

A

Ab Initio Methods

The Latin phrase *ab initio* means (loosely) ‘from scratch’. It is applied to calculations of the electronic structures and properties of molecules starting from only the atomic numbers of the elements and the mass and charge of an electron. They are in contrast to semi-empirical methods, which import empirical information into the calculation as a substitute for calculating certain integrals.

Absorption

In spectroscopy, *absorption* is the process by which electromagnetic radiation excites an atom or molecule into a state of higher energy. Absorption is most intense when the energy, $h\nu$, of a photon of the incident radiation matches the energy difference, ΔE , between the initial and final states. For electric dipole transitions, the intensity of absorption is proportional to the square of the transition dipole moment. The intensity is reported as the *absorbance* (at a specified frequency, wavelength, or wavenumber) or, when the absorption spans a range of frequencies, as the *integrated absorption coefficient*. When the upper state is already populated, the net intensity of absorption is the difference between the intensity of absorption from the ground state and the intensity of emission from the upper state.

Accommodation

Accommodation in surface science is the dissipation of energy that leads to the adsorption of a gas-phase molecule on to a substrate.

Acid

An *Arrhenius acid* is a compound that releases hydrogen ions in aqueous solution. A *Brønsted acid*, HA, is a proton donor (with ‘proton’, in this context, a hydrogen ion, H^+). Loss of the proton results in the formation of the *conjugate base* of the acid, A^- . Conversely, the acquisition of a proton by a base, B, result in the formation of its *conjugate acid*, HB^+ . A *strong acid* is effectively fully deprotonated in solution; a *weak acid* is only partially deprotonated at normal concentrations. In terms of acidity constants, K_a , a weak acid has $K_a \ll 1$. A *Lewis acid* is an electron-pair acceptor. A *hard acid* is a Lewis acid that tends to bond strongly to a hard base; a *soft acid* is a Lewis acid that tends to bond strongly to a soft base. Hard acid–hard base combinations are largely ionic whereas soft acid–soft base combinations are largely covalent.

Acid–Base Indicator

An *acid–base indicator* is a water-soluble organic dye that changes colour according to the pH of the solution. The indicator is a weak acid with acidity constant K_{In} (and $pK_{In} = -\log K_{In}$); the relative molar concentrations of the protonated and deprotonated form depend on pH as

$$\log \frac{[HIn^+, \text{colour1}]}{[In, \text{colour2}]} = pH - pK_{In}$$

See Figure A.1. The *end point* of a titration is the stage at which HIn^+ and In are present in equal concentrations, and occurs at $pH = pK_{In}$. For precise results, an indicator should be chosen with an end point that coincides with the pH of the stoichiometric point (or ‘equivalence point’).

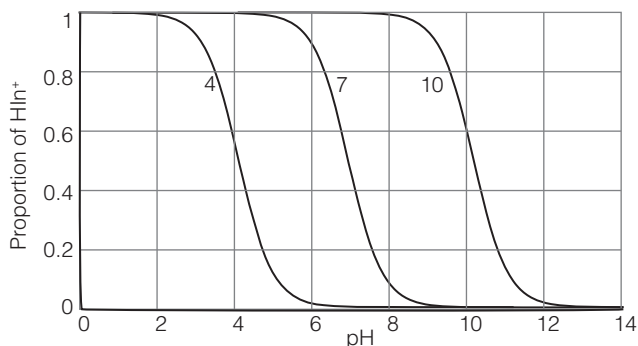


Figure A.1 Indicator concentration curves for $pK_{In}=4, 7,$ and 10 .

Acidity Constant

The *acidity constant*, K_a , of an acid HA (including the conjugate acid of a base) is defined as

$$K_a = \frac{a(\text{H}_3\text{O}^+)a(\text{A}^-)}{a(\text{HA})}, \quad pK_a = -\log K_a$$

where $a(\text{J})$ is the activity of J in solution. In elementary applications, the activities are replaced by the numerical values of the molar concentrations:

$$K_a \approx \frac{([\text{H}_3\text{O}^+]/c^\ominus)([\text{A}^-]/c^\ominus)}{[\text{HA}]/c^\ominus} = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]c^\ominus}$$

The acidity constant is a measure of the proton-donating strength of the acid to water. A low value of K_a , and therefore a high value of pK_a , indicates a weak acid.

