardment by high energy subatomic particles or photons. If this modifies the number of protons in a nucleus, the atom changes to a different chemical element.[43][44]

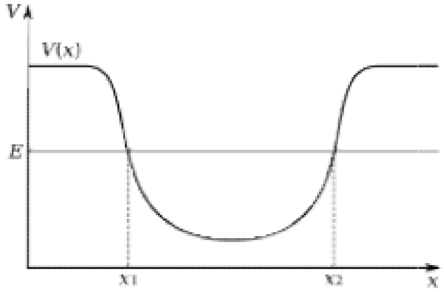
If the mass of the nucleus following a fusion reaction is less than the sum of the masses of the separate particles, then the difference between these two values can be emitted as a type of usable energy (such as a gamma ray, or the kinetic energy of a beta particle), as described by Albert Einstein's mass–energy equivalence formula, $e=mc^2$, where m is the mass loss and c is the speed of light. This deficit is part of the binding energy of the new nucleus, and it is the non-recoverable loss of the energy that causes the fused particles to remain together in a state that requires this energy to separate.[45]

The fusion of two nuclei that create larger nuclei with lower atomic numbers than iron and nickel—a total nucleon number of about 60—is usually an exothermic process that releases more energy than is required to bring them together.[46] It is this energy-releasing process that makes nuclear fusion in stars a self-sustaining reaction. For heavier nuclei, the binding energy per nucleon begins to decrease. That means that a fusion process producing a nucleus that has an atomic number higher than about 26, and a mass number higher than about 60, is an endothermic process. Thus, more massive nuclei cannot undergo an energy-producing fusion reaction that can sustain the hydrostatic equilibrium of a star.[41]

Electron cloud

Main articles: Electron configuration, Electron shell, and Atomic orbital

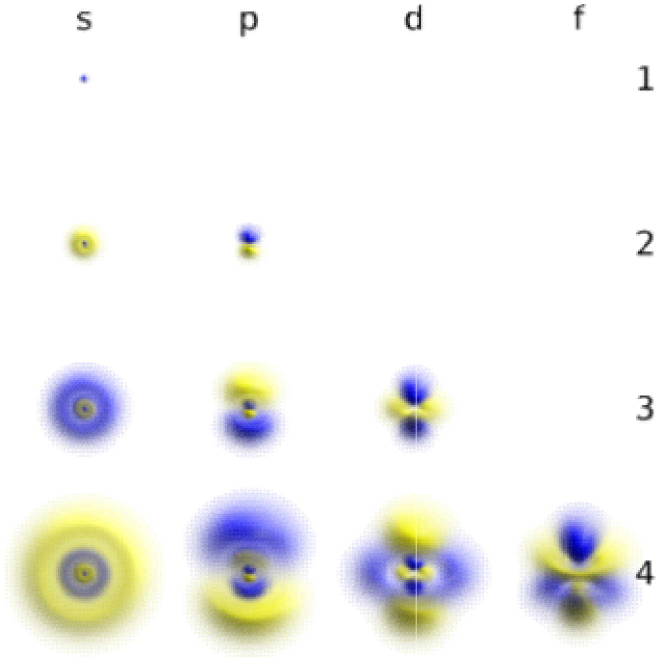
See also: Electronegativity



A potential well, showing, according to classical mechanics, the minimum energy $V(x)$ needed to reach each position x. Classically, a particle with energy E is constrained to a range of positions between x_1 and x_2.

The electrons in an atom are attracted to the protons in the nucleus by the electromagnetic force. This force binds the electrons inside an electrostatic potential well surrounding the smaller nucleus, which means that an external source of energy is needed for the electron to escape. The closer an electron is to the nucleus, the greater the attractive force. Hence electrons bound near the center of the potential well require more energy to escape than those at greater separations.

Electrons, like other particles, have properties of both a particle and a wave. The electron cloud is a region inside the potential well where each electron forms a type of three-dimensional standing wave—a wave form that does not move relative to the nucleus. This behavior is defined by an atomic orbital, a mathematical function that characterises the probability that an electron appears to be at a particular location when its position is measured.[47] Only a discrete (or quantized) set of these orbitals exist around the nucleus, as other possible wave patterns rapidly decay into a more stable form.[48] Orbitals can have one or more ring or node structures, and differ from each other in size, shape and orientation.[49]



3D views of some hydrogen-like atomic orbitals showing probability density and phase (**g** orbitals and higher are not shown)

Each atomic orbital corresponds to a particular energy level of the electron. The electron can change its state to a higher energy level by absorbing a photon with sufficient energy to boost it into the new quantum state. Likewise, through spontaneous emission, an electron in a higher energy state can drop to a lower energy state while radiating the excess energy as a photon. These characteristic energy values, defined by the differences in the energies of the quantum states, are responsible for atomic spectral lines.[48]

The amount of energy needed to remove or add an electron—the electron binding energy—is far less than the binding energy of nucleons. For example, it requires only 13.6 eV to strip a ground-state electron from a hydrogen atom,[50] compared to 2.23 *million* eV for splitting a deuterium nucleus.[51] Atoms are electrically neutral if they have an equal number of protons and electrons. Atoms that have either a deficit or a surplus of electrons are called ions. Electrons that are farthest from the nucleus may be transferred to other nearby atoms or shared between atoms. By this mechanism, atoms are able to bond into molecules and other types of chemical compounds like ionic and covalent network crystals.[52]

Properties

Nuclear properties

Main articles: Isotope, Stable isotope, List of nuclides, and List of elements by stability of isotopes

By definition, any two atoms with an identical number of *protons* in their nuclei belong to the same chemical element. Atoms with equal numbers of protons but a different number of *neutrons* are different isotopes of the same element. For example, all hydrogen atoms admit exactly one proton, but isotopes exist with no neutrons (hydrogen-1, by far the most common form,[53] also called protium), one neutron (deuterium), two neutrons (tritium) and more than two neutrons. The known elements form a set of atomic numbers, from the single-proton element hydrogen up to the 118-proton element oganesson.[54] All known isotopes of elements with atomic numbers greater than 82 are radioactive, although the radioactivity of element 83 (bismuth) is so slight as to be practically negligible.[55][56]

