

Diffusion

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The transport of matter from one point to another by random molecular motions. It occurs in gases, liquids, and solids.

Diffusion plays a key role in processes as diverse as permeation through membranes, evaporation of liquids, dyeing textile fibers, drying timber, doping silicon wafers to make semiconductors, and transporting of thermal neutrons in nuclear power reactors. Rates of important chemical reactions are limited by how fast diffusion can bring reactants together or deliver them to reaction sites on enzymes or catalysts. The forces between molecules and molecular sizes and shapes can be studied by making diffusion measurements. See also: [Evaporation \(/content/evaporation/247100\)](#); [Integrated circuits \(/content/integrated-circuits/347600\)](#); [Semiconductor \(/content/semiconductor/614010\)](#); [Thermal neutrons \(/content/thermal-neutrons/689600\)](#)

Fluids

Molecules in fluids (gases and liquids) are constantly moving. Even in still air, for example, nitrogen and oxygen molecules ricochet off each other at bullet speeds. Molecular diffusion is easily demonstrated by pouring a layer of water over a layer of ink in a narrow glass tube. The boundary between the ink and water is sharp at first, but it slowly blurs as the ink diffuses upward into the clear water. Eventually, the ink spreads evenly along the tube without any help from stirring.

Diffusion equations

Adolph Fick discovered the mathematical laws of diffusion in 1855. He found that the rate of diffusion of a substance is proportional to the gradient in its concentration (C). This is expressed in his first law, Eq. (1),

$$J = -D \frac{\partial C}{\partial z} \quad (1)$$

where J is the flux density, the amount of substance diffusing parallel to the z coordinate axis per unit time per unit area. The minus sign reflects the natural tendency of substances to diffuse down concentration gradients, from higher to lower concentrations. Similar equations can be written for diffusion along the x and y coordinates in three-dimensional space.

The quantity D is called the diffusion coefficient or the diffusivity. It measures the flux produced by a given concentration gradient. If the concentration is expressed in units of moles per cubic centimeter and the flux in moles per square centimeter per second, the units of D are square centimeters per second. Mass concentrations (grams per cubic centimeter) and mass fluxes (grams per square centimeter per second) are also used. Since J is the rate of diffusion per unit area, the amount of substance diffusing per second through area A is AJ .

Fick's law for the flow of matter in a concentration gradient is analogous to Fourier's law for heat conduction in a temperature gradient. See also: [Conduction \(heat\) \(/content/conduction-heat/155700\)](#)

Fick's second law

Diffusion changes the distribution of molecules as time passes. Each second, $AJ(z)$ moles of substance diffuse into a slab of solution of area A and thickness Δz (**Fig. 1**) across its left face. Simultaneously, $AJ(z + \Delta z)$ moles per second diffuse out of the slab across its right face. The net rate of diffusion into the slab is $AJ(z) - AJ(z + \Delta z)$.

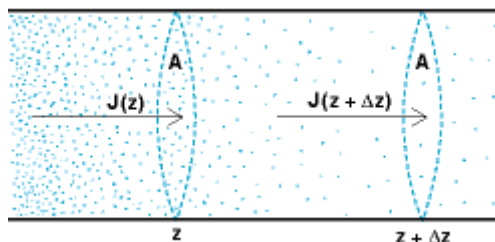


Fig. 1 Diffusion in a tube of cross-sectional area A . The net rate of diffusion into the fluid between z and $z + \Delta z$ is $AJ(z) - AJ(z + \Delta z)$.

Dividing the rate of diffusion into the slab by its volume $A\Delta z$ gives the rate of change of concentration, as in Eq. (2), and combining Eqs. (1) and (2)

$$\frac{\Delta C}{\Delta t} = - \frac{AJ(z + \Delta z) - AJ(z)}{A\Delta z} \quad (2)$$

gives Fick's second law of diffusion, Eq. (3).

$$\frac{\partial C}{\partial t} = - \frac{\partial J}{\partial z} = \frac{\partial}{\partial z} \left[D \frac{\partial C}{\partial z} \right] \quad (3)$$

As time passes, the concentration changes in proportion to the change in the concentration gradient along the diffusion path. This illustrates diffusion's fundamental role: smoothing out gradients in composition.

Diffusion coefficients can be treated as constants if the concentration gradients are not too large. The simpler version of Fick's second law, Eq. (4),

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} \quad (4)$$

then applies. This equation is used to predict the concentrations of diffusing substances in hundreds of different applications. Slightly different equations are used for diffusion in cylindrical or spherical geometries. See also: [Differential equation \(/content/differential-equation/193500\)](#)

Onsager's equation

Just as positive charge flows from higher to lower electric potential, molecules diffuse from regions of higher to lower chemical potential (a thermodynamic property). Gradients in the chemical potential, not concentration gradients, are the true driving forces for diffusion. A more fundamental description of diffusion states that the flux of a diffusing substance is proportional to the gradient in its chemical potential, as in Eq. (5).

$$J = -L \frac{\partial \mu}{\partial z} \quad (5)$$

The thermodynamic diffusion coefficient L is proportional to the mobility of a diffusing substance, the ease with which it moves through a fluid. Small molecules in low-viscosity fluids have the largest mobilities. Fick's diffusion coefficient D equals $L\partial\mu/\partial C$. This result shows that diffusion coefficients are not purely kinetic quantities because they depend on thermodynamic properties too. See also: [Chemical thermodynamics \(/content/chemical-thermodynamics/128200\)](#)

Diffusion processes

These comprise chemical interdiffusion, self-diffusion, and intradiffusion.