Activation Energy

The *activation energy* of a chemical reaction is the parameter E_a that occurs in the Arrhenius expression for the temperature-dependence of the rate constant, $\ln k_r = \ln A - E_a/RT$, and is determined from an Arrhenius plot. The molecular interpretation of the activation energy is that it represents the height of the energy barrier on the reaction coordinate between reactants and products (Figure A.2). A high activation energy signifies a rate constant that is very sensitive to temperature; a low activation energy signifies a rate constant that varies

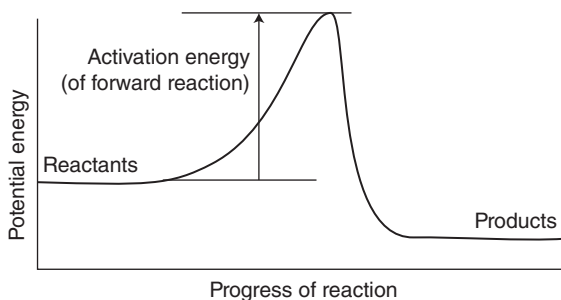


Figure A.2 The energy barrier on the reaction coordinate.

only little with temperature. In a multistep reaction the overall activation energy is a combination of the activation energies of the individual steps. That leaves open the possibility that the sensitivity of the rate to temperature is dominated by one step with a high activation energy. Another possibility is that an activation energy may be negative, such as when the reverse reactions in a sequence are more sensitive to temperature than the forward reactions. The formal definition of activation energy, which allows for the possibility that the Arrhenius plot is not a straight line and therefore that in some sense the activation energy varies with temperature, is

$$E_a = RT^2 \frac{d \ln k_r}{dT}$$

Activation Parameters

The standard *Gibbs energy of activation*, $\Delta^\ddagger G^\ominus$, the standard *enthalpy of activation*, $\Delta^\ddagger H^\ominus$, and the standard *entropy of activation*, $\Delta^\ddagger S^\ominus$, are defined by analogy with the corresponding expressions for chemical equilibria. Thus, by analogy with the thermodynamic relation $\Delta_r G^\ominus = -RT \ln K$, the standard Gibbs energy of activation is defined as $\Delta^\ddagger G^\ominus = -RT \ln k_r$. The thermodynamic relation $\Delta G = \Delta H - T\Delta S$ is then mirrored by writing $\Delta^\ddagger G^\ominus = \Delta^\ddagger H^\ominus - T\Delta^\ddagger S^\ominus$. These relations then imply that the parametrization of the rate constant is

$$k_r = e^{-\Delta^\ddagger G^\ominus/RT} = e^{\overbrace{\Delta^\ddagger S^\ominus/R}^A} e^{-\Delta^\ddagger H^\ominus/RT}$$

Note that the entropy of activation maps on to the Arrhenius frequency factor, A , and the enthalpy of activation replaces the activation energy.

Activity

Thermodynamic expressions are typically developed for ideal solutions and perfect gases, with expressions such as $\mu_J = \mu_J^\ominus + RT \ln x_J$ (where μ_J^\ominus is the standard chemical potential and x_J is the mole fraction of J). The *activity* of a species J, a_J or $a(J)$, is introduced principally to retain the form of these expressions for systems that are not ideal. Thus, for a real solution the chemical potential is written $\mu_J = \mu_J^\ominus + RT \ln a_J$. The activity is therefore an ‘effective’ version of the mole fraction (or other measures of abundance, such as molar concentration $[J]$ and molality b_J). Activities are dimensionless. For reversion to ideal expressions (as in many elementary applications) given an expression in terms of activity, use the relations $a_J = p_J/p^\ominus$ (for a gas) and either $a_J = [J]/c^\ominus$ or $a_J = b_J/b^\ominus$ for a solute; for any pure solid, $a_J = 1$.

Activities can be measured by making observations on the vapour pressure of a solvent and comparing it with the vapour pressure of the pure solvent (at the same temperatures): $a_J = p_J/p_J^*$. The activity of the solute can then be inferred from this value by using the Gibbs–Duhem equation. Electrochemical measurements in conjunction with the Nernst equation can be used if the solute is ionic.

Thermodynamic equations expressed in terms of activities are exact (by definition). For them to be useful, activities need to be related to measures of abundance. To do so, it is common to introduce the *activity coefficient*, γ_J , by the relation $a_J = \gamma_J x_J$ (or analogous expressions in terms of molar concentration and molality), and to focus on the activity coefficient. For the solvent, Raoult’s law implies that $\gamma_J \rightarrow 1$ as $x_J \rightarrow 1$. For the solute, Henry’s law implies that $\gamma_J \rightarrow 1$ as $x_J \rightarrow 0$. Models and theories are then needed to relate γ_J to measurable properties. Typically, these theories are limiting laws, reliable only in the Raoult’s or Henry’s law limits. An example is the Debye–Hückel limiting law for electrolyte solutions. The utility of these limiting-law expressions is best regarded as a guide to how measurements should be extrapolated to low concentrations rather than as the basis for making reliable estimates of numerical values.

