

Chapter 1 Atomic Structure

Lecture 1 Classical Theory of Atomic Structure

1 MATTER IS MADE OF ATOMS

Richard Feynman used to say that¹, if all of scientific knowledge were to be destroyed in a catastrophe, and only one sentence passed on to the next generations of creatures, the statement containing the most information in the fewest words would be

All things are made of atoms.

The primitive idea that the universe is made of small building blocks, called atoms, dates back to the ancient greek philosopher Democritus (c. 460 BC – c. 370 BC). The atomic theory was only casted in its modern form in the 1800s by John Dalton.

There are only about 10^2 types of atoms in nature, which combine with one another to make about 10^4 compounds. The compounds of carbon is on the order of 10^6 , from which life is constructed. The substances around us can be devided into different categories based on whether they contain more than one type of molecules or elements (Figure 1).

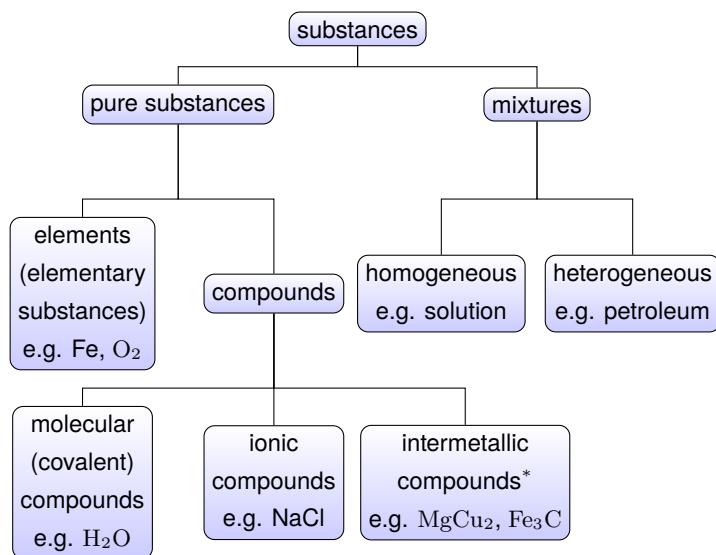


Figure 1: Classification of substances.

element

Atoms/ions that have the same atomic number (positive charges in the nucleus) belong to the same type of element.

molecule

A molecule is made of atom(s) and is the smallest unit that still preserves the chemical properties of substances.

– Linus Pauling, *General Chemistry*

Chemistry is mainly concerned with entities and phenomena on *molecular scale*. That is on length scales 10^{-10} – 10^{-6} m, which is why chemistry is sometimes called the “central science”, although subatomic processes ($< 10^{-10}$ m) lay the foundation for chemical properties (Table 1).

Table 1: Length scales relevant to chemistry in unit of meter m.

prefix	symbol	factor	example
femto	f	10^{-15}	size of nucleus
pico	p	10^{-12}	
	Å	10^{-10}	size of atom
nano	n	10^{-9}	macromolecule
micro	μ	10^{-6}	colloidal particle
milli	m	10^{-3}	thin films
centi	c	10^{-2}	bulk materials
deci	d	10^{-1}	laboratory reaction
	meter	10^0	industrial production
kilo	k	10^3	geochemistry

Modern chemistry began to mature during the 18th century and to find possible applications in the late 19th century when petroleum became a major industrial fuel and resource. Into the 20th century, synthetic plastics, rubbers and fibers from petroleum and chemical engineering industries generate huge impacts on human life. Today, chemistry is indispensable to many economic sectors such as agriculture, food, pharmaceutical and cosmetic. (Table 2). Chemistry also finds its applications in the manufacture of hightech products, such as integrated circuits (lithography), solar cells and fuel cells.

Table 2: Industrial applications of chemistry and chemical engineering

sector	molecule	application
petroleum	plastic: polyethylene (PE)	packaging
	rubber: polyisoprene	tire
	fiber: nylon	clothing
agriculture	$\text{NH}_3 \longrightarrow (\text{NH}_4)_2\text{SO}_4$	fertilizer
	DDT	pesticide
food	aspartame	sweeteners
	$\text{NaNO}_3 / \text{NaNO}_2$	preservative
pharmaceutical	tartrazine	food dye
	aspirin	fever reducer
personal care	penicillin	antibiotics
	parabens	preservative
	sodium lauryl sulfate	shampoo

This course focuses on two themes of chemistry: structure and dynamics. Starting from laws of quantum mechanics, we first examine the static structure of atoms, molecules and matter including

¹The Feynman Lectures on Physics 1-2

life. Then, based on laws of statistical thermodynamics, we explore the kinetics and equilibrium properties of chemical reactions.

Why should you learn this chemistry course?

- develop a molecular perspective about life
- become scientifically literate

3 SUBATOMIC PARTICLES

So far, our knowledge of atomic structure reveals that atoms are made of several types of elementary particles² (Table 3 and Figure 2). An atom is quite empty with majority of its mass concentrated on a tiny core, called *nucleus*.

Table 3: Timeline of major discoveries in atomic structure and quantum mechanics

year	scientist	discovery
1803	Dalton	atom
1896	Rontgen	X-ray
1898	JJ Thomson	electron
1900	Planck	quanta h
1905	Einstein	photon $E = h\nu$
1908	Millikan	elementary charge e
1909	Rutherford	nucleus
1913	Bohr	Bohr atomic model E_n
1924	de Broglie	matter wave $\lambda = h/p$
1926	Shroedinger	wave mechanics
1926	Born	meaning of wave function $ \psi ^2$
1927	Heisenberg	uncertainty principle $\Delta x \Delta p \geq \frac{\hbar}{2}$
1931	Chadwick	neutron

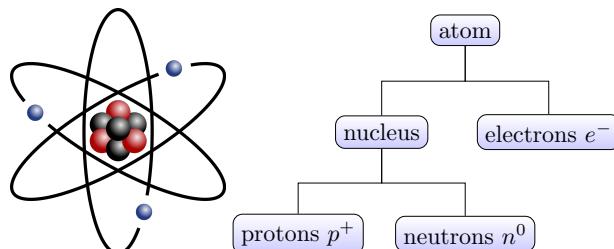


Figure 2: Schematic picture of atom (Wikipedia) and subatomic particles.

electron

charge $-e = -1.602 \times 10^{-19} \text{ C}$

rest mass $m_e = 9.11 \times 10^{-31} \text{ kg}$

(classical radius $a_e < 2.82 \times 10^{-15} \text{ m}$; quantum-mechanical radius $< 10^{-18} \text{ m}$. We view electrons as sizeless points.)^{*}

proton p^+ or ${}_1^1H^+$

charge $+e$

mass $m_p = 1.6726 \times 10^{-27} \text{ kg} \approx 1836m_e$

neutron

mass $m_n = 1.6749 \times 10^{-27} \text{ kg} \approx 1838m_e$

$n^0 \rightarrow p^+ + e^- + \dots$

nucleus

diameter $10^{-15}\text{--}10^{-14} \text{ m}$

mass $> 99.95\% m_a$

atom

diameter $10^{-10} \text{ m} = \text{\AA}$: 10000–100000 times of the nucleus size

atomic number Z : number of protons, defines the element type.

neutron number N

mass number $A = Z + N$

isotope ${}_Z^AX$ (or ${}_Z^AX_N$)

atomic mass (atomic weight) m_a of atom ($m_a \approx A$) or element (weighted average), measured in unit of u or Da

Dalton Da is 1/12 of the mass of ${}_6^{12}C$ at rest, used as atomic mass unit (u). (Why not use proton mass m_p as atomic mass unit?)

ion: cation (X^{n+}) / anion (X^{n-})

mole

Avogadro number (Avogadro constant) $N_A = 6.022 \times 10^{23}$

A mole of substance is defined as N_A molecules of the substance.

Vector

A *vector* \mathbf{a} (or \vec{a}) is a quantity with both magnitude (length) ($a = |\mathbf{a}|$) and direction. A unit vector \hat{u} is a vector with magnitude one. A vector in three-dimensional Cartesian coordinate system can be decomposed as $\mathbf{a} = (a_x, a_y, a_z) = a_x \hat{x} + a_y \hat{y} + a_z \hat{z}$, where a_x, a_y, a_z are the coordinates or components. The magnitude a is given by the Pythagorean theorem $a^2 = a_x^2 + a_y^2 + a_z^2$. Force \mathbf{F} , electric field \mathbf{E} and magnetic field \mathbf{B} are vectors.

In contrast, a *scaler* is a quantity with only magnitude but no direction. Energy U , mass m and electric charge q are scalars.

4 CLASSICAL THEORY OF ATOMIC STRUCTURE

Coulomb's law: the magnitude of the electrostatic force between two stationary charges q_1 and q_2 in vacuum that are a distance r apart is

$$f_e = k_e \frac{q_1 q_2}{r^2} = \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{r^2} \sim \frac{1}{r^2}, \quad (\text{inverse-square law}) \quad (1)$$

where $k_e = 9 \times 10^9 \text{ N} \cdot \text{C}^{-2} \cdot \text{m}^2$ and $\epsilon_0 = 8.854 \times 10^{-12} \text{ C}^2 \cdot \text{N}^{-1} \cdot \text{m}^{-2}$ is the vacuum permittivity³. The corresponding potential energy⁴ is

$$U_e = -\frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{r}. \quad (2)$$

In analogy to Newton's law of universal gravity⁵ between two masses m_1 and m_2

$$f_G = G \frac{m_1 m_2}{r^2} \sim \frac{1}{r^2}, \quad (\text{inverse-square law}) \quad (3)$$

²For particle physicists, even protons are not "elementary", because they can still be broken into smaller pieces. There exist more fundamental particles like quarks.

³By choosing appropriate unit systems, it is possible to set $\epsilon_0 = 1$ (natural units) or $\epsilon_0 = 1/4\pi$ (Gaussian units) such that $f_e = \frac{q_1 q_2}{r^2}$.

⁴The definition of potential energy is subject to an arbitrary additive constant determined by the choice of the reference point of zero potential energy. Here, the reference point is customarily set at infinity, i.e. $U_e(\infty) = 0$.

⁵There are four types of fundamental interactions, gravitational, weak, strong and electromagnetic interaction.

where $G = 6.67 \times 10^{-11} \text{ N}\cdot\text{m}^2\cdot\text{kg}^{-2}$ is the gravitational constant. **Uniform circular motion** is a motion along a circle of radius r with constant angular speed ω (or linear speed $v = \omega r$).

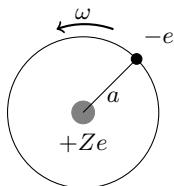


Figure 3: The classical picture of atoms: an electron orbits around the nucleus.

Centripetal force is a force which keeps a body moving along a circular path and is directed along the radius towards the center. For an object of mass m moving at linear speed $v = \omega r$ along a path with radius of curvature r ,

$$f_C = \frac{mv^2}{r} = m\omega^2 r \quad (4)$$

In the classical theory of hydrogen-like atom/cation (only one electron), an electron orbits around the nucleus (nearly held still for it is much heavier than electrons) in uniform circular motion⁶, in the same fashion as the Earth orbits around the Sun (Figure 3). In the case of atom, the Coulomb attraction serves as the centripetal force. If the radius of this orbit is a and the atomic number is Z , then

$$\frac{m_e v^2}{a} = m_e a \omega^2 = \frac{1}{4\pi\epsilon_0} \frac{Z e^2}{a^2}. \quad (5)$$

This equation means that, the electron can revolve faster (large ω) along a smaller orbit (small a) or slower along a larger orbit. But the choice of (a, ω) pairs can be *arbitrary* and *continuous*.

The total energy E of an electron in such a motion consists of its kinetic energy $\frac{m_e}{2} a^2 \omega^2$ and its potential energy $-\frac{1}{4\pi\epsilon_0} \frac{Z e^2}{a}$. By the conservation of energy,

$$\frac{m_e}{2} a^2 \omega^2 - \frac{1}{4\pi\epsilon_0} \frac{Z e^2}{a} = E \quad (6)$$

where $E(a, \omega)$ is a constant determined by ω and a . Using equation (5) as a constraint, E is determined by one quantity, either a or ω .

$$E = -\frac{1}{4\pi\epsilon_0} \frac{Z e^2}{2a} \sim -\frac{1}{a}, \quad (7)$$

or

$$a = -\frac{1}{4\pi\epsilon_0} \frac{Z e^2}{2E}. \quad (8)$$

To every a (or ω), there corresponds a definite value E , but again, E can be *continuous*.

- The energy E of revolving electrons continuously changes with the orbit radius a . Energy emitted or absorbed (in terms of light) by electrons should thus be continuous, which is not the case in reality.

Maxwell Equations* (in vacuum)

$$\nabla \times \mathbf{B} = \mu_0 \mathbf{j} + \mu_0 \epsilon_0 \frac{\partial \mathbf{E}}{\partial t} \quad (9)$$

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \quad (10)$$

where $\mu_0 = 1.257 \times 10^{-6} \text{ N/A}^2$ is the vacuum permeability. A electric field \mathbf{E} changing with time induces a magnetic field \mathbf{B} perpendicular to it, and vice versa. \mathbf{E} and \mathbf{B} can thus alternatively generate each other and propagate through space, resulting in electromagnetic waves or radiation.

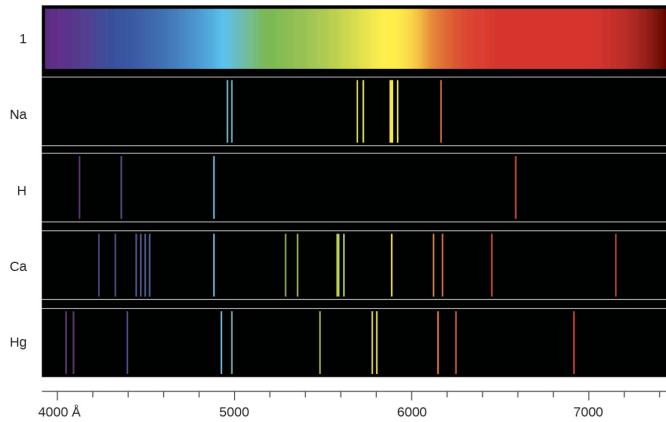


Figure 4: Emission line spectra of excited atoms (*Chemistry, OpenStax*).

The “golden rule” of science

It doesn't matter how beautiful your theory is, it doesn't matter how smart you are. If it doesn't agree with experiment, it's wrong. In that simple statement is the key to science. – Richard Feynman, The Character of Physical Law

Classical Newtonian mechanics holds the views that physical quantities take continuous values and the motion of body follows deterministic trajectories (Table 4). It turns out that both of these views are invalid in the microscopic atomic world. To find theories in consistent with experiments, we have to adopt the quantum-mechanical perspective.

Table 4: Comparison of classical and quantum-mechanical views.

physical quantities		path of motion
classical	continuous	deterministic
old quantum (Bohr)	discrete	deterministic
new quantum	discrete	probabilistic

⁶A more delicate treatment allows elliptical orbits.

⁷ $\nabla \times \mathbf{A}$ is a vector perpendicular to the vector \mathbf{A} .

Chapter 1 Atomic Structure

Lecture 2 Old Quantum Theory of Atomic Structure

1 HARMONIC WAVE*

Generally, a **wave** is a periodic distribution of matter or energy in space and time, often caused by the periodic oscillation of a source.

- **wavelength** λ : the periodicity in space
- **wave number** $k = \frac{2\pi}{\lambda}$
- **wave vector** \mathbf{k} : a vector of magnitude k and of direction of the propagation of the wave
- **time period** T : the periodicity in time
- **frequency** $\nu = \frac{1}{T}$
- **angular frequency** $\omega = 2\pi\nu = \frac{2\pi}{T}$
- **amplitude** A : maximum magnitude of oscillation
- **(phase) speed** v of propagation: $v = \nu\lambda = \frac{\omega}{k}$

A (one dimensional) simple *harmonic wave* can be described by sinusoidal functions

$$u(x, t) = A \cos(kx - \omega t) \quad (1)$$

or equivalently,

$$\tilde{u}(x, t) = Ae^{i(kx - \omega t)} \quad (2)$$

satisfying the *wave equation* (one dimensional)

$$\frac{\partial^2 u(x, t)}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 u(x, t)}{\partial t^2}. \quad (3)$$

Complex Number

A complex number $z = x + iy$ has its real part $\Re z = x$ and imaginary part $\Im z = y$. When written in exponential form $z = |z|e^{i\theta}$, with the modulus $|z| = \sqrt{x^2 + y^2}$. The *complex conjugate* z^* of z is $z^* = x - iy$ and $z^*z = |z|^2$.

Euler Formula

$$e^{i\theta} = \cos \theta + i \sin \theta. \quad (4)$$

2 OLD QUANTUM PHYSICS: QUANTIZATION

Experiments in the late 19th and early 20th century showed that, physical quantities do not take continuous values when we keep dividing them into smaller parts. For instance, the smallest unit of electric charge is $e = 1.6 \times 10^{-19} \text{ C}$, carried by one electron or proton, all charges encountered in nature are integral multiples of e .

Angular Momentum*

A translational motion carries with it a (linear) momentum $\mathbf{p} = m\mathbf{v}$. A rotational motion carries with it an angular momentum

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} \quad (5)$$

or $L = rp$ for circular motion. The direction of \mathbf{L} is perpendicular to the plane of rotation satisfying the right-hand rule by convention. Angular momentum has the dimension of [length][momentum] or [energy][time].

2.1 Max Planck's idea of quanta

All physical quantities are quantized into small units. The scale of each unit, called a *quanta* (量子), is characterized by Planck constant

$$h = 6.626 \times 10^{-34} \text{ J}\cdot\text{s}$$

$$\hbar = \frac{h}{2\pi} = 1.055 \times 10^{-34} \text{ J}\cdot\text{s}$$

Note that, Planck constant has the dimension of angular momentum. Thus, h is the quanta of angular momentum.

2.2 Photoelectric effect and photons

Classical electrodynamics says that light is an electromagnetic wave – a continuous distribution of radiation energy in space, which contradicts with the experiment of photoelectric effect.

Einstein (1905): light is not just an electromagnetic wave, but also can be viewed as being made of small discrete particles, called *photons*, each with energy

$$E = h\nu = \hbar\omega, \quad (6)$$

where ν is the frequency of the light wave. This is to say, energy is quantized.

3 BOHR MODEL

The emission line spectrum of hydrogen atom empirically obeys

$$\frac{1}{\lambda} = R_H \left(\frac{1}{n^2} - \frac{1}{m^2} \right) \quad (7)$$

where λ is the wavelength of the emitted light, (n, m) are small integers ($n < m$) and the Rydberg constant for hydrogen is $R_H = 109678 \text{ cm}^{-1}$.

Assumption: quantization of angular momentum

$$L = n\hbar, \quad n = 1, 2, 3, \dots \quad (8)$$

namely, $m_e v a = n\hbar$. Square this equation, $m_e^2 v^2 a^2 = n^2 \hbar^2$, and recall the result from classical theory

$$m_e v^2 a = \frac{1}{4\pi\epsilon_0} Ze^2 \quad (9)$$

we obtain the radius of Bohr orbit (Figure 1)

$$a(Z, n) = \frac{4\pi\epsilon_0 n^2 \hbar^2}{Z m_e e^2} = \frac{n^2}{Z} a_0, \quad (10)$$

where the Bohr radius for ground state ($n = 1$) orbit in hydrogen atom ($Z = 1$) is

$$a_0 = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2} = \frac{4\pi \times 8.854 \times 10^{-12} \times (1.055 \times 10^{-34})^2}{9.11 \times 10^{-31} \times (1.6 \times 10^{-19})^2} \text{ m} = 0.53 \text{ \AA} \quad (11)$$

n is called a *quantum number* and here it only takes positive integer values $1, 2, \dots$ ¹.

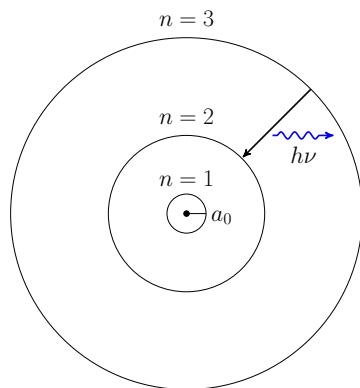


Figure 1: Bohr electron orbits and photon emission.

The corresponding energy levels are, $E_n = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{2a_0} \frac{Z^2}{n^2}$, or

$$E_n = -\frac{m_e e^4}{2(4\pi\epsilon_0)^2 \hbar^2} \frac{Z^2}{n^2} = -2.18 \times 10^{-18} \text{ J} \times \frac{Z^2}{n^2} \quad (12)$$

or more conveniently

$$E_n = -13.6 \text{ eV} \times \frac{Z^2}{n^2} \quad (13)$$

The energy of absorbed/emitted photons, when atoms make transitions between energy levels E_m and E_n , follows the *Bohr frequency rule* (Figure 1)

$$h\nu = h\frac{c}{\lambda} = E_m - E_n, \quad (14)$$

where $c = 2.998 \times 10^8 \text{ m/s}$ is the speed of light in vacuum. Bohr model predicts that²

$$R_H = \frac{m_e e^4}{2(4\pi\epsilon_0)^2 \hbar^2} \frac{1}{hc} = \frac{2\pi^2 m_e e^4}{(4\pi\epsilon_0)^2 h^3 c} = 109737 \text{ cm}^{-1} \quad (15)$$

4 SOMMERFELD ELLIPTICAL ORBITS*

Generally, the electron orbit is an ellipse³ with major and minor semiaxes (Figure 2)

$$a = \frac{n^2}{Z} a_0, \quad b = \frac{nk}{Z} a_0, \quad (16)$$

characterized by three quantum numbers

- total quantum number $n = 1, 2, 3, \dots$
- azimuthal quantum number $k = 1, 2, 3, \dots, n$
- magnetic quantum number $m = \pm 1, \pm 2, \dots, \pm k$.

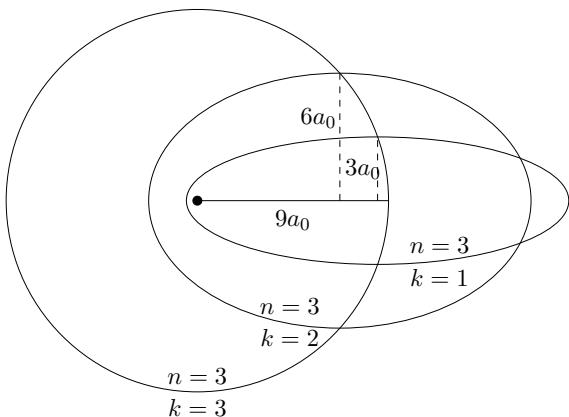


Figure 2: Sommerfeld electron orbits in hydrogen atom for $n = 3$.

For hydrogen-like atom/cations (one electron), the energy level is solely determined by n

$$E_n = -13.6 \text{ eV} \times \frac{Z^2}{n^2}. \quad (17)$$

k determines the orbit angular momentum

$$L = k\hbar \quad (18)$$

For multi-electron atoms, (n, k) determine energy levels together.

m determines the projection of L along an external magnetic field,

$$L_z = m\hbar, \quad (19)$$

thus the plane of the orbit rotation after applying the field.

Because Sommerfeld wants to include the circular orbit ($k = n$) as one special case of elliptical orbits, the value of quantum numbers defined in the Sommerfeld elliptical orbit theory gives wrong predictions about angular momentum. We will see in next lecture that, if one gives up the circular orbit, it is possible to construct elliptical orbits with appropriate quantum numbers in agreement with experimental observations (i.e. Bohr elliptical orbits).

5 LIMITATION OF OLD QUANTUM THEORY: DETERMINISTIC VS PROBABILISTIC

Predictions from the old quantum theory are in disagreement with experimental energy levels for atoms other than hydrogen. It turns out that, quantum angular momentum takes the form of $\sqrt{J(J+1)}\hbar$, where the quantum number J can even be half-integer. So, the old quantum theory partially solved the discrete spectrum problem based on quantization assumptions.

However, the old quantum theory still holds the belief that particle motion should be described by **deterministic** paths, like motion of macroscopic bodies in classical mechanics, therefore, does not

¹There are cases in which quantum numbers are zero, negative integers or even half-integers.

²Discrepancy due to the assumption that the H nucleus is held still, while the true picture is that the electron and the nucleus rotate about their common center of mass.

³Similarly, planetary orbits around the Sun are generally ellipses with circle being one particular case. Circular orbit is ONE solution to the Newtonian mechanics does not mean it is the ONLY solution.

explain the discrepancy that electrons do not fall into the nucleus. More and more evidences suggest that motion in the microscopic world is **wave-like** and of **probabilistic** nature.

5.1 Matter wave: electron moves like a wave

Associated with any motion with momentum $p = mv$, there is a wave-like behavior with de Broglie wavelength

$$\lambda_B = \frac{h}{p} \quad (p = \hbar k) \quad (20)$$

Electron diffraction

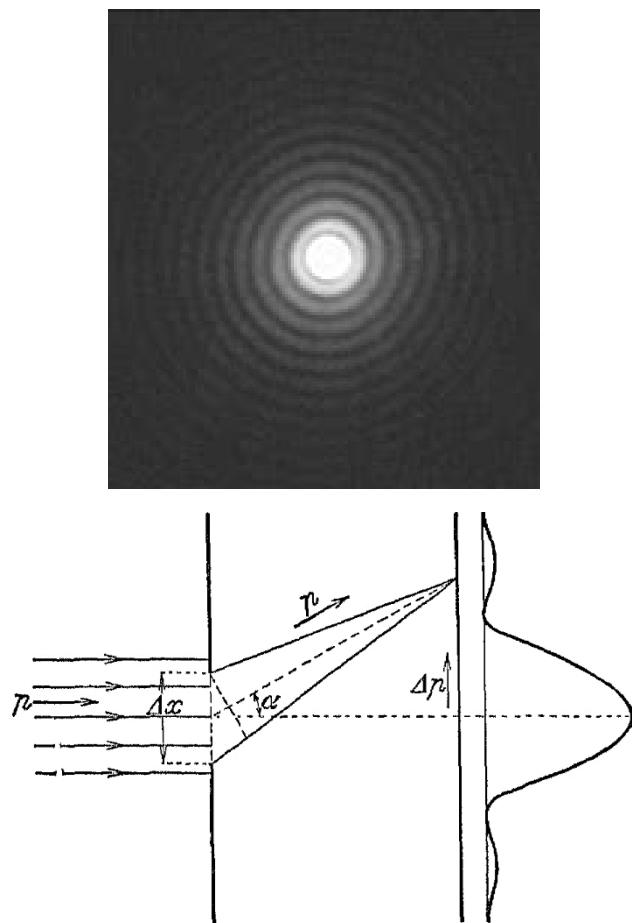


Figure 3: (Top) Fraunhofer diffraction of electrons at a circular hole⁴. (Bottom) Diffraction of electrons at a single slit (*Atomic Physics*, Max Born).