Chemical interdiffusion

By far the most frequently studied diffusion process is the molecular mixing of two different chemical substances. An example is the interdiffusion of oxygen and nitrogen. At first glance, there are two diffusion coefficients to consider, one for each substance. However, there is no bulk movement of fluid during diffusion. This restriction leads to the surprising result that the interdiffusion of two substances is described by a single diffusion coefficient, D : $J_1 = -D\partial C_1/\partial z$ and $J_2 = -D\partial C_2/\partial z$. The quantity D is called the interdiffusion coefficient or the mutual diffusion coefficient.

Gas molecules travel over distances of many molecular diameters before being deflected by collisions with other molecules. This gives gas mixtures the largest interdiffusion coefficients, about $0.1 \text{ cm}^2 \text{ s}^{-1}$ at room temperature and atmospheric pressure. A gas molecule diffuses about 0.1–0.5 cm in 1 s. Diffusion in liquids is about 10,000 times slower because the molecules are packed more closely. Solid-state diffusion is even slower because the molecules are locked in position by their neighbors, except for infrequent jumps.

Self-diffusion

Diffusion occurs in pure substances too, and is called self-diffusion. It can be studied by tagging some of the diffusing molecules with isotopes. For example, the self-diffusion coefficient of water is measured by releasing trace amounts of water labeled with radioactive tritium ($^3\text{H}^1\text{HO}$) at one end of a tube filled with ordinary water ($^1\text{H}_2\text{O}$) and then monitoring the

spread of radioactivity along the tube. Magnetized molecules also serve as tagged species. See *also*: [Isotope \(/content/isotope/357000\)](#); [Nuclear magnetic resonance \(NMR\) \(/content/nuclear-magnetic-resonance-nmr/459000\)](#)

Intradiffusion

The term intradiffusion refers to the interchange of tagged and untagged species in systems of uniform chemical composition. To measure the intradiffusion coefficient of benzene in a benzene-heptane mixture containing 1 mole of benzene per liter, a 1-mole-per-liter solution of benzene in heptane is brought into contact with another 1-mole-per-liter benzene solution in which a portion of the total benzene molecules are tagged with radioactive ^{14}C .

Gases

A number of techniques are used to measure diffusion in gases. In a two-bulb experiment, two vessels of gas are connected by a narrow tube through which diffusion occurs. Diffusion is followed by measuring the subsequent changes in the composition of gas in each vessel. Excellent results are also obtained by placing a lighter gas mixture on top of a denser gas mixture in a vertical tube and then measuring the composition along the tube after a timed interval.

Rates of diffusion in gases increase with the temperature (T) approximately as $T^{3/2}$ and are inversely proportional to the pressure. The interdiffusion coefficients of gas mixtures are almost independent of the composition.

Kinetic theory shows that the self-diffusion coefficient of a pure gas is inversely proportional to both the square root of the molecular weight and the square of the molecular diameter. Interdiffusion coefficients for pairs of gases can be estimated by taking averages of the molecular weights and collision diameters. Kinetic-theory predictions are accurate to about 5% at pressures up to 10 atm (1 megapascal). Theories which take into account the forces between molecules are more accurate, especially for dense gases. See *also*: [Kinetic theory of matter \(/content/kinetic-theory-of-matter/364600\)](#)

Liquids

The most accurate diffusion measurements on liquids are made by layering a solution over a denser solution and then using optical methods to follow the changes in refractive index along the column of solution. Excellent results are also obtained with cells in which diffusion occurs between two solution compartments through a porous diaphragm. Many other reliable experimental techniques have been devised.

Room-temperature liquids usually have diffusion coefficients in the range $0.5\text{--}5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. Diffusion in liquids, unlike diffusion in gases, is sensitive to changes in composition but relatively insensitive to changes in pressure. Diffusion of high-viscosity, syrupy liquids and macromolecules is slower. The diffusion coefficient of aqueous serum albumin, a protein of molecular weight 60,000 atomic mass units, is only $0.06 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ at 25°C (77°F).

When solute molecules diffuse through a solution, solvent molecules must be pushed out of the way. For this reason, liquid-phase interdiffusion coefficients are inversely proportional to both the viscosity of the solvent and the effective radius of the solute molecules. Accurate theories of diffusion in liquids are still under development. See *also*: [Viscosity \(/content/viscosity/733900\)](#)

Applications

Diffusion is involved in a great diversity of processes.

Tracer diffusion

If tracer molecules are released in a fluid in which there is no convection, such as stirring, Fick's second equation can be integrated to predict how rapidly the tracer molecules spread out by random thermal motions.

If tracer molecules are released at position $z = 0$ in a tube of cross-sectional area A , they will cluster near the origin initially, and slowly disperse (**Fig. 2a**). The bell-shaped concentration profiles are identical to the gaussian distribution of random errors employed in statistical sciences. This is not accidental, but a direct consequence of the random motions of diffusing molecules. In fact, the standard deviation of the tracer profile, a measure of its width, is $\sqrt{2Dt}$ after diffusion for time t . See [also: Statistics \(/content/statistics/652400\)](#)