Adiabatic

A boundary is *adiabatic* if it does not allow the exchange of energy as heat between the system and its surroundings. A process is adiabatic

if $q = 0$. The practical realization of an adiabatic boundary is that of a container with efficiently insulated walls, such as a Dewar vessel. For the adiabatic, reversible expansion of a perfect gas, the initial and final states are related by

$$p_i V_i^\gamma = p_f V_f^\gamma, \quad T_i V_i^{1/c} = T_f V_f^{1/c}$$

where $\gamma = C_p/C_V$ is the *heat capacity ratio* (or *adiabatic constant*) and $c = C_{V,m}/R$. The two graphs (Figures A.3 and A.4) show how the pressure (for $\gamma = 2$) and temperature (for $C_{V,m} = 2R$) change (the dotted line is for isothermal expansion).

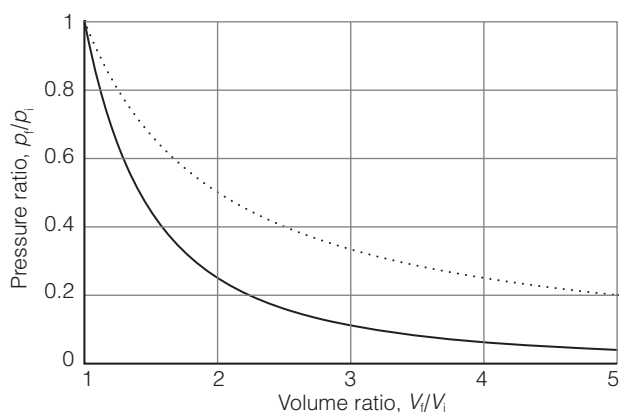


Figure A.3 The pressure variation for a reversible adiabatic expansion of a perfect gas. The dotted line is for a reversible isothermal expansion.

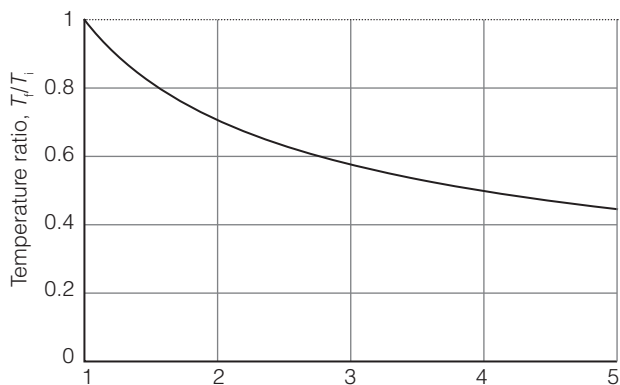


Figure A.4 The temperature variation for a reversible adiabatic expansion of a perfect gas.

Adiabatic Demagnetization

Adiabatic demagnetization is a procedure for cooling objects to very low temperatures. A sample of electron or nuclear spins (on their parent atoms or ions) at a given temperature has a certain entropy. The application of a magnetic field on the sample in thermal contact with its surroundings partially aligns the spins and therefore lowers the entropy of the spin system. Then, with the thermal contact broken to make the subsequent step adiabatic, the field is slowly reduced to zero (Figure A.5). This step is adiabatic and reversible, so it is also isentropic (that is, occurs without change of entropy). The result of this step is a sample in which the newly partially aligned spins survive in the absence of a magnetic field. The lower entropy of this spin distribution corresponds to a temperature lower than it was initially. The process can be repeated to reach successively lower temperatures. When the spins are those of nuclei, the technique is called *adiabatic nuclear demagnetization*.

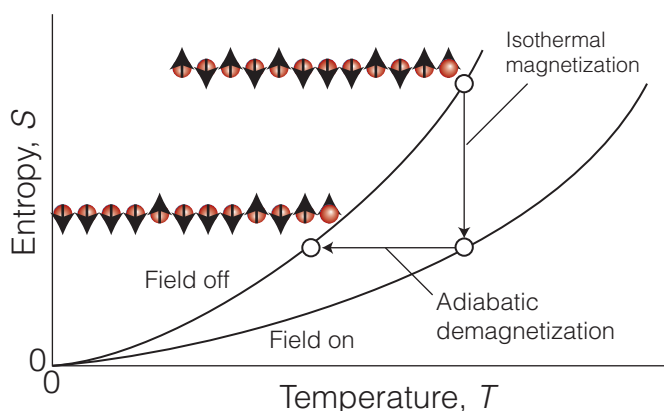


Figure A.5 The steps in the process of adiabatic demagnetization.