Periodic boundary condition $2\pi a = n\lambda_B$ ($n = 1, 2, \dots$) with de Broglie wavelength $\lambda_B = h/(m_e v)$ of electron matter wave naturally leads to the quantization or discreteness of angular momentum $L = nh$. Here we see one example of quantization imposed automatically by boundary conditions, once wave-like behaviors are assumed.

5.2 Uncertainty principle

The product of the uncertainty of experimental measurements of a pair of non-commuting quantities⁵, like position-momentum or

energy-time, is roughly greater than \hbar^6 .

$$\Delta x \Delta p \gtrsim \hbar \quad (21)$$

This can be illustrated from the diffraction of electrons at a single slit. The uncertainty of position is $\Delta x \sin \alpha \sim \lambda_B = \frac{h}{p}$ ⁷ and on the order of the de Broglie wavelength. Correspondingly, the uncertainty of the momentum is $p \sin \alpha \sim \Delta p$ (Figure 3). Together, their product is on the order of \hbar .

5.3 Wave function and superposition principle

When we say the motion of electron is described by a **wave function** $\Psi(x, t)$, what is the meaning of this wave function? In quantum mechanics, this wave is a probabilistic wave. Although $\Psi(x, t)$, called *probability amplitude*, has no physical meaning by itself, $I = |\Psi(x, t)|^2 = \Psi^*(x, t)\Psi(x, t)$ ⁸ is the probability density for the electron to be observed at position x and time t .

When adding effects of two quantum mechanic events, we should use superposition of probability amplitude $\Psi = \Psi_1 + \Psi_2$ and find the overall probability density to be $I = |\Psi_1 + \Psi_2|^2 = |\Psi_1|^2 + |\Psi_2|^2 + \Psi_1^*\Psi_2 + \Psi_1\Psi_2^* = I_1 + I_2 + \Psi_1^*\Psi_2 + \Psi_1\Psi_2^* \neq I_1 + I_2$. The last two terms account for the interference, which is a characteristic phenomenon for waves. In summary, superposition of intensity or probability applies to classical macroscopic bodies $I = I_1 + I_2$. But for quantum-mechanical microscopic bodies, superposition applies to probability amplitude or wave functions

$$\Psi = \Psi_1 + \Psi_2. \quad (22)$$

The overall intensity or probability should be computed after the superposition of wave functions.

Double-slit interference

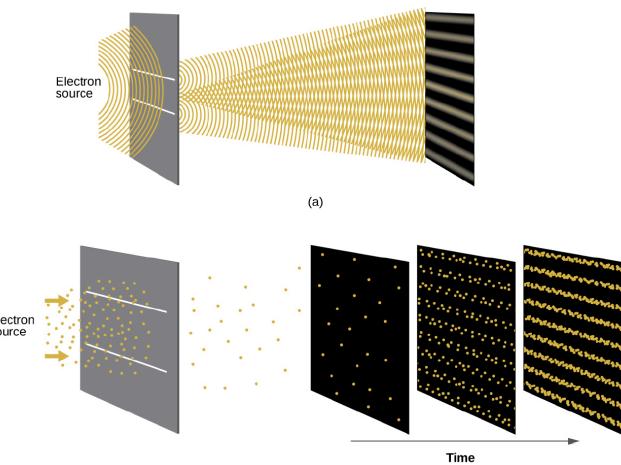


Figure 4: (a) Double-slit interference of electrons. (b) Interference pattern built up gradually under low-intensity electron source. Bright stripes are where the intensity I of electron beam is high, or the probability of observing electrons is high. (*Chemistry, OpenStax*)

⁴Matteucci, G., Ferrari, L., and Migliori, A. (2010). The Heisenberg uncertainty principle demonstrated with an electron diffraction experiment. *European Journal of Physics*, 31(5), 1287.

⁵Two quantities A and B commute if $AB = BA$, when applied to others as operators.

⁶More rigorous treatment gives a smaller lower bound

⁷~ here means on the order of, or is approximately equal to.

⁸ z^* is the complex conjugate of z

Chapter 1 Atomic Structure

Lecture 3 Quantum-Mechanical Theory of Atomic Structure and Atomic Orbital

1 BOHR ELLIPTICAL ORBITS*

Before we look at the correct quantum-mechanical atomic orbitals, we show here that, by making slight modifications to quantum numbers k and m , it is possible to adapt the Sommerfeld elliptical orbits for a formally correct description of atomic structure. These improved Bohr elliptical orbits (Figure 1) are now characterized by three quantum numbers (n, l, m)

- total quantum number $n = 1, 2, 3, \dots$
- azimuthal quantum number $l = 0, 1, 2, \dots, n - 1$
- magnetic quantum number $m = 0, \pm 1, \pm 2, \dots, \pm l$.

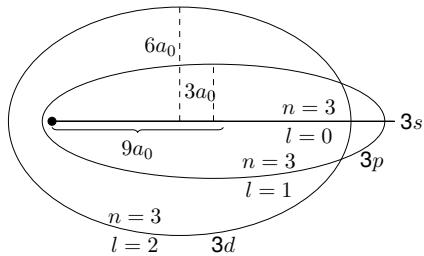


Figure 1: Bohr elliptical electron orbits in hydrogen atom for $n = 3$. Orbit with $l = 0, 1, 2, \dots$ can be mapped onto quantum-mechanical s, p, d, \dots atomic orbitals, to be shown later.

Still, the major and minor semiaxes of the ellipse is $a = \frac{n^2}{Z} a_0$ and $b = \frac{nl}{Z} a_0$. But the $l = n$ circular orbit is excluded and a new $l = 0$ line orbit (a limit ellipse) is added. Again, for one-electron hydrogen-like atom/ions, the energy level is purely determined by n : $E_n = -13.6 \text{ eV} \times \frac{Z^2}{n^2}$. But the orbit angular momentum is changed to

$$L = \sqrt{l(l+1)}\hbar \quad (1)$$

to agree with experiment. The z component under a field along z -axis, $L_z = m\hbar$, can now take the zero value for $m = 0$ is included.

Most of the features of Bohr ellipses are valid and equivalent to quantum-mechanical atomic orbitals, except the deterministic path idea and the strange line orbit $l = 0$ which says the electron will collide onto the nucleus.

2 STANDING WAVE*

A classical one-dimensional standing wave satisfies the wave equation

$$\frac{\partial^2 u(x,t)}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 u(x,t)}{\partial t^2}. \quad (2)$$

and constrained by boundary conditions

$$u(0,t) = 0, \quad u(L,t) = 0, \quad (3)$$

which imply that

$$L = n \frac{\lambda_n}{2}, \quad n = 1, 2, 3, \dots \quad (4)$$

or equivalently,

$$k_n = \frac{n\pi}{L}, \quad n = 1, 2, 3, \dots \quad (5)$$

Here we see another example of

Boundary conditions impose quantization.

The solution is

$$u_n(x,t) = A \sin\left(\frac{n\pi}{L}x\right) \sin\left(\frac{n\pi}{L}vt\right). \quad (6)$$

nodes: positions x_0 with $u(x_0, t) = 0$ for all time. There are $n - 1$ non-trivial nodes (not at boundaries) for mode n (Figure 2).

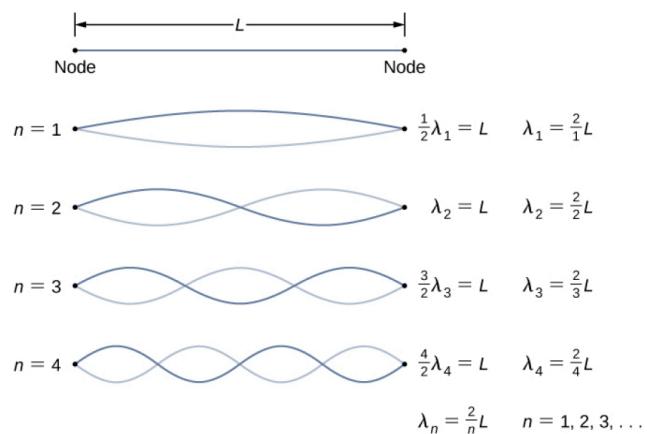


Figure 2: One-dimensional classical standing waves. (*Physics, OpenStax*)

Classification of Waves*

Waves can be classified into different types depending on whether physical medium is involved

- mechanical wave (机械波)

- electromagnetic wave (电磁波)

whether the peak amplitude profile travels in space

- traveling wave (行波), e.g. pulse signal

- standing wave (驻波), e.g. drumhead, guitar string.

whether the oscillation direction is perpendicular to the propagation direction

- transverse wave (横波) (perpendicular), e.g. electromagnetic wave, water wave, earthquake S-wave (secondary shear wave)

- longitudinal wave (纵波) (parallel), e.g. sound wave, earthquake P-wave (primary pressure wave)

Derivative Formulas*

$$\frac{d(cx)}{dx} = c \quad (7)$$

$$\frac{de^x}{dx} = e^x \quad (8)$$

$$\frac{d \sin x}{dx} = \cos x \quad \frac{d \cos x}{dx} = -\sin x \quad (9)$$

$$\frac{df(y(x))}{dx} = \frac{df}{dy} \frac{dy}{dx} \text{ (chain rule)} \quad (10)$$

Verification of One-Dimensional Standing Wave*

$$\frac{\partial u_n(x,t)}{\partial x} = A \frac{n\pi}{L} \cos\left(\frac{n\pi}{L}x\right) \sin\left(\frac{n\pi}{L}vt\right)$$

$$\frac{\partial^2 u_n(x,t)}{\partial x^2} = -A \left(\frac{n\pi}{L}\right)^2 \sin\left(\frac{n\pi}{L}x\right) \sin\left(\frac{n\pi}{L}vt\right)$$

$$\frac{\partial u_n(x,t)}{\partial t} = A \frac{n\pi}{L} v \sin\left(\frac{n\pi}{L}x\right) \cos\left(\frac{n\pi}{L}vt\right)$$

$$\frac{\partial^2 u_n(x,t)}{\partial t^2} = -A \left(\frac{n\pi}{L}v\right)^2 \sin\left(\frac{n\pi}{L}x\right) \sin\left(\frac{n\pi}{L}vt\right)$$

4 A PARTICLE IN A BOX: MODEL ONE-DIMENSIONAL ATOM*

Consider the potential

$$V(x) = \begin{cases} \infty, & x < 0 \\ 0, & 0 < x < L \\ \infty, & x > L \end{cases} \quad (13)$$

the full wave function $\Psi(x,t)$ can be factored into the product of the spatial and temporal contributions

$$\Psi(x,t) = \psi(x)e^{-i\frac{E}{\hbar}t}, \quad (14)$$

where $\psi(x)$ solves the time-independent Schrödinger equation

$$\left[-\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x)}{\partial x^2} + V(x)\psi(x) = E\psi(x) \right]. \quad (15)$$

Together with boundary conditions $\psi(0) = 0$ and $\psi(L) = 0$, it can be determined that

$$\psi_n(x) = \begin{cases} 0, & x < 0 \\ \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right), & 0 < x < L \\ 0, & x > L \end{cases}, \quad (16)$$

with energy levels

$$E_n = \frac{n^2 \hbar^2}{8mL^2}, \quad n = 1, 2, 3, \dots \quad (17)$$

Here, we have a model one-dimensional atom, whose quantized energy levels E_n is set by the *quantum number* n and whose electron is bounded within the range $[0, L]$. In this 1D atom, the electron moves in a certain *state* $\psi_n(x)$, or *atomic orbital*. The n th orbital has $n - 1$ non-trivial nodes. $|\psi_n(x)|^2$ is the probability density of finding the electron at position x .

5 ATOMIC ORBITALS IN HYDROGEN-LIKE IONS

"The general theory of quantum mechanics is now almost complete, the imperfections that still remain being in connection with the exact fitting in of the theory with relativity ideas. These give rise to difficulties only when high-speed particles are involved, and are therefore of no importance in the consideration of atomic and molecular structure and ordinary chemical reactions, in which it is, indeed, usually sufficiently accurate if one neglects relativity variation of mass with velocity and assumes only Coulomb forces between the various electrons and atomic nuclei. The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble." – Paul Dirac, Quantum mechanics of many-electron systems, 1929.

In real 3D hydrogen-like atom/ions (one electron), the spatial part of the wave function $\psi(\mathbf{r})$ is often expressed in spherical coordinates $\psi(r, \theta, \phi)$. The potential is of Coulomb form, $V(r) = -\frac{1}{4\pi\epsilon_0 r} \frac{e^2}{r}$. The solution to the Schrödinger equation, characterized by three *quantum numbers* (n, l, m) ,

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r)\Theta_{lm}(\theta)\Phi_m(\phi) \quad (18)$$

$$\Psi(x,t) = Ae^{i(kx-\omega t)} = Ae^{i(\frac{p}{\hbar}x - \frac{E}{\hbar}t)}. \quad (11)$$

From

$$\frac{\partial \Psi(x,t)}{\partial t} = \Psi \left(-i\frac{E}{\hbar} \right)$$

$$\frac{\partial \Psi(x,t)}{\partial x} = \Psi \left(i\frac{p}{\hbar} \right) \text{ and } \frac{\partial^2 \Psi(x,t)}{\partial x^2} = -\Psi \left(\frac{p}{\hbar} \right)^2,$$

it can be seen that

$$i\hbar \frac{\partial \Psi(x,t)}{\partial t} = i\hbar \Psi \left(-i\frac{E}{\hbar} \right) = E\Psi$$

and

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x,t)}{\partial x^2} = \frac{\hbar^2}{2m} \Psi \left(\frac{p}{\hbar} \right)^2 = \frac{p^2}{2m} \Psi.$$

Because $E = \frac{p^2}{2m} + V$, we arrive at the one-dimensional (time-dependent) Schrödinger equation of a particle of mass m under a steady potential field $V(x)$

$$i\hbar \frac{\partial \Psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x,t)}{\partial x^2} + V(x)\Psi(x,t). \quad (12)$$

are *atomic orbitals*(原子轨道), which the electron can occupy.

The possible integer values of (n, l, m) are the same as in Bohr ellipse orbits: $n = 1, 2, \dots$ determines energy levels E_n in one-electron hydrogen-like atom/ions; $l = 0, 1, \dots, n - 1$ determines the orbital angular momentum $L = \sqrt{l(l+1)}\hbar$; $m = 0, \pm 1, \pm 2, \dots, \pm l$ determines the projection of L along the direction of an external field $L_z = m\hbar$. Again, in multi-electron atoms, n and l determine energy levels of orbitals together E_{nl} . Orbitals with different l have different shapes and we assign symbols s, p, d, f, \dots to those with $l = 0, 1, 2, 3, \dots$. The number of nodes (planes or cones or spheres where $\psi_{nlm} = 0$) equals $n - 1$ (Figure 3), including $n - l - 1$ nodal spheres ($R_{nl}(r) = 0$) and l nodal planes or nodal cones ($\Theta_{lm}(\theta)\Phi_m(\phi) = 0$).

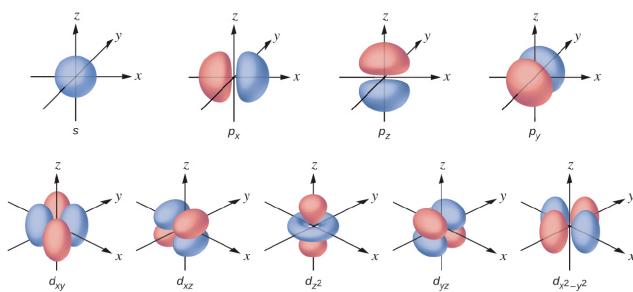


Figure 3: Schematic representation of s, p, d atomic orbitals with blue (red) lobes corresponding to $\psi > 0 (< 0)$. (Chemistry, Openstax)

Orbitals with the same n form a *shell*. Under each shell, those with the same l form a *subshell*.

$|\psi_{nlm}(r, \theta, \phi)|^2$ gives the probability density of finding the electron at position (r, θ, ϕ) when it moves in state (n, l, m) . For instance, in hydrogen atom, the $1s$ orbital

$$\psi_{100} = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0} \right)^{3/2} e^{-\frac{r}{a_0}} \quad (19)$$

is independent of θ and ϕ , thus spherically symmetric. The probability density at a distance r , after averaged over all directions, is $4\pi r^2 \psi_{100}^2$, which has its maximum value at $r = a_0$, the Bohr radius. The motion of electrons around the nucleus is in a probabilistic fashion in orbitals looking more like *electron clouds*, instead of deterministic paths. Accumulation of electron positions over time provides a map of electron density in proportion to $|\psi_{nlm}|^2$ (Figure 3).

6 ORBITAL ANGULAR MOMENTUM AND ZEEMAN

EFFECT*

In quantum mechanics, incompatible quantities, like position p and local x , cannot be determined simultaneously, but can only be measured with accuracy set by the uncertainty principle. For the same reason, any two components of the angular momentum vector $\mathbf{L} = (L_x, L_y, L_z)$ cannot be determined at the same time. Therefore, when we specify the angular quantum number l , we can only affirm the *magnitude* $L = \sqrt{l(l+1)}\hbar$ of \mathbf{L} but not its direction.

For instance, the five d orbitals for $l = 2$ all have the same energy and angular momentum magnitude, but the orientation of \mathbf{L} is arbitrary. When an external magnetic field is applied (say along the z direction), the energy of the five d orbitals become different and the original spectral line are splitted into five different lines, called (normal) Zeeman effect¹. After the symmetry is broken by the external field, the projection of \mathbf{L} along z direction, L_z can be determined. Its value is quantized, $L_z = m\hbar$ with $m = -l, -l+1, \dots, l-1, l$. That is to say, $L = |\mathbf{L}|$ and L_z are compatible and determined at the same time. But the direction of \mathbf{L} is arbitrary, which means it can rotate freely along the surface of a cone (Figure 4).

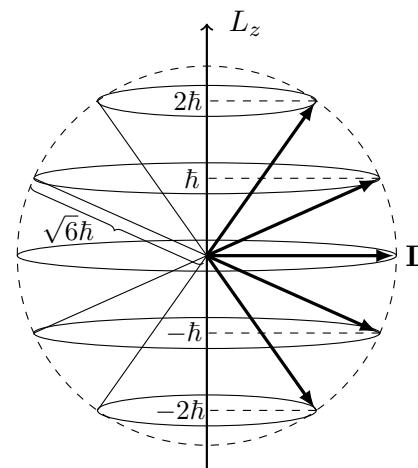


Figure 4: Orbital angular momentum \mathbf{L} states for $l = 2$ (d orbitals). The magnitude of \mathbf{L} is $\sqrt{2(2+1)}\hbar = \sqrt{6}\hbar$ but the direction cannot be determined. Only one component $L_z = m\hbar$ can be determined with $m = 0, \pm 1, \pm 2$ if an external field is applied. In each state, \mathbf{L} can still rotate about the z axis along the surface of the cone.

¹In reality, a strong magnetic field can split the spectral line into more than $2l + 1$ lines, when spin angular momentum is also taken into account. This is called anomalous Zeeman effect.

Chapter 1 Atomic Structure

Lecture 4 Electron Configuration and Periodic Table

1 ENERGY LEVELS IN MULTI-ELECTRON ATOMS

For one-electron hydrogen-like atom/ions, the energy level E_n is solely determined by n , and s, p, d, \dots orbitals for the same n are degenerate¹. In multi-electron atoms, both n and l affect energy E_{nl} , because each electron not only feels the attraction from the nucleus but also experiences repulsion from other electrons. When other electrons *penetrate* into inner space of the atom, they can *screen* part of the Z positive charges of the nucleus. The total effective positive charge Z_{eff} acting on outer layer electrons is thus smaller than the original Z , causing their energies to be higher. A useful empirical rule, called Goudsmit rule or Bose rule, to rank atomic orbitals (n, l, m) by their energies, is to use the pair

$$(n + l, n). \quad (1)$$

Generally, E_{nl} increases with $n + l$ and, in case of equal $n + l$, with n (see reading materials²). This leads to the energy sequence of

$$1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s \dots, \quad (2)$$

which can be traced with following diagram.

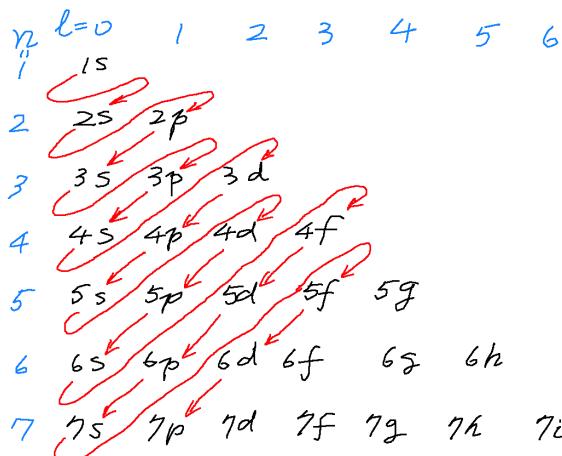


Figure 1: A diagram to help remember the energy levels of atoms when filling electrons under the aufbau principle

However, a lot of exceptions to the *aufbau principle* exist, which says that ground state electron configurations of atoms should have all electrons filled from low to high energy levels, due to other complexities (electron-electron interaction, spin-orbit coupling, relativity effects etc.).

2 ELECTRON SPIN AND PAULI EXCLUSION PRINCIPLE

Several experiments suggest that, besides orbital angular momentum, each electron also carries a *spin angular momentum* with magnitude

$$S = \sqrt{s(s+1)}\hbar, \quad s = \frac{1}{2}. \quad (3)$$

Note that here the quantum number is a half-integer. Like the orbital angular momentum, the direction of the vector S cannot be determined, but its projection along a certain direction z can be measured.

$$S_z = m_s \hbar, \quad m_s = \pm \frac{1}{2}. \quad (4)$$

By convention, electrons with $m_s = +\frac{1}{2}$ or $-\frac{1}{2}$ are called *spin up* or *down*, and denoted by \uparrow or \downarrow . Adding the spin quantum number m_s to the other three orbital quantum numbers, we find that the state of electrons in atoms is characterized by four quantum numbers

$$(n, l, m, m_s). \quad (5)$$

Although the analogy is often drawn between the spin of electron and the rotation of the Earth about its axis, current evidences suggest that the electron is a structureless point particle. And spin is an *intrinsic* property of elementary particles including electrons.

Pauli exclusion principle⁴

No more than two electrons can occupy the same orbital in an atom and these two must have opposite spins. In another word, no two electrons in an atom can have the same values of the four quantum numbers n, l, m, m_s .

When electrons fill in atomic orbitals from low to high energy levels, they tend to form pairs with opposite spins as much as they can. There are cases that several orbitals are singly occupied with parallel spins due to the coupling between orbital L and spin S , which are explained by Hund's rules*.

Each unpaired electron spin carries a net magnetic moment and responds to external magnetic fields. The overall magnetic properties of materials are determined by the number and orientation of unpaired electron spins in each atom/molecule.

- diamagnetic: all electrons are paired with opposite spins.
- paramagnetic: there are unpaired electron spins but in random orientations.

¹ means having the same energy

²Lowdin, Per-Olov. Some comments on the periodic system of the elements. International Journal of Quantum Chemistry 3.S3A S3a (1969): 331-334.

³In general, a quantum-mechanical angular momentum has a magnitude $J = \sqrt{j(j+1)}\hbar$ and z component $J_z = m_j \hbar$ with m_j running from $-j$ to j with increment 1.

⁴This is true for all fermions-particles with half-integral spin. It comes from the quantum-mechanical rule that the wave function representing a state of a system containing two or more electrons must be *antisymmetric*, i.e. change its sign, on interchanging the coordinates of any two electrons.

- ferromagnetic: there are unpaired electron spins, which are almost aligned in the same direction.

3 PERIODIC TABLE

Combining atomic orbital energy levels with electron spins, we can build up elements and derive their *electron configuration* sequentially as the atomic number Z increases.

The properties of the chemical elements are not arbitrary, but depend upon the electron configuration of the atom and vary with the atomic number in a systematic and somewhat periodic way.

Not all electrons in atoms affect the chemical properties of the element.

- **inner electrons:** paired and buried deep inside in inner shells of atoms that do not participate in bonding or chemical reactions. Often omitted or brief as noble gas core, e.g. [He] and [Ar], in electron configurations.
- **valence electrons:** outer electrons that actively affect chemical properties of elements. defines the group of the element.

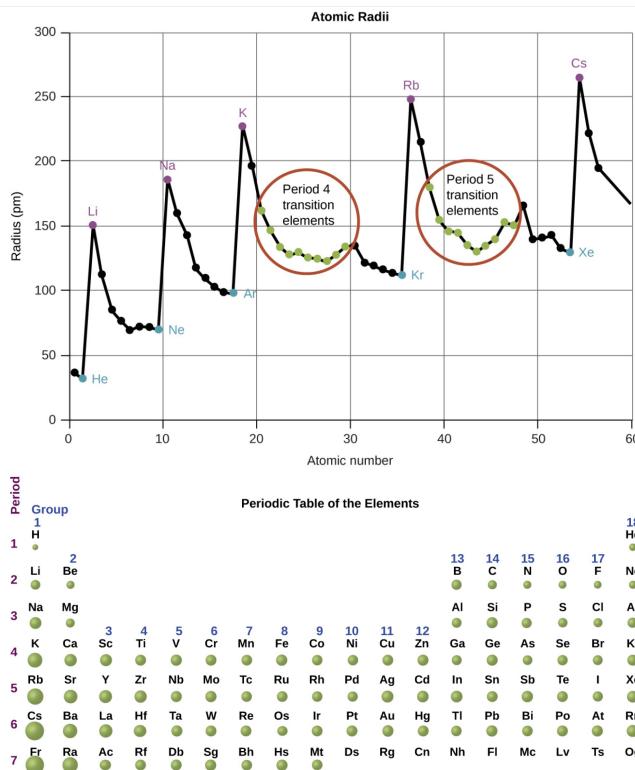


Figure 2: The Atomic radius⁵ decreases with Z within each period, but increases with Z within each group. (Chemistry, OpenStax)

If we arrange the elements in a table reflecting the periodicity of their properties, we have a *periodic table*. The most common style of the periodic table has 7 *periods* and 18 *groups*.

- **period(周期):** a horizontal row goes from most metal-like elements to least metal-like elements. From the 1st to the 7th period, there are 2, 8, 8, 18, 18, 32, 32 (not all found) elements.
- **group (family)(族):** a vertical column containing elements with closely related physical and chemical properties.