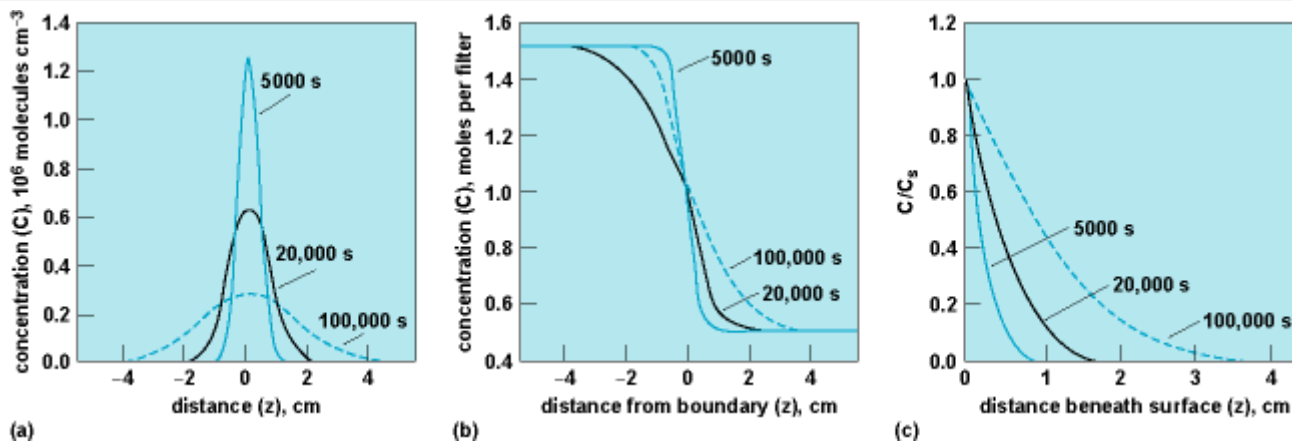


Fig. 2 Concentration profiles. (a) Diffusion of 10^6 tracer molecules in a tube of 1-cm^2 cross-sectional area. The molecules are initially located at position $z = 0$. $D = 1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. (b) Interdiffusion of a solution of concentration 1.5 moles per liter into a solution of concentration 0.5 mole per liter across a sharp initial boundary. (c) Absorption of a gas into a convection-free liquid. Concentration (C) of dissolved gas is given in terms of saturation concentration at liquid surface.

Mixing without convection

Two fluids of different composition can be rapidly mixed by stirring. Without convection, the rate of mixing is diffusion controlled and much slower. As time passes, interdiffusion gradually smooths out a sharp initial boundary between two solutions (**Fig. 2b**).

Gas absorption

Concentration profiles can also be measured for the absorption and diffusion of a soluble gas into a convection-free liquid (**Fig. 2c**). The surface of the liquid is saturated with dissolved gas. After exposure for time t , the dissolved gas penetrates the absorbent to an average depth of about \sqrt{Dt} .

The diffusion flux at the surface of the liquid gives the rate of dissolution of gas per unit surface area of liquid. This rate is proportional to the solubility of the gas and the square root of the diffusion coefficient. The adsorption process slows down as time passes as $t^{-1/2}$. Identical results are obtained for the dissolution of a solid into a stagnant liquid.

Brownian motion

Colloidal particles suspended in a liquid move by a series of small, chaotic jumps. This kind of diffusion is called brownian motion. It was first observed by looking at suspensions of pollen grains in water under a microscope.

A. Einstein analyzed the motion of a randomly jumping particle. He showed that a particle making ν jumps per second of length ℓ has diffusion coefficient $\nu\ell^2/2$. This result provides a useful physical model of the diffusion process. It also accounts for the slowness of diffusion in liquids relative to gases: The distance between collisions, ℓ , is relatively small for liquids. Diffusion in solids is even slower because both the step size and jump frequency are small.

If a particle is allowed to diffuse freely in one dimension, its root-mean-square displacement after time t is $\sqrt{2Dt}$. This result is frequently used to estimate the distances covered by diffusing molecules. A molecule with diffusion coefficient $1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ diffuses about 1 cm in a day but only about 25 cm in a year. The root-mean-square displacement for three-dimensional diffusion is $\sqrt{6Dt}$ (**Fig. 3**). See also: [Brownian movement \(/content/brownian-movement/097200\)](/content/brownian-movement/097200); [Colloid \(/content/colloid/149100\)](/content/colloid/149100)

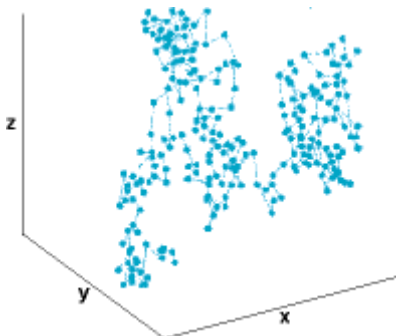


Fig. 3 Brownian motion of a particle in three dimensions.

Porous materials

Diffusion through a porous solid is slower than diffusion through an equal volume of homogeneous fluid for two reasons. First, the diffusing molecules must travel greater distances to move around solid obstructions. Second, diffusion can occur only through the pore fraction of the total cross-sectional area.

A practical approach to this problem is to treat the porous medium as a homogeneous phase with an effective diffusion coefficient, D_{eff} . Values of D_{eff} are typically 3–10 times smaller than the diffusion coefficient D for the pore fluid. The D_{eff}/D ratio depends on the void fraction and details of the pore network, such as the number of interconnections and dead ends.