Adsorption

Adsorption is the attachment of a species, the *adsorbent*, to a surface, the *substrate*. If no chemical bonds are formed between adsorbent and substrate, it is called *physisorption*; if chemical bonds are formed, then the process is called *chemisorption*. The reverse of adsorption is *desorption*.

Adsorption Isotherm

An *adsorption isotherm* is the relation between the *fractional coverage*, θ (which is the ratio of occupied adsorption sites to the total number of sites), and the partial pressure of the overlying gas. The simplest version is the *Langmuir isotherm*:

$$\theta = \frac{Kp}{1 + Kp}$$

where K is an empirical constant, with dimensions of 1/pressure, which can be identified with the ratio of the rate constants for adsorption and desorption, $K = k_{\text{ads}}/k_{\text{des}}$. The Langmuir isotherm (Figure A.6) is based on the assumption that all adsorption sites are equivalent, that there are no interactions between neighbouring adsorbed molecules (so the ability to adsorb is independent of the fractional coverage), and that adsorption does not proceed beyond monolayer coverage. Multilayer adsorption is modelled by the BET isotherm.

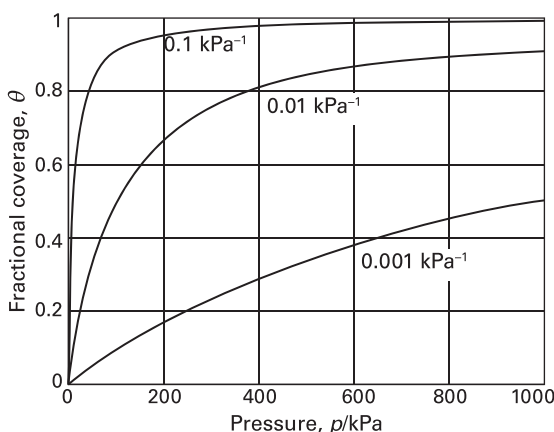


Figure A.6 The Langmuir isotherm for three values of K .

Affinity of Reaction

The *affinity of reaction*, A , is the quantity

$$A = \left(\frac{\partial G}{\partial \xi} \right)_{T, p} = - \sum_{\text{J}} \nu_{\text{J}} \mu_{\text{J}}, \quad A = - \mathbf{v} \cdot \boldsymbol{\mu}$$

where G is the Gibbs energy of the system, ξ is the extent of reaction,

and the ν_j are (signed) stoichiometric numbers. A reaction proceeds spontaneously towards products if $A > 0$ and is at equilibrium when $A = 0$. Don't confuse this A with the Helmholtz energy, also denoted A .

Allowed Transition

An *allowed transition* is a spectroscopic transition that is permitted by the selection rules. A transition that is forbidden may become allowed by perturbations or departures from the assumed symmetry of the molecule. Allowed transitions are identified by consideration of the transition dipole moment, which in turn can be assessed by considerations of symmetry.

Amount of Substance

The *amount of substance*, n , is a measure of the number of specified entities in a sample of matter. It is the physical quantity that is measured in moles, and hence is still widely colloquially referred to as the 'number of moles'. The term 'amount of substance' is somewhat unwieldy, so it is often abbreviated to 'amount' or, preferably, 'chemical amount'. For a sample of a substance of mass m and molar mass M , $n = m/M$. To avoid ambiguity, the value of n should always include the identity of the species; thus 1 mol H(g) or 1 mol H₂(g), not 1 mol of hydrogen.

Amphiprotic

An *amphiprotic species* is one that can act as both a proton donor and a proton acceptor. Water is an example. See autoprotolysis.

Angular Momentum

In classical mechanics, *angular momentum* is the moment of momentum of a body about a point. It is defined as $\mathbf{l} = \mathbf{r} \times \mathbf{p}$, where \mathbf{r} is the location of the centre of mass of the body on its orbit and \mathbf{p} is its linear momentum (Figure A.7). The angular momentum is commonly represented by a vector that depicts the sense of rotation, its orientation, and magnitude. In classical mechanics, all

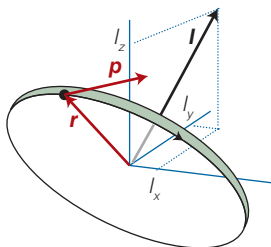


Figure A.7 The vector representation of classical angular momentum.