About 339 nuclides occur naturally on Earth,[57] of which 251 (about 74%) have not been observed to decay, and are referred to as "stable isotopes". Only 90 nuclides are stable theoretically, while another 161 (bringing the total to 251) have not been observed to decay, even though in theory it is energetically possible. These are also formally classified as "stable". An additional 35 radioactive nuclides have half-lives longer than 100 million years, and are long-lived enough to have been present since the birth of the Solar System. This collection of 286 nuclides are known as primordial nuclides. Finally, an additional 53 short-lived nuclides are known to occur naturally, as daughter products of primordial nuclide decay (such as radium from uranium), or as products of natural energetic processes on Earth, such as cosmic ray bombardment (for example, carbon-14).[58][note 1]

For 80 of the chemical elements, at least one stable isotope exists. As a rule, there is only a handful of stable isotopes for each of these elements, the average being 3.1 stable isotopes per element. Twenty-six "monoisotopic elements" have only a single stable isotope, while the largest number of stable isotopes observed for any element is ten, for the element tin. Elements 43, 61, and all elements numbered 83 or higher have no stable isotopes.[59]:1–12

Stability of isotopes is affected by the ratio of protons to neutrons, and also by the presence of certain "magic numbers" of neutrons or protons that represent closed and filled quantum shells.

These quantum shells correspond to a set of energy levels within the shell model of the nucleus; filled shells, such as the filled shell of 50 protons for tin, confers unusual stability on the nuclide. Of the 251 known stable nuclides, only four have both an odd number of protons *and* odd number of neutrons: hydrogen-2 (deuterium), lithium-6, boron-10, and nitrogen-14. (Tantalum-180m is odd-odd and observationally stable, but is predicted to decay with a very long half-life.) Also, only four naturally occurring, radioactive odd-odd nuclides have a half-life over a billion years: potassium-40, vanadium-50, lanthanum-138, and lutetium-176. Most odd-odd nuclei are highly unstable with respect to beta decay, because the decay products are even-even, and are therefore more strongly bound, due to nuclear pairing effects.[60]

Mass

Main articles: Atomic mass and mass number

The large majority of an atom's mass comes from the protons and neutrons that make it up. The total number of these particles (called "nucleons") in a given atom is called the mass number. It is a positive integer and dimensionless (instead of having dimension of mass), because it expresses a count. An example of use of a mass number is "carbon-12," which has 12 nucleons (six protons and six neutrons).

The actual mass of an atom at rest is often expressed in daltons (Da), also called the unified atomic mass unit (u). This unit is defined as a twelfth of the mass of a free neutral atom of carbon-12, which is approximately 1.66×10^{-27} kg.[61] Hydrogen-1 (the lightest isotope of hydrogen which is also the nuclide with the lowest mass) has an atomic weight of 1.007825 Da.[62] The value of this number is called the atomic mass. A given atom has an atomic mass approximately equal (within 1%) to its mass number times the atomic mass unit (for example the mass of a nitrogen-14 is roughly 14 Da), but this number will not be exactly an integer except (by definition) in the case of carbon-12.[63] The heaviest stable atom is lead-208,[55] with a mass of 207.9766521 Da.[64]

As even the most massive atoms are far too light to work with directly, chemists instead use the unit of moles. One mole of atoms of any element always has the same number of atoms (about 6.022×10^{23}). This number was chosen so that if an element has an atomic mass of 1 u, a mole of atoms of that element has a mass close to one gram. Because of the definition of the unified atomic mass unit, each carbon-12 atom has an atomic mass of exactly 12 Da, and so a mole of carbon-12 atoms weighs exactly 0.012 kg.[61]

Shape and size

Main article: Atomic radius

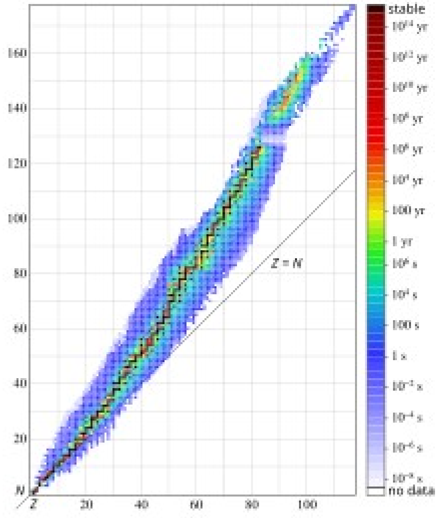
Atoms lack a well-defined outer boundary, so their dimensions are usually described in terms of an atomic radius. This is a measure of the distance out to which the electron cloud extends from the nucleus.[65] This assumes the atom to exhibit a spherical shape, which is only obeyed for atoms in vacuum or free space. Atomic radii may be derived from the distances between two nuclei when the two atoms are joined in a chemical bond. The radius varies with the location of an atom on the atomic chart, the type of chemical bond, the number of neighboring atoms (coordination number) and a quantum mechanical property known as spin.[66] On the periodic table of the elements, atom size tends to increase when moving down columns, but decrease when moving across rows (left to right).[67] Consequently, the smallest atom is helium with a radius of 32 pm, while one of the largest is caesium at 225 pm.[68]

When subjected to external forces, like electrical fields, the shape of an atom may deviate from spherical symmetry. The deformation depends on the field magnitude and the orbital type of outer shell electrons, as shown by group-theoretical considerations. Aspherical deviations might be elicited for instance in crystals, where large crystal-electrical fields may occur at low-symmetry lattice sites.[69][70] Significant ellipsoidal deformations have been shown to occur for sulfur ions[71] and chalcogen ions[72] in pyrite-type compounds.

Atomic dimensions are thousands of times smaller than the wavelengths of light (400–700 nm) so they cannot be viewed using an optical microscope, although individual atoms can be observed using a scanning tunneling microscope. To visualize the minuteness of the atom, consider that a typical human hair is about 1 million carbon atoms in width.[73] A single drop of water contains about 2 sextillion (2×10^{21}) atoms of oxygen, and twice the number of hydrogen atoms.[74] A single carat diamond with a mass of 2×10^{-4} kg contains about 10 sextillion (10^{22}) atoms of carbon.[note 2] If an apple were magnified to the size of the Earth, then the atoms in the apple would be approximately the size of the original apple.[75]

Radioactive decay

Main article: Radioactive decay



This diagram shows the half-life ($T_{1/2}$) of various isotopes with Z protons and N neutrons.