Effusion

At low pressures, gas molecules can escape through a pinhole in the wall of a container without colliding with other molecules. This process is called effusion. It is used to measure the vapor pressure of solids and liquids at high temperatures. The rate of effusion is inversely proportional to the square root of the molecular weight of the gas. Gases such as $^{235}\text{UF}_6$ and $^{238}\text{UF}_6$ can therefore be separated by effusion through porous membranes. See also: [Isotope separation \(/content/isotope-separation/357100\)](/content/isotope-separation/357100)

Interdiffusion coefficients of electrolytes are sensitive to changes in concentration. For a dilute solution of a 1:1 salt, such as NaCl, the interdiffusion is the harmonic average of the diffusion coefficients of the ions: $D = 2D_+ D_- / (D_+ + D_-)$. See also: [Electrolyte \(/content/electrolyte/221800\)](#); [Electrolytic conductance \(/content/electrolytic-conductance/221900\)](#)

Multicomponent interdiffusion

Mixtures of three or more components are of considerable practical importance. Diffusion in these systems differs in important ways from diffusion in simpler two-component mixtures. Adding a new component to an existing mixture changes the rates of diffusion of all the components in the mixture. Also, a new feature appears: coupled diffusion, where the gradient in concentration of each substance causes diffusion of the other substances in the mixture. Coupled diffusion can drive substances from regions of lower to higher concentration, opposite to the expected direction. Diffusion in multicomponent mixtures is described by adding coupled-diffusion terms to Fick's equations.

Coupled diffusion is important in concentrated solutions and in mixed electrolytes because the forces between the diffusing materials are significant. For example, in aqueous solutions of potassium chloride (KCl) and hydrogen chloride (HCl), owing to electrostatic forces, the flux of potassium chloride caused by the gradient in hydrogen chloride can be larger than the flux of potassium chloride caused by its own gradient. Hydrogen chloride diffuses much more rapidly in water-KCl-HCl mixtures than in binary water-HCl mixtures.

Diffusion with convection

In moving fluids, substances are transported by diffusion as well as convection. If the concentration of a substance is C and the solution moves with velocity U_z in the z direction, the flux of substance due to the bulk movement of the solution is CU_z . The net flux is the sum of the contributions from diffusion and convection, as in Eq. (6).

$$J = -D \frac{\partial C}{\partial z} + CU_z \quad (6)$$

See also: [Convection \(heat\) \(/content/convection-heat/160000\)](#)

Dispersion in pipelines

The dispersion of a tracer in a liquid carrier stream is an interesting example of combined diffusive and convective transport. The liquid near the center of the tube moves more quickly than the liquid near the tube wall. This causes an injected tracer to spread out along the axis of the tube. If the flow rate is low enough to prevent turbulence, the combined actions of axial convection and radial diffusion shape the dispersed tracer into a bell-shaped plume. Dispersion is minimized by using short, narrow tubes. Diffusion coefficients of liquids and gases are determined by measuring dispersion profiles.

Ionic diffusion in electric fields

When a salt solution is placed between charged electrodes, electrical forces draw the positive ions toward the negative electrode and the negative ions toward the positive electrode. The flux of an ion caused by an electric field is proportional to the field strength and to the ion's charge, diffusion coefficient, and concentration.

Dividing the drift velocity of a migrating ion by the electric field gives the ion's electric mobility. The electric mobilities of aqueous ions are usually in the range 0.0003 – $0.001 \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$. Thus, a 10 V cm^{-1} electric field generates ionic drift velocities of about 0.003 – 0.01 cm s^{-1} .

Thermal diffusion

If one end of a convection-free column of solution is heated and the other end cooled, solute spontaneously migrates to the cooler regions and solvent migrates to the warmer regions, or vice versa. Diffusion caused by temperature gradients is called thermal diffusion.

Diffusion in nonisothermal solutions is described by adding the term $-CD_T\partial T/\partial z$ to the right-hand side of Eq. (1) to allow for the flux caused by the temperature gradient, giving Eq. (7).

$$J = -D \frac{\partial C}{\partial z} - CD_T \frac{\partial T}{\partial z} \quad (7)$$

The quantity D_T is the thermal diffusion coefficient. Positive values of D_T indicate migration to the cooler parts of a mixture. Substances with negative D_T values migrate to warmer regions.

The accumulation of material at the ends of the solution column produces concentration gradients. Eventually, thermal migration is balanced by ordinary diffusion down the concentration gradient, and a steady state is reached in which there are no further changes in concentration. The ratio of the thermal diffusion coefficient to the interdiffusion coefficient gives the fractional change in solute concentration per degree at steady state, as in Eq. (8).

$$\frac{D_T}{D} = -\frac{1}{C} \left(\frac{dC}{dT} \right)_{\text{steady state}} \quad (8)$$

Typical D_T/D values are about 0.001 K^{-1} , which corresponds to a 1% concentration difference for a 10 K (18°F) temperature difference.

Thermal diffusion is used to purify isotopes and to fractionate polymers, but for most solutions the separations are too small to compete with other techniques. A few solutions have D_T/D values as large as 0.03 K^{-1} . Thus, a 10 K (18°F) temperature difference can produce a 30% change in concentration, which is not negligible. Thermal diffusion effects can be significant if large temperature gradients are imposed on a solution.