three components l_q ($q = x, y, z$) may be specified simultaneously. The magnitude, l , of angular momentum is $l = I\omega$ where I is the moment of inertia of the body travelling with angular velocity ω (in radians per second) on a circular path. If the mass of the body is m and the path has radius r , the moment of inertia is $I = mr^2$. The magnitude of angular momentum is related to its components by

$$l^2 = l_x^2 + l_y^2 + l_z^2$$

In quantum mechanics, the angular momentum is a physical observable that is represented by a set of three operators with the commutation relations

$$[\hat{l}_x, \hat{l}_y] = i\hbar\hat{l}_z, \quad [\hat{l}_y, \hat{l}_z] = i\hbar\hat{l}_x, \quad [\hat{l}_z, \hat{l}_x] = i\hbar\hat{l}_y; \quad [\hat{l}^2, \hat{l}_q] = 0$$

The three components are mutually complementary variables, so only one of them can be specified (together with the magnitude). The quantum numbers that specify the angular momentum are denoted l, m_l for orbital angular motion, s, m_s for spin, and j, m_j in general. The commutation relations imply the following restrictions to the values of the observables for spatial motion (as distinct from intrinsic spin):

$$\text{Magnitude of angular momentum} = \sqrt{l(l+1)}\hbar, \quad l = 0, 1, 2, \dots$$

$$\text{z-component of angular momentum} = m_l\hbar, \quad m_l = 0, \pm 1, \pm 2, \dots, \pm l$$

See also vector model and spin.

Anharmonicity

An oscillator is mechanically *anharmonic* if its potential energy differs from the parabolic form characteristic of a harmonic oscillator.

One model that is used to express anharmonicity is the *Morse potential energy*:

$$V(x) = hc\tilde{D}_e(1 - e^{-ax})^2, \quad a = \left(\frac{k_f}{2hc\tilde{D}_e}\right)^{1/2}$$

The energy levels of a *Morse oscillator* of mass m are

$$E_v = \left(v + \frac{1}{2}\right)\hbar\omega - \left(v + \frac{1}{2}\right)^2\hbar\omega x_e, \quad \omega = \left(\frac{k_f}{m}\right)^{1/2}, \quad \omega x_e = \frac{\hbar a^2}{2m}$$

with $v = 0, 1, \dots, v_{\max}$, where v_{\max} is the highest integer below $(2hc\tilde{D}_e/\hbar\omega) - \frac{1}{2}$ (Figure A.8).

Note that the levels converge with increasing v and that there is a finite number of bound states. The zero-point energy is

$$E_0 = \frac{1}{2}\left(1 - \frac{1}{2}x_e\right)\hbar\omega$$

and

$$hc\tilde{D}_e = \frac{\hbar\omega}{4x_e}$$

The dissociation energy $hc\tilde{D}_0$ (which is measured from the zero-point energy) is at $hc\tilde{D}_0 = hc\tilde{D}_e - E_0$. For a more general potential energy, the Morse expression is extended to

$$E_v = \left(v + \frac{1}{2}\right)\hbar\omega - \left(v + \frac{1}{2}\right)^2\hbar\omega x_e + \left(v + \frac{1}{2}\right)^3\hbar\omega y_e + \dots$$

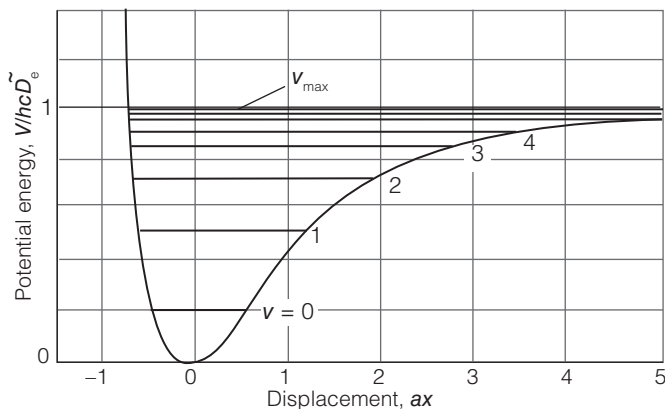


Figure A.8 The potential energy and the allowed energies of a Morse oscillator.

where the empirical *anharmonicity constants* x_e, y_e, \dots are characteristic of the molecule. Another consequence of anharmonicity is that the selection rule $\Delta v = \pm 1$ weakens and transitions with $\Delta v = \pm 2, \pm 3, \dots$, become allowed. Anharmonicity mixes normal modes, so they are no longer independent. One consequence of this mixing is that a forbidden transition may borrow intensity from an allowed transition and so become weakly allowed.