Every element has one or more isotopes that have unstable nuclei that are subject to radioactive decay, causing the nucleus to emit particles or electromagnetic radiation. Radioactivity can occur when the radius of a nucleus is large compared with the radius of the strong force, which only acts over distances on the order of 1 fm.[76]

The most common forms of radioactive decay are:[77][78]

- Alpha decay: this process is caused when the nucleus emits an alpha particle, which is a helium nucleus consisting of two protons and two neutrons. The result of the emission is a new element with a lower atomic number.
- Beta decay (and electron capture): these processes are regulated by the weak force, and result from a transformation of a neutron into a proton, or a proton into a neutron. The neutron to proton transition is accompanied by the emission of an electron and an antineutrino, while proton to neutron transition (except in electron capture) causes the

emission of a positron and a neutrino. The electron or positron emissions are called beta particles. Beta decay either increases or decreases the atomic number of the nucleus by one. Electron capture is more common than positron emission, because it requires less energy. In this type of decay, an electron is absorbed by the nucleus, rather than a positron emitted from the nucleus. A neutrino is still emitted in this process, and a proton changes to a neutron.

- Gamma decay: this process results from a change in the energy level of the nucleus to a lower state, resulting in the emission of electromagnetic radiation. The excited state of a nucleus which results in gamma emission usually occurs following the emission of an alpha or a beta particle. Thus, gamma decay usually follows alpha or beta decay.

Other more rare types of radioactive decay include ejection of neutrons or protons or clusters of nucleons from a nucleus, or more than one beta particle. An analog of gamma emission which allows excited nuclei to lose energy in a different way, is internal conversion—a process that produces high-speed electrons that are not beta rays, followed by production of high-energy photons that are not gamma rays. A few large nuclei explode into two or more charged fragments of varying masses plus several neutrons, in a decay called spontaneous nuclear fission.

Each radioactive isotope has a characteristic decay time period—the half-life—that is determined by the amount of time needed for half of a sample to decay. This is an exponential decay process that steadily decreases the proportion of the remaining isotope by 50% every half-life. Hence after two half-lives have passed only 25% of the isotope is present, and so forth.[76]

Magnetic moment

Main articles: Electron magnetic moment and Nuclear magnetic moment

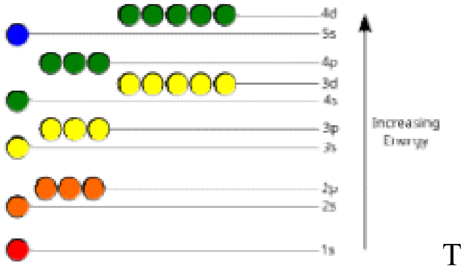
Elementary particles possess an intrinsic quantum mechanical property known as spin. This is analogous to the angular momentum of an object that is spinning around its center of mass, although strictly speaking these particles are believed to be point-like and cannot be said to be rotating. Spin is measured in units of the reduced Planck constant (ħ), with electrons, protons and neutrons all having spin ½ ħ, or "spin-½". In an atom, electrons in motion around the nucleus possess orbital angular momentum in addition to their spin, while the nucleus itself possesses angular momentum due to its nuclear spin.[79]

The magnetic field produced by an atom—its magnetic moment—is determined by these various forms of angular momentum, just as a rotating charged object classically produces a magnetic field, but the most dominant contribution comes from electron spin. Due to the nature of electrons to obey the Pauli exclusion principle, in which no two electrons may be found in the same quantum state, bound electrons pair up with each other, with one member of each pair in a spin up state and the other in the opposite, spin down state. Thus these spins cancel each other out, reducing the total magnetic dipole moment to zero in some atoms with even number of electrons.[80]

In ferromagnetic elements such as iron, cobalt and nickel, an odd number of electrons leads to an unpaired electron and a net overall magnetic moment. The orbitals of neighboring atoms overlap and a lower energy state is achieved when the spins of unpaired electrons are aligned with each other, a spontaneous process known as an exchange interaction. When the magnetic moments of ferromagnetic atoms are lined up, the material can produce a measurable macroscopic field. Paramagnetic materials have atoms with magnetic moments that line up in random directions when no magnetic field is present, but the magnetic moments of the individual atoms line up in the presence of a field.[80][81]

The nucleus of an atom will have no spin when it has even numbers of both neutrons and protons, but for other cases of odd numbers, the nucleus may have a spin. Normally nuclei with spin are aligned in random directions because of thermal equilibrium, but for certain elements (such as xenon-129) it is possible to polarize a significant proportion of the nuclear spin states so that they are aligned in the same direction—a condition called hyperpolarization. This has important applications in magnetic resonance imaging.[82][83]

Energy levels

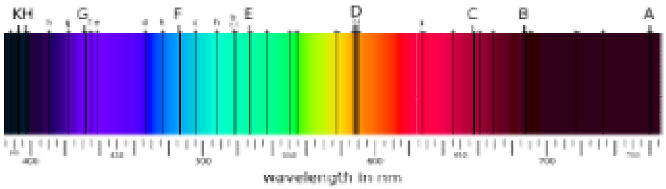


These electron's energy levels (not to scale) are sufficient for ground states of atoms up to cadmium ($5s^2\ 4d^{10}$) inclusively. Do not forget that even the top of the diagram is lower than an unbound electron state.

The potential energy of an electron in an atom is negative relative to when the distance from the nucleus goes to infinity; its dependence on the electron's position reaches the minimum inside the nucleus, roughly in inverse proportion to the distance. In the quantum-mechanical model, a bound electron can occupy only a set of states centered on the nucleus, and each state corresponds to a specific energy level; see time-independent Schrödinger equation for a theoretical explanation. An energy level can be measured by the amount of energy needed to unbind the electron from the atom, and is usually given in units of electronvolts (eV). The lowest energy state of a bound electron is called the ground state, i.e. stationary state, while an electron transition to a higher level results in an excited state.[84] The electron's energy increases along with n because the (average) distance to the nucleus increases. Dependence of the energy on ℓ is caused not by the electrostatic potential of the nucleus, but by interaction between electrons.

For an electron to transition between two different states, e.g. ground state to first excited state, it must absorb or emit a photon at an energy matching the difference in the potential energy of those levels, according to the Niels Bohr model, what can be precisely calculated by the Schrödinger equation. Electrons jump between orbitals in a particle-like fashion. For example, if a single photon strikes the electrons, only a single electron changes states in response to the photon; see Electron properties.