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Solids

Diffusion in solids is an important topic of physical metallurgy and materials science since diffusion processes are ubiquitous in solid matter at elevated temperatures. They play a key role in the kinetics of many microstructural changes that occur during the processing of metals, alloys, ceramics, semiconductors, glasses, and polymers. Typical examples of such changes include nucleation of new phases, diffusive phase transformations, precipitation and dissolution of a second phase, recrystallization, high-temperature creep, and thermal oxidation. Direct technological applications concern diffusion doping during the fabrication of microelectronic devices, solid electrolytes for battery and fuel cells, surface hardening of steels through carburization or nitridation, diffusion bonding, and sintering. See also: [Creep \(materials\) \(/content/creep-materials/167300\)](#); [Fuel cell \(/content/fuel-cell/274100\)](#); [Heat treatment \(metallurgy\) \(/content/heat-treatment-metallurgy/311200\)](#); [Metal, mechanical properties of \(/content/metal-mechanical-properties-of/417810\)](#); [Phase transitions \(/content/phase-transitions/506100\)](#); [Plastic deformation of metals \(/content/plastic-deformation-of-metals/526600\)](#); [Sintering \(/content/sintering/625200\)](#); [Solid-state battery \(/content/solid-state-battery/634700\)](#); [Surface hardening of steel \(/content/surface-hardening-of-steel/671000\)](#)

The atomic mechanisms of diffusion are closely connected with defects in solids. Point defects such as vacancies and interstitials are the simplest defects and often mediate diffusion in an otherwise perfect crystal. Dislocations, grain boundaries, phase boundaries, and free surfaces are other types of defects in a crystalline solid. They can act as diffusion short circuits because the mobility of atoms along such defects is usually much higher than in the lattice. See also: [Crystal defects \(/content/crystal-defects/171300\)](/content/crystal-defects/171300)

Diffusion coefficients

The diffusion of atoms through a solid can be described by Fick's equations (1) and (3). For a constant (concentration-independent) diffusivity, solutions of these equations exist for a wide variety of initial and boundary conditions and permit a determination of the diffusion coefficient (D) either from measurements of the concentration distribution as function of the position and time or from measurements of diffusion fluxes and concentration gradients. For example, if a diffusing species is initially concentrated in a thin layer, then after a time t it will have a bell-shaped concentration profile whose width depends on D and t in the same manner as in tracer diffusion.

For diffusion in a material with a chemical composition gradient, solutions of Eq. (3) in closed form are usually not possible. Then numerical methods are often used to deduce interdiffusion coefficients.

Any diffusion coefficient is a material parameter, which depends on the composition, slightly on pressure, and strongly on temperature T . Very often the temperature dependence for a given material is described by an Arrhenius equation (9),

$$D = D_0 \exp\left(-\frac{Q}{RT}\right) \quad (9)$$

where Q is the activation enthalpy, D_0 is a preexponential factor, and R is the gas constant. See also: [Enthalpy \(/content/enthalpy/234900\)](/content/enthalpy/234900)

The most fundamental diffusion process in a solid is self-diffusion and refers to diffusion of A atoms in a solid element A or in an A-B alloy or compound. Following Eq. (9), the self-diffusion coefficients of many metals increase by 7 to 10 orders of magnitude as the absolute temperature is increased from half the melting temperature to the melting temperature. Diffusion of a solute B in a very dilute A-B alloy with the solvent A is denoted as impurity diffusion. Self-diffusion and impurity diffusion in a homogeneous solid can be studied, for example, by utilizing small amounts of radioactive trace atoms. Diffusion in an inhomogeneous solid with a composition gradient is denoted as interdiffusion or sometimes as chemical diffusion.

Crystalline solids differ from gases and liquids in that the symmetry of the atomic arrangement can give rise to different values of D in different directions of the crystal lattice. In isotropic materials such as glasses and polycrystals with random orientation of the individual grains and in cubic single crystals, only one D value characterizes the material. Two diffusion coefficients are necessary for uniaxial (hexagonal, tetragonal, and trigonal) crystals, and three D values characterize diffusion in single crystals of lower symmetry. For example, the D value for diffusion in the basal plane of a hexagonal single crystal is different from the D value perpendicular to this plane. See also: [Crystal structure \(/content/crystal-structure/171700\)](/content/crystal-structure/171700)

Mechanisms

Diffusion in crystalline matter takes place by a series of jumps of individual atoms from site to site throughout the crystal. Because of the lattice vibrations, atoms in a crystal oscillate around their equilibrium (substitutional or interstitial) positions with frequencies, ν_0 , of the order of the Debye frequency (typically 10^{12} – 10^{13} Hz). Usually an atom is confined to a certain

site by a potential barrier with barrier height G^M , which corresponds to the Gibbs free-energy difference between the configuration with the jumping atom at the saddlepoint and with that at its equilibrium position. Diffusion is thermally activated, meaning that a fluctuation of thermal energy pushes the atom over the energy barrier which exists between two neighboring sites. From reaction rate theory, the jump frequency ω at which an atomic jump will occur into an empty neighboring site may be written in the form of Eq. (10).

$$\omega = \nu_0 \exp\left(-\frac{G^M}{RT}\right) \quad (10)$$

See also: [Boltzmann statistics \(/content/boltzmann-statistics/089900\)](#); [Free energy \(/content/free-energy/271300\)](#); [Lattice vibrations \(/content/lattice-vibrations/373400\)](#); [Specific heat of solids \(/content/specific-heat-of-solids/641900\)](#); [Statistical mechanics \(/content/statistical-mechanics/652300\)](#)

At an atomic level, the diffusivity of (for example, radioactive) tagged atoms in a cubic crystal can be described by Eq. (11),

$$D = \frac{1}{6} f d^2 \omega p \quad (11)$$

where d is the jump distance (some fraction of the lattice parameter), p is the probability that the neighboring site of the jumping atom is empty, and f is the correlation factor, a term which expresses the degree of randomness of successive jumps. Various atomic mechanisms have been identified for bulk diffusion in crystals.