– **Group 1 hydrogen and alkali metals(碱金属)** ns¹: H and Li, Na, K, etc.

– **Group 2 alkaline (earth) metals(碱土金属)** ns²: Be, Mg, Ca, etc.

– **Group 3-12 transition metals(过渡金属)** (n-1)d¹⁻¹⁰s⁰⁻²: Fe, Co, Ni, Cu, Zn, Ag, Pt, Au, Hg, etc.

* **Group 3 Period 6 lanthanoids(镧系)** (n-2)f⁰⁻¹⁴(n-1)d⁰⁻¹ns²: La, Er, etc.

* **Group 3 Period 7 actinoids(锕系)** (n-2)f⁰⁻¹⁴(n-1)d⁰⁻²ns²: Ac, U, etc.

– **Group 13 ns²np¹:** B, etc.

– **Group 14 ns²np²:** C, Si, etc.

– **Group 15 ns²np³:** N, P, etc.

– **Group 16 ns²np⁴:** O, S, etc.

– **Group 17 halogens(卤素)** ns²np⁵: F, Cl, Br, I, etc.

– **Group 18 noble (inert) gases(惰性气体)** ns²np⁶: He, Ne, Ar, Kr, Xe, Rn, etc.

The transition from metals to non-metals is gradual, with boundary elements (metalloids: B, Si, Ge, etc.) going diagonally on the periodic table.

Depending on which subshell is involved in valence electrons, the periodic table can be divided into several zones or blocks: s, p, d and f zone.

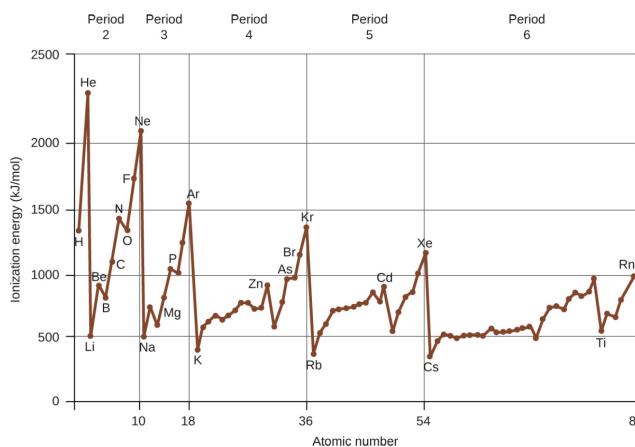
4 ATOMIC WEIGHT

Weighted average (by abundance) of atomic masses of the element, measured in unit of Da (1/12 of the mass of ^{12}C atom).

We define one *mole* as the number $N_A = 6.022 \times 10^{23}$ such that 1 mole of ^{12}C atoms is of mass 12 grams. The advantage of using mole is that the weight of substances tends to be a numerical value close to integers (mass numbers).

5 PERIODIC PROPERTIES

First ionization energy IE₁: energy required to remove one electron from the atom. The smaller IE₁ is, the easier for the element to lose one electron and the more metal-like the element is.



⁵For most elements, atoms do not naturally exist in an isolated state but bond or couple with other elements. The definition of atomic radius changes with the bonding type.

Figure 3: The periodicity of the first ionization energy. (*Chemistry, OpenStax*)

Electronegativity: an artificial numerical scale representing the el-

ements' power of attraction for electrons in a covalent bond. Non-metals have larger electronegativity, e.g. F 4.0, O 3.5, N 3.0, thus stronger tendency to attract and acquire electrons.

Chapter 2 Molecular Structure

Lecture 5 Empirical Valence Bond Theory 价键理论

1 CHEMICAL BONDS

Except for noble gases, atoms are not the basic units that can preserve the chemical properties of substances. In fact, by sharing or exchanging (valence) electrons with other atoms (of the same or different element), atoms form *chemical bonds* with each other and build up molecules, that are more natural units for analyzing chemical properties.

For instance, water is made of H_2O molecules but not isolated H and O atoms. Discussing chemical properties of water, such as its boiling point, reactivity with Na, etc, is more meaningful on the molecular level.

There is a chemical bond between two atoms or groups of atoms in case that the forces acting between them are such as to lead to the formation of an aggregate with sufficient stability to make it convenient for the chemist to consider it as an independent molecular species. – Linus Pauling, *The Nature of the Chemical Bond*

Based on their nature, chemical bonds can be classified into three different types: covalent, ionic and metallic bonds (Figure 1).

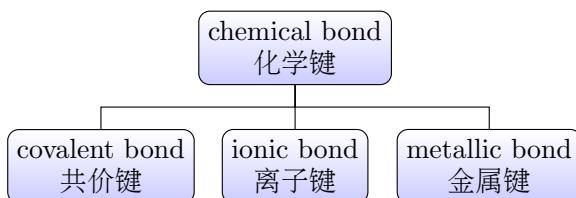


Figure 1: Types of chemical bonds.

- **covalent bond** involves *sharing* of one or multiple pairs of electrons by the two bonded atoms. Covalent bonds can only be formed in certain directions (directionality). The total number of covalent bonds is limited by the atom's *valence* (saturation). Atoms form molecules via covalent bonds. e.g. $\text{H}-\text{O}-\text{H}$, $\text{Cl}-\text{Cl}$
- **ionic bond** results from the Coulomb attraction of the excess electric charges of oppositely charged ions. Metallic atoms tend to lose their valence electrons easily to form *cations*, whereas nonmetallic atoms tend to add additional electrons in the outer shell to form *anions*. Ionic bonds are long-ranged, non-saturating, and can be formed in any direction. The whole ionic crystal may be viewed as one giant molecule. e.g. Na^+Cl^-
- **metallic bond*** In metals, valence electrons from each atoms can move inside the entire system and become *free electrons*, which serve as glue to hold all the atoms together.

Quantum-mechanical band theory in solid physics is needed to explain metallic bond.

valence of an element is its combining power, that is, the number of valence bonds formed by an atom of the element with other atoms.

2 LEWIS STRUCTURE

Starting from 1916, before quantum mechanics was fully developed, Gilbert Lewis¹ and Irving Langmuir developed an empirical² *valence bond theory* that can successfully explain electron structures of many compounds, especially those involving the first 20 elements (before *d* orbital electrons are encountered). Note that, when this theory was invented, people did not know about wave functions or atomic orbitals yet.

In Lewis's theory

- Each atom X has a *kernel* X^{n+} which remains unaltered during ordinary chemical changes. In our language, X^{n+} consists of the nucleus and the inner electrons. The positive charge number *n* equals the ordinal number of the group (族序数) in the periodic table to which the element X belongs. For instance, the kernel of the C atom is C^{4+} – the carbon nucleus plus two $1s$ inner electrons.
- Electrons in the *outer shell*, namely, valence electrons, affect the chemical properties of the elements, whose number may vary between 0 and 8.
- When forming compounds, atoms tend to combine in such a way that each atom has eight electrons in its valence shell, through sharing electron pairs or donating-accepting electrons. (**octet rule**) (八电子规则)

Lewis structure

I would suggest the use of a colon, or two dots arranged in some other manner, to represent the two electrons which act as the connecting links between the two atoms. Thus we may write Cl_2 as $\text{Cl}:\text{Cl}$ We may go further and give a complete formula for each compound by using the symbol of the kernel and by adjoining to each symbol a number of dots corresponding to the number of electrons in the atomic shell. Thus we may write $\text{H}:\text{H}$, $\text{H}:\ddot{\text{O}}:\text{H}$, $\text{H}:\ddot{\text{O}}:\text{H}$ and $\ddot{\text{O}}:\ddot{\text{O}}:$ – Lewis 1916.

Here we use the element symbol to represent the kernel. Those electron pair(s) shared between two or more atoms are covalent bond(s) which sometimes are represented by short line(s), for instance, $\text{H}-\ddot{\text{O}}-\text{H}$. Those unshared electron pair(s) are called *lone pair(s)* (孤对电子).

¹Lewis, Gilbert N. "The atom and the molecule." Journal of the American Chemical Society 38.4 (1916): 762-785.

²neither very quantitative nor of first principle, but formally works for most cases, based on experience.

Two atoms sharing one, two or three electron pairs form *single*, *double* or *triple bond*. For instance, $\text{:N}\equiv\text{N:}$, $\text{:O}=\ddot{\text{O}}:$, ethylene
 $\begin{array}{c} \text{H} & \text{H} \\ | & | \\ \text{H}-\text{C}=\text{C}-\text{H}, \text{acetylene H}-\text{C}\equiv\text{C}-\text{H}. \end{array}$

Limitations of Lewis structure and theory

- Octet rule may give rise to wrong electron structures, e.g. $\text{:O}=\ddot{\text{O}}:$, and in most cases, does not apply to heavy elements with *d* or *f* electrons.
- does not reflect actual bond angles or spatial conformation of molecules, e.g. $\begin{array}{c} \text{H} & \text{H} \\ | & | \\ \text{H}-\text{C}=\text{C}-\text{H} \end{array}$
- does not explain the origin of the bonding force resulted from the shared electron pair(s).

Lewis's Cubical Atom*

To account for the octet rule, Lewis proposed a cubical atom model, in which one valence electron can occupy one corner of a cube (Figure 2). This model is purely phenomenological – there is no evidence suggesting that valence electrons should move on a cubic shape shell. Nevertheless, it formally captures some of the bonding rules and can even adapt for the tetrahedral geometry of carbon-hydrogen bonds in organic compounds, by moving valence electrons to four of the twelve edges of the cube. That is why we say Lewis's theory is empirical.

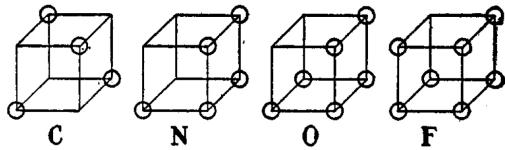


Figure 2: The imagined cubical atoms of Lewis. (Lewis, 1916)

and direction points from the negative to the positive charge³ (Figure 3).

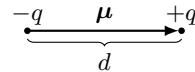


Figure 3: Electric dipole moment of magnitude $\mu = qd$.

Given bond polarity, the molecule as a whole can be *polar* or *nonpolar*, depends on how all the bond dipole moments add up together. Note that μ 's are vectors thus follow the rule of vector addition. Molecular polarity is determined by the spatial conformation of the molecule.

Molecular polarity affects solubility. Polar solutes tend to be well dissolved in polar solvent but poorly in nonpolar solvent. Polar molecules that tend to attract and mix with water (which is polar) are called *hydrophilic*, while nonpolar molecules that tend to repel and demix from water are called *hydrophobic*. *Surfactants*, or amphiphilic molecules, are small rod-like molecules made up of a hydrophilic head-group and a hydrophobic tail, which tend to stay at the interfaces of polar (water) and nonpolar (oil) solvents. Hydrophobicity (being hydrophilic or hydrophobic) can also refer to a particular part of the molecule – a chemical group.

Formal charge is the net charge each atom would carry, if shared electrons were divided equally between the bonded atoms in a Lewis structure (Figure 4).

When there is a confusion between different possible Lewis structures, we use the one obeys the **electroneutrality principle**, which says that *stable molecules have electronic structures such that the formal charge of each atom is close to zero, in particular, often between -1 and +1*.

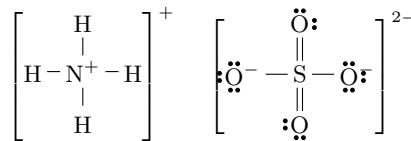


Figure 4: Stable Lewis structures of ammonium ion NH_4^+ and sulfate ion SO_4^{2-} with correctly assigned formal charges.

Oxidation number (oxidation state) is a number that represents the electric charge that the atom would have if the electrons in a compound were assigned to the atoms in a conventional way. In covalent compound, each shared electron pair is assigned completely to the more electronegative atom of the two bonded atoms. An electron pair shared by two atoms of the same element is usually split between them (Figure 5).

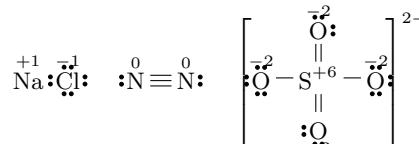


Figure 5: Oxidation numbers of elements in NaCl , N_2 and sulfate ion SO_4^{2-} .

3 BOND AND MOLECULAR POLARITY

When a pair of electrons are shared between two atoms of different types, they lean towards the atom with stronger attraction for electrons. The covalent bond becomes *polar* and the two bonded atoms carry partial charges $A^{\delta+} \rightarrow B^{\delta-}$. In the extreme case that one atom completely loses its electron and the other accepts it, the bond becomes an ionic bond $A^+:B^-$.

The energy released when an extra electron is attached to an atom to form an anion is called the *electron affinity* (电子亲和势). Larger electron affinity implies stronger attraction for electrons. In practice, it is more convenient to use the artificial *electronegativity* (电负性) scale. Elements with larger electronegativity have stronger attraction for electrons.

When a positive charge $+q$ is separated from a negative charge $-q$ by a distance d , it is useful to define a vector quantity called *electric dipole moment* (电偶极矩) μ , whose magnitude is $\mu = qd$

³In physics, the convention is to define μ pointing from minus to plus charge $- \rightarrow +$. For bond dipoles in chemistry, as in Pauling's book, the convention is the opposite $+ \rightarrow -$, i.e. along the inclination direction of electron pairs. You can choose either convention, but remember to be consistent. The physics convention has the advantage that, when placed in an external electric field \mathbf{E} , the energy $U = -\mu \cdot \mathbf{E}$ of the dipole μ is minimized when it is aligned with \mathbf{E} .

4 VSEPR

Valence shell electron pair repulsion (VSEPR) theory is an empirical model to predict the geometry of molecules from the number

of electron pairs surrounding the central atom⁴.

For any molecule AX_nE_m with a central atom A, n ligands X and m lone pairs E, the shape of AX_n can be predicted from the number of bonding and nonbonding (lone) electron pairs (Figure 6).

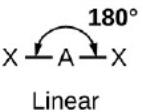
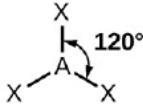
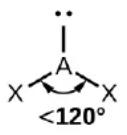
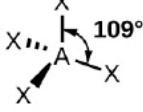
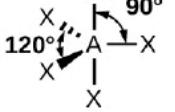
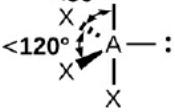
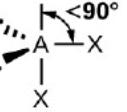
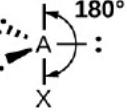
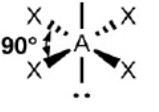
Number of electron pairs	Electron pair geometries: 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2	 Linear				
3	 Trigonal planar	 Bent or angular			
4	 Tetrahedral	 Trigonal pyramidal	 Bent or angular		
5	 Trigonal bipyramidal	 Sawhorse or seesaw	 T-shape	 Linear	
6	 Octahedral	 Square pyramidal	 Square planar	 T-shape	 Linear

Figure 6: Typical cases of molecular structures in VSEPR theory. (Chemistry, Openstax)

⁴Gillespie, Ronald James. "The electron-pair repulsion model for molecular geometry." Journal of Chemical Education 47.1 (1970): 18.

Chapter 2 Molecular Structure

Lecture 6 Quantum-Mechanical Nature of Covalent Bond

The covalent bond consists of a pair of electrons shared between two atoms, and occupying two stable [atomic] orbitals, one of each atom. — Linus Pauling

1 RESONANCE

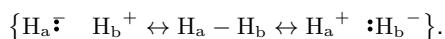
How does the shared electron pairs stabilize the molecule? What provides the force for covalent bonding? Electron pairs act as glue to hold two bonded atoms together, but there is no good explanation in classical mechanics for this.

To describe covalent bond, Linus Pauling borrowed the idea of superposition in quantum mechanics¹ and introduced the theory of *resonance* (共振). According to this theory, the actual structure of the molecule is a hybrid structure resulted from its resonance between two or more electronic structures. As a consequence of the resonance, the molecule can be stabilized by a certain amount of energy², called *resonance energy*.

In the hydrogen molecule-ion H_2^+ , the one electron resonates between two nuclei (*a* and *b*) and resonance structures of H_2^+ are



In hydrogen molecule H_2 , we consider following resonance Lewis structures



Similarly, the CO molecule resonates between three structures



Note that, the valid resonance Lewis structures should obey the electroneutrality principle.

2 QUANTUM-MECHANICAL VALENCE BOND THEORY

The valence bond theory (VB) of covalent bond is also a shared-electron-pair theory, in which each resonance Lewis structure corresponds to the product of two atomic orbitals occupied by two electrons. For one-electron covalent bond, the idea is similar as shown below.

In the quantum-mechanical treatment of H_2^+ , where the one electron is denoted by “1”, the resonance structures are represented by wavefunctions

$$\begin{aligned}\psi_a(1) &: \text{H}_a \cdot \text{H}_b^+ \\ \psi_b(1) &: \text{H}_a^+ \cdot \text{H}_b\end{aligned}$$

and the actual stable state of the system, $\{\text{H}_a \cdot \text{H}_b^+ \leftrightarrow \text{H}_a^+ \cdot \text{H}_b\}$, is the superposition of $\psi_a(1)$ and $\psi_b(1)$

$$\psi_{\text{VB}}(\text{H}_2^+) = \psi_a(1) + \psi_b(1).$$

For a normal two-electron covalent bond in hydrogen molecule H_2 , it is necessary to differentiate the two electrons, “1” and “2”, in each quantum state. They can also be understood as two electrons with different spins, \uparrow and \downarrow . The resonance Lewis structures, after considering the two electrons differently, are



The corresponding quantum states are

$$\psi_a(1)\psi_a(2) \leftrightarrow \psi_a(1)\psi_b(2) \leftrightarrow \psi_a(2)\psi_b(1) \leftrightarrow \psi_b(1)\psi_b(2).$$

Here the two structures $\psi_a(1)\psi_b(2)$ and $\psi_a(2)\psi_b(1)$ are of covalent nature, while the two structures $\psi_a(1)\psi_a(2)$ and $\psi_b(1)\psi_b(2)$ are of ionic nature. The meaning of each of these four forms, e.g. $\psi_a(1)\psi_b(2)$, is that electron 1 is in atomic orbital ψ_a and electron 2 is in atomic orbital ψ_b , etc. If we assume these four structures contribute equally to the final quantum state, the valence bond wavefunction of the entire H_2 molecule is then

$$\psi_{\text{VB}}(\text{H}_2) = \psi_a(1)\psi_a(2) + \psi_a(1)\psi_b(2) + \psi_a(2)\psi_b(1) + \psi_b(1)\psi_b(2).$$

Note that, this form is equivalent to

$$[\psi_a(1) + \psi_b(1)][\psi_a(2) + \psi_b(2)],$$

which is later to be recognized in molecular orbital theory.

3 HYBRIDIZATION

To understand the geometry of molecules, it is sometimes helpful to use the idea of *hybridization* (杂化) of atomic orbitals. For instance, methane CH_4 is of tetrahedral symmetry with four equivalent C–H bonds. The four valence electrons of carbon atom $[\text{He}]2s^2 2p^2$ originally stays in *s* and *p* orbitals. It is not obvious to see how one spherical *s* orbital plus three mutually perpendicular *p* orbitals could give rise to four tetrahedral bonds.

In hybridization theory, by linear combination, several atomic orbitals first reorganize into a new set of *hybrid orbitals*, which possess the correct symmetry of the molecule, and then form covalent bonds with other orbitals. In the case of CH_4 , the *s*, p_x , p_y and p_z orbitals of carbon form four sp^3 hybrid orbitals by (see also Appendix VII of [Pauling])

$$\left\{ \begin{array}{l} \psi_1 = \frac{1}{2}(\psi_s + \psi_{p_x} + \psi_{p_y} + \psi_{p_z}) \\ \psi_2 = \frac{1}{2}(\psi_s + \psi_{p_x} - \psi_{p_y} - \psi_{p_z}) \\ \psi_3 = \frac{1}{2}(\psi_s - \psi_{p_x} + \psi_{p_y} - \psi_{p_z}) \\ \psi_4 = \frac{1}{2}(\psi_s - \psi_{p_x} - \psi_{p_y} + \psi_{p_z}) \end{array} \right. . \quad (1)$$

¹Recall the double-slit interference discussed before. The state of the overall pattern is the superposition of two separate states $\psi = \psi_1 + \psi_2$.

²The total energy for a superposition state $\psi_a + \psi_b$ under Hamiltonian \hat{H} is $E = \int (\psi_a^* + \psi_b^*) \hat{H} (\psi_a + \psi_b) d\mathbf{r} = \int \psi_a^* \hat{H} \psi_a d\mathbf{r} + \int \psi_b^* \hat{H} \psi_b d\mathbf{r} + \int \psi_b^* \hat{H} \psi_a d\mathbf{r} + \int \psi_a^* \hat{H} \psi_b d\mathbf{r} = E_a + E_b + J_{ab} + J_{ab}^*$. The exchange energy $J_{ab} = \int \psi_a^* \hat{H} \psi_b d\mathbf{r}$ is the source of extra stability and resonance energy.

Each sp^3 hybrid orbital forms a C–H σ -bond by head-to-head overlapping with the s orbital of hydrogen atom. The bond angle of perfect tetrahedral symmetry is 109.5° . sp^3 hybridization also occurs in other small molecules, such as NH_3 and H_2O , in which the existence of electron lone pair(s) distorts the tetrahedral arrangement (Figure 1).

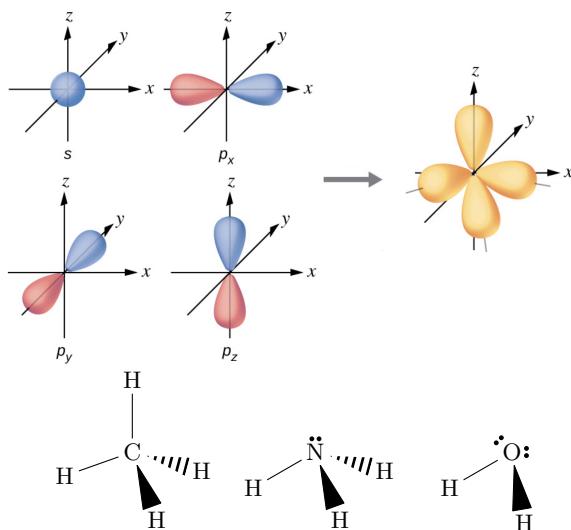


Figure 1: sp^3 hybridization in CH_4 , NH_3 and H_2O (Chemistry, Openstax).

In organic chemistry, it is also often to see sp^2 hybridization in ethylene $\text{H}_2\text{C}=\text{CH}_2$ and sp hybridization in acetylene $\text{HC}\equiv\text{CH}$. When double or triple bonds are involved, only one of them is σ -bond while the remaining are π -bonds from side-to-side overlap of p orbitals.

Arrangement		Hybridization	
-----	linear	sp	
	trigonal planar	sp^2	
	tetrahedral	sp^3	
	trigonal bipyramidal	sp^3d	
	octahedral	sp^3d^2	

Figure 2: The shapes of hybrid orbitals (Chemistry, Openstax).

There are other forms of hybridization involving d orbitals. The geometry of hybrid orbitals can be used together with VSEPR to explain molecular geometry (Figure 2).

Vector Decomposition with Different Basis*

A 2D vector \mathbf{r} can be decomposed into a linear combination of base vectors (\hat{x}, \hat{y}) with coordinates (a, b) , $\mathbf{r} = a\hat{x} + b\hat{y}$. If different base vectors (\hat{x}', \hat{y}') are used, which come from a counterclockwise rotation of (\hat{x}, \hat{y}) by an angle θ , the decomposition has different coordinates $\mathbf{r} = a'\hat{x}' + b'\hat{y}'$ (Figure 3).

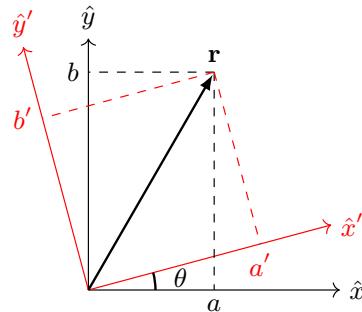


Figure 3: Vector decomposition in two sets of basis.

The new base vectors can be viewed as linear combination of the old ones

$$\begin{cases} \hat{x}' = \cos \theta \hat{x} + \sin \theta \hat{y} \\ \hat{y}' = -\sin \theta \hat{x} + \cos \theta \hat{y} \end{cases}.$$

The coordinates in the new and old reference frame are also related by

$$\begin{cases} a' = \cos \theta a + \sin \theta b \\ b' = -\sin \theta a + \cos \theta b \end{cases}.$$

Appropriate choice of base vectors can lead to well-behaved coordinates, in this case, of same magnitude $a' = b'$.

The ideal of hybrid orbitals can be understood using the analogy of vector decomposition. The state of the atom described by an overall wavefunction Ψ is like a vector \mathbf{r} . The original atomic orbitals s , p_x , p_y and p_z are like the original base vectors \hat{x} and \hat{y} , while hybrid orbitals ψ_1 – ψ_4 are like the new base vectors \hat{x}' and \hat{y}' . Expressing Ψ in different base orbitals is similar to decomposing \mathbf{r} in different base vectors.

Chapter 2 Molecular Structure

Lecture 7 Molecular Orbital Theory 分子轨道理论

1 MOLECULAR ORBITAL FROM LCAO

So far, in valence bond theory, the pairing of two bonding electrons is described by the product of two atomic orbitals. The overall state of the covalent bond is then viewed as superposition or resonance of these product states. This picture of shared electron pairs, in some cases, disagrees with the real situation. For instance, the Lewis structure for oxygen molecule is $\text{:}\ddot{\text{O}}=\ddot{\text{O}}\text{:}$, in which all electrons are paired, in order to obey the octet rule. However, experiments show that unpaired electron spins exist in oxygen.