The energy of an emitted photon is proportional to its frequency, so these specific energy levels appear as distinct bands in the electromagnetic spectrum.[85] Each element has a characteristic spectrum that can depend on the nuclear charge, subshells filled by electrons, the electromagnetic interactions between the electrons and other factors.[86]



An example of absorption lines in a spectrum

When a continuous spectrum of energy is passed through a gas or plasma, some of the photons are absorbed by atoms, causing electrons to change their energy level. Those excited electrons that remain bound to their atom spontaneously emit this energy as a photon, traveling in a random direction, and so drop back to lower energy levels. Thus the atoms behave like a filter that forms a series of dark absorption bands in the energy output. (An observer viewing the atoms from a view that does not include the continuous spectrum in the background, instead sees a series of emission lines from the photons emitted by the atoms.) Spectroscopic measurements of the strength and width of atomic spectral lines allow the composition and physical properties of a substance to be determined.[87]

Close examination of the spectral lines reveals that some display a fine structure splitting. This occurs because of spin–orbit coupling, which is an interaction between the spin and motion of the outermost electron.[88] When an atom is in an external magnetic field, spectral lines become split into three or more components; a phenomenon called the Zeeman effect. This is caused by the interaction of the magnetic field with the magnetic moment of the atom and its electrons. Some atoms can have multiple electron configurations with the same energy level, which thus appear as a single spectral line. The interaction of the magnetic field with the atom shifts these electron configurations to slightly different energy levels, resulting in multiple spectral lines.[89] The presence of an external electric field can cause a comparable splitting and shifting of spectral lines by modifying the electron energy levels, a phenomenon called the Stark effect.[90]

If a bound electron is in an excited state, an interacting photon with the proper energy can cause stimulated emission of a photon with a matching energy level. For this to occur, the electron must drop to a lower energy state that has an energy difference matching the energy of the interacting photon. The emitted photon and the interacting photon then move off in parallel and with matching phases. That is, the wave patterns of the two photons are synchronized. This physical property is used to make lasers, which can emit a coherent beam of light energy in a narrow frequency band.[91]

Valence and bonding behavior

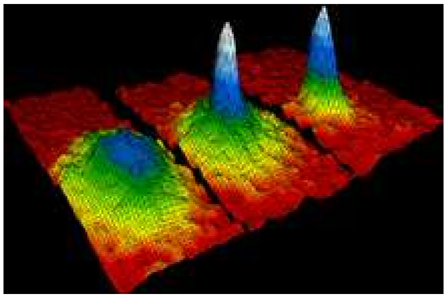
Main articles: Valence (chemistry) and Chemical bond

Valency is the combining power of an element. It is determined by the number of bonds it can form to other atoms or groups.[92] The outermost electron shell of an atom in its uncombined state is known as the valence shell, and the electrons in that shell are called valence electrons. The number of valence electrons determines the bonding behavior with other atoms. Atoms tend to chemically react with each other in a manner that fills (or empties) their outer valence shells.[93] For example, a transfer of a single electron between atoms is a useful approximation for bonds that form between atoms with one-electron more than a filled shell, and others that are one-electron short of a full shell, such as occurs in the compound sodium chloride and other chemical ionic salts. Many elements display multiple valences, or tendencies to share differing numbers of electrons in different compounds. Thus, chemical bonding between these elements takes many forms of electron-sharing that are more than simple electron transfers. Examples include the element carbon and the organic compounds.[94]

The chemical elements are often displayed in a periodic table that is laid out to display recurring chemical properties, and elements with the same number of valence electrons form a group that is aligned in the same column of the table. (The horizontal rows correspond to the filling of a quantum shell of electrons.) The elements at the far right of the table have their outer shell completely filled with electrons, which results in chemically inert elements known as the noble gases.[95][96]

States

Main articles: State of matter and Phase (matter)

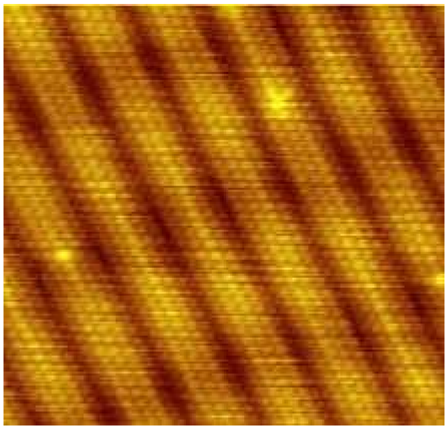


Graphic illustrating the formation of a Bose–Einstein condensate

Quantities of atoms are found in different states of matter that depend on the physical conditions, such as temperature and pressure. By varying the conditions, materials can transition between solids, liquids, gases and plasmas.[97] Within a state, a material can also exist in different allotropes. An example of this is solid carbon, which can exist as graphite or diamond.[98] Gaseous allotropes exist as well, such as dioxygen and ozone.

At temperatures close to absolute zero, atoms can form a Bose–Einstein condensate, at which point quantum mechanical effects, which are normally only observed at the atomic scale, become apparent on a macroscopic scale.[99][100] This super-cooled collection of atoms then behaves as a single super atom, which may allow fundamental checks of quantum mechanical behavior.[101]

Identification



Scanning tunneling microscope image showing the individual atoms making up this gold (100) surface. The surface atoms deviate from the bulk crystal structure and arrange in columns several atoms wide with pits between them (See surface reconstruction).

While atoms are too small to be seen, devices such as the scanning tunneling microscope (STM) enable their visualization at the surfaces of solids. The microscope uses the quantum tunneling phenomenon, which allows particles to pass through a barrier that would be insurmountable in the classical perspective. Electrons tunnel through the vacuum between two biased electrodes, providing a tunneling current that is exponentially dependent on their separation. One electrode is a sharp tip ideally ending with a single atom. At each point of the scan of the surface the tip's height is adjusted so as to keep the tunneling current at a set value. How much the tip moves to and away from the surface is interpreted as the height profile. For low bias, the microscope images the averaged electron orbitals across closely packed energy levels—the local density of the electronic states near the Fermi level.[102][103] Because of the distances involved, both electrodes need to be extremely stable; only then periodicities can be observed that correspond to individual atoms. The method alone is not chemically specific, and cannot identify the atomic species present at the surface.