Interstitial mechanism

Solute atoms which are much smaller than the lattice atoms, as for example, hydrogen, carbon, nitrogen, and oxygen in metals, are incorporated in interstitial sites. They diffuse by jumping from interstitial site to interstitial site (**Fig. 4a**). For a dilute interstitial alloy, the probability p in Eq. (10) is unity. The magnitude of the barrier height G^M is also relatively small, with the result that the diffusion coefficients for interstitial diffusion can be many orders of magnitude larger than those for the self-diffusion of lattice atoms. Interstitial diffusivities near the melting temperature of the solvent can be as high as diffusivities in liquids.

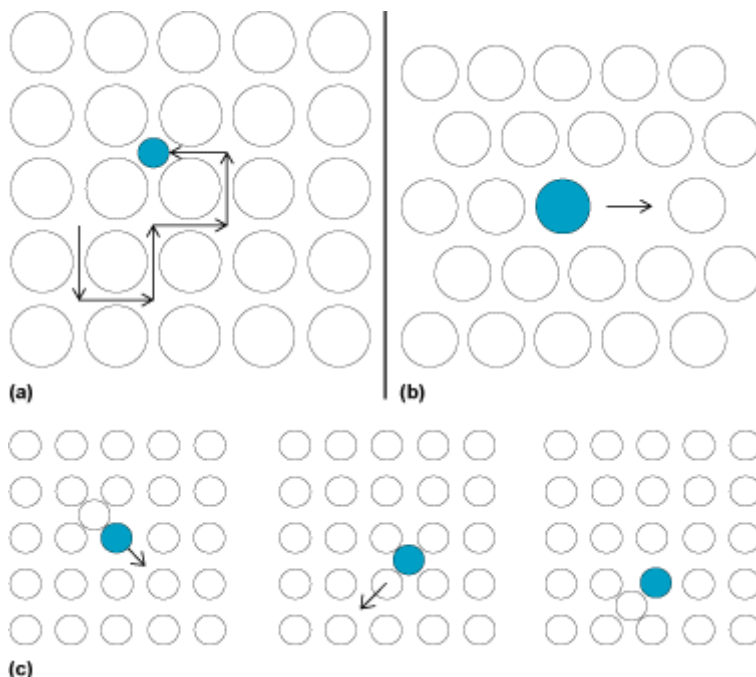


Fig. 4 Diffusion mechanisms. (a) Direct interstitial mechanism. (b) Vacancy mechanism. (c) Self-interstitial mechanism.

Vacancy mechanism

Self-atoms or substitutional solute atoms migrate by jumping into a neighboring vacant site. Self-diffusion in metals and alloys, and in many ionic crystals and ceramic materials, occurs via the vacancy mechanism (Fig. 4b). Attractive or repulsive interactions between the vacancy and substitutional solute atoms may lead to higher or lower diffusivities compared with self-diffusion of the pure solvent. See also: [Ionic crystals \(/content/ionic-crystals/352100\)](/content/ionic-crystals/352100)

In crystals with ionic bonding characteristics such as alkali halides, in ceramics, and in some intermetallic compounds, atoms do not jump between the sublattices of the constituents. This implies that the diffusion coefficients of the various atomic species can differ significantly.

Self-interstitial mechanism

In this case, self-interstitials—extra atoms located between lattice sites—act as diffusion vehicles. A self-interstitial replaces an atom on a substitutional site which then replaces again a neighboring lattice atom (Fig. 4c). Self-interstitials are responsible for diffusion in the silver sublattice of silver halides. In silicon, the base material of microelectronic devices, the interstitialcy mechanism dominates self-diffusion and plays a prominent role in the diffusion of many solute atoms, including the most important doping elements. In the close-packed metals, this mechanism is unimportant under thermal equilibrium conditions because of the fairly high formation enthalpy of self-interstitials. It is, however, important for radiation-damage-induced diffusion, where self-interstitials and vacancies are created athermally by irradiation of a crystal with energetic particles. See also: [Radiation damage to materials \(/content/radiation-damage-to-materials/566800\)](/content/radiation-damage-to-materials/566800)

Interstitial-substitutional exchange mechanisms

Some solute atoms (B) may be dissolved on interstitial (B_i) and substitutional sites (B_s) of a solvent crystal (A). For hybrid solutes the diffusivity of B_i is much higher than the diffusivity of B_s , whereas the opposite is true for the solubilities. Under such conditions, the incorporation of B atoms can occur by the fast diffusion of B_i and the subsequent change-over to B_s .

If the change-over involves vacancies (V) according to reaction (12),



the mechanism is denoted as the dissociative mechanism (sometimes also known as the Frank-Turnbull mechanism or the Longini mechanism). The rapid diffusion of copper in germanium and of some foreign metallic elements in polyvalent metals like lead, titanium, and zirconium has been attributed to this mechanism.

If the change-over involves a self-interstitial of the solvent (A_i) according to reaction (13),



the mechanism is denoted as the kick-out mechanism. Examples of this mechanism have been established for some rapidly diffusing foreign elements (for example, gold, platinum, and zinc) in silicon.