An alternative, more natural view is to consider the molecule as a whole with its *molecular orbitals* (MOs). Then electrons from *all* bonding atoms fill in these MOs from low to high energy levels. To find these MOs, it is convenient to use the approximation of linear combination of atomic orbitals (LCAOs), i.e.

$$\text{MO} \approx \text{LCAO}.$$

In case of hydrogen-molecule ion H_2^+ or hydrogen molecule H_2 , it is straightforward to find two MOs ψ_I and ψ_{II} from linear combinations of two atomic orbitals ψ_a and ψ_b , with coefficients (1, 1) and (1, -1), respectively¹ (Figure 1)

$$\begin{cases} \psi_I = \psi_a + \psi_b \\ \psi_{II} = \psi_a - \psi_b \end{cases}. \quad (1)$$

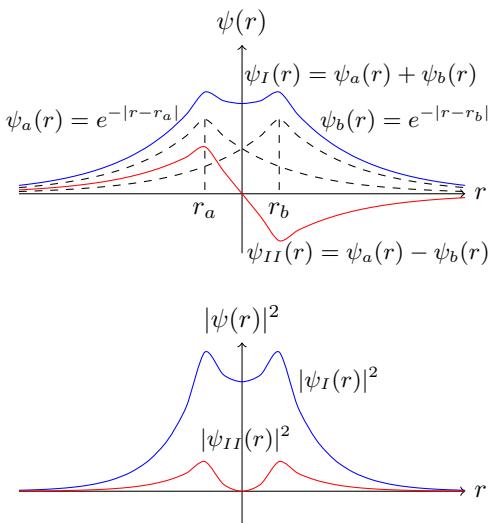


Figure 1: Superposition of two 1s atomic orbitals ψ_a and ψ_b gives rise to a bonding ψ_I and an anti-bonding ψ_{II} state. High electron density $|\psi|^2$ in the middle of two atoms in state I signifying covalent bonding of the two atoms.

Electrons in state ψ_I has an enhanced probability density in between the two bonded hydrogen atoms. Thus the ψ_I molecular orbital has lower energy (than the original constituting atomic orbital ψ_a , ψ_b) and is called, a *bonding orbital* (成键轨道). On the other hand, electrons in state ψ_{II} have zero probability showing

up in the middle of the two bonded atoms. The ψ_{II} molecular orbital has higher energy and is called, an *antibonding orbital* (反键轨道). This process is often illustrated by a molecular orbital diagram (Figure 2). The symbol σ_{1s} for the bonding orbital indicates that it is a σ -bond from head-to-head overlap of *s* orbitals. The * is used to denote the corresponding antibonding orbital.

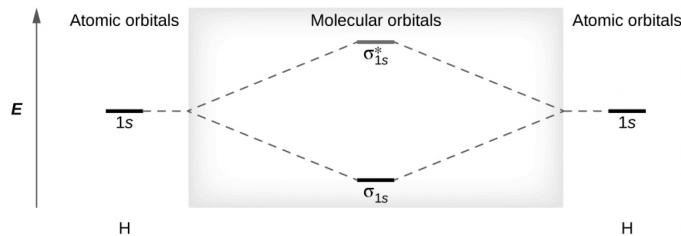


Figure 2: Two molecular orbitals made from two 1s atomic orbitals (Chemistry, OpenStax).

After having the two MOs at hand, we can construct the total wavefunction of the molecule, for instance,

$$\psi_{\text{MO}}(\text{H}_2^+) = \psi_I(1) = \psi_a(1) + \psi_b(1)$$

and

$$\psi_{\text{MO}}(\text{H}_2) = \psi_I(1)\psi_I(2) = [\psi_a(1) + \psi_b(1)][\psi_a(2) + \psi_b(2)].$$

Note that $\psi_{\text{MO}}(\text{H}_2)$ is equivalent to $\psi_{\text{VO}}(\text{H}_2)$ if ionic contributions are included in valence bond theory.

It is thus convenient to view covalent bonding as the constructive overlap of atomic orbitals (of the same sign), which enhances the electron density between the two bonded atoms.

- σ bond: head-to-head overlap of atomic orbitals; strong; free rotation about internuclear axis
- π bond: side-to-side overlap of atomic orbitals; weak; cannot rotate

2 MOLECULAR ORBITAL THEORY

In molecular orbital theory

- Linear combination of n atomic orbitals generates n molecular orbitals.
- Electrons fill in molecular orbitals with the same rules as filling in atomic orbitals. That is (1) from lower to higher energy levels; (2) Pauli exclusion principle (no more than two electrons per MO); (3) Hund's rules (singly occupied orbitals with spins in parallel).
- The stability of the covalent bond is determined by the net number of electrons in bonding orbitals, i.e. the *bond order* (B.O.):

¹Generally, $z = c_1x + c_2y$ is a linear combination of x and y with coefficients c_1 and c_2 .

$$\frac{\text{number of bonding electrons} - \text{number of antibonding electrons}}{2} \quad (2)$$

With molecular orbital theory, it is possible to predict the existence of unpaired electrons (Figure 3). The Lewis structure for O_2 should thus be written as $\ddot{\bullet}O-\ddot{\bullet}O\bullet$, where two two-center-three-electron Π_2^3 bonds² are formed upon the one σ -bond. The B.O. for O_2 is 2 (net pairs of bonding electrons).

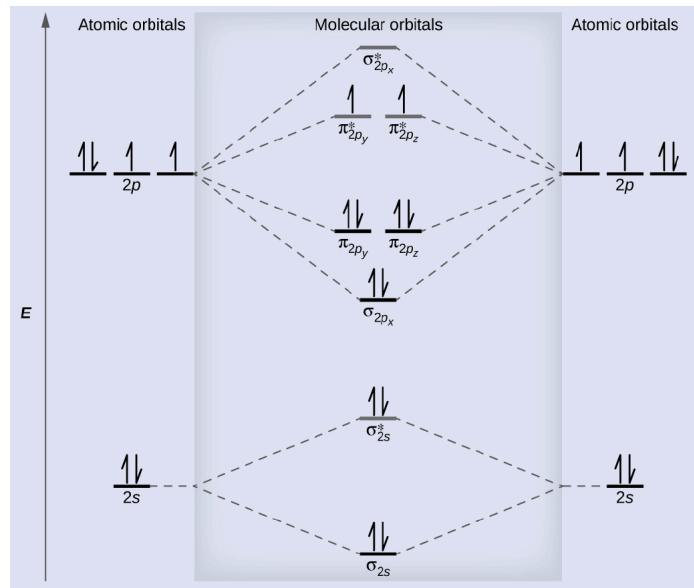


Figure 3: Molecular orbital diagram for O_2 (only valence electrons are shown) (*Chemistry, Openstax*).

We can use our vector decomposition analogy to understand the motivation for molecular orbital theory. The state of the entire molecule is described by a wavefunction Ψ , which is like a vector r . The valence bond theory uses atomic orbitals (AO) as base vectors to decompose Ψ . The molecular orbital theory uses MOs as base vectors, which are LCAOs.

HOMO: highest occupied molecular orbital

LUMO: lowest unoccupied molecular orbital

Many chemical and electrical properties of molecules, such as reactivity, color and conductivity, are determined by the states of HOMO and LUMO, and in particular, the energy gap between them.

3 BOND ENERGY

Bond energy is the energy required to break a chemical bond or energy released to form a chemical bond, which is an indicator of bond strength. There are more rigorous definition based on chemical reactions with specified conditions, which will be covered in later chapters.

The bond energy for just one bond is too small. Practically, it is convenient to use bond energy of one mole of bonds or express bond energy in unit of kJ/mol or kcal/mol (1 cal = 4.184 J). Typically, the chemical bond energy is on the order of 100 kJ/mol.

See [Pauling] Appendix VIII to have a sense of bond energy for common bonds.

4 MOLECULAR FORMULA AND NOMENCLATURE

For covalent (molecular) compounds, molecular formula gives the actual composition of the molecule, in terms of how many number of atoms of each type in the molecule, e.g. H_2O , H_2SO_4 and $C_6H_{12}O_6$.

For ionic compounds, molecular formula only gives the ratio of cations and anions in irreducible integers, e.g. $NaCl$ and $MgCl_2$.

Example of compound nomenclature:

N_2O_3 dinitrogen trioxide

PCl_5 phosphorus pentachloride

$FeCl_3$ iron(III) chloride ("ferrous, ferric" etc. is obsolete)

H_2O_2 hydrogen peroxide (dihydrogen dioxide)

See *Chemistry, Openstax* Chapter 2.7 for more rules and examples (binary acids and oxyacids). For instance, prefix

1-mono, 2-di, 3-tri, 4-tetra, 5-penta, 6-hexa, 7-hepta, 8-octa, 9-nona, 10-deca, etc.

²In empirical Lewis valence bond theory, a covalent bond contains a pair of electrons. In quantum-mechanical molecular orbital theory, the concept of covalent bond can be generalized to contain other numbers of electrons, for instance, one-electron bond in H_2^+ , three-electron bond in O_2 and six-electron bond in benzene C_6H_6 etc.

Chapter 2 Molecular Structure

Lecture 8 Intermolecular Forces

1 VAN DER WAALS FORCES

In addition to strong chemical bonds with bond energy of several hundreds kJ/mol, there are other weaker interactions between molecules that contribute to the formation of condensed matter (liquid and solid). Such ubiquitous attractions between all molecules are called, *van der Waals forces*, which include three major components¹ (Figure 1):

- permanent dipole-dipole attraction (Keesom force)
- permanent dipole + induced dipole attraction (Debye force)
- dispersion force (London force)

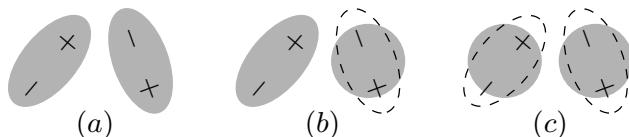


Figure 1: The (a) Keesom, (b) Debye and (c) London contributions to van der Waals forces.

The London dispersion force is usually the dominant term, except for extremely polar molecules. The strength of London dispersion force roughly increases with molecular weight.

Van der Waals forces are

- weaker than covalent and ionic bonds, with energy often in the range of 10-20 kJ/mol.
- not directional
- not saturated
- shorter-ranged than ionic bonds ($\frac{1}{r^6}$ v.s. $\frac{1}{r}$)

Van der Waals forces can be modeled by the Lennard-Jones potential

$$u_{\text{LJ}}(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] \quad (1)$$

whose attraction well depth ϵ is on the order of 10 kJ/mol and attraction range is about 2-3 times of the molecular size $\sigma \sim \text{\AA}$ (Figure 2).

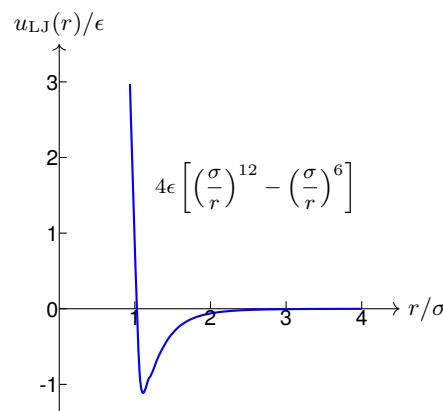


Figure 2: Lennard-Jones potential.

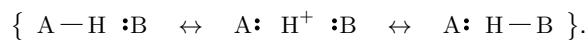
Van der Waals forces are responsible for the condensation of molecules into molecular liquids and crystals, therefore, determine their *melting points* T_m ² and *boiling points* T_b .

2 HYDROGEN BOND

When a hydrogen atom is closely attracted by two atoms of large electronegativity (i.e. N, O, F), it acts as a bridge bringing the two atoms together almost in a straight line and forms a *hydrogen bond*. Hydrogen bond

- only forms in between N, O, F.
- (with energy ~ 20 kJ/mol) is weaker than ionic and covalent bonds, but stronger than ordinary van der Waals forces.
- is short-ranged and directional, i.e. only along the A—H…B line.
- can be saturated

The H in a hydrogen bond is not permanently bonded to one of the two atoms next to it, but can be transferred between the two atoms. In another word, a A—H…B hydrogen bond involves resonance among three structures



Hydrogen bonds give rise to anomalous properties for compounds containing N, O and F. For instance, the boiling point of H₂O is much higher than it should be, if only ordinary van der Waals forces were in action (Figure 3). The very reason for the Earth to have life is that water is in its liquid state in the normal temperature range here (0-100 °C) (Figure 4).

Hydrogen bonds are also crucial for many biological structures and processes. For instance, the binding of base pairs in DNA uses two (A-T) or three (C-G) hydrogen bonds. The folding of peptide chain into functional α -helix relies on hydrogen bonds.

¹Sometimes the definition of van der Waal force only narrowly includes the London dispersion term.

²In case of melting of crystals into liquids, the shape of molecules and their packing efficiency also play an important role.

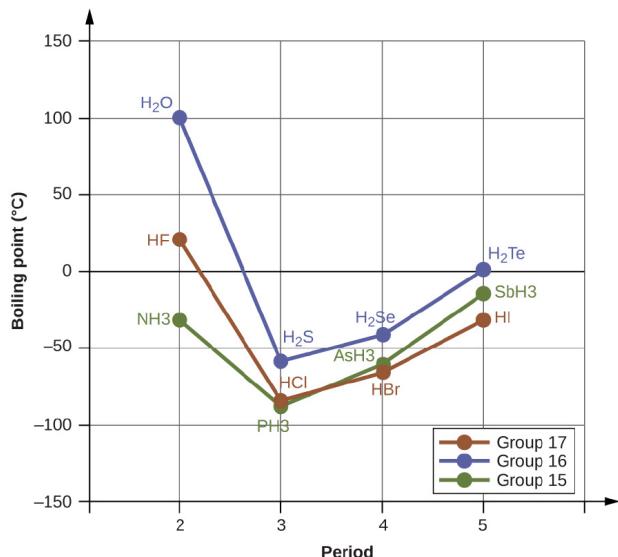


Figure 3: NH₃, H₂O and HF exhibit anomalously high boiling points comparing with other compounds in their group. (*Chemistry, OpenStax*)

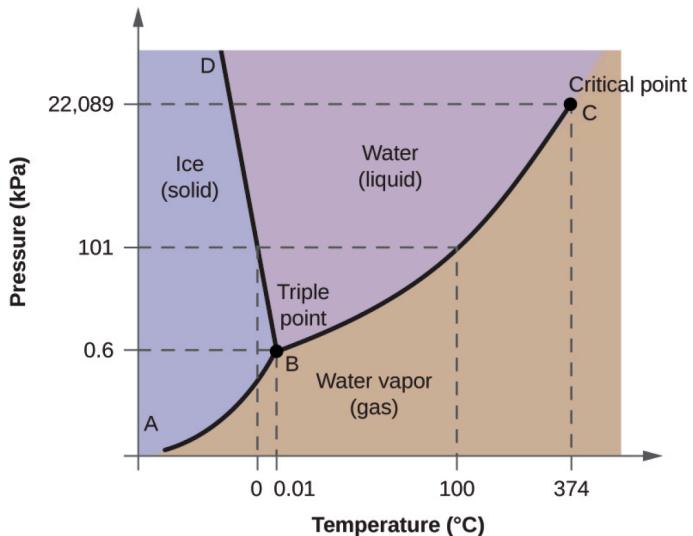


Figure 4: The phase diagram of water. (*Chemistry, OpenStax*)

Chapter 3 Structure of Matter and Life

Lecture 9 Crystal Structure

"How can the universe start with a few types of elementary particles at the big bang, and end up with life, history, economics, and literature? ... Why did the big bang not form a simple gas of particles, or condense into one big crystal?"

— Per Bak, How Nature Works

1 STATES OF MATTER

A substance often exists in one of its three states, gas, liquid and solid. In gaseous state, molecules are far apart from each other and can travel from place to place. In liquid state, molecules are condensed into contact but still can travel within the system. In solid state, molecules are confined within the cages formed by neighboring molecules and can only vibrate within cages. Gas and liquid together are called *fluid* (流体) ; liquid and solid together are called *condensed matter* (凝聚态) (Figure 1). An easy macroscopic criterion to distinguish between liquid and solid is to test whether the material yields to external shearing, namely, flows.

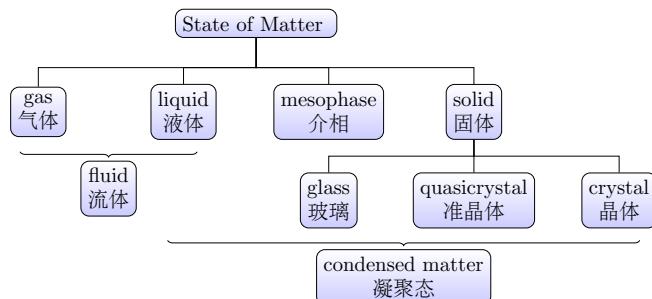


Figure 1: States of matter.

Pure gas, liquid, or solid constitutes a phase. A **phase** (相) is a homogeneous part of a system, separated from other parts by physical boundaries. A homogeneous *solution* is also one phase. A mixture of water and oil contains two phases. *Homogeneous* means that molecules are uniformly mixed on the molecular level.

2 CRYSTALS

Crystals are ordered solids in which atoms/molecules are arranged regularly on a lattice. A *lattice* (晶格) is a geometric abstraction of the crystal, for which each atom/molecule is viewed as a sizeless point.

Depending on the interactions between constituent particles, crystals can be classified into metallic, ionic, covalent and molecular crystals (Figure 2). Note that previously we named "covalent and molecular compound" indistinguishably. Here covalent crystals refer to those in which atoms are connected by covalent bonds throughout the entire system, forming a network, e.g. in diamond. On the other hand, in molecular crystals, covalent bonds are only

within each molecule and different molecules are held together by much weaker van der Waals attractions (sometimes including hydrogen bonds).

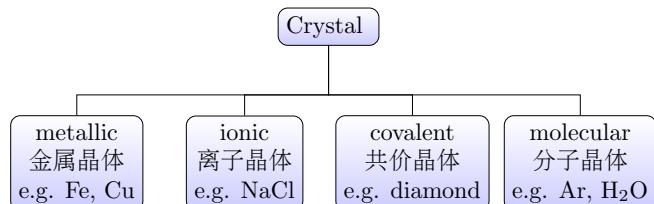


Figure 2: Types of crystals.

The types of interactions can affect the melting point T_m of crystals. Ionic and covalent crystals tend to have very high T_m (upto several thousands degree) because of the strength of ionic and covalent bonds (several hundreds kJ/mol). In contrast, the melting point of molecular crystals are much lower (often below several hundreds degree), because van der Waals forces are much weaker (10-20 kJ/mol).

In addition, the shape of molecules and their packing also affect T_m . Molecules of more symmetric and regular shapes can pack more efficiently on a lattice, thus are more difficult to melt (higher T_m). Branches, protrusions or surface roughness tend to frustrate molecular packing thus reduce T_m .

3 PACKING OF SPHERES ON LATTICES

Regardless of the bonding type, particles of different crystals share some common packing (堆积) motifs from a geometric point of view. For simple atoms/molecules that can be approximated as spheres¹, four common packing motifs are often encountered.

- **simple cubic (SC)** (简单立方): $\eta = 0.52$, $z = 6$
- **body-centered cubic (BCC)** (体心立方): $\eta = 0.68$, $z = 8+6$
- **face-centered cubic (FCC)** (面心立方): $\eta = 0.74$, $z = 12$
- **hexagonal close packed (HCP)** (六方): $\eta = 0.74$, $z = 12$

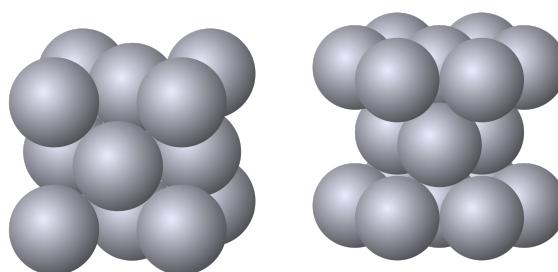


Figure 3: FCC and HCP structure (wikimedia).

¹ Most organic compounds and large molecules are not sphere-like.

Packing efficiency (volume fraction) η : fraction of volume occupied by the packing spheres.

Coordination number z : number of nearest neighbors on a lattice².

In absence of other effects, dense packings tend to be more stable, thus most crystals adopt the FCC or HCP lattice (Figure 3).

4 IONIC CRYSTALS

Ionic crystals contain at least two types of ions: cations A^{n+} and anions B^{m-} . The crystal structure of binary ionic compounds A_mB_n is determined by the charge number m, n and the ratio $\frac{r_B}{r_A}$ of radii of A^{n+} and B^{m-} .

In the same period, the radius of anion r_B is larger than that of cation r_A (see Figure 6-20 and 6-21 in [Pauling]). What lattice structure for the ionic crystal to use depends on how the small cations can fit in the cavities formed by large surrounding anions (18-2 [Pauling]). See the example of NaCl (FCC+FCC = SC) and CsCl (SC+SC = BCC) (Figure 4).

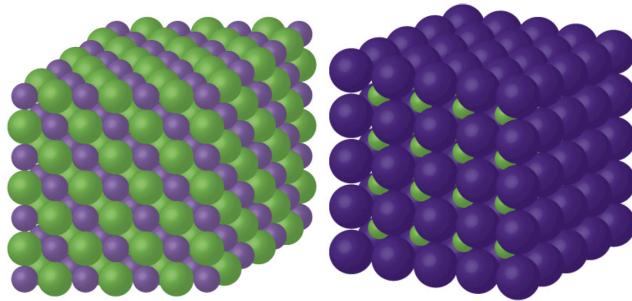


Figure 4: Crystal structure of NaCl and CsCl (Chemistry, Openstax).

Hydration of ions (12-6 [Pauling]) As a polar solvent, water molecules can often use their partially negative O end to combine with positively charged cations, especially bipositive and terpositive ones, forming *hydrated ions*. Depending on the relative size of the cation, four or six H_2O molecules may surround the central cation in tetrahedral or octahedral geometry. If the electrostatic attractions between waters and cations are strong enough, a layer of water molecules may remain around each cation during crystallization. For instance, $MgCl_2 \cdot 6 H_2O$ or $KAl(SO_4)_2 \cdot 12 H_2O$. This water is *water of crystallization* and is binded inside the crystal lattice.

5 MOLECULAR CRYSTALS

The two O–H bonds and two electron lone pairs in water molecule are roughly in the tetrahedral arrangement. When freezing into Ice (I_h), water molecules can form a diamond-like network³ with hydrogen bonds (Figure 6). Because of this extended network structure, ice has lower density than liquid water thus can float above oceans to help protect the Earth from being overheated.

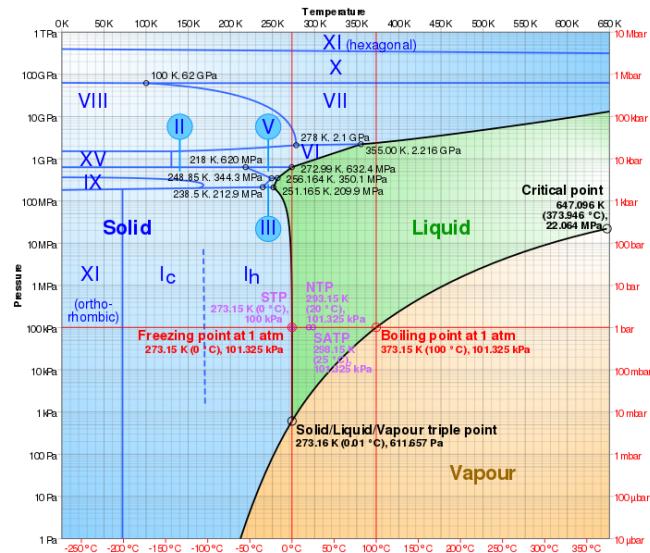


Figure 5: Phase diagram of water showing several types of ices (Wikipedia).

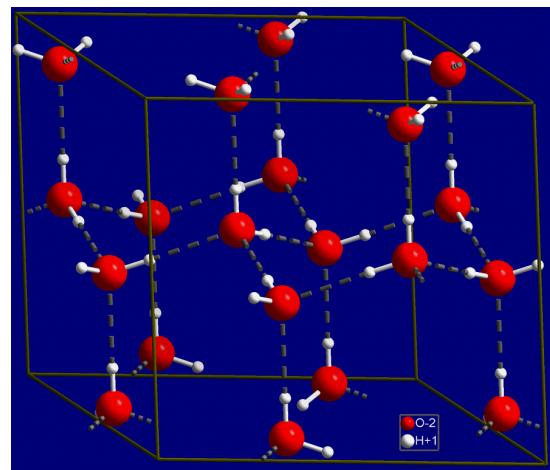


Figure 6: The structure of hexagonal ice I_h (wikimedia).

6 OTHER STATES*

Besides typical liquid and crystal states, many other complex structures occur in nature.

Liquid crystals are mesophases that in some directions are ordered and deprived of translational movement, but in other directions are disordered and open to translational movement. In this sense, biomembranes are liquid crystals, in which rod-like lipid molecules are confined within a quasi-two-dimensional surface but are able to move freely in it.

Glasses are amorphous (disordered) solids. Structurally, they are like liquids, but dynamically, they cannot flow.

Quasicrystals are solids intermediate between purely disordered glasses and purely ordered crystals. They are ordered (possess rotational symmetry) but not periodic (lack translational symmetry).

²Sometimes it is useful to include next-nearest neighbors, as in the case of BCC.

³Not exactly the same. But with an alternative rotation of layers.

Chapter 3 Structure of Matter and Life

Lecture 10 Organic Molecules, Polymers and Biomolecules

1 ORGANIC MOLECULES

Carbon C is an element with chemical properties intermediate between metals and nonmetals, and thus tends to form chemical bonds with many other types of elements.

Organic chemistry is the study of compounds of carbon. Because life on Earth is carbon-based, organic molecules are often related to biological structures and processes. In the early days, it was thought that life, or organisms, are made of different materials than the “inorganic” compounds that chemists first studied. It is now agreed that “life molecules” can be united with other types of molecules, all in the realm of chemistry.

There are only a handful of elements involved in organic compounds, of which the most common ones are C, H, O, N, P, S etc. However, through elongation and rearrangement of carbon chains, these small number of elements make up $\sim 10^6$ different types of organic molecules.

The valence of elements in organic compounds is usually the typical value. That is, carbon forms 4 bonds (double bond counts as two), hydrogen forms 1 bond, oxygen forms 2 bonds, and nitrogen forms 3 bonds, etc.

1.1 Hydrocarbon

Hydrocarbons (烃) are compounds of hydrogen and carbon alone. Depending on whether double or triple bonds are contained, hydrocarbons are classified as

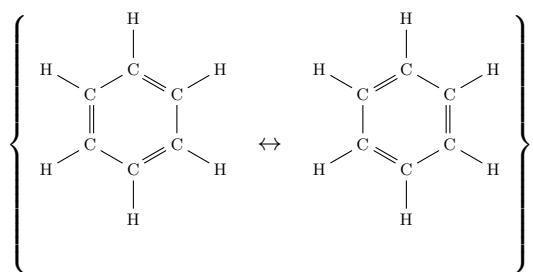
- **alkane (烷烃)** contains only C–C single bond and is said to be *saturated*¹ (饱和). For instance, methane CH₄, ethane C₂H₆ (or H₃C–CH₃) etc. The group obtained by removing a hydrogen atom from an alkane is called a *alkyl group* (烷基) and often represented by R–.