Atoms can be easily identified by their mass. If an atom is ionized by removing one of its electrons, its trajectory when it passes through a magnetic field will bend. The radius by which the trajectory of a moving ion is turned by the magnetic field is determined by the mass of the atom. The mass spectrometer uses this principle to measure the mass-to-charge ratio of ions. If a sample contains multiple isotopes, the mass spectrometer can determine the proportion of each isotope in the sample by measuring the intensity of the different beams of ions. Techniques to vaporize atoms include inductively coupled plasma atomic emission spectroscopy and inductively coupled plasma mass spectrometry, both of which use a plasma to vaporize samples for analysis.[104]

The atom-probe tomograph has sub-nanometer resolution in 3-D and can chemically identify individual atoms using time-of-flight mass spectrometry.[105]

Electron emission techniques such as X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES), which measure the binding energies of the core electrons, are used to identify the atomic species present in a sample in a non-destructive way. With proper focusing both can be made area-specific. Another such method is electron energy loss spectroscopy (EELS), which measures the energy loss of an electron beam within a transmission electron microscope when it interacts with a portion of a sample.

Spectra of excited states can be used to analyze the atomic composition of distant stars. Specific light wavelengths contained in the observed light from stars can be separated out and related to the quantized transitions in free gas atoms. These colors can be replicated using a gas-discharge lamp containing the same element.[106] Helium was discovered in this way in the spectrum of the Sun 23 years before it was found on Earth.[107]

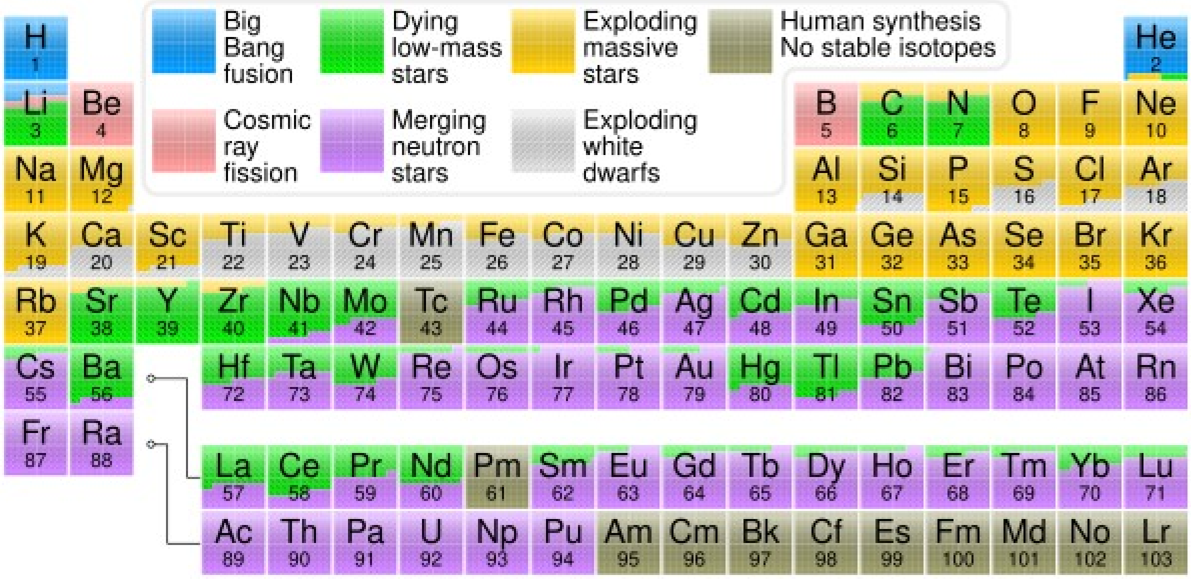
Origin and current state

Baryonic matter forms about 4% of the total energy density of the observable universe, with an average density of about 0.25 particles/m^3 (mostly protons and electrons).[108] Within a galaxy such as the Milky Way, particles have a much higher concentration, with the density of matter in the interstellar medium (ISM) ranging from 10^5 to 10^9 atoms/m^3.[109] The Sun is believed to be inside the Local Bubble, so the density in the solar neighborhood is only about 10^3 atoms/m^3.[110] Stars form from dense clouds in the ISM, and the evolutionary processes of stars result in the steady enrichment of the ISM with elements more massive than hydrogen and helium.

Up to 95% of the Milky Way's baryonic matter are concentrated inside stars, where conditions are unfavorable for atomic matter. The total baryonic mass is about 10% of the mass of the galaxy;[111] the remainder of the mass is an unknown dark matter.[112] High temperature inside stars makes most "atoms" fully ionized, that is, separates *all* electrons from the nuclei. In stellar remnants—with exception of their surface layers—an immense pressure make electron shells impossible.

Formation

Main article: Nucleosynthesis



Periodic table showing the origin of each element. Elements from carbon up to sulfur may be made in small stars by the alpha process. Elements beyond iron are made in large stars with slow neutron capture (s-process). Elements heavier than iron may be made in neutron star mergers or supernovae after the r-process.

Electrons are thought to exist in the Universe since early stages of the Big Bang. Atomic nuclei forms in nucleosynthesis reactions. In about three minutes Big Bang nucleosynthesis produced most of the helium, lithium, and deuterium in the Universe, and perhaps some of the beryllium and boron.[113][114][115]

Ubiquitousness and stability of atoms relies on their binding energy, which means that an atom has a lower energy than an unbound system of the nucleus and electrons. Where the temperature is much higher than ionization potential, the matter exists in the form of plasma—a gas of positively charged ions (possibly, bare nuclei) and electrons. When the temperature drops below the ionization potential, atoms become statistically favorable. Atoms (complete with bound electrons) became to dominate over charged particles 380,000 years after the Big Bang—an epoch called recombination, when the expanding Universe cooled enough to allow electrons to become attached to nuclei.[116]

Since the Big Bang, which produced no carbon or heavier elements, atomic nuclei have been combined in stars through the process of nuclear fusion to produce more of the element helium, and (via the triple-alpha process) the sequence of elements from carbon up to iron;[117] see stellar nucleosynthesis for details.

Isotopes such as lithium-6, as well as some beryllium and boron are generated in space through cosmic ray spallation.[118] This occurs when a high-energy proton strikes an atomic nucleus, causing large numbers of nucleons to be ejected.