Antibonding Orbital

An *antibonding orbital* is a molecular orbital with an energy higher than that of its constituent atomic orbitals. In dihydrogen, the antibonding orbital is $\psi = \psi_{A1s} - \psi_{B1s}$. When discussing polyatomic molecules, it is appropriate to refer to the antibonding character of a molecular orbital in relation to pairs of neighbouring atoms and to identify an orbital as antibonding between two atoms if there is an internuclear nodal plane (Figure A.9).

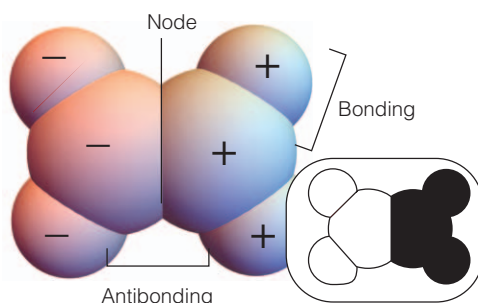


Figure A.9 The regions of bonding and antibonding in a polyatomic molecule.

Antisymmetric

A mathematical function $f(x)$ is *antisymmetric* if $f(-x) = -f(x)$. A many-particle wavefunction is said to be antisymmetric with respect to particle interchange if it changes sign under the interchange of the labels of two identical particles: $\psi(\dots, i, \dots, j, \dots) = -\psi(\dots, j, \dots, i, \dots)$. See Pauli principle. A normal mode of vibration of a centrosymmetric polyatomic molecule is classified as antisymmetric if the extension of

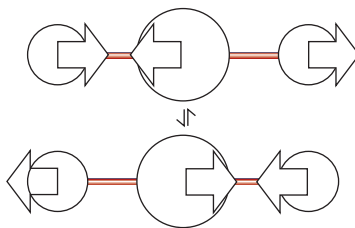


Figure A.10 The antisymmetric stretching mode of an AB_2 molecule.

one bond is mirrored by the contraction of an equivalent bond (as in Figure A.10). The term antisymmetry should be distinguished from *asymmetry*, which means the absence of symmetry.

Arrhenius Parameters

The Arrhenius parameters are the *activation energy*, E_a , and the *frequency factor* (formerly the *pre-exponential factor*), A , which occur in the expression $k_r = Ae^{-E_a/RT}$ or equivalently $\ln k_r = \ln A - E_a/RT$ for the temperature dependence of the rate constant of a chemical reaction. They are determined experimentally by making an Arrhenius plot of $\ln k_r$ against $1/T$, the intercept at $1/T=0$ being $\ln A$ and the slope $-E_a/R$. A high activation energy signifies a strong dependence of the rate constant on the temperature (Figure A.11).

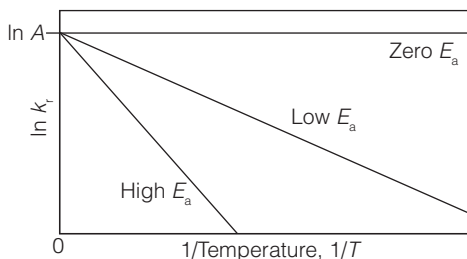


Figure A.11 The dependence of the rate constant on temperature for different activation energies.

Asymmetric unit

An *asymmetric unit* is the entity (an atom, ion, or molecule) from which a crystal is built. The location of an asymmetric unit is

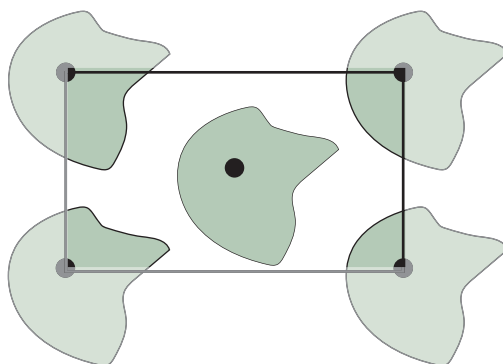


Figure A.12 An asymmetric unit associated with lattice points.

denoted by a lattice point. The crystal structure itself is the array of asymmetric units obtained by associating each one with a lattice point (Figure A.12).

atmosphere (the unit)

The *atmosphere* (atm) is a unit of pressure defined as $1 \text{ atm} = 101\,325 \text{ Pa}$ exactly. The unit is used in the current definitions of normal melting and boiling points. It is a component of the definition of standard temperature and pressure (STP).

Atomic Number

The *atomic number*, Z , of an element is the number of protons in the nucleus of one of its atoms. The nuclear charge is Ze , where e is the fundamental charge. It follows that the number of electrons in an electrically neutral atom is also Z . See also effective nuclear charge.