- **alkene (烯烃)** contains C=C double bond and is said to be *unsaturated*. For instance, ethylene H₂C=CH₂ and isoprene H₂C=CH–CH=CH₂.

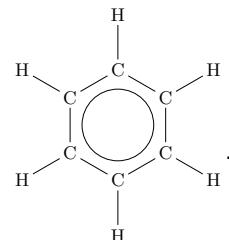


- **alkyne (炔烃)** contains C≡C triple bond and is also *unsaturated*. For instance, acetylene HC≡CH.

- **aromatic hydrocarbon (芳香烃)²** contains benzene C₆H₆ or benzene ring C₆H₅– and is also *unsaturated*. The benzene molecule can be considered to resonate among two structures



Therefore, each carbon-carbon bond in benzene is a superposition of C–C and C=C bonds. The alternative molecular orbital theory says that each *sp*² hybridized carbon contributes its one remaining *p*_z orbital and the six parallel *p*_z orbitals form a large conjugate Π_6^6 bond. The structure of benzene is thus also represented by



1.2 Functional groups

The chemical properties of organic molecules, regardless of their size and complexity, are often characterized by a small representative group of bonded atoms, called a *functional group* (官能团). The nomenclature and classification of organic molecules are often based on their functional groups.

Table 1: Common functional groups*.

notation	structure	name	example
–R	—R	alkyl 烷基	—CH ₂ CH ₃
–OH	—O—H	hydroxyl 羟基	CH ₃ CH ₂ OH
—CO—	—C=O	carbonyl 羰基	CH ₃ COCH ₃
—CHO	—C=O	aldehyde 醛基	CH ₃ CHO
—COR	—C=O—R	acyl 酰基	aspirin
—COOH	—C=O—O—H	carboxyl 羧基	CH ₃ COOH
—COOR	—C=O—O—R	ester 酯基	CH ₃ COOC ₂ H ₅
—NH ₂	—N—H	amino 氨基	CH ₂ (NH ₂)COOH

¹For in this case, carbon connects to maximum number of hydrogen atoms.

²Non-aromatic hydrocarbons are also called *aliphatic* hydrocarbons (脂肪烃).

1.3 Isomerism

Isomerism (同分异构) is the existence of two or more compounds (isomers) having the same composition (molecular formula) but different way that atoms are bonded together.

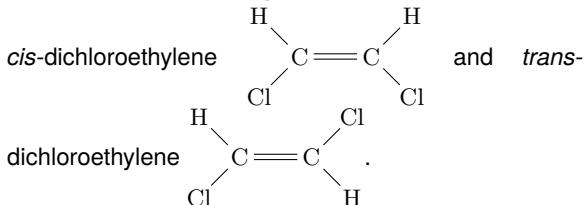
- *constitutional (structural) isomerism* (构造异构): due to different bond connectivity, e.g.

n-butane (正丁烷) $\text{H}_3\text{C} - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$ and isobutane (异丁烷) $\text{H}_3\text{C} - \underset{\text{CH}_3}{\text{CH}} - \text{CH}_3$.



- *stereoisomerism* (立体异构): same bond connectivity but different stereoscopic arrangement.

- *cis/trans isomerism* (顺反异构): one same or different sides of double bond, e.g.



- *enantiomerism* (对映异构): due to chirality

1.4 Chirality (handedness)

When four different atoms or groups (ligands) are connected to one tetrahedral center³, normally a sp^3 carbon, they can be arranged in two different configurations that are mutual mirror images but not able to completely overlap in space (Figure 1). We can use wedge and dash bonds to represent the stereochemical structure of a chiral center⁴.

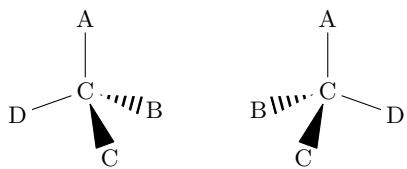


Figure 1: Left-handed (L) and right-handed (D) isomers.

Naturally occurring amino acids are left-handed.

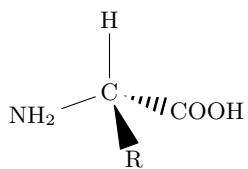


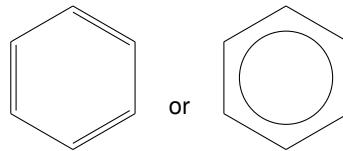
Figure 2: Left-handed (L) amino acid.

1.5 Structural formula

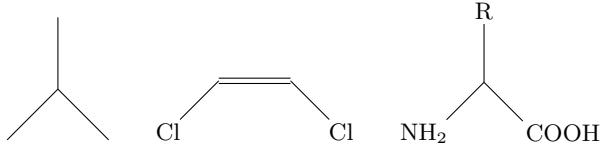
Since the valence of elements in organic compounds are often very regular, it is possible to derive how many hydrogen atoms should be in the molecule, if all other types of atoms are specified. Even writing all carbon symbols C explicitly is unnecessary. In structural formula of organic compounds, it is customary to omit some or all C atoms and omit some or all H atoms. It is defined that each vertex

of the graph, being a terminal, a kink or a intersection, represents a carbon atom.

Under this convention, called *skeletal formula*, the structural formula of benzene can be simplified to



And some compounds mentioned above can be represented by



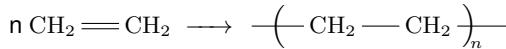
2 POLYMERS

Polymers or *macromolecules* are large molecules (with molecular weight $>10^4$ Da and size $\gtrsim 10$ nm), composed of many similar repeated units, *monomers* (单体).

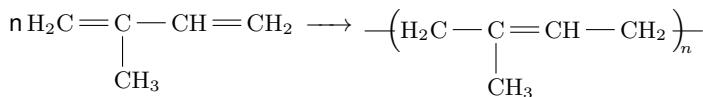
Polymerization are often through

- *addition* (加成)

polyethylene

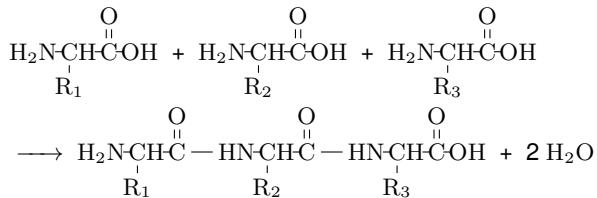


natural rubber, polyisoprene



- *condensation* (缩合)

polypeptide (多肽)



If only a few ($\lesssim 10$) monomers are connected, the resulted polymer is called an *oligomer* (寡聚物), specifically, dimer (2), trimer (3), tetramer (4), etc.

3 BIOMOLECULES

3.1 Small biomolecules

- sugars (糖): small carbohydrates. Carbohydrates (碳水化合物): $\text{C}_x(\text{H}_2\text{O})_y$.

– ribose

– glucose $\text{C}_6\text{H}_{12}\text{O}_6$

- organic acids

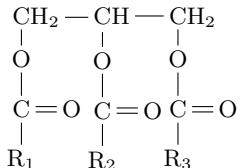
– palmitic acid $\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$

– stearic acid $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$

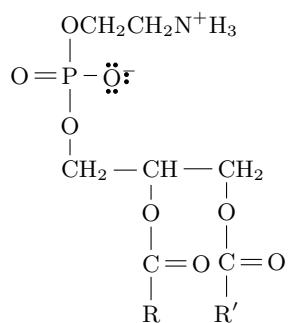
³Another common scenario of chirality involves cyclic structures. Generally, a molecule is chiral if it has neither symmetry center nor symmetry plane, e.g. H_2O_2 .

⁴It is also possible to show chirality with planar structures following pre-defined rules about clockwise/counterclockwise rotation along the ligand sequence. We avoid using this confusing convention here.

- oleic acid $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$
- lactic acid
- amino acid
- glycerol (甘油) $\begin{array}{c} \text{CH}_2 - \text{CH} - \text{CH}_2 \\ | \quad | \quad | \\ \text{OH} \quad \text{OH} \quad \text{OH} \end{array}$
- lipids (类脂)
 - fats and oils



- phospholipids (磷脂) : lecithin, cephalin, sphingomyelin



- purines: adenine (A) and guanine (G)
- pyrimidines: thymine (T) and cytosine (C) and uracil (U)

3.2 Macro biomolecules

- polysaccharides
 - starch
 - glycogen
 - cellulose
 - chitin
- proteins (primary, secondary, tertiary, quaternary structures)
- nucleic acids
 - deoxyribonucleic acid (DNA)
 - ribonucleic acid (RNA)

Chapter 4 Statistical Thermodynamics

Lecture 11 Entropy and Constant Energy Systems

1 MICROSTATES AND MACROSTATES

A thermodynamic system is the object under concern that normally contains a large number ($\sim N_A = 6.023 \times 10^{23}$) of particles (atoms, molecules, ions etc). Everything else is the *surrounding* or environment. The system plus its surrounding is the universe.

A *microstate* of the system is characterized by a set of microscopic mechanical variables, for instance, all the position and momentum vectors, $(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N; \mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_N) \equiv (\mathbf{r}^N, \mathbf{p}^N)$, for a N particle system. Therefore, a microstate of a classical N -particle system corresponds to a point in this $2dN$ -dimensional *phase space* ($d = 3$) (相空间).

A *macrostate* of the system is characterized by a set of experimentally measurable macroscopic *thermodynamic variables*, such as temperature T , pressure p , volume V etc. The system visits different microstates j 's with different probability p_j 's with $\sum_j p_j = 1$. The whole set of p_j 's, $\{p_j\} \equiv \{p_1, p_2, \dots, p_j, \dots\}$, is called a *distribution*. A macrostate of the system can also be described by a certain distribution $\{p_j\}$.

The value of an experimentally measurable macroscopic thermodynamic quantity A (in a macrostate), such as energy, volume, temperature, etc., can often be expressed as the *thermal average* $\langle A \rangle = \sum_j A_j p_j$ of a mechanical quantity A_j over all microstates j 's.

2 A TWO-PARTICLE NINE-CELL LATTICE MODEL

Consider a square lattice with $M = 9$ cells (sites) and $N = 2$ identical particles. Each cell can be empty or occupied by one particle. We now assume that there is no interaction energy between this pair of particles except that they cannot occupy the same cell. In another word, the energy of the system is always zero.

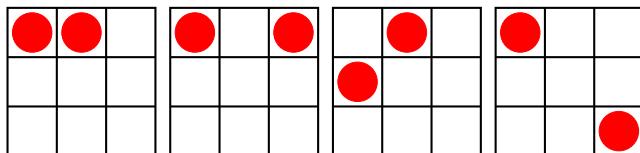


Figure 1: Examples of microstates of $N = 2$ and $M = 9$ lattice model.

A microstate of this system corresponds to a particular configuration or arrangement of the two particles sitting on two of the nine cells. The two particles are identical in a sense that interchanging them does not give rise to a new microstate. The total number of microstates Ω for this system is the combination number

$$\Omega = C_9^2 = \frac{9 \times 8}{1 \times 2} = 36.$$

Each microstate, index by $j = 1, 2, \dots, 36$, has the same energy $E = 0$.

Exercise Draw all these 36 microstates.

Among all these 36 microstates, $\Omega_A = 12$ of them (say they are microstates $j = 1-12$) have two particles on neighboring or connected cells. The remaining $\Omega_B = 24$ microstates ($j = 13-36$) have two particles that are disconnected. We call the collection of microstates with connected particles, macrostate A , characterized by the distribution,

$$\{p_j\}_A = (p_1, p_2, \dots, p_{12}; 0, 0, \dots, 0)$$

and the collection of microstates with disconnected particles, macrostate B , characterized by the distribution,

$$\{p_j\}_B = (0, 0, \dots, 0; p_{13}, p_{14}, \dots, p_{36})$$

We may define other types of macrostates using other parameters or methods. The *equilibrium* macrostate, characterized by $\{p_j\}_{eq}$, is a special distribution that maximizes/minimizes certain thermal quantities (to be shown soon). An arbitrary distribution $\{p_j\}$ generally corresponds to a *non-equilibrium* macrostate.

3 BOLTZMANN ENTROPY FOR CONSTANT ENERGY SYSTEMS

The **postulate of equal a priori probabilities** of statistical mechanics says that, at thermodynamic equilibrium, all Ω microstates with the same energy are equally likely to be visited by the system, i.e.

$$p_j = \frac{1}{\Omega}. \quad (1)$$

Under postulate of equal a priori probabilities, the equilibrium macrostate of the system above has the distribution

$$\{p_j\}_{eq} = \left(\frac{1}{36}, \frac{1}{36}, \dots, \dots, \dots, \dots, \frac{1}{36} \right)$$

Boltzmann's entropy formula

The thermodynamic or Boltzmann *entropy* of an equilibrium constant energy E system is

$$S_E = k_B \ln \Omega(E), \quad (2)$$

where k_B is Boltzmann constant has a unit of energy/temperature. $\Omega(E)$, the number of microstates in a system with constant energy E , is also called the *degeneracy* at energy level E .

Exercise What is the Boltzmann entropy of the equilibrium macrostate S_{eq} of the model above?

4 GIBBS ENTROPY AND MAXIMUM ENTROPY PRINCIPLE

Gibbs entropy

For any system, even at non-equilibrium, that visits each microstate j with probability p_j , the generalized Gibbs entropy is

$$S_G = -k_B \sum_j p_j \ln p_j. \quad (3)$$

We can verify that, the Boltzmann entropy is just a special case of the Gibbs entropy, for which the system of constant energy is at equilibrium and every microstate is equally probable, i.e.

$$-k_B \sum_{j=1}^{\Omega} \frac{1}{\Omega} \ln \frac{1}{\Omega} = k_B \ln \Omega \sum_{j=1}^{\Omega} \frac{1}{\Omega} = k_B \ln \Omega.$$

If macrostate A and macrostate B has the distribution

$$\{p_j\}_A = \left(\frac{1}{12}, \frac{1}{12}, \dots, \frac{1}{12}; 0, 0, \dots, 0 \right)$$

$$\{p_j\}_B = \left(0, 0, \dots, 0; \frac{1}{24}, \frac{1}{24}, \dots, \frac{1}{24} \right)$$

their Gibbs entropy, obtained similarly as with Boltzmann entropy formula, is

$$S_A = k_B \ln 12$$

$$S_B = k_B \ln 24$$

Note that, equilibrium macrostate has higher entropy than that of macrostate A or macrostate B . In fact, any distribution $\{p_j\}$ different from the equilibrium one will leads to a smaller entropy.

Maximum entropy principle

When the system reaches equilibrium, the Gibbs entropy is maximized (under certain constraints if required). In this case, the probability p_j takes the equilibrium value and the Gibbs entropy is the thermodynamic entropy $S_G = S$. That is to say, we can find the equilibrium probability by maximizing S_G with respect to p_j (under certain constraints).

Method of Lagrange Multipliers *

For a function $f(x)$ of x with a constraint $g(x) = 0$, the extreme value of $f(x)$ satisfying the constraint occurs by minimizing or maximizing

$$f(x) + \alpha g(x), \quad (4)$$

where α is an undetermined lagrange multiplier. That is, to solve

$$\frac{d[f(x) + \alpha g(x)]}{dx} = \frac{df(x)}{dx} + \alpha \frac{dg(x)}{dx} = 0. \quad (5)$$

Problem Find the equilibrium p_j in constant energy E systems from maximum entropy principle.

Solution We need to maximize $S_G = -k_B \sum_j p_j \ln p_j$ under the normalization constraint $\sum_{j=1}^{\Omega} p_j = 1$, i.e. to maximize

$$S' = -k_B \sum_j p_j \ln p_j + \bar{\alpha} \left(1 - \sum_j p_j \right), \quad (6)$$

or

$$S'/k_B = - \sum_j p_j \ln p_j + \alpha \left(1 - \sum_j p_j \right), \quad (\alpha = \bar{\alpha}/k_B). \quad (7)$$

Solving

$$0 = \frac{\partial S'/k_B}{\partial p_k} = -\ln p_k - p_k \frac{1}{p_k} - \alpha,$$

we find that

$$p_k = e^{-(1+\alpha)} = C.$$

From $1 = \sum_{j=1}^{\Omega} p_j = \sum_{j=1}^{\Omega} C = C\Omega$, we know $C = \frac{1}{\Omega}$. Therefore

$$p_k = \frac{1}{\Omega},$$

in agreement with the assumption of equal a priori probabilities.

Second law of thermodynamics

In an isolated system, a spontaneous process occurs in the direction of increasing entropy¹. In another word, entropy can never decrease in an isolated system, i.e. $\Delta S \geq 0$. The entropy is maximized when the system reaches equilibrium.

Exercise For the same model, consider a macrostate L in which the two particles are confined in the left most row of the cells, what is number of microstates in this macrostate, Ω_L ? What is the entropy of this macrostate S_L ? How to use macrostate L and the equilibrium macrostate to understand the expansion of gas molecules from one side of container to the entire volume?

5 SHANNON ENTROPY IN INFORMATION THEORY*

$$S_I = - \sum_j p_j \log_2 p_j \quad (8)$$

For a N -bit equal probable binary string $\dots 0101010100111000 \dots$, $p_j = \frac{1}{2^N}$,

$$S_I = \log_2 2^N = N \text{ bits.} \quad (9)$$

¹ Here the definition of entropy also includes non-equilibrium macrostates, i.e. to be understood as Gibbs entropy. Technically, thermodynamic entropy is only defined for equilibrium macrostates.

Chapter 4 Statistical Thermodynamics

Lecture 12 Boltzmann Distribution and Constant Temperature Systems

1 A TWO-PARTICLE NINE-CELL LATTICE MODEL WITH INTERACTION

We consider the $N = 2$ particle and $M = 9$ cell model again but with a modification — now the two particles attract each other when they are neighbors. We define the interaction energy between a pair of connected particles to be $-\epsilon$, where $\epsilon > 0$ is the strength of attraction used as the unit of energy.

Due to particle-particle interaction, the total energy of the system for different microstates can be different. Now, microstate $j = 1\text{-}12$ has a energy $E = -\epsilon$ and microstate $j = 13\text{-}36$ has a energy $E = 0$. Since the 36 microstates of this system may have different energies, the distribution of the equilibrium macrostate is no longer constant, i.e. $p_j \neq \frac{1}{36}$.

We will show next that, in this case (of microstates at different energy levels), it is natural to consider a system at constant temperature T , or equivalently, a system whose average energy $\langle E \rangle = \sum_j p_j E_j$ is a constant. In addition to temperature T , we fix the number of particles N and volume V of the system too. This is called a *closed system*¹, which exchanges energy with surroundings.

2 BOLTZMANN DISTRIBUTION IN CONSTANT TEMPERATURE SYSTEMS

We apply the maximum entropy principle under two constraints, $\sum_j p_j = 1$ and $\sum_j E_j p_j = \langle E \rangle$, to find the equilibrium distribution $\{p_j\}$ of microstates. That is to maximize

$$S' = -k_B \sum_j p_j \ln p_j + \bar{\alpha} \left(1 - \sum_j p_j \right) + \bar{\beta} \left(\langle E \rangle - \sum_j E_j p_j \right)$$

or

$$S'/k_B = - \sum_j p_j \ln p_j + \alpha \left(1 - \sum_j p_j \right) + \beta \left(\langle E \rangle - \sum_j E_j p_j \right). \quad (1)$$

The solution is

$$p_k = C e^{-\beta E_k}.$$

From normalization condition $\sum_j p_j = 1$, it becomes

$$p_k = \frac{e^{-\beta E_k}}{\sum_j e^{-\beta E_j}}.$$

It was later recognized that²

$$\beta = \frac{1}{k_B T}. \quad (2)$$

Therefore, a fixed volume closed system that has fixed average energy $\langle E \rangle$, the temperature is constant. In a constant NVT system, the probability p_k visiting each microstate k follows the

Boltzmann distribution law

$$p_k = \frac{e^{-\frac{E_k}{k_B T}}}{\sum_j e^{-\frac{E_j}{k_B T}}}. \quad (3)$$

This is the distribution of the equilibrium macrostate of a constant temperature system. The Boltzmann distribution can also be written as

$$p_j = \frac{e^{-\frac{E_j}{k_B T}}}{Q}. \quad (4)$$

If we define the *canonical partition function*

$$Q(N, V, T) = \sum_j e^{-\frac{E_j}{k_B T}}. \quad (5)$$

This is a summation of microstates j 's. If microstates have degeneracy $\Omega(E)$ on energy level E , it is also possible to write the partition function as a summation over energy levels

$$Q(N, V, T) = \sum_E \Omega(E) e^{-\frac{E}{k_B T}}. \quad (6)$$

In this sense, the microstates of a constant temperature system can be viewed as the collection of microstates of many constant energy systems.

3 INTERNAL ENERGY

The *internal energy* $\langle E \rangle$ in a constant NVT system is the thermal average of energy over different microstates

$$\langle E \rangle = \frac{\sum_j E_j e^{-\frac{E_j}{k_B T}}}{Q}. \quad (7)$$

In the context of thermodynamics, we often omit the average symbol $\langle \cdot \rangle$ and just use E to represent internal energy, if there is no confusion with microstate energy.

Exercise

For the two-particle nine-cell lattice model with particle-particle interactions, compute partition function Q at temperature $T = 1.0\epsilon/k_B$ and Boltzmann distribution p_j for those 36 microstates. Compute internal energy $\langle E \rangle$ of the system at this temperature.

The first law of thermodynamics (conservation of energy)

$$\Delta E = Q + W, \quad (8)$$

¹This corresponds to the canonical ensemble in statistical mechanics.

²through dimension analysis and thermodynamics relationships.

where Q is the *heat* absorbed by the system (not to be confused with the partition function mentioned above) and W is the *work* done on the system. For an infinitesimal change of internal energy

$$dE = \delta Q + \delta W^3 \quad (9)$$

The infinitesimal *heat* δQ (absorbed by the system) and *work* δW (done on the system⁴) during a quasistatic process are

$$\delta Q = TdS \begin{cases} < 0, \text{ releasing heat or exothermic} \\ > 0, \text{ absorbing heat or endothermic} \end{cases} \quad (10)$$

$$\delta W = -pdV \begin{cases} < 0, \text{ expansion, work } |\delta W| \text{ done by the system} \\ > 0, \text{ compression, work } |\delta W| \text{ done on the system} \end{cases} \quad (11)$$

A *quasistatic process* is a process taking place infinitely slowly such that at any stage the system is at equilibrium. A quasistatic process is *reversible*. In fact, one thermodynamics definition of entropy change dS is the quotient of δQ in a reversible process by T , $dS = \frac{\delta Q_{\text{rev}}}{T}$. Because the heat under constant volume is

$$Q_V = \Delta E \quad (12)$$

the constant volumne heat capacity is

$$C_V = \frac{Q_V}{\Delta T} = \left(\frac{\partial E}{\partial T} \right)_V. \quad (13)$$

Specific heat at constant volume, which is the heat required to raise the temperature of the unit mass (or other unit quantities) by one degree,

$$c_v = \frac{Q_V}{m\Delta T}. \quad (14)$$

Combining equations (9), (10) and (11), we can write

$$dE = TdS - pdV. \quad (15)$$

Thus, S and V are natural variables for the thermodynamic function E , namely, $E(N, V, S)$ and

$$\left(\frac{\partial E}{\partial S} \right)_V = T^5 \quad (16)$$

$$\left(\frac{\partial E}{\partial V} \right)_S = -p. \quad (17)$$

that it is more convenient to define a new quantity, Helmholtz free energy, to find Boltzmann distribution for constant temperature systems.

Define the *Helmholtz free energy*

$$F(N, V, T) = -k_B T \ln Q(N, V, T). \quad (18)$$

The thermodynamic definition of the Helmholtz free energy is

$$F = E - TS. \quad (19)$$

From the energy differential relationship, we find that

$$dF = -SdT - pdV \quad (20)$$

and the thermodynamic definition of pressure

$$p = - \left(\frac{\partial F}{\partial V} \right)_T. \quad (21)$$

The thermodynamic Helmholtz free energy is only defined for equilibrium macrostate. But we can generalize to define F for any macrostates with distribution $\{p_j\}$, which is

$$\tilde{F} = \sum_j E_j p_j + k_B T \sum_j p_j \ln p_j \quad (22)$$

Minimizing ⁷ this \tilde{F} with respect to p_j under the normalization constraint $\sum_j p_j = 1$, namely

$$\frac{\partial}{\partial p_k} \left(\sum_j E_j p_j + k_B T \sum_j p_j \ln p_j + \tilde{\alpha}(1 - \sum_j p_j) \right) = 0, \quad (23)$$

also gives the equilibrium Boltzmann distribution $p_k = e^{-\frac{E_k}{k_B T}} / Q$. We can thus say that, at the equilibrium macrostate, the Helmholtz free energy is minimized. Note that we do not require the average energy $\sum_j E_j p_j$ to be fixed here. A macrostate at constant NVT is thermodynamically more *stable* if its energy E is lower and its entropy S is higher ($-TS$ lower).

Free energy minimization principle

In the constant NVT system, the equilibrium macrostate has the minimum Helmholtz free energy F . Any non-equilibrium macrostate tends to relax to the equilibrium one spontaneously, to reduce its Helmholtz free energy \tilde{F} ⁸.

Exercise

Compute equilibrium (internal) energy, entropy, and free energy of the lattice model with particle-particle interactions at temperatures $T = 0.1, 0.5, 0.7, 1.0, 10.0\epsilon/k_B$. Extrapolate the results to $T = 0$ and $T = \infty$. Recall the two energy levels are $E_A = -\epsilon$ with degeneracy $\Omega_A = 12$ and $E_B = 0$ with degeneracy $\Omega_B = 24$. You may compute partition function more efficiently with $Q = \Omega_A e^{-\frac{E_A}{k_B T}} + \Omega_B e^{-\frac{E_B}{k_B T}}$.

Exercise

Consider two non-equilibrium macrostates A and B , what is their average energy $\langle E \rangle$ and entropy S ? What is their free energy as a function of temperature ?

4 HELMHOLTZ FREE ENERGY

For constant energy system, we can use entropy alone to find equilibrium distribution under maximum entropy principle. For constant temperature system allowing energy fluctuations (E changes around $\langle E \rangle$), we have shown that adding the constant $\langle E \rangle$ constraint to maximum entropy principle allows us to find the equilibrium distribution – the Boltzmann distribution. Below, we will see

³Using δ not d before Q and W because they depend on the path.

⁴In some other textbooks, δW is defined as work done by the system pdV . Then the first law has the form of $dE = \delta Q - \delta W$.

⁵This gives another definition of temperature, i.e. if $S(E, N, V)$ is viewed as a function of E , $\left(\frac{\partial S}{\partial E} \right)_V = \frac{1}{T}$.