Elements heavier than iron were produced in supernovae and colliding neutron stars through the r-process, and in AGB stars through the s-process, both of which involve the capture of neutrons by atomic nuclei.[119] Elements such as lead formed largely through the radioactive decay of heavier elements.[120]

Earth

Most of the atoms that make up the Earth and its inhabitants were present in their current form in the nebula that collapsed out of a molecular cloud to form the Solar System. The rest are the result of radioactive decay, and their relative proportion can be used to determine the age of the Earth through radiometric dating.[121][122] Most of the helium in the crust of the Earth (about 99% of the helium from gas wells, as shown by its lower abundance of helium-3) is a product of alpha decay.[123]

There are a few trace atoms on Earth that were not present at the beginning (i.e., not "primordial"), nor are results of radioactive decay. Carbon-14 is continuously generated by cosmic rays in the atmosphere.[124] Some atoms on Earth have been artificially generated either deliberately or as by-products of nuclear reactors or explosions.[125][126] Of the transuranic elements—those with atomic numbers greater than 92—only plutonium and neptunium occur naturally on Earth.[127][128] Transuranic elements have radioactive lifetimes shorter than the current age of the Earth[129] and thus identifiable quantities of these elements have long since decayed, with the exception of traces of plutonium-244 possibly deposited by cosmic dust.[121] Natural deposits of plutonium and neptunium are produced by neutron capture in uranium ore.[130]

The Earth contains approximately 1.33×10^{50} atoms.[131] Although small numbers of independent atoms of noble gases exist, such as argon, neon, and helium, 99% of the atmosphere is bound in the form of molecules, including carbon dioxide and diatomic oxygen and nitrogen. At the surface of the Earth, an overwhelming majority of atoms combine to form various compounds, including water, salt, silicates and oxides. Atoms can also combine to create materials that do not consist of discrete molecules, including crystals and liquid or solid metals.[132][133] This atomic matter forms networked arrangements that lack the particular type of small-scale interrupted order associated with molecular matter.[134]

Rare and theoretical forms

Superheavy elements

Main article: Superheavy element

All nuclides with atomic numbers higher than 82 (lead) are known to be radioactive. No nuclide with an atomic number exceeding 92 (uranium) exists on Earth as a primordial nuclide, and heavier elements generally have shorter half-lives. Nevertheless, an "island of stability" encompassing relatively long-lived isotopes of superheavy elements[135] with atomic numbers 110 to 114 might exist.[136] Predictions for the half-life of the most stable nuclide on the island range from a few minutes to millions of years.[137] In any case, superheavy elements (with $Z > 104$) would not exist due to increasing Coulomb repulsion (which results in spontaneous fission with increasingly short half-lives) in the absence of any stabilizing effects.[138]

Exotic matter

Main article: Exotic matter

Each particle of matter has a corresponding antimatter particle with the opposite electrical charge. Thus, the positron is a positively charged antielectron and the antiproton is a negatively charged equivalent of a proton. When a matter and corresponding antimatter particle meet, they annihilate each other. Because of this, along with an imbalance between the number of matter and antimatter particles, the latter are rare in the universe. The first causes of this imbalance are not yet fully understood, although theories of baryogenesis may offer an explanation. As a result, no antimatter atoms have been discovered in nature.[139][140] In 1996, the antimatter counterpart of the hydrogen atom (antihydrogen) was synthesized at the CERN laboratory in Geneva.[141][142]

Other exotic atoms have been created by replacing one of the protons, neutrons or electrons with other particles that have the same charge. For example, an electron can be replaced by a more massive muon, forming a muonic atom. These types of atoms can be used to test fundamental predictions of physics.[143][144][145]

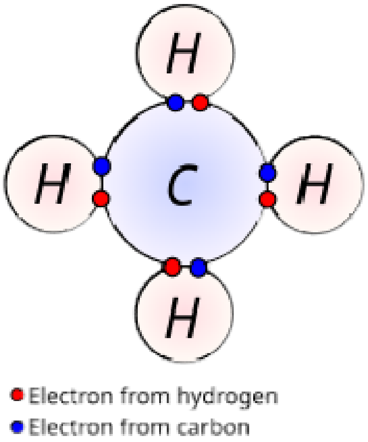
A **covalent bond** is a chemical bond that involves the sharing of electrons to form electron pairs between atoms. These electron pairs are known as **shared pairs** or **bonding pairs**. The stable balance of attractive and repulsive forces between atoms, when they share electrons, is known as covalent bonding.[1] For many molecules, the sharing of electrons allows each atom to attain the equivalent of a full valence shell, corresponding to a stable electronic configuration. In organic chemistry, covalent bonding is much more common than ionic bonding.

Covalent bonding also includes many kinds of interactions, including σ-bonding, π-bonding, metal-to-metal bonding, agostic interactions, bent bonds, three-center two-electron bonds and three-center four-electron bonds.[2][3] The term *covalent bond* dates from 1939.[4] The prefix *co-* means *jointly, associated in action, partnered to a lesser degree,* etc.; thus a "co-valent bond", in essence, means that the atoms share "valence", such as is discussed in valence bond theory.

In the molecule H_2, the hydrogen atoms share the two electrons via covalent bonding.[5] Covalency is greatest between atoms of similar electronegativities. Thus, covalent bonding does not necessarily require that the two atoms be of the same elements, only that they be of comparable electronegativity. Covalent bonding that entails the sharing of electrons over more than two atoms is said to be delocalized.

History

[edit]



Early concepts in covalent bonding arose from this kind of image of the molecule of methane. Covalent bonding is implied in the Lewis structure by indicating electrons shared between atoms.

The term *covalence* in regard to bonding was first used in 1919 by Irving Langmuir in a *Journal of the American Chemical Society* article entitled "The Arrangement of Electrons in Atoms and Molecules". Langmuir wrote that "we shall denote by the term *covalence* the number of pairs of electrons that a given atom shares with its neighbors."[6]

The idea of covalent bonding can be traced several years before 1919 to Gilbert N. Lewis, who in 1916 described the sharing of electron pairs between atoms[7] (and in 1926 he also coined the term "photon" for the smallest unit of radiant energy). He introduced the *Lewis notation* or *electron dot notation* or *Lewis dot structure*, in which valence electrons (those in the outer shell) are represented as dots around the atomic symbols. Pairs of electrons located between atoms represent covalent bonds. Multiple pairs represent multiple bonds, such as double bonds and triple bonds. An alternative form of representation, not shown here, has bond-forming electron pairs represented as solid lines.[8]