Short-circuit diffusion

Any real crystalline material usually contains extended defects such as dislocations, grain boundaries in polycrystals, interphase boundaries in polyphase materials, and free surfaces. These regions are more open structures than the adjoining crystal lattice. The jump frequency of atoms in these regions is much higher and the activation enthalpy of diffusion lower than in the perfect crystal. Because of the lower activation enthalpy, the mobility of atoms along extended defects decreases less rapidly with decreasing temperature than in the bulk. The result is that at low temperatures (below about half of the melting temperature) diffusion through the lattice becomes slower than diffusion along the extended defects. Then these defects constitute paths of high diffusivity which at low enough temperatures are said to short circuit lattice diffusion.

The rapid diffusion along high-diffusivity paths is often important in surface- and thin-film technologies. In thin-film microelectronic devices, shortcircuit diffusion among various components of the multilayered structures is one of the principal modes of device failure. The fast diffusion character of grain-phase and interphase boundaries also results in the fact that many solid-state reactions at lower temperatures, such as discontinuous precipitation and eutectoid transformations, are controlled by diffusion along boundaries.

Superionic conductors

Superionic conductors, sometimes referred to as fast-ion conductors or solid electrolytes, are solids which have an exceptionally high ionic conductivity over a reasonable temperature range. In some cases the conductivity approaches the magnitude found in molten salts and aqueous solutions of strong electrolytes. Typical values of the conductivity of a superionic conductor are in the range of 0.001 to 10 $(\Omega \text{ cm})^{-1}$. The conductivity of copper near room temperature is 6×10^5 $(\Omega \text{ cm})^{-1}$; a typical ionic crystal has a conductivity of 10^{-4} $(\Omega \text{ cm})^{-1}$ close to the melting temperature; an aqueous solution of 0.1 N NaCl has a conductivity of 10^{-2} $(\Omega \text{ cm})^{-1}$. Diffusivity D and ionic conductivity σ are related via the Nernst-Einstein equation (14),

$$D = \frac{\sigma k_B T}{q^2 N} \quad (14)$$

where k_B denotes Boltzmann's constant, T absolute temperature, q the ionic charge, and N the volume density of mobile ions. Superionic conduction implies fast diffusion of the ions. Typically a conductivity of 1 $(\Omega \text{ cm})^{-1}$ corresponds to a diffusivity of about 10^{-5} $\text{cm}^2 \text{ s}^{-1}$, which is in the same order of magnitude as diffusion in liquids. Because of their high conductivity, superionic conductors are thought of as solid electrolytes with many applications, both realized and potential, for example, in batteries, fuel cells, and sensors. See also: [Battery \(/content/battery/075200\)](#); [Fuel cell \(/content/fuel-cell/274100\)](#)

The high ionic conductivity, depending on the material, can be of either cationic or anionic character. As a general rule, superionic conductors are materials with an open structure, which allows the rapid motion of relatively small ions. The most important classes of superionic conductors are the following:

1. Many superionic conductors have a fixed anion lattice and a three-dimensionally disordered cation lattice. Example are those of the silver iodide type (reported as early as 1913), which display a first-order phase transition between a superionic phase at high temperatures and a normal conducting phase at low temperatures. In the case of pure silver iodide (AgI), the high-temperature phase α -AgI exists above 146°C (295°F) with a body-centered cubic sublattice of fixed I^- ions. Each unit cell presents 42 interstitial sites over which the two Ag^+ ions can distribute themselves (**Fig. 5**). Since there are many more sites than Ag^+ ions, the latter can migrate easily. Materials derived from α -AgI with the formula $\text{M}\text{Ag}_4\text{I}_5$, where $\text{M} = \text{K}, \text{Rb}, \text{Cs},$ and NH_4 , are superionic at ambient temperature.

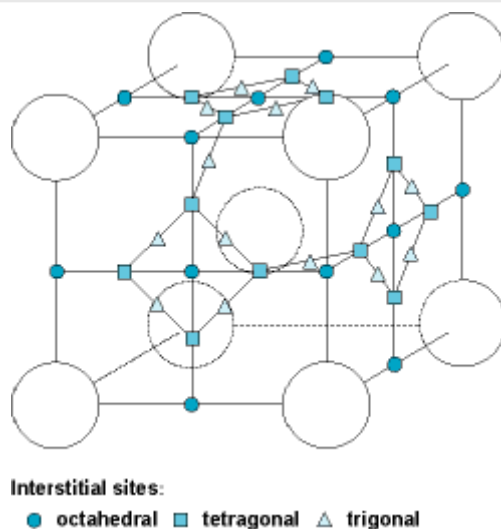


Fig. 5 Crystal structure of α -silver iodide.

- Some fast-ion conductors have a hexagonal structure in which small cations can move either two-dimensionally in layers or one-dimensionally in channels. Materials in which two-dimensional diffusion occurs are the β -aluminas, which are nonstoichiometric aluminates with the formula $M_2O_nAl_2O_3$, where $M = Na, Li, Ag, \dots$ and n ranges from 5 to 11. A material with one-dimensional diffusion is β -eucryptite, an aluminosilicate ($LiAlSiO_4$), in which the lithium ions are located in channels parallel to the hexagonal axis.
- Zeolites are natural or synthetic hydrated aluminosilicates with an open three-dimensional structure, in which ions are incorporated in cavities of the lattice. See also: [Zeolite \(/content/zeolite/754600\)](/content/zeolite/754600)
- Superionic conductors are also found among compounds with the fluorite structure, such as some halides ($SrCl_2, CaF_2, PbF_2$) and oxides like ZrO_2 (zirconia), and exhibit fast-ion conductivity. Zirconia is stabilized in the cubic structure by additions of CaO and Y_2O_3 .
- A number of glasses, including lithium borate glass, have been examined as fast-ion conductors.
- Solutions of ionic salts in certain polymers (polymer electrolytes) can exhibit conductivities in the intermediate range. The fact that these materials can be cast as thin, flexible foils led to applications as battery electrolytes.