⁶The internal energy $\langle E \rangle$ is technically a thermal average over different microstates. But the $\langle \dots \rangle$ are often omitted in thermodynamics without causing confusion.

⁷It is a minimum because $\frac{\partial^2}{\partial p_k^2} > 0$.

⁸Often we just drop the tilde and use F for any macrostates.

T	$e^{-\frac{E_A}{k_B T}}$	$e^{-\frac{E_B}{k_B T}}$	Q	$p_A = \frac{e^{-\frac{E_A}{k_B T}}}{Q}$	$p_B = \frac{e^{-\frac{E_B}{k_B T}}}{Q}$	$\Omega_A p_A$	$\Omega_B p_B$	$\langle E \rangle$	$S (=S_G)$	$F = \langle E \rangle - TS = -k_B T \ln Q$
0.0	∞	1	12∞	$\frac{1}{12}$	0	1	0	$-\epsilon$	$k_B \ln 12$	
0.1	$e^{10} = 22026.5$	1								
1.0	$e^1 = 2.718$	1								
10.0	$e^{0.1} = 1.105$	1								
∞	1	1	36	$\frac{1}{36}$	$\frac{1}{36}$	$\frac{12}{36}$	$\frac{24}{36}$	$-\frac{\epsilon}{3}$	$k_B \ln 36$	

For macrostate A and B , energy

$$\langle E \rangle_A = E_A = -\epsilon$$

$$\langle E \rangle_B = E_B = 0$$

entropy

$$S_A = k_B \ln \Omega_A = k_B \ln 12$$

$$S_B = k_B \ln \Omega_B = k_B \ln 24$$

and free energy

$$F_A = \langle E \rangle_A - TS_A = -\epsilon - k_B T \ln 12$$

$$F_B = \langle E \rangle_B - TS_B = -k_B T \ln 24$$

Chapter 4 Statistical Thermodynamics

Lecture 13 Classical Statistical Thermodynamics of Gases

1 MICROSTATES IN CLASSICAL SYSTEMS*

A *microstate* of a classical system of monoatomic gases is characterized by a set of microscopic mechanical variables, for instance, all the position and momentum vectors, $(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N; \mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_N) \equiv (\mathbf{r}^N, \mathbf{p}^N)$, for a N particle system. Therefore, a microstate corresponds to a point in this $2dN$ -dimensional *phase space* ($d = 3$) (相空间).

At a microstate, we can define the instantaneous kinetic energy

$$\mathcal{K}(\mathbf{p}^N) = \sum_{i=1}^N \frac{1}{2} m v_i^2 = \sum_{i=1}^N \frac{p_i^2}{2m} \quad (1)$$

and the instantaneous potential energy

$$\mathcal{U}(\mathbf{r}^N) = \sum_{i=1}^{N-1} \sum_{j=i+1}^N u(r_{ij}) = \sum_{j>i} u(r_{ij}) \quad (2)$$

of the system. The total instantaneous energy, or *Hamiltonian*,

$$\mathcal{H}(\mathbf{r}^N, \mathbf{p}^N) = \mathcal{K} + \mathcal{U} = \sum_{i=1}^N \frac{p_i^2}{2m} + \sum_{j>i} u(r_{ij}). \quad (3)$$

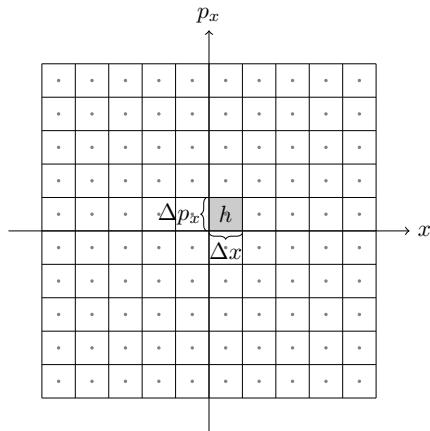


Figure 1: The 2-dimensional phase space (x, p_x) of a one-dimensional particle, whose resolution is set by the uncertainty principle $\Delta x \Delta p_x \sim h$. The total number of points (microstates) in this phase space is $\frac{\int dx \int dp_x}{h}$.

Integration*

The area of a rectangle with length a and width b can be expressed by an integral

$$A = \int_0^a dx \int_0^b dy = ab, \quad (4)$$

If the rectangle is placed in a Cartesian coordinate system with x running from 0 to a and y from 0 to b . Here “ dx ” means a small segment of x .

To count the total number of points, or microstates, in phase space, we can use

$$\frac{1}{N!} \frac{1}{h^{3N}} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \cdots \int d\mathbf{r}_N \int d\mathbf{p}_1 \int d\mathbf{p}_2 \cdots \int d\mathbf{p}_N = \frac{1}{N!} \frac{1}{h^{3N}} \int d\mathbf{r}^N \int d\mathbf{p}^N = \sum_j 1 \quad (5)$$

where the factor $\frac{1}{N!}$ is due to the indistinguishability of particles and the factor $\frac{1}{h^{3N}}$ corresponds to the resolution of the phase space set by the uncertainty principle (Figure 1). Because of the finite resolution $\sim h$, the counting can also be written as a sum over microstate index j .

2 CLASSICAL PARTITION FUNCTION*

Recall the definition of partition function at constant temperature

$$Q(N, V, T) = \sum_j e^{-\frac{E_j}{k_B T}}$$

where the sum is over microstates j 's. In the classical form of Q , we replace the summation over discrete microstates \sum_j with integration over phase space vectors

$$\begin{aligned} Q(N, V, T) &= \frac{1}{N!} \frac{1}{h^{3N}} \int d\mathbf{r}^N \int d\mathbf{p}^N e^{-\frac{\mathcal{H}(\mathbf{r}^N, \mathbf{p}^N)}{k_B T}} \\ &= \frac{1}{N!} \frac{1}{h^{3N}} \int d\mathbf{p}^N e^{-\frac{\mathcal{K}(\mathbf{p}^N)}{k_B T}} \int d\mathbf{r}^N e^{-\frac{\mathcal{U}(\mathbf{r}^N)}{k_B T}} \\ &= \frac{1}{N!} \frac{1}{h^{3N}} \left(\int d\mathbf{p} e^{-\frac{p_x^2 + p_y^2 + p_z^2}{2mk_B T}} \right)^N \int d\mathbf{r}^N e^{-\frac{\mathcal{U}(\mathbf{r}^N)}{k_B T}} \\ &= \frac{1}{N!} \frac{1}{h^{3N}} \left(\int_{-\infty}^{\infty} dp_x e^{-\frac{p_x^2}{2mk_B T}} \right)^{3N} \int d\mathbf{r}^N e^{-\frac{\mathcal{U}(\mathbf{r}^N)}{k_B T}} \\ &= \frac{1}{N!} \frac{1}{h^{3N}} \left(m \int_{-\infty}^{\infty} dv_x e^{-\frac{mv_x^2}{2k_B T}} \right)^{3N} \int d\mathbf{r}^N e^{-\frac{\mathcal{U}(\mathbf{r}^N)}{k_B T}} \\ &= \frac{1}{N!} \frac{1}{h^{3N}} \left(\sqrt{2\pi mk_B T} \right)^{3N} \int d\mathbf{r}^N e^{-\frac{\mathcal{U}(\mathbf{r}^N)}{k_B T}} \\ &= \frac{1}{N!} \frac{1}{\left(\sqrt{\frac{h^2}{2\pi mk_B T}} \right)^{3N}} \int d\mathbf{r}^N e^{-\frac{\mathcal{U}(\mathbf{r}^N)}{k_B T}} \\ &= \frac{1}{N!} \frac{1}{\Lambda^{3N}} Z, \end{aligned} \quad (6)$$

where the *thermal de Broglie wavelength*

$$\Lambda = \sqrt{\frac{h^2}{2\pi mk_B T}} \quad (7)$$

and the *configuration integral*

$$Z = \int d\mathbf{r}^N e^{-\frac{\mathcal{U}(\mathbf{r}^N)}{k_B T}}. \quad (8)$$

Gaussian Distribution and Integrals*

$$\int_{-\infty}^{\infty} dx e^{-ax^2} = \sqrt{\frac{\pi}{a}} \quad (9)$$

$$\frac{1}{\sqrt{2\pi\sigma^2}} \int_{-\infty}^{\infty} dx e^{-\frac{x^2}{2\sigma^2}} = 1 \quad (10)$$

$$\frac{1}{\sqrt{2\pi\sigma^2}} \int_{-\infty}^{\infty} dx x^2 e^{-\frac{x^2}{2\sigma^2}} = \sigma^2 \quad (11)$$

$$\frac{1}{\sqrt{2\pi\sigma^2}} \int_{-\infty}^{\infty} dx x^4 e^{-\frac{x^2}{2\sigma^2}} = 3\sigma^4 \quad (12)$$

freedom (x, y, z motions) and a N -atom system has $3N$ degrees of freedom in total².

Other characteristic speeds are, the root-mean-square speed v_{rms} , the average speed v_{avg} and the most probable speed v_{max}

$$v_{\text{rms}} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3k_B T}{m}} \quad (18)$$

$$v_{\text{avg}} = \langle v \rangle = \sqrt{\frac{8k_B T}{\pi m}} \quad (19)$$

$$v_{\text{max}} = \sqrt{\frac{2k_B T}{m}}, \quad (20)$$

which satisfies $v_{\text{max}} < v_{\text{avg}} < v_{\text{rms}}$.

3 MAXWELL VELOCITY DISTRIBUTION LAW

From the form of partition function in constant NVT systems

$$Q = \frac{1}{N!} \frac{1}{h^{3N}} \left(m \int_{-\infty}^{\infty} dv_x e^{-\frac{mv_x^2}{2k_B T}} \right)^{3N} \int d\mathbf{r}^N e^{-\frac{U(\mathbf{r})}{k_B T}},$$

the kinetic and configurational factors are decoupled. That is the probability for the velocity of the particle to take a certain value is purely determined by the Boltzmann factor $e^{-\frac{mv^2}{2k_B T}}$ but not affected by its position vector \mathbf{r} or potential energy.

Maxwell velocity distribution law¹

The probability density to observe a velocity vector \mathbf{v} for a particle in the system at constant NVT is

$$f(\mathbf{v}) = f(v_x, v_y, v_z) = \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-\frac{m(v_x^2 + v_y^2 + v_z^2)}{2k_B T}}, \quad (13)$$

where $-\infty < v_x, v_y, v_z < \infty$. The probability density of the speed $v = |\mathbf{v}|$ is

$$f_v(v) = 4\pi v^2 f(\mathbf{v}) = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^2 e^{-\frac{mv^2}{2k_B T}}, 0 < v < \infty \quad (14)$$

We can show that the mean square speed is

$$\begin{aligned} \langle v^2 \rangle &= \int_0^{\infty} v^2 f_v(v) dv \\ &= 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} \int_0^{\infty} v^4 e^{-\frac{mv^2}{2k_B T}} dv \\ &= \frac{3k_B T}{m}. \end{aligned} \quad (15)$$

Therefore,

$$\frac{1}{2} m \langle v^2 \rangle = \frac{1}{2} m \frac{1}{N} \sum_{i=1}^N v_i^2 = \frac{3}{2} k_B T \quad (16)$$

$$\text{or } K = \frac{1}{2} m \sum_{i=1}^N v_i^2 = \frac{3N}{2} k_B T. \quad (17)$$

We can see that temperature T is related to the total kinetic energy of the system.

Law of equipartition of energy

At equilibrium, the total kinetic energy is equally distributed among all degrees of freedom, with $\frac{1}{2} k_B T$ per degree of freedom.

In monoatomic systems, each atom has 3 translational degrees of

Ideal gas is an abstract model for gases that has zero interaction potential energy $u(r) = 0$. Thus ideal gas particles are sizeless point masses that do not collide nor attract each other. Most gases in the low density limit approach the ideal gas. For ideal gas,

$$Z_{\text{id}} = \int d\mathbf{r}^N = V^N, \quad (21)$$

the partition function

$$Q_{\text{id}}(N, V, T) = \frac{1}{N!} \frac{1}{\Lambda^{3N}} V^N \quad (22)$$

and the Helmholtz free energy³

$$\begin{aligned} F_{\text{id}}(N, V, T) &= -k_B T \ln Q_{\text{id}} = Nk_B T \left[\ln \left(\frac{N}{V} \Lambda^3 \right) - 1 \right] \\ &= Nk_B T [\ln (\rho \Lambda^3) - 1], \end{aligned} \quad (23)$$

where $\rho = \frac{N}{V}$ is the number density of the ideal gas.

So the pressure p for ideal gas is

$$p = - \left(\frac{\partial F_{\text{id}}}{\partial V} \right)_T = -Nk_B T \left(\frac{\partial \ln \frac{1}{V}}{\partial V} \right)_T = \frac{Nk_B T}{V}. \quad (24)$$

4.1 Ideal gas law

Ideal gas law

$$pV = Nk_B T = nRT \quad (25)$$

where the number of moles $n = \frac{N}{N_A}$ and the gas constant

$$R = k_B N_A = 8.314 \text{ J/K/mol} = 0.082 \text{ atm} \cdot \text{L/K/mol}.$$

¹Although first derived for gases, it is also obeyed in liquids and solids.

²We neglect the constraints from the conservation of center of mass.

³Stirling's approximation is used. For large N , $\ln N! = N \ln N - N$.

5 ENTROPY OF MIXING*

Bernoulli's Formula: Derivation of Ideal Gas Law*

Consider a cubic rigid box of side length L and volume $V = L^3$. For one particle traveling at constant x -speed $|v_x|$ along x -direction, the number of collisions per unit time per wall is $\frac{|v_x|}{2L}$ (divided by 2 because there are two walls).

Each elastic collision exerts a momentum of $2m|v_x|$ to the wall ($\mathbf{p}_x - (-\mathbf{p}_x)$). So, the force of one particle on one wall ($\mathbf{f} = \frac{d\mathbf{p}}{dt}$) is $\frac{|v_x|}{2L} 2m|v_x| = \frac{mv_x^2}{L}$.

The pressure on that wall from all N particles is $p_{xx} = \frac{\sum_{i=1}^N \frac{mv_{ix}^2}{L}}{L^2} = \frac{2\sum_{i=1}^N \frac{1}{2}mv_{ix}^2}{V} = \frac{2\frac{1}{2}Nk_B T}{V} = \frac{Nk_B T}{V}$. So the bulk pressure averaged over three directions is $p = \frac{1}{3}(p_{xx} + p_{yy} + p_{zz})$.

For a mixture of m types of ideal gases, each of n_i mole, $i = 1, 2, \dots, m$, with $\sum_{i=1}^m n_i = n$, the total pressure $p = \sum_{i=1}^m p_i$ obeys the ideal gas law

$$pV = (n_1 + n_2 + \dots + n_m)RT \quad (26)$$

Each component i obeys its own ideal gas law with *partial pressure*

$$p_i V = n_i RT. \quad (27)$$

4.2 Entropy of Ideal gas

$$S_{\text{id}}(N, V, T) = (E - F_{\text{id}})/T = \left(\frac{3N}{2}k_B T - F_{\text{id}}\right)/T$$

$$S_{\text{id}}(N, V, T) = \frac{5}{2}Nk_B - Nk_B \ln(\rho\Lambda^3) \quad (28)$$

or

$$\frac{S_{\text{id}}(N, V, T)}{N} = k_B \ln V - k_B \ln N + \frac{3}{2}k_B \ln m + \frac{3}{2}k_B \ln T + \frac{5}{2}k_B + \frac{3}{2}k_B \ln \frac{2\pi k_B}{h^2}. \quad (29)$$

The entropy of ideal gas can be written as $S_{\text{id}} = Nk_B \ln V + S_0(N, T, m)$, where S_0 is a V -independent constant. Consider a rigid box of volume V separated by a wall into two compartments of volume V_1 and V_2 such that $V_1 + V_2 = V$. There are N_1 molecules of gas A in V_1 and N_2 molecules of gas B in V_2 ($N_1 + N_2 = N$) at the same temperature T . $\frac{N_1}{V_1} = \frac{N_2}{V_2}$ such that the two gases have the same initial pressure $p = \frac{N_1 k_B T}{V_1}$. The mole fraction of each gas is $x_i = \frac{N_i}{N} = \frac{V_i}{V}$ ($i = 1, 2$) (Figure 2).

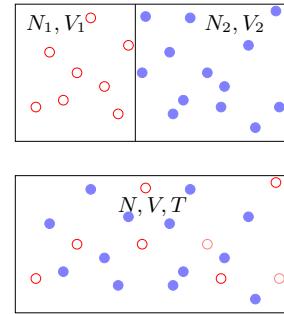


Figure 2: Before (top) and after (bottom) mixing of two gases.

Now remove the wall so that each gas can expand to the other compartment. When final equilibrium is established, what is the *entropy of mixing* ΔS_{mix} ?

Initially,

$$S_{1,i} = N_1 k_B \ln V_1 + S_{1,0} \text{ and } S_{2,i} = N_2 k_B \ln V_2 + S_{2,0}$$

Finally,

$$S_{1,f} = N_1 k_B \ln V + S_{1,0} \text{ and } S_{2,f} = N_2 k_B \ln V + S_{2,0}.$$

So the entropy change for each gas after the expansion is

$$\begin{aligned} \Delta S_1 &= N_1 k_B \ln \frac{V}{V_1} = -N x_1 k_B \ln x_1 \\ \Delta S_2 &= N_2 k_B \ln \frac{V}{V_2} = -N x_2 k_B \ln x_2. \end{aligned}$$

The total entropy change, i.e. entropy of mixing $\Delta S_{\text{mix}} = \Delta S_1 + \Delta S_2$ is

$$\boxed{\Delta S_{\text{mix}} = -Nk_B(x_1 \ln x_1 + x_2 \ln x_2)}. \quad (30)$$

Chapter 4 Statistical Thermodynamics

Lecture 14 Gibbs Free Energy and Phase Equilibrium

1 CONSTANT NpT SYSTEMS

In a constant NpT system, absorbed heat not only increases the internal energy but is also used to do pV work during thermal expansion¹. It is thus convenient to define a thermodynamic variable **enthalpy**

$$H(N, p, S) = E + pV, \quad (1)$$

such that the heat under constant pressure is

$$Q_p = \Delta H. ^2 \quad (2)$$

Heat capacity at constant pressure

$$C_p = \frac{Q_p}{\Delta T} = \left(\frac{\partial H}{\partial T} \right)_p. \quad (3)$$

$C_p > C_V$ because, at constant pressure, part of the heat is consumed to do pV work.

The free energy in a constant NpT system is the *Gibbs free energy*

$$G(N, p, T) = H - TS = F + pV, \quad (4)$$

which has the differential relationship

$$dG = -SdT + Vdp \quad (5)$$

and thus

$$\left(\frac{\partial G}{\partial p} \right)_T = V. \quad (6)$$

For ideal gases

$$\begin{aligned} \int_{G_0(p_0, T)}^{G(p, T)} dG &= \int_{p_0}^p Vdp' = \int_{p_0}^p \frac{nRT}{p'} dp' \\ G(p, T) - G(p_0, T) &= nRT \int_{p_0}^p \frac{dp'}{p'} = nRT \ln \frac{p}{p_0} \end{aligned}$$

$$G(p, T) = G_0 + nRT \ln \frac{p}{p_0} \quad (\text{gas phase}) \quad (7)$$

where $G_0 \equiv G(p_0, T)$ is the Gibbs free energy at the reference pressure p_0 .

Free energy minimization

In the constant NpT system, the equilibrium macrostate has the minimum Gibbs free energy G . At constant p and T , any non-equilibrium macrostate tends to relax to the equilibrium one spontaneously, to reduce its Gibbs free energy.

¹A constant NpT system is also a *closed* system that exchanges energy (through both heat and pV work) but not matter with surroundings.

²At constant p , $\Delta H = \Delta E + p\Delta V = Q_p + W + p\Delta V = Q_p - p\Delta V + p\Delta V = Q_p$.

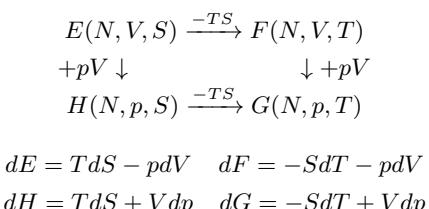
Isothermal–Isobaric Ensemble*

Isothermal–isobaric partition function

$$\begin{aligned} \Delta(N, p, T) &= \int_0^\infty dV e^{-\frac{pV}{k_B T}} Q(N, V, T) \\ &= \int_0^\infty dV e^{-\frac{pV}{k_B T}} \sum_j e^{-\frac{E_j}{k_B T}} \\ &= \sum_i \sum_j e^{-\frac{E_j + pV_i}{k_B T}} = \sum_k e^{-\frac{H_k}{k_B T}} \end{aligned} \quad (8)$$

$$G(N, p, T) = -k_B T \ln \Delta(N, p, T) \quad (9)$$

Summary of Thermodynamic Potentials



2 CHEMICAL POTENTIAL AND OSMOTIC PRESSURE

In an *open* system, not only energy but also matter flows between the system and surroundings. The balance of heat flow implies equating temperature, the balance of volume implies equating pressure and the balance of matter implies equating chemical potential. *Chemical potential* μ is the Gibbs free energy cost of inserting one particle into the system at constant T and p , i.e.

$$\mu = \left(\frac{\partial G}{\partial N} \right)_{T, p} \quad (10)$$

which suggests the differential form, if particle number is allowed to change,

$$dG = -SdT + Vdp + \mu dN. \quad (11)$$

At constant T and p , each additional particle add the same amount to G , because the density of the system remains constant. Thus

$$G = \mu N, \quad (12)$$

which says chemical potential is just the Gibbs free energy per particle.

2.1 Osmotic pressure

A *semipermeable membrane* is a membrane with very small holes of such a size that only molecules of the solvent are able to pass through but (large) molecules of the solute are not. When a solution of large molecules is separated from pure solvent by a semipermeable membrane, the pressure of in the solution becomes higher than that of the pure solvent by an amount, $\Pi > 0$, called osmotic pressure ([Pauling] 13-9).

In a dilute solution, osmotic pressure is related to the concentration (molarity c_1) of solute (component 1) in the solution, by the ideal-gas law like **van't Hoff equation**

$$\Pi = \frac{n_1}{V} RT = c_1 RT. \quad (13)$$

This is a result of the equilibrium transfer of water between the two sides of the membrane, i.e. equating the chemical potential of water (component 2)

$$(\text{pure water}) \mu_2^*(T, p, 0) = \mu_2(T, p + \Pi, x_1) \quad (\text{solution})^3 \quad (14)$$

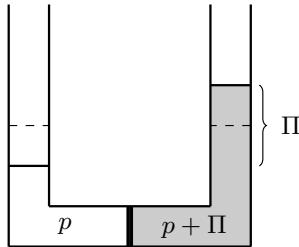


Figure 1: Osmotic pressure between pure water and dilute solution.

3 PHASE EQUILIBRIUM

A *phase* is a uniform portion of matter where the physical and chemical properties are everywhere alike. A phase can be characterized by several (maybe redundant) thermodynamic variables such as temperature T , pressure p , chemical potential μ_i and concentration (molar fraction) x_i of each of the multiple components, if the system is not a pure substance.

Two or more phases can coexist in thermodynamic equilibrium, if certain conditions are satisfied, including (in case of two phases α and β , C components)

- no heat flow: $T_\alpha = T_\beta = T$
- no volume change: $p_\alpha = p_\beta = p$
- no matter flow: $\mu_{i,\alpha} = \mu_{i,\beta} = \mu_i$ ($i = 1, 2, \dots, C$)
- chemical equilibrium, if reactions among different species exist.

Generally, not all these thermodynamic variables are independent – knowing some of them will automatically pin down others. The number f of independent thermodynamic variables needed to describe a system of multiple phases at phase equilibrium is called, *thermodynamic degrees of freedom*.

$$\int_p^{p+\Pi} \left(\frac{\partial \mu_2^*}{\partial p} \right)_T dp' = \int_p^{p+\Pi} v_2 dp' = v_2 \Pi. \quad x_1 = n_1/(n_1 + n_2) \approx n_1/n_2. \quad n_2 v_2 = V_2 \approx V.$$

$$\int_p^{p+\Pi} \left(\frac{\partial \mu_2^*}{\partial p} \right)_T dp' = \mu_2^*(T, p + \Pi, 0) - \mu_2^*(T, p, 0) = RT \ln(1 - x_1) = RT \ln(n_1/n_2).$$

The Gibbs Phase Rule ([Pauling] 11-9)

For every system in phase equilibrium (in absence of chemical reactions), the degrees of freedom f is related to the number of phases P and the number of components C by

$$f = C - P + 2. \quad (15)$$

For example

- one-phase pure substances: $P = 1$ and $C = 1$, $f = 2$. Therefore, (T, p) are needed to define the state of pure water, pure water vapor, pure ice, etc.
- two-phase pure substances: $P = 2$ and $C = 1$, $f = 1$. T or p alone can determine the liquid-gas, solid-liquid, solid-gas equilibrium. Given the pressure, there is a definite boiling point T_b and melting point T_m .
- three-phase pure substances: $P = 3$ and $C = 1$, $f = 0$. No need to specify T or p or any other variables. The triple point (T_t, p_t) of gas-liquid-solid coexistence is intrinsic and unique for each pure substance.
- one-phase two-component mixtures: $P = 1$ and $C = 2$, $f = 3$. We need three (T, p, x_1) variables to define a water (component 2) solution of sugar (component 1). The solubility x_1 changes with T and p .
- two-phase two-component mixtures: $P = 2$ and $C = 2$, $f = 2$. We can choose (T, p) or $(T, x_{1,\alpha})$ or $(p, x_{2,\alpha})$ or $(x_{1,\alpha}, x_{1,\beta})$ etc. to define a water-oil mixture.

A *phase diagram* is a 2D projection of all possible phases of the system onto two of the many possible thermodynamic variables $(T, p, \mu_1, \mu_2, \dots, x_{1,\alpha}, x_{2,\alpha}, \dots)$. A simplified T - p phase diagram of water (Figure 2) shows the gas, liquid and solid states of water.