Lewis proposed that an atom forms enough covalent bonds to form a full (or closed) outer electron shell. In the diagram of methane shown here, the carbon atom has a valence of four and is, therefore, surrounded by eight electrons (the octet rule), four from the carbon itself and four from the hydrogens bonded to it. Each hydrogen has a valence of one and is surrounded by two electrons (a duet rule) – its own one electron plus one from the carbon. The numbers of electrons correspond to full shells in the quantum theory of the atom; the outer shell of a carbon atom is the $n = 2$ shell, which can hold eight electrons, whereas the outer (and only) shell of a hydrogen atom is the $n = 1$ shell, which can hold only two.[9]

While the idea of shared electron pairs provides an effective qualitative picture of covalent bonding, quantum mechanics is needed to understand the nature of these bonds and predict the structures and properties of simple molecules. Walter Heitler and Fritz London are credited with the first successful quantum mechanical explanation of a chemical bond (molecular hydrogen) in 1927.[10] Their work was based on the valence bond model, which assumes that a chemical bond is formed when there is good overlap between the atomic orbitals of participating atoms.

Types of covalent bonds

[edit]

Atomic orbitals (except for s orbitals) have specific directional properties leading to different types of covalent bonds. Sigma (σ) bonds are the strongest covalent bonds and are due to head-on overlapping of orbitals on two different atoms. A single bond is usually a σ bond. Pi (π) bonds are weaker and are due to lateral overlap between p (or d) orbitals. A double bond between two given atoms consists of one σ and one π bond, and a triple bond is one σ and two π bonds.[8]

Covalent bonds are also affected by the electronegativity of the connected atoms which determines the chemical polarity of the bond. Two atoms with equal electronegativity will make nonpolar covalent bonds such as H–H. An unequal relationship creates a polar covalent bond such as with H−Cl. However polarity also requires geometric asymmetry, or else dipoles may cancel out, resulting in a non-polar molecule.[8]

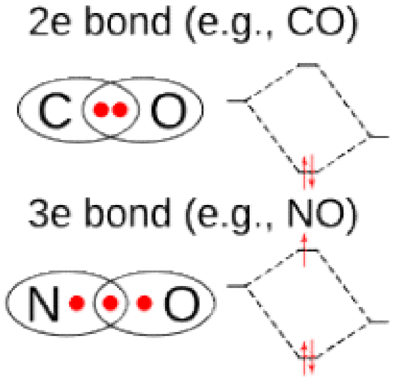
Covalent structures

[edit]

There are several types of structures for covalent substances, including individual molecules, molecular structures, macromolecular structures and giant covalent structures. Individual molecules have strong bonds that hold the atoms together, but generally, there are negligible forces of attraction between molecules. Such covalent substances are usually gases, for example, HCl, SO_2, CO_2, and CH_4. In molecular structures, there are weak forces of attraction. Such covalent substances are low-boiling-temperature liquids (such as ethanol), and low-melting-temperature solids (such as iodine and solid CO_2). Macromolecular structures have large numbers of atoms linked by covalent bonds in chains, including synthetic polymers such as polyethylene and nylon, and biopolymers such as proteins and starch. Network covalent structures (or giant covalent structures) contain large numbers of atoms linked in sheets (such as graphite), or 3-dimensional structures (such as diamond and quartz). These substances have high melting and boiling points, are frequently brittle, and tend to have high electrical resistivity. Elements that have high electronegativity, and the ability to form three or four electron pair bonds, often form such large macromolecular structures.[11]

One- and three-electron bonds

[edit]



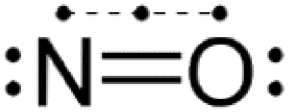
Lewis and MO diagrams of an individual $2e^-$ bond and $3e^-$ bond

Bonds with one or three electrons can be found in radical species, which have an odd number of electrons. The simplest example of a 1-electron bond is found in the dihydrogen cation, H_2^+. One-electron bonds often have about half the bond energy of a 2-electron bond, and are therefore called "half bonds". However, there are exceptions: in the case of dilithium, the bond is actually stronger for the 1-electron Li_2^+ than for the 2-electron Li_2. This exception can be explained in terms of hybridization and inner-shell effects.[12]

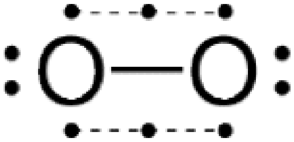
The simplest example of three-electron bonding can be found in the helium dimer cation, He_2^+. It is considered a "half bond" because it consists of only one shared electron (rather than two);[13] in molecular orbital terms, the third electron is in an anti-bonding orbital which cancels out half of the bond formed by the other two electrons. Another example of a molecule containing a 3-electron bond, in addition to two 2-electron bonds, is nitric oxide, NO. The oxygen molecule, O_2 can also be regarded as having two 3-electron bonds and one 2-electron bond, which accounts for its paramagnetism and its formal bond order of 2.[14] Chlorine dioxide and its heavier analogues bromine dioxide and iodine dioxide also contain three-electron bonds.

Molecules with odd-electron bonds are usually highly reactive. These types of bond are only stable between atoms with similar electronegativities.[14]

Modified Lewis structures with 3e bonds



Nitric oxide



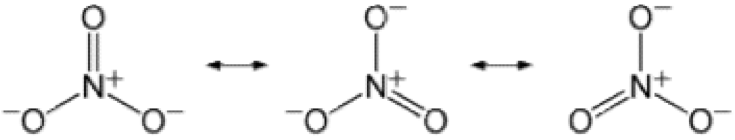
Dioxygen

Resonance

[edit]

Main article: Resonance (chemistry)

There are situations whereby a single Lewis structure is insufficient to explain the electron configuration in a molecule and its resulting experimentally-determined properties, hence a superposition of structures is needed. The same two atoms in such molecules can be bonded differently in different Lewis structures (a single bond in one, a double bond in another, or even none at all), resulting in a non-integer bond order. The nitrate ion is one such example with three equivalent structures. The bond between the nitrogen and each oxygen is a double bond in one structure and a single bond in the other two, so that the average bond order for each N–O interaction is $2 + 1 + 1/3 = 4/3$.[8]



Aromaticity

[edit]