Surface diffusion

Surface diffusion is the motion of atoms or molecules on top of the surface of a solid material. The diffusivity of an atom on the surface is usually much higher than the diffusivity of the same atom in the interior of the solid, and its activation enthalpy is lower than in the bulk material.

The surface of a crystalline solid has a complicated but well-defined crystallographic structure, which can be described in terms of terraces (low-indexed, vicinal planes), steps, and kinks (**Fig. 6**). Adatoms on the terraces and at steps and surface vacancies occur in thermal equilibrium. More complex defects, such as dislocation emerging points, impurity clusters, high-index facets, and hillocks, may be present. The structure of a real surface will give rise to a mobility of atoms that depends on their position. It will be different, for example, on terraces and on steps. Often an anisotropy of diffusion is also observed, depending on the orientation of vicinal surfaces.

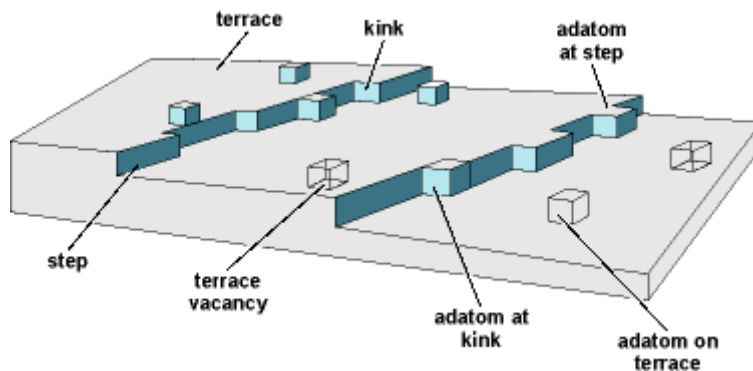


Fig. 6 Model of the surface of a single crystal.

Surface diffusion at temperatures that are not too high occurs via elementary jumps of surface vacancies and adatoms over one atomic distance. When the temperature rises, multiple jumps of adatoms over several atomic distances are possible. Near the melting temperature, even pseudo-liquid behavior has been observed in molecular-dynamic simulations.

Various methods can be used to study surface diffusion. Among them are observations of the migration of single adatoms by means of field-ion microscopy and scanning tunneling microscopy; observations of the redistribution of radiotracer atoms initially deposited on one part of a surface; and topographic methods that monitor the diffusion-induced change in the shape of a solid, which is driven by surface tension.

Radiation-enhanced diffusion

The diffusion coefficient of atoms in solids is dominated by the product of the equilibrium concentration of the diffusion-relevant defects times their mobility. Equilibrium concentration and defect mobility drop steeply with decreasing temperature. As a consequence of this strong temperature dependence, hardly any atomic diffusivity will remain below about 40% of the melting temperature.

In radiation-enhanced diffusion, additional point defects are produced by the incident radiation. High-energy electrons (available, for example, in a high-voltage electron microscope) colliding with the lattice atoms can produce pairs of vacancies and self-interstitials (Frenkel pairs). Irradiation with heavier particles, such as protons, fast neutrons, alpha particles, and heavy ions, causes radiation damage to the crystal lattice which introduces many Frenkel pairs per incident particle. Therefore, not only will the usual diffusion path be enhanced, but also new channels can be opened by way of defects (such as self-interstitials in the case of metals) which are not available in normal thermally activated diffusion. Radiation-enhanced diffusion can occur at relatively low temperatures provided that thermal activation permits sufficient mobility of at least one of the defect species produced during irradiation. Radiation-enhanced diffusion is of importance in materials science since it affects the properties of materials exposed to particle irradiation.

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Bibliography

E. L. Cussler, *Diffusion: Mass Transfer in Fluid Systems*, 2d ed., 1997

B. Gebhart, *Heat Conduction and Mass Diffusion*, 1993

M. E. Glicksman, *Diffusion in Solids*, Wiley, 1999

H. Mehrer (ed.), *Diffusion in Solid Metals and Alloys*, 1990

H. Mehrer, C. Herzig, and N. A. Stolwijk (eds.), *Diffusion in Materials*, Scitec Publications, 1997

G. Murch (ed.), *Diffusion in Solids: Unsolved Problems*, 1992

J. S. Newman, *Electrochemical Systems*, 2d ed., 1991

J. Philibert, *Atom Movements: Diffusion and Mass Transport in Solids*, 1991

B. W. Rossiter and J. F. Hamilton (eds.), *Physical Methods of Chemistry*, vol. 6, 2d ed., 1992

P. Shewmon, *Diffusion in Solids*, 1989

Additional Readings

G. Hou et al., Spin diffusion driven by R-symmetry sequences: Applications to homonuclear correlation spectroscopy in MAS NMR of biological and organic solids, *J. Am. Chem. Soc.*, 133(11):3943–3953, 2011 DOI: [10.1021/ja108650x](https://doi.org/10.1021/ja108650x)
(<http://dx.doi.org/10.1021/ja108650x>)

H. Kuhn, H. D. Försterling, and D. H. Waldeck, *Principles of Physical Chemistry*, 2d ed., John Wiley & Sons, Hoboken, NJ, 2009

R. M. A. Roque-Malherbe, *The Physical Chemistry of Materials*, CRC Press, Boca Raton, FL, 2010