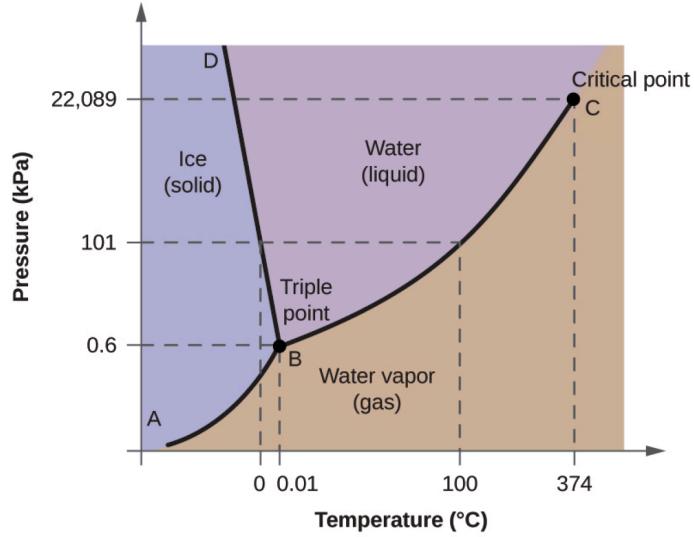


Figure 2: The phase diagram of water. (Chemistry, OpenStax)

During the process of a *phase transition* from one to another phase, phase equilibrium is maintained, which reduces the degrees of freedom of the system. That is why the temperature of a boiling water stays constantly at 100°C under 1 atm.

Chapter 5 Chemical Equilibrium

Lecture 15 Chemical Reactions

1 INTRODUCTION TO CHEMICAL REACTIONS

Chemical reactions are processes that convert substances to other substances. Chemical reactions involve changes of molecule types through rearrangement of atoms or ions, accompanied by breaking/formation of chemical bonds or transfer of electrons. Element types (or atom types) do not change during chemical reactions¹. In the reaction,



chemicals on the left side are *reactants*, while chemicals on the right side are *products*. The *reaction coefficients* a, b, c, d , often rounded to integers, are chosen so that the number of each type of atom is conserved before and after the reaction—the *law of conservation of mass*. *Stoichiometry* is concerned with the relative quantities (mass or mole ratio) of reactants and products in chemical reactions, from the reaction coefficients after balancing the reaction.

Two important types of reactions are widely seen:

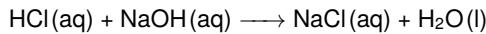
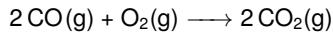
- acid-base reaction
- oxidation and reduction reaction (redox)

The study of chemical reactions often focuses on two aspects:

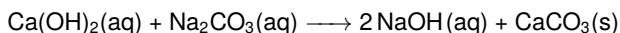
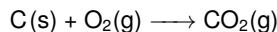
- extent of reaction – thermodynamics
- rate of reaction – kinetics

1.1 States of reacting substances

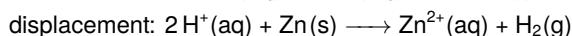
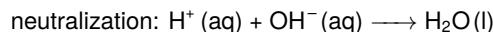
- *homogeneous reaction*: reactants and products are in the same phase, for instance, in gas state (g) or aqueous solution (aq).



- *heterogeneous reaction*: more than one phases are involved.



For reactions in solution, it is also customary to use the *net ionic equation*, which lists only those species participating in the reaction. For instance,

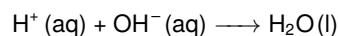


1.2 Reaction conditions

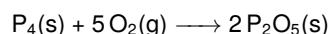
To enable or accelerate chemical reactions, different reaction conditions are used.

- **spontaneous** fast reaction (at ambient conditions, $T \sim 300\text{K}$ and $p \sim 1\text{atm}$). Some reactions occur instantly just after reactants are mixed.

Neutralization of strong acid and base

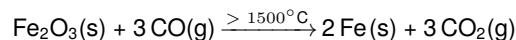


Spontaneous combustion of white phosphorus

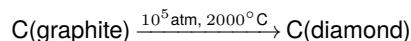


- **high temperature** or heating

Metallurgy of iron in blast furnace

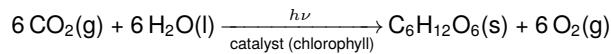


- **high pressure**



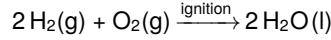
- **light**

Photosynthesis



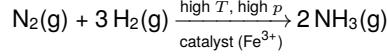
- **ignition**

Combustion reactions

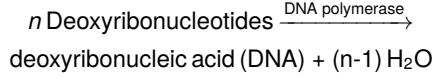


- **catalyst**

Ammonia production (Haber process)



Enzyme-catalyzed biochemical reactions



- **electricity**

Electrolytic production of aluminum



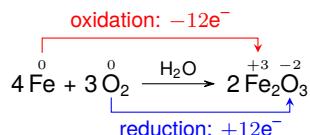
- **mechanical force** (mechanochemistry)

ultrasound, splat

¹Otherwise, it is a nuclear reaction.

2 OXIDATION AND REDUCTION REACTION

An oxidation and reduction reaction, or *redox*, is a reaction in which the oxidation number of elements changes due to electron transfer. *Oxidation* is accompanied by an increase in oxidation number and loss of electrons, while *reduction* is accompanied by a decrease in oxidation number and acquisition of electrons. For example, in the rusting reaction of iron,



Fe is oxidized (by O_2) and O_2 is reduced (by Fe).

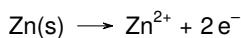
2.1 Combustion: chemical to thermal energy



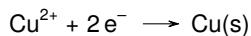
2.2 Voltaic cell (Battery): chemical to electrical energy

Copper-zinc cell

negative electrode reaction (oxidation)



positive electrode reaction (reduction)



overall reaction

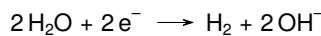


2.3 Electrolysis: electrical to chemical energy

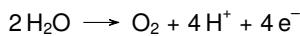
Electrolysis of water

- **cathode** (阴极) connected to the negative electrode receiving electrons
- **anode** (阳极) connected to the positive electrode donating electrons

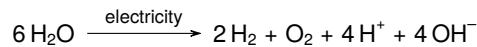
cathode reaction (reduction)



anode reaction (oxidation)

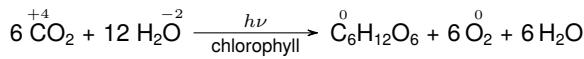


overall reaction



2.4 Photosynthesis: solar to chemical energy

Overall photosynthesis reaction



3 ENERGY CONVERSION

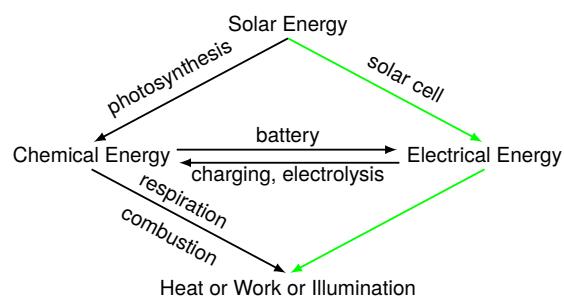


Figure 1: Energy conversion through electron transfer reactions.

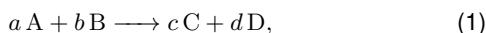
Chapter 5 Chemical Equilibrium

Lecture 16 Chemical Thermodynamics

Chemical reactions often occur at constant p not constant V . That is why we use H instead of E , G instead of F , to analyze the thermodynamics of chemical reactions.

1 ENTHALPY CHANGE ΔH

The enthalpy change for a chemical reaction, or reaction enthalpy, is the difference between the total enthalpy of the products and the total enthalpy of the reactants, $\Delta H = H_{\text{prod}} - H_{\text{react}}$. For a general reaction,



$$\Delta H = cH_C + dH_D - aH_A - bH_B. \quad (2)$$

In chemistry, it is more convenient to use 1 mol of reaction (1), that is, a mol of A reacts with b mol of B . Then ΔH is expressed in units of kJ/mol. Although absolute enthalpy H_A , H_B etc. are theoretically defined, they cannot be measured in experiment. In practice, it is the change of enthalpy ΔH_A , ΔH_B etc. with respect to certain reference states that are used.

- **endothermic:** absorbing heat $\Delta H > 0$
- **exothermic:** releasing heat $\Delta H < 0$

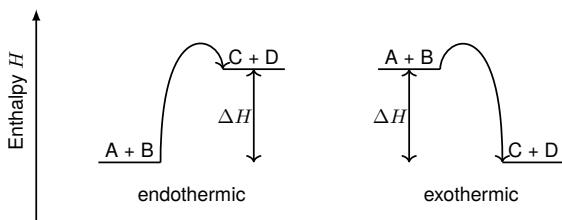


Figure 1: Enthalpy change ΔH of endothermic and exothermic reactions.

The **standard reaction enthalpy** ΔH° is the enthalpy change of a chemical reaction with all its reactants and products in their standard states.

The **standard state** refers to a pure substance at standard pressure and temperature, for instance, $p = 1 \text{ atm}$ and $T = 25^\circ\text{C}$ (298.15 K)¹.

Standard molar enthalpy of formation ΔH_f° is the **standard reaction enthalpy** for the formation of one mole of a molecule from its constituent elements². Since the reactants and the products in one reaction share the same types of elements, namely reference, ΔH_f° can be used to calculate the ΔH° of that reaction (Figure 2).

¹Different conventions may be used, for instance, $p = 1 \text{ bar}$, $T = 273.15 \text{ K}$. 1 bar = 10^5 Pa . 1 atm = 101325 Pa.

²For allotropic elements, it is the more stable one, for instance C(graphite).

³Note that, it is not "products - reactants" here, because of the relationship $E_b = -\Delta H$.

⁴If a crystal has a non-zero entropy at $T = 0 \text{ K}$, namely the *residual entropy*, it is due to its non-perfect structure, for instance, multiple orientations of molecules that leads to $\Omega > 1$.

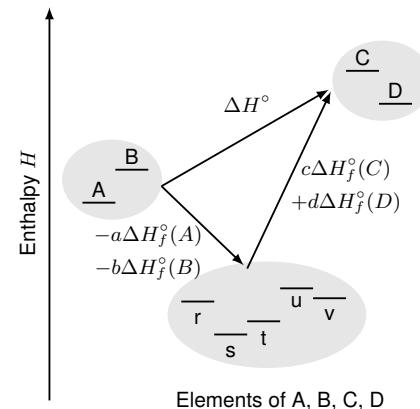


Figure 2: Standard reaction enthalpy ΔH° can be calculated from standard molar enthalpy of formation ΔH_f° .

$$\Delta H^\circ = c\Delta H_f^\circ(C) + d\Delta H_f^\circ(D) - a\Delta H_f^\circ(A) - b\Delta H_f^\circ(B). \quad (3)$$

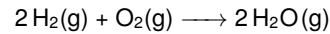
Bond energy E_b is literally defined as the energy needed ($E_b > 0$) to break a chemical bond or one mole of chemical bonds (in units of kJ/mol). In practice, it can be related to the enthalpy change $\Delta H (< 0)$ of a reaction from isolated gas atoms to form a gas compound $E_b = -\Delta H$. For instance, the reaction



has $\Delta H = -436 \text{ kJ/mol}$, which indicates the bond energy for the H–H bond is $E_b(\text{H–H}) = 436 \text{ kJ/mol}$. Knowing all the bond energies in reactants and products allows us to compute the reaction enthalpy ΔH (in gasous state) by

$$\Delta H = \sum E_b(\text{reactants}) - \sum E_b(\text{products})^3. \quad (4)$$

For instance, $E_b(\text{H–H}) = 436 \text{ kJ/mol}$, $E_b(\text{O–H}) = 463 \text{ kJ/mol}$ and $E_b(\text{O=O}) = 498 \text{ kJ/mol}$, the reaction



has

$$\begin{aligned} \Delta H &= 2E_b(\text{H–H}) + E_b(\text{O=O}) - 2 \times 2E_b(\text{O–H}) \\ &= 2 \times 436 + 498 - 4 \times 463 = -482 \text{ kJ/mol}. \end{aligned}$$

From the table of thermodynamic properties, we find that $\Delta H_f^\circ(\text{H}_2\text{O(g)}) = -241.83 \text{ kJ/mol}$, which gives $\Delta H^\circ = -483.66 \text{ kJ/mol}$ for the above reaction.

2 ENTROPY CHANGE ΔS

Third law of thermodynamics

The entropy of a pure substance in the form of a perfect crystal is zero at the absolute zero temperature, i.e. $S_{\text{crystal}}(0K) = 0$. This is a result from the number of microstates being unity $\Omega = 1^4$.

Because of the third law of thermodynamics, one can obtain the *absolute* entropy of substances.

Standard molar entropy S° is the molar entropy of a substance at its standard state, given in units of J/mol/K.

The **standard reaction entropy** is

$$\Delta S^\circ = cS^\circ(C) + dS^\circ(D) - aS^\circ(A) - bS^\circ(B). \quad (5)$$

3 GIBBS FREE ENERGY CHANGE ΔG

Standard molar Gibbs free energy of formation ΔG_f° is defined similarly as ΔH_f° .

The **standard reaction Gibbs free energy** can be calculated either from ΔG_f° 's

$$\Delta G^\circ = c\Delta G_f^\circ(C) + d\Delta G_f^\circ(D) - a\Delta G_f^\circ(A) - b\Delta G_f^\circ(B), \quad (6)$$

or from ΔH° and ΔS°

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ. \quad (7)$$

If reactants and products are viewed as two macrostates, “react” and “prod”, of the system, their relative thermodynamic probability is proportional to the Boltzmann factor $e^{-\frac{G_{\text{react}}}{k_B T}}$ and $e^{-\frac{G_{\text{prod}}}{k_B T}}$. Thus the relative probability of products versus reactants is

$$e^{-\frac{G_{\text{prod}}}{k_B T}} / e^{-\frac{G_{\text{react}}}{k_B T}} = e^{-\frac{G_{\text{prod}} - G_{\text{react}}}{k_B T}} = e^{-\frac{\Delta G}{k_B T}}.$$

- **non-spontaneous:** reactants are thermodynamically favored $\Delta G > 0$. Endothermic ($\Delta H > 0$) and entropy decreasing $\Delta S < 0$ reactions tend to be non-spontaneous.
- **spontaneous:** products are thermodynamically favored $\Delta G < 0$. Exothermic ($\Delta H < 0$) and entropy increasing $\Delta S > 0$ reactions tend to be spontaneous.
- **equilibrium:** reactants and products macrostates are equally favored $\Delta G = 0$.

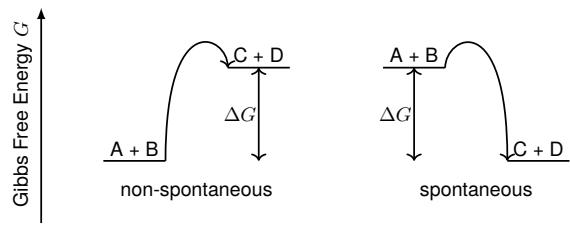


Figure 3: Gibbs free energy change ΔG of non-spontaneous and spontaneous reactions.

4 TEMPERATURE DEPENDENCE OF ΔH , ΔS AND ΔG^*

For each reactant and product, use following relationships to connect H and S between two temperatures (if no phase transition encountered between T_1 and T_2),

$$H(T_2) - H(T_1) = \int_{T_1}^{T_2} C_p dT \quad (8)$$

and

$$S(T_2) - S(T_1) = \int_{T_1}^{T_2} \frac{C_p}{T} dT. \quad (9)$$

For Gibbs free energy

$$\frac{G(T_2)}{T_2} - \frac{G(T_1)}{T_1} = - \int_{T_1}^{T_2} \frac{H(T)}{T^2} dT. \quad (10)$$

If the temperature dependence of H is neglected, then

$$\frac{G(T_2)}{T_2} - \frac{G(T_1)}{T_1} = H \left(\frac{1}{T_2} - \frac{1}{T_1} \right). \quad (11)$$

If a phase transition from α phase to β phase with enthalpy ΔH_{trans} occurs at $T_{\text{trans}} \in (T_1, T_2)$, we need to use

$$H(T_2) - H(T_1) = \int_{T_1}^{T_{\text{trans}}} C_p^\alpha dT + \Delta H_{\text{trans}} + \int_{T_{\text{trans}}}^{T_2} C_p^\beta dT \quad (12)$$

and

$$S(T_2) - S(T_1) = \int_{T_1}^{T_{\text{trans}}} \frac{C_p^\alpha}{T} dT + \frac{\Delta H_{\text{trans}}}{T_{\text{trans}}} + \int_{T_{\text{trans}}}^{T_2} \frac{C_p^\beta}{T} dT. \quad (13)$$

Chapter 5 Chemical Equilibrium

Lecture 17 Chemical Equilibrium

1 CONDITION FOR CHEMICAL EQUILIBRIUM

Theoretically, any chemical reaction occurs in both directions, forward and backward. Some reactions are dominantly towards the products, for which we use \longrightarrow as the reaction symbol. Other reactions are roughly balanced between reactants and products, for which we write



Consider the above reaction initially with n_{j0} moles of species j , $j \in \{A, B, C, D\}$. Define the *extent of reaction* ξ , in units of mole, such that the numbers of moles of reactants and products during reaction are given by

$$\text{reactants: } n_A = n_{A0} - a\xi, \quad n_B = n_{B0} - b\xi$$

$$\text{products: } n_C = n_{C0} + c\xi, \quad n_D = n_{D0} + d\xi.$$

The change in moles of each species satisfies

$$d\xi = \frac{dn_C}{c} = \frac{dn_D}{d} = -\frac{dn_A}{a} = -\frac{dn_B}{b}. \quad (2)$$

If G_j is the molar Gibbs free energy of species j , the deviation of the total Gibbs free energy of the reaction system from equilibrium (at constant T and p), due to changes in n_j , is

$$\begin{aligned} dG &= G_A dn_A + G_B dn_B + G_C dn_C + G_D dn_D \\ &= -aG_A d\xi - bG_B d\xi + cG_C d\xi + dG_D d\xi \\ &= (-aG_A - bG_B + cG_C + dG_D)d\xi \\ &= \Delta G d\xi. \end{aligned} \quad (3)$$

At chemical equilibrium, G is minimized with respect to ξ ,

$$\frac{dG}{d\xi} = [\Delta G = 0]. \quad (4)$$

2 EQUILIBRIUM CONSTANT K

2.1 Definition of equilibrium constant

For ideal gas, the molar Gibbs free energy at an arbitrary pressure p is related to that at a reference pressure p_0 (often chosen as 1 atm) by

$$G(p, T) = G^\circ(p_0 = 1 \text{ atm}, T) + RT \ln p/p_0. \quad (5)$$

Similar relationship applies to ideal or low-concentration solutions, where the reference concentration is often chosen as 1 mol/L = 1 M.

$$G(c, T) = G^\circ(c_0 = 1 \text{ M}, T) + RT \ln c/c_0. \quad (6)$$

This is because solutes at low concentrations behave like ideal "gas molecules" in solution.

¹If it is agreed that, in the context of chemical equilibrium, p and c are expressed in units of p_0 and c_0 , then these standard quantities can be omitted in the reaction quotient, i.e. $Q_p = \frac{p_C^c p_D^d}{p_A^a p_B^b}$ and $Q_c = \frac{c_C^c c_D^d}{c_A^a c_B^b}$. The latter is also written as $Q_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$ when using $[\cdot]$ to denote molarity.

Applying Equation (5) to reaction (1) at arbitrary condition, where all reactants and products are assumed to be in gas state,

$$\begin{aligned} \Delta G &= c \left(G_C^\circ + RT \ln \frac{p_C}{p_0} \right) + d \left(G_D^\circ + RT \ln \frac{p_D}{p_0} \right) \\ &\quad - a \left(G_A^\circ + RT \ln \frac{p_A}{p_0} \right) - b \left(G_B^\circ + RT \ln \frac{p_B}{p_0} \right) \\ &= (cG_C^\circ + dG_D^\circ - aG_A^\circ - bG_B^\circ) \\ &\quad + RT \left[\ln \left(\frac{p_C}{p_0} \right)^c + \ln \left(\frac{p_D}{p_0} \right)^d - \ln \left(\frac{p_A}{p_0} \right)^a - \ln \left(\frac{p_B}{p_0} \right)^b \right] \\ &= \Delta G^\circ + RT \ln \frac{(p_C/p_0)^c (p_D/p_0)^d}{(p_A/p_0)^a (p_B/p_0)^b}. \end{aligned}$$

Define *reaction quotient*

$$Q_p = \frac{(p_C/p_0)^c (p_D/p_0)^d}{(p_A/p_0)^a (p_B/p_0)^b}, \quad (7)$$

or similarly for solution reactions

$$Q_c = \frac{(c_C/c_0)^c (c_D/c_0)^d}{(c_A/c_0)^a (c_B/c_0)^b}, \quad (8)$$

then

$$\boxed{\Delta G = \Delta G^\circ + RT \ln Q}. \quad (9)$$

The *equilibrium constant* K is the reaction quotient at chemical equilibrium with equilibrium values of pressure or concentration,

$$\boxed{K_p = \left(\frac{p_C^c p_D^d}{p_A^a p_B^b} \right)_{\text{eq}}} \quad (10)$$

or

$$\boxed{K_c = \left(\frac{c_C^c c_D^d}{c_A^a c_B^b} \right)_{\text{eq}}}. \quad (11)$$

The subscript "eq", which is normally omitted, emphasizes that equilibrium values of p or c should be used. Pure solids (s) and liquids (l) do not appear in the expression of K .

At chemical equilibrium, $\Delta G = 0$ and $Q = K$. Therefore,

$$\boxed{\Delta G^\circ = -RT \ln K} \quad (12)$$

or

$$\boxed{K = e^{-\frac{\Delta G^\circ}{RT}}}. \quad (13)$$

where ΔG° is the change of standard molar Gibbs free energy of the reaction. ΔG° can be calculated from $\Delta G^\circ = c\Delta G_f^\circ(C) + d\Delta G_f^\circ(D) - a\Delta G_f^\circ(A) - b\Delta G_f^\circ(B)$ or $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$.

2.2 K_c and K_p

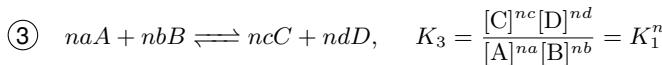
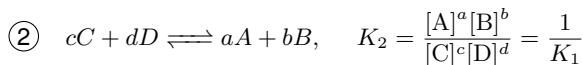
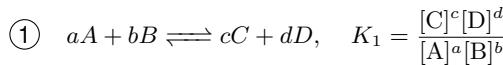
Not only in solutions, K_c can also be defined in gas reactions. Following the ideal gas assumption, $pV = nRT \Rightarrow p = cRT$ with $R = 8.314 \text{ J/mol/K} = 0.082 \text{ atm}\cdot\text{L/mol/K}$ ², we find that

$$K_p = \frac{p_C^c p_D^d}{p_A^a p_B^b} = \frac{[C]^c [D]^d}{[A]^a [B]^b} (RT)^{c+d-a-b} = K_c (RT)^{\Delta n} \quad (14)$$

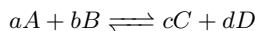
Comments

K_c and K_p are dimensionless because the concentrations and pressures in use are divided by standard unit M and atm, and thus are unitless.

2.3 Reverse, multiply and sum of reactions



If the reaction



is the sum of reactions



then

$$K_4 K_5 = \frac{[C]^c [N]^n}{[A]^a [M]^m} \frac{[M]^m [D]^d}{[N]^n [B]^b} = \frac{[C]^c [D]^d}{[A]^a [B]^b} = K_1.$$

2.4 Temperature dependence of $K(T)$

$$\ln K = -\frac{\Delta H^\circ}{R} \frac{1}{T} + \frac{\Delta S^\circ}{R} \quad (15)$$

equilibrium constants at two different temperatures T_1 and T_2 are related by the **van't Hoff equation**

$$\ln \frac{K_1(T_1)}{K_2(T_2)} = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right), \quad (16)$$

where the temperature dependence of ΔH° and ΔS° are weak and thus neglected.

3 LE CHÂTELIER'S PRINCIPLE

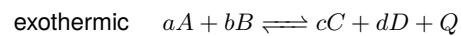
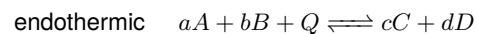
If the conditions of a reaction, initially at equilibrium, are changed, the equilibrium will shift in such a direction as to tend to restore the original conditions, if such a shift is possible.

The changes may include

- add or remove reactants or products
- increase or decrease temperature T
- expand or compress volume (thus change total pressure and partial pressures)
- add a non-reacting noble gas at constant volume (thus increase total pressure but not partial pressures) or constant pressure (thus change partial pressures)

Effect of changing temperature

Consider heat $Q > 0$ as a reactant (endothermic) or a product (exothermic), then increasing or decreasing T is like to add Q to or remove Q from the system. That is



	$T \uparrow$	$T \downarrow$
$\Delta H > 0$	\rightarrow	\leftarrow
$\Delta H < 0$	\leftarrow	\rightarrow

Effect of changing pressure

Initially,

$$K_p = \frac{p_C^c p_D^d}{p_A^a p_B^b}$$

and total pressure $p = p_A + p_B + p_C + p_D$. Now suddenly rescale the total pressure by a factor $\gamma > 0$, $p' = \gamma p$ such that the reaction quotient becomes

$$Q_p = \frac{(\gamma p_C)^c (\gamma p_D)^d}{(\gamma p_A)^a (\gamma p_B)^b} = \frac{p_C^c p_D^d}{p_A^a p_B^b} \gamma^{c+d-a-b} = \frac{p_C^c p_D^d}{p_A^a p_B^b} \gamma^{\Delta n} = K_p \gamma^{\Delta n}$$

So, if $\gamma > 1$ (compression) and $\Delta n > 0$ (forward reaction generates more gases), then $\gamma^{\Delta n} > 1$ and $Q_p > K_p$, thus reaction moves backward (reduce amount of gases).

compression $\gamma > 1$	expansion $\gamma < 1$
$\Delta n > 0$	\leftarrow
$\Delta n < 0$	\rightarrow

²Use the later because p and c are expressed in units of atm and mol/L in equilibrium constant

Chapter 5 Chemical Equilibrium

Lecture 18 Oxygen Equilibrium with Myoglobin and Hemoglobin

1 STRUCTURE OF MYOGLOBIN AND HEMOGLOBIN

Myoglobin (Mb) is a protein found in muscle tissue of animals with an iron-centered heme ligand in it (Figure 2). Each Mb can bind to one O_2 to form a complex MbO_2 with its heme group, at which Fe^{2+} is oxidized by O_2 into Fe^{3+} .



Figure 1: A model of myoglobin. (*The Three-dimensional Structure of a Protein Molecule*, *Scientific American* by John Kendrew, 1961)

Hemoglobin (Hb_4) is a protein in the red blood cells responsible for oxygen transport in the blood of vertebrates. Hemoglobin contains four protein subunits (two α and two β units), each with one heme ligand. Each heme ligand (or Hb subunit) can bind to one O_2 molecule, so a Hb_4 may absorb none, one, two, three or four O_2 molecules.