Atomic Orbital

An atomic orbital is a one-electron wavefunction for an atom. Most developments in chemistry are based on hydrogenic atomic orbitals, which are the orbitals found by solving the Schrödinger equation for a hydrogenic atom. Each of these wavefunctions can be expressed as

the product of a radial wavefunction, $R(r)$, and an angular wavefunction, $Y(\theta, \phi)$, where r , θ , and ϕ are the polar coordinates of a point relative to the nucleus. Each orbital is specified by three quantum numbers:

principal quantum number n , with $n = 1, 2, \dots$
 orbital angular momentum quantum number l , with $l = 0, 1, 2, \dots, n - 1$
 magnetic quantum number $m_l = 0, \pm 1, \pm 2, \dots, \pm l$

It follows that there are n^2 orbitals that can have the quantum number n and which in a hydrogenic atom are degenerate.

Atomic orbitals are referred to according to the following notation:

l	0	1	2	3	4...
Orbital	s	p	d	f	g...

The value of l specifies the orbital angular momentum of the electron it describes. The angular wavefunctions are the spherical harmonics. See that entry and also the entries for individual types of orbital for their shapes. The radial wavefunction has $n - l - 1$ nodes where the wavefunction passes through zero. An s orbital is unique in having a nonzero value at the nucleus: in classical terms, there is no orbital angular momentum to fling an electron away from the nucleus. An electron that 'occupies' (that is, is described by) an atomic orbital with quantum number n is called an ns -electron (if $l = 0$) an np -electron (if $l = 1$), and so on. See also shell, subshell, and hydrogenic atom.

Atomic Structure

According to the *nuclear model*, an atom consists of a small, central, positively charged, massive nucleus surrounded by shells of electrons. The electronic structures of atoms are expressed in terms of the atomic orbitals that are occupied by the Z electrons that are present in a neutral atom of atomic number Z . The structure is reported in terms of the electron *configuration*, the list of occupied orbitals such as $1s^1$ for hydrogen, $1s^2$ for helium, $1s^2 2s^1$ for lithium, and so on. The electron configuration is determined spectroscopically and magnetically and can be rationalized in terms of the building-up

principle. The orbitals available to the electrons lie in a series of concentric shells labelled as follows:

n	1	2	3	4...
Shell	K	L	M	N...

Attractive and Repulsive Surfaces

An *attractive surface* is a potential energy surface for a chemical reaction in which the saddle point occurs early in the *reaction coordinate* (Figure A.13). Reactions with attractive surfaces take place more readily if the energy of the reactants is principally in their relative translational motion. A surface is *repulsive* if the saddle point occurs late in the reaction coordinate (right illustration). Reactions with such surfaces take place most readily if the excess energy of the reactants is in the form of molecular vibration.

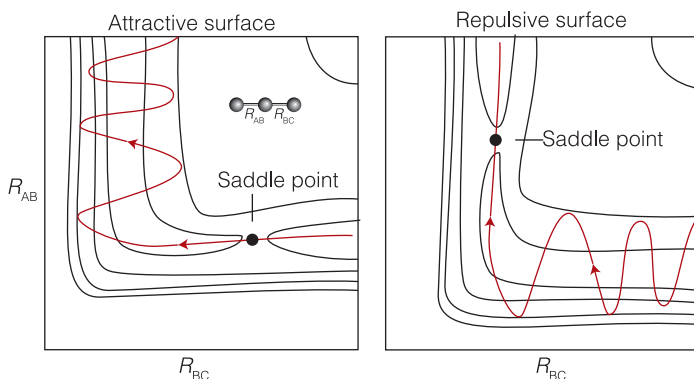


Figure A.13 Attractive (left) and repulsive (right) potential energy surfaces.

Auger Effect

The *Auger effect* is the emission of a secondary electron after high-energy radiation (either X-ray or, more commonly, a beam of fast electrons) has expelled another electron. The first electron to depart leaves a vacancy in the low-lying orbital and an electron falls into it from an upper level (Figure A.14). The energy released ejects the secondary electron. The latter's kinetic energy is characteristic of the solid. Its use in determining composition is called *Auger electron*

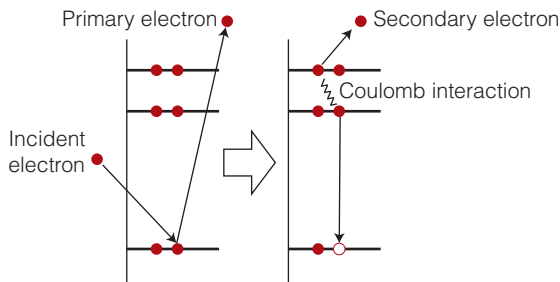


Figure A.14 The processes involved in the Auger effect.

spectroscopy (AES). Instead of the released energy ejecting a second electron, it might result in the generation of an X-ray photon, which is observed as *X-ray fluorescence*.