Main article: Aromaticity

In organic chemistry, when a molecule with a planar ring obeys Hückel's rule, where the number of π electrons fit the formula 4*n* + 2 (where *n* is an integer), it attains extra stability and symmetry. In benzene, the prototypical aromatic compound, there are 6 π bonding electrons (*n* = 1, 4*n* + 2 = 6). These occupy three delocalized π molecular orbitals (molecular orbital theory) or form conjugate π bonds in two resonance structures that linearly combine (valence bond theory), creating a regular hexagon exhibiting a greater stabilization than the hypothetical 1,3,5-cyclohexatriene.[9]

In the case of heterocyclic aromatics and substituted benzenes, the electronegativity differences between different parts of the ring may dominate the chemical behavior of aromatic ring bonds, which otherwise are equivalent.[9]

Hypervalence

[edit]

Main article: Hypervalent molecule

Certain molecules such as xenon difluoride and sulfur hexafluoride have higher co-ordination numbers than would be possible due to strictly covalent bonding according to the octet rule. This is explained by the three-center four-electron bond ("3c–4e") model which interprets the molecular wavefunction in terms of non-bonding highest occupied molecular orbitals in molecular orbital theory and resonance of sigma bonds in valence bond theory.[15]

Electron deficiency

[edit]

Main article: Electron deficiency

In three-center two-electron bonds ("3c–2e") three atoms share two electrons in bonding. This type of bonding occurs in boron hydrides such as diborane (B_2H_6), which are often described as electron deficient because there are not enough valence electrons to form localized (2-centre 2-electron) bonds joining all the atoms. However the more modern description using 3c–2e bonds does provide enough bonding orbitals to connect all the atoms, so that the molecules can instead be classified as electron-precise.

Each such bond (2 per molecule in diborane) contains a pair of electrons which connect the boron atoms to each other in a banana shape, with a proton (the nucleus of a hydrogen atom) in the middle of the bond, sharing electrons with both boron atoms. In certain cluster compounds, so-called four-center two-electron bonds also have been postulated.[16]

Quantum mechanical description

[edit]

After the development of quantum mechanics, two basic theories were proposed to provide a quantum description of chemical bonding: valence bond (VB) theory and molecular orbital (MO) theory. A more recent quantum description[17] is given in terms of atomic contributions to the electronic density of states.

Comparison of VB and MO theories

[edit]

The two theories represent two ways to build up the electron configuration of the molecule.[18] For valence bond theory, the atomic hybrid orbitals are filled with electrons first to produce a fully bonded valence configuration, followed by performing a linear combination of contributing structures (resonance) if there are several of them. In contrast, for molecular orbital theory a linear combination of atomic orbitals is performed first, followed by filling of the resulting molecular orbitals with electrons.[8]

The two approaches are regarded as complementary, and each provides its own insights into the problem of chemical bonding. As valence bond theory builds the molecular wavefunction out of localized bonds, it is more suited for the calculation of bond energies and the understanding of reaction mechanisms. As molecular orbital theory builds the molecular wavefunction out of delocalized orbitals, it is more suited for the calculation of ionization energies and the understanding of spectral absorption bands.[19]

At the qualitative level, both theories contain incorrect predictions. Simple (Heitler–London) valence bond theory correctly predicts the dissociation of homonuclear diatomic molecules into separate atoms, while simple (Hartree–Fock) molecular orbital theory incorrectly predicts dissociation into a mixture of atoms and ions. On the other hand, simple molecular orbital theory correctly predicts Hückel's rule of aromaticity, while simple valence bond theory incorrectly predicts that cyclobutadiene has larger resonance energy than benzene.[20]

Although the wavefunctions generated by both theories at the qualitative level do not agree and do not match the stabilization energy by experiment, they can be corrected by configuration interaction.[18] This is done by combining the valence bond covalent function with the functions describing all possible ionic structures or by combining the molecular orbital ground state function with the functions describing all possible excited states using unoccupied orbitals. It can then be seen that the simple molecular orbital approach overestimates the weight of the ionic structures while the simple valence bond approach neglects them. This can also be described as saying that the simple molecular orbital approach neglects electron correlation while the simple valence bond approach overestimates it.[18]

Modern calculations in quantum chemistry usually start from (but ultimately go far beyond) a molecular orbital rather than a valence bond approach, not because of any intrinsic superiority in the former but rather because the MO approach is more readily adapted to numerical computations. Molecular orbitals are orthogonal, which significantly increases the feasibility and speed of computer calculations compared to nonorthogonal valence bond orbitals.

Covalency from atomic contribution to the electronic density of states

[edit]

In COOP,[21] COHP[22] and BCOOP,[23] evaluation of bond covalency is dependent on the basis set. To overcome this issue, an alternative formulation of the bond covalency can be provided in this way.

The mass center of an atomic orbital with quantum numbers for atom A is defined as where is the contribution of the atomic orbital of the atom A to the total electronic density of states of the solid

where the outer sum runs over all atoms A of the unit cell. The energy window is chosen in such a way that it encompasses all of the relevant bands participating in the bond. If the range to select is unclear, it can be identified in practice by examining the molecular orbitals that describe the electron density along with the considered bond.

The relative position of the mass center of levels of atom A with respect to the mass center of levels of atom B is given as

where the contributions of the magnetic and spin quantum numbers are summed. According to this definition, the relative position of the A levels with respect to the B levels is

where, for simplicity, we may omit the dependence from the principal quantum number in the notation referring to

In this formalism, the greater the value of the higher the overlap of the selected atomic bands, and thus the electron density described by those orbitals gives a more covalent A−B bond. The quantity is denoted as the *covalency* of the A−B bond, which is specified in the same units of the energy .

Analogous effect in nuclear systems

[edit]

An analogous effect to covalent binding is believed to occur in some nuclear systems, with the difference that the shared fermions are quarks rather than electrons.[24] High energy proton-proton scattering cross-section indicates that quark interchange of either u or d quarks is the dominant process of the nuclear force at short distance. In particular, it dominates over the Yukawa interaction where a meson is exchanged.[25] Therefore, covalent binding by quark interchange is expected to be the dominating mechanism of nuclear binding at small distance when the bound hadrons have covalence quarks in common.[26]

See also

[edit]

- Bonding in solids
- Bond order
- Coordinate covalent bond, also known as a dipolar bond or a dative covalent bond
- Covalent bond classification (or LXZ notation)
- Covalent radius
- Disulfide bond
- Hybridization
- Hydrogen bond
- Ionic bond
- Linear combination of atomic orbitals
- Metallic bonding
- Noncovalent bonding
- Resonance (chemistry)