Autocatalysis

Autocatalysis is the acceleration of a reaction as a result of a product acting as a reactant. Thus, the reaction $A + B \rightarrow C$ followed by $C \rightarrow A + D$ is autocatalytic.

Autoprotolysis

The term *autoprotolysis* means the transfer of a proton between like molecules, with a molecule acting both as a proton donor (acid) and proton acceptor (base), as in the autoprotolysis of water, $2 \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-(\text{aq})$. The equilibrium constant of this reaction is called the *autoprotolysis constant* (of water), K_w :

$$K_w = a_{\text{H}_3\text{O}^+} a_{\text{OH}^-}, \quad \text{p}K_w = -\log K_w$$

At 25 °C, $\text{p}K_w = 14.01$. In elementary applications the activities in the definition of K_w are interpreted as $[J]/c^\ominus$, where $[J]$ is the molar concentration of J and $c^\ominus = 1 \text{ mol dm}^{-3}$.

Avogadro's Constant

Avogadro's constant, N_A , is the number of entities per mole of a substance. It has the defined value $N_A = 6.022\,140\,76 \times 10^{23} \text{ mol}^{-1}$ (a value chosen to be close to the traditional definition, which was the number of atoms in exactly 12 g of carbon-12). See mole.

Axilrod-Teller Formula

The *Axilrod-Teller formula* is an approximate form of the potential energy of interaction of three molecules:

$$V = -\frac{C_6}{r_{AB}^6} - \frac{C_6}{r_{BC}^6} - \frac{C_6}{r_{CA}^6} - \frac{C'(\theta_A, \theta_B, \theta_C)}{(r_{AB}r_{BC}r_{CA})^3}, \quad C'(\theta_A, \theta_B, \theta_C) = a(1 + 3 \cos \theta_A \cos \theta_B \cos \theta_C)$$

where a is a parameter that is approximately equal to $\frac{3}{4} \alpha' C_6$ with α' the polarizability volume of the molecule. The angles are depicted in Figure A.15.

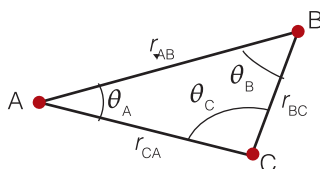


Figure A.15 The angles used in the Axilrod-Teller formula.

Axis of Symmetry

An *axis of symmetry* is the symmetry element corresponding to a symmetry rotation of a body. An *n-fold axis of symmetry* is the symmetry element associated with a rotation through $2\pi/n$.

Azeotrope

An azeotrope is a liquid mixture that boils to give a vapour of the same composition as the liquid. A *high-boiling azeotrope* has a boiling

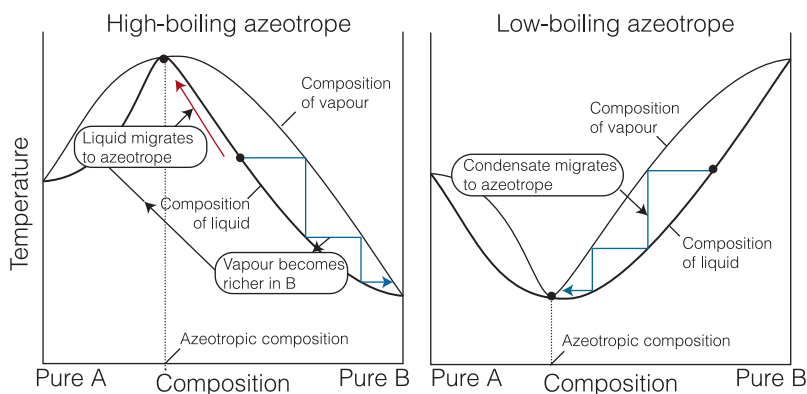


Figure A.16 High-boiling (left) and low-boiling (right) azeotrope phase diagrams.

temperature higher than that of both its components (Figure A.16). A *low boiling azeotrope* has a boiling point that is lower than that of both its components. Azeotropes have important consequences for fractional distillation. When a mixture that forms a high-boiling azeotrope is fractionally distilled, the more volatile component vaporizes until the remaining liquid has reached its azeotropic composition; the mixture then distills unchanged. When a mixture that forms a low-boiling azeotrope is distilled, the vapour has the composition of the azeotropic mixture.