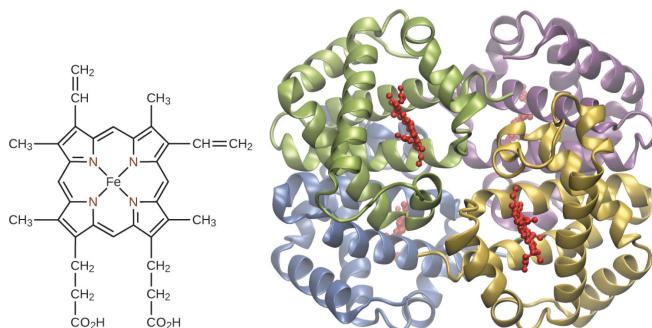


Figure 2: Left: A heme ligand with an iron center. Right: Hemoglobin contains four protein subunits, each with a heme ligand. (*Chemistry*, OpenStax)

2 ABSORPTION CURVE OF O_2 IN MYOGLOBIN AND HEMOGLOBIN

When studying oxygen absorption in myoglobin or hemoglobin, we are interested in the oxygen saturation y , which is defined as,

$$y = \frac{\text{amount of } O_2 \text{ has been absorbed}}{\text{total amount of } O_2 \text{ can be absorbed}} < 1$$

as a function of oxygen partial pressure p given in mmHg. The absorption curve of O_2 in myoglobin is “elbow” like. The absorption curve of O_2 in hemoglobin is typically S-shaped, or sigmoidal.

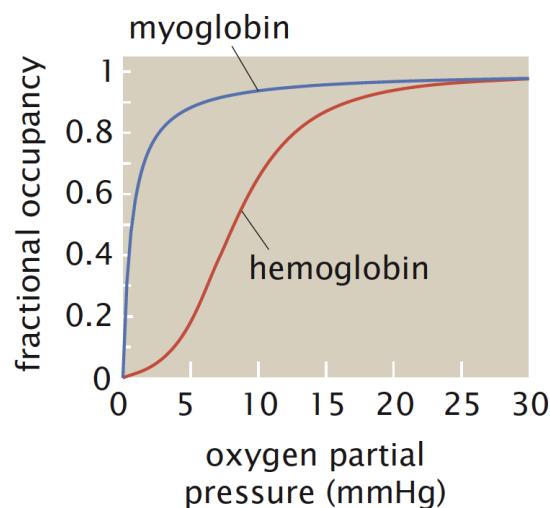


Figure 3: Absorption curve of O_2 in myoglobin and hemoglobin at different O_2 partial pressure p . (*Physical Biology of the Cell* by Rob Phillips, Jane Kondev, Julie Theriot and Hernan G. Garcia)

The physiological effect of myoglobin having higher oxygen saturation at low pressure is to allow O_2 to be transferred from hemoglobin to myoglobin in the muscle.

3 CHEMICAL EQUILIBRIUM OF O_2 WITH MYOGLOBIN

One O_2 binds to one Mb

$$Mb + O_2 \rightleftharpoons MbO_2, \quad K = \frac{[MbO_2]}{[Mb] p}$$

$$y = \frac{[MbO_2]}{[Mb] + [MbO_2]} = \frac{Kp[Mb]}{[Mb] + Kp[Mb]}$$

That is

$$y = \frac{Kp}{1 + Kp} \quad (1)$$

which explains the elbow trend of the absorption curve.

4 ADAIR MODEL FOR O_2 ABSORPTION BY HEMOGLOBIN

O_2 binds to Hb_4 in four cumulative, not successive, steps.

$$Hb_4 + O_2 \rightleftharpoons Hb_4O_2, \quad K_1 = \frac{[Hb_4O_2]}{[Hb_4] p}$$

$$Hb_4 + 2 O_2 \rightleftharpoons Hb_4(O_2)_2, \quad K_2 = \frac{[Hb_4(O_2)_2]}{[Hb_4] p^2}$$

$$Hb_4 + 3 O_2 \rightleftharpoons Hb_4(O_2)_3, \quad K_3 = \frac{[Hb_4(O_2)_3]}{[Hb_4] p^3}$$

$$Hb_4 + 4 O_2 \rightleftharpoons Hb_4(O_2)_4, \quad K_4 = \frac{[Hb_4(O_2)_4]}{[Hb_4] p^4}$$

Because

$$K_1 p = \frac{[Hb_4O_2]}{[Hb_4]}, \quad K_2 p^2 = \frac{[Hb_4(O_2)_2]}{[Hb_4]}$$

$$K_3 p^3 = \frac{[Hb_4(O_2)_3]}{[Hb_4]}, \quad K_4 p^4 = \frac{[Hb_4(O_2)_4]}{[Hb_4]}$$

the total concentration of Hb₄

$$\begin{aligned} [\text{Hb}_4]_0 &= [\text{Hb}_4] + [\text{Hb}_4\text{O}_2] + [\text{Hb}_4(\text{O}_2)_2] + [\text{Hb}_4(\text{O}_2)_3] + [\text{Hb}_4(\text{O}_2)_4] \\ &= [\text{Hb}_4] (1 + K_1 p + K_2 p^2 + K_3 p^3 + K_4 p^4) \\ &= [\text{Hb}_4] Z. \end{aligned}$$

Here, $1, K_1 p, K_2 p^2, K_3 p^3, +K_4 p^4$ can be understood as the relative abundance of Hb₄, Hb₄O₂, Hb₄(O₂)₂, Hb₄(O₂)₃, Hb₄(O₂)₄ at equilibrium. These five species have oxygen saturation, 0, 0.25, 0.5, 0.75, 1.0 respectively. So the true oxygen saturation in the system is the weighted average

$$\begin{aligned} y &= \frac{[\text{Hb}_4\text{O}_2]}{[\text{Hb}_4]_0} \frac{1}{4} + \frac{[\text{Hb}_4(\text{O}_2)_2]}{[\text{Hb}_4]_0} \frac{1}{2} + \frac{[\text{Hb}_4(\text{O}_2)_3]}{[\text{Hb}_4]_0} \frac{3}{4} + \frac{[\text{Hb}_4(\text{O}_2)_4]}{[\text{Hb}_4]_0} \frac{1}{1} \\ &= \frac{K_1 p}{Z} \frac{1}{4} + \frac{K_2 p^2}{Z} \frac{1}{2} + \frac{K_3 p^3}{Z} \frac{3}{4} + \frac{K_4 p^4}{Z} \\ y &= \frac{K_1 p + 2K_2 p^2 + 3K_3 p^3 + 4K_4 p^4}{4(1 + K_1 p + K_2 p^2 + K_3 p^3 + K_4 p^4)} \quad (2) \end{aligned}$$

5 PAULING MODEL FOR O₂ ABSORPTION BY HEMOGLOBIN

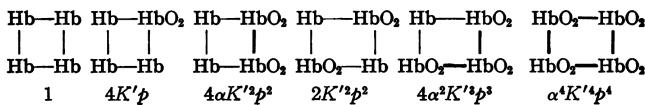


Figure 4: Pauling's model of oxygen binding to hemoglobin [Pauling 1935]¹. The relative probability of seeing each state is given by the number below each state. We will use k in place of K' below for clear notation.

Binding energy ϵ of one O₂ to Hb group introduces a Boltzmann factor $k = e^{-\frac{\epsilon}{k_B T}}$; interacting energy δ of two neighboring HbO₂ groups introduces a Boltzmann factor $\alpha = e^{-\frac{\delta}{k_B T}}$ ($\delta < 0$

and $\alpha > 1$, positive cooperation; $\delta > 0$ and $\alpha < 1$, negative cooperation).

The molar fraction of each species above is, e.g.

$$y = \frac{1}{1 + 4kp + (4\alpha + 2)k^2p^2 + 4\alpha^2k^3p^3 + \alpha^4k^4p^4}$$

fraction of Hb₄

$$y = \frac{4kp}{1 + 4kp + (4\alpha + 2)k^2p^2 + 4\alpha^2k^3p^3 + \alpha^4k^4p^4}$$

fraction of Hb₄O₂. Knowing all the molar fractions, we can calculate the oxygen saturation as weighted average

$$y = \frac{kp + (2\alpha + 1)k^2p^2 + 3\alpha^2k^3p^3 + \alpha^4k^4p^4}{1 + 4kp + (4\alpha + 2)k^2p^2 + 4\alpha^2k^3p^3 + \alpha^4k^4p^4} \quad (3)$$

Allotropy (变构) and cooperativity

Cooperativity refers to the fact that binding of ligands on different sites on the same molecule is not independent. Instead, binding of one ligand promotes (positive cooperation) or inhibits (negative cooperation) binding of others.

Allotropy refers to the change of structure of proteins, in particular enzymes, when a ligand binds to one site and affects properties at a distant site. Such a ligand is an allosteric *activator* or *inhibitor* that can enhance or suppress enzyme activity.

Comments

Although models like Adair's or Pauling's can provide good fits to the experimental data, it does not mean the actual mechanism works this way. In fact, there are many other models that also fit the data very well, for instance, the Hill equation² with non-integer n ,

$$y = \frac{Kp^n}{1 + Kp^n}. \quad (4)$$

¹ Pauling, Linus. "The oxygen equilibrium of hemoglobin and its structural interpretation." Proceedings of the National Academy of Sciences of the United States of America 21.4 (1935): 186.

² Hill, Archibald Vivian. "The possible effects of the aggregation of the molecules of haemoglobin on its dissociation curves." j. physiol. 40 (1910): 4-7.

Chapter 6 Acids and Bases

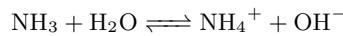
Lecture 19 Chemical Equilibrium of Acids and Bases in Aqueous Solution

1 DEFINITIONS OF ACIDS AND BASES

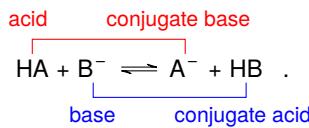
A *acid* is a hydrogen-containing substance that dissociates on solution in water to produce hydrogen ions¹, and a *base* is a substance containing the hydroxide ion or the hydroxyl group that dissociates in aqueous solution as the hydroxide ion.

More generally, in the Brønsted-Lowry theory, an acid is a *proton donor* and a base is a *proton acceptor*.

Still more generally, in the Lewis theory, an acid is an *electron-lone-pair acceptor*, for instance $\text{B}(\text{OH})_3$, and a base is an *electron-lone-pair donor*, for instance :NH_3 .



Conjugate acid-base pair

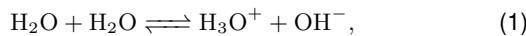


Concentration of ions in aqueous solutions

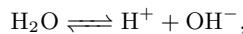
- molarity *c*: mole per liter of solution, $1 \text{ M} = 1 \text{ mol/L}$
- molality *b*: mole per kg of solvent, $1 \text{ m} = 1 \text{ mol/kg}$
- normality: *N*
- formality: *F*

2 SELF-IONIZATION OF WATER

The self-ionization, or autoprotolysis, of water involves the following process



sometimes shortened as



which establishes chemical equilibrium with equilibrium constant

$$K_{\text{eq}} = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2}.$$

Because $[\text{H}_2\text{O}]$ is nearly the same as that in pure water and thus remains effectively constant, it is customary to group $[\text{H}_2\text{O}]^2$ with K_{eq} and define the dissociation constant of water, $K_w = K_{\text{eq}}[\text{H}_2\text{O}]^2$,

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]. \quad (2)$$

¹In water, H^+ ions do not exist in isolated state, but bind to water molecules to form hydronium ions H_3O^+ . It is often customary to use H^+ in place of H_3O^+ .

²We often only use pH and pOH when dealing with dilute solutions, in which $[\text{H}^+], [\text{OH}^-] \lesssim 1 \text{ mol/L}$.

At room temperature 25°C , in pure water, $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.00 \times 10^{-7} \text{ mol/L}$, thus $K_w = 1.00 \times 10^{-14}$. In acidic or basic solutions, the relationship still holds.

Because the concentration of ions in aqueous solution can vary by orders of magnitude, it is convenient to define and use

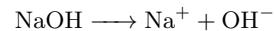
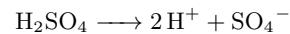
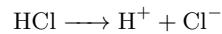
$$\text{pH} = -\log [\text{H}^+] \quad \text{and} \quad \text{pOH} = -\log [\text{OH}^-], \quad (3)$$

which satisfies $\text{pH} + \text{pOH} = 14$.

In pure water at room temperature, $\text{pH} = \text{pOH} = 7$, which is said to be *neutral*. *Acidic* solutions have more H^+ than OH^- , thus $0 < \text{pH} < 7$; *basic* solutions have more OH^- than H^+ , thus $14 > \text{pH} > 7$ ².

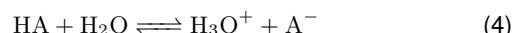
3 STRONG ACIDS AND BASES

Strong acids and bases dissociate almost completely into ions in dilute aqueous solution, such as

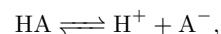


4 WEAK ACIDS AND BASES

A weak acid HA, e.g. HF, releases H^+ in aqueous solution by



sometimes shortened as



for which, we define the *acid constant* K_a

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{[\text{H}^+][\text{conjugate base}]}{[\text{weak acid}]} \quad (5)$$

The larger K_a is, the more acidic HA is.

A weak base MOH, e.g. NH_4OH , releases OH^- in aqueous solution by



for which, we define the *basic constant* K_b

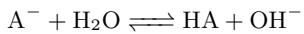
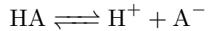
$$K_b = \frac{[\text{M}^+][\text{OH}^-]}{[\text{MOH}]} = \frac{[\text{conjugate acid}][\text{OH}^-]}{[\text{weak base}]} \quad (7)$$

The larger K_b is, the more basic MOH is.

For a conjugate acid-base pair

$$K_a K_b = K_w. \quad (8)$$

This is because



can add up to an overall reaction

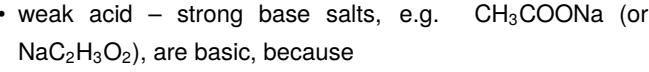
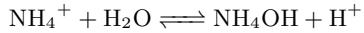


$$K_a K_b = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]} = K_w.$$

5 SALTS

Salts are products of the neutralization reaction of acids and bases, which are often ionic compounds consisting of metal cations and non-metal anions, such as NaCl, CaCO₃, etc. When put into water, some salts are insoluble and become precipitates, while others are soluble and dissociate into ions. Salts can be classified according to their sources of acids and bases. In aqueous solution,

- strong acid – strong base salts, e.g. NaCl, are neutral
- strong acid – weak base salts, e.g. NH₄Cl, are acidic, because
- weak acid – strong base salts, e.g. CH₃COONa (or NaC₂H₃O₂), are basic, because



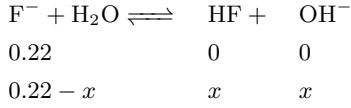
Example

Determine the [OH⁻] and pH of a 0.22 M NaF solution, given the acid constant for HF is $K_a = 6.8 \times 10^{-4}$.

Solution

$$K_b = \frac{10^{-14}}{6.8 \times 10^{-4}} = 1.47 \times 10^{-11}$$

Method 1

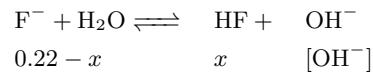


$$\frac{x^2}{0.22 - x} = K_b \Rightarrow x = \frac{-K_b + \sqrt{K_b^2 + 4 \times 0.22 \times K_b}}{2} = 1.8 \times 10^{-6}$$

If we approximate $0.22 - x \approx 0.22$ by considering $x \ll 0.22$, then $x = \sqrt{0.22 K_b} = 1.8 \times 10^{-6}$, which validates the approximation.

Method 2

Exactly speaking, $[\text{OH}^-] \neq [\text{HF}]$ for a small amount of OH⁻ comes from dissociation of $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$.



We have three equations and three unknown's x , $[\text{H}^+]$ and $[\text{OH}^-]$

$$\begin{aligned} \frac{x[\text{OH}^-]}{0.22 - x} &= K_b \\ [\text{H}^+][\text{OH}^-] &= K_w \\ [\text{OH}^-] &= x + [\text{H}^+] \end{aligned}$$

The third equation says the total OH⁻ concentration comes from two contributions: from F⁻ and from H₂O.

To solve this system of equations, we get

$$\frac{\left([\text{OH}^-] - \frac{K_w}{[\text{OH}^-]}\right)[\text{OH}^-]}{0.22 - \left([\text{OH}^-] - \frac{K_w}{[\text{OH}^-]}\right)} = K_b$$

We need to approximate $0.22 - \left([\text{OH}^-] - \frac{K_w}{[\text{OH}^-]}\right) \approx 0.22$. Otherwise, we will have a third order equation. Then

$$\begin{aligned} \frac{([\text{OH}^-]^2 - K_w)}{0.22} &= K_b \Rightarrow \\ [\text{OH}^-] &= \sqrt{0.22 K_b + K_w} \\ &= \sqrt{3.23 \times 10^{-12} + 10^{-14}} \\ &= 1.8 \times 10^{-6} \end{aligned}$$

It appears that for this problem, the contribution of H₂O to [OH⁻] is negligible and Method 1 works just fine.

It is often true that, in acidic solutions we can neglect H⁺ coming from water self-ionization; in basic solutions we can neglect OH⁻ coming from water self-ionization.

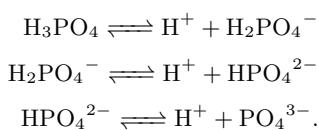
Chapter 6 Acids and Bases

Lecture 20 Amphotericism 两性

An amphoteric compound is a molecule or ion that can react both as an acid and as a base. An amphiprotic molecule can both lose a proton and add a proton.

1 POLYPROTIC ACIDS

Polyprotic acids are able to dissociate more than one H^+ per molecule, which have several acid constants. The acidity of polyprotic acids becomes weaker and weaker, eventually basic, as hydrogen ions are released successively. For instance, the triprotic phosphoric acid H_3PO_4 can



Correspondingly,

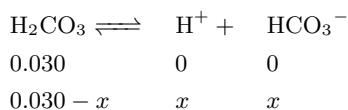
$$\begin{aligned}K_1 &= \frac{[\text{H}^+][\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]} = 7.5 \times 10^{-3} \\ K_2 &= \frac{[\text{H}^+][\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = 6.2 \times 10^{-8} \\ K_3 &= \frac{[\text{H}^+][\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]} = 10^{-12}.\end{aligned}$$

Example

Determine the pH of a 0.030 M H_2CO_3 solution, given the successive acid constants for carbonic acid are $K_1 = 4.5 \times 10^{-7}$ and $K_2 = 4.7 \times 10^{-11}$.

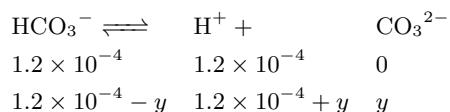
Solution

First ionization:



$$\frac{x^2}{0.030 - x} \approx \frac{x^2}{0.030} = K_1 \Rightarrow x = \sqrt{0.030 K_1} = 1.2 \times 10^{-4}.$$

Second ionization:



$$\frac{(1.2 \times 10^{-4} + y)y}{1.2 \times 10^{-4} - y} \approx \frac{1.2 \times 10^{-4}y}{1.2 \times 10^{-4}} = K_2 \Rightarrow y = K_2 = 4.7 \times 10^{-11}.$$

In summary, $y \ll x$, H^+ mainly comes from the first ionization step. At equilibrium, $[\text{H}_2\text{CO}_3] = 0.030 \text{ M}$, $[\text{HCO}_3^-] = 1.2 \times 10^{-4} \text{ M}$ and $[\text{CO}_3^{2-}] = 4.7 \times 10^{-11} \text{ M}$. $[\text{H}^+] = 1.2 \times 10^{-4} \text{ M}$ and $\text{pH} = 3.9$.

2 BUFFER SOLUTIONS

A *buffer solution* (缓冲溶液), or a buffer, contains an equimolar weak conjugate acid-base pair, whose pH remains relatively stable when considerably large amounts of strong acids or bases are added. For instance, a buffer solution may contain or be made from

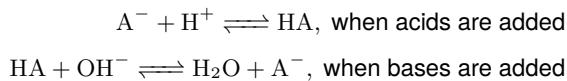
- 0.10 M acetic acid $\text{HC}_2\text{H}_3\text{O}_2$ and 0.10 M sodium acetate $\text{NaC}_2\text{H}_3\text{O}_2$.
- 0.10 M KH_2PO_4 and 0.10 M Na_2HPO_4 , or equivalently, 0.20 M H_3PO_4 and 0.30 M NaOH

At $\text{pH} \approx 7$ ($[\text{H}^+] = 10^{-7} \text{ M}$),

$$\begin{aligned}\frac{[\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]} &= \frac{K_3}{[\text{H}^+]} = \frac{10^{-5}}{10^{-7}} = 10^{-5} \ll 1 \\ \frac{[\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]} &= \frac{K_1}{[\text{H}^+]} = \frac{7.5 \times 10^4}{10^{-7}} = 7.5 \times 10^4 \gg 1 \\ \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} &= \frac{K_2}{[\text{H}^+]} = \frac{0.62}{10^{-7}} = 0.62 \approx 1\end{aligned}$$

the buffer solution is nearly neutral, with $[\text{H}_2\text{PO}_4^-] \approx \text{HPO}_4^{2-}] \approx 0.1 \text{ M}$ and $[\text{PO}_4^{3-}] \approx [\text{H}_3\text{PO}_4] \approx 0 \text{ M}$.

A buffer of the acid-base pair of HA/A^- works through



The operating pH that the buffer can stabilize is estimated from the **Henderson-Hasselbalch equation**

$$\text{pH} = pK_a + \log \frac{[\text{A}^-]}{[\text{HA}]} \quad (1)$$

2.1 pH in buffered solution

Example

Consider a 100 mL buffer containing 0.10 M $\text{HC}_2\text{H}_3\text{O}_2$ and 0.10 M $\text{NaC}_2\text{H}_3\text{O}_2$. The acid constant of acetic acid is $K_a = 1.8 \times 10^{-5}$.

(a) What is the pH of the solution?

(b) If 1.0 mL of 0.10 M NaOH is added into the buffer, what does the pH become?

(c) If 2.0 mL of 0.10 M HCl is added into the buffer, what does the pH become?

Solution

(a) $\text{pH} = pK_a + \log \frac{0.10}{0.10} = pK_a = -\log(1.8 \times 10^{-5}) = 4.74$

(b) Before mixing,

$$0.10 \times 1.0 \times 10^{-3} = 1.0 \times 10^{-4} \text{ mol NaOH}$$

$$0.10 \times 1.0 \times 10^{-1} = 1.0 \times 10^{-2} \text{ mol } \text{HC}_2\text{H}_3\text{O}_2 \text{ and } \text{NaC}_2\text{H}_3\text{O}_2.$$

After mixing, NaOH consumes same amount of $\text{HC}_2\text{H}_3\text{O}_2$, leaving

$$1.0 \times 10^{-2} - 1.0 \times 10^{-4} = 0.99 \times 10^{-2} \text{ mol HC}_2\text{H}_3\text{O}_2$$

$$1.0 \times 10^{-2} + 1.0 \times 10^{-4} = 1.01 \times 10^{-2} \text{ mol NaC}_2\text{H}_3\text{O}_2.$$

The new concentrations are

$$[\text{HC}_2\text{H}_3\text{O}_2] = \frac{0.99 \times 10^{-2}}{0.101} = 0.098 \text{ M}$$

$$[\text{NaC}_2\text{H}_3\text{O}_2] = \frac{1.01 \times 10^{-2}}{0.101} = 0.10 \text{ M.}$$

So the new pH is

$$\text{pH} = \text{pK}_a + \log \frac{0.10}{0.098} = \text{pK}_a = 4.74 + 0.01 = 4.75.$$

(c) Before mixing,

$$0.10 \times 2.0 \times 10^{-3} = 2.0 \times 10^{-4} \text{ mol HCl}$$

$$0.10 \times 1.0 \times 10^{-1} = 1.0 \times 10^{-2} \text{ mol HC}_2\text{H}_3\text{O}_2 \text{ and NaC}_2\text{H}_3\text{O}_2.$$

After mixing, HCl consumes the same amount of NaC₂H₃O₂,

leaving

$$1.0 \times 10^{-2} - 2.0 \times 10^{-4} = 0.98 \times 10^{-2} \text{ mol NaC}_2\text{H}_3\text{O}_2$$

$$1.0 \times 10^{-2} + 2.0 \times 10^{-4} = 1.02 \times 10^{-2} \text{ mol HC}_2\text{H}_3\text{O}_2.$$

The new concentrations are

$$[\text{HC}_2\text{H}_3\text{O}_2] = \frac{1.02 \times 10^{-2}}{0.102} = 0.10 \text{ M}$$

$$[\text{NaC}_2\text{H}_3\text{O}_2] = \frac{0.98 \times 10^{-2}}{0.102} = 0.096 \text{ M.}$$

So the new pH is

$$\text{pH} = \text{pK}_a + \log \frac{0.096}{0.10} = \text{pK}_a = 4.74 - 0.02 = 4.72.$$

2.2 pH in unbuffered solution

Example

Consider a 100 mL HCl solution at pH = 4.74.

(a) If 1.0 mL of 0.10 M NaOH is added into the solution, what does the pH become?

(b) If 2.0 mL of 0.10 M HCl is added into the solution, what does the pH become?

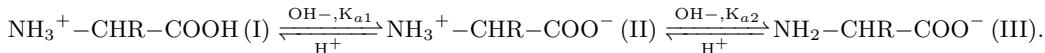
Solution

Initially, $[\text{H}^+] = 1.8 \times 10^{-5} \text{ M}$ and $1.8 \times 10^{-6} \text{ mol H}^+$ in the 100 mL solution.

(a) The $1.0 \times 10^{-4} \text{ mol NaOH}$ consumes all H^+ and leaves $0.982 \times 10^{-4} \text{ mol OH}^-$.

$$[\text{OH}^-] = \frac{0.982 \times 10^{-4}}{0.101} = 9.72 \times 10^{-4} \text{ M}, \text{pOH} = 3.01$$

$$\text{pH} = 14 - 3.01 = 9.99.$$



In acidic solution, amino acids mainly exist in the form of positive ion (I); in basic solution, amino acids mainly exist in the form of negative ion (III); at certain moderate pH, the **isoelectric point (pl)**, the concentrations of (I) and (III) are equal and amino acids mainly exist in the form of zwitterion (II), leaving no net charge in solution. The charging property can be used to separate amino acids, peptides or even proteins, by tuning the pH value of the solution under an external electric field — *electrophoresis*. The isoelectric point can be estimated using the acid constants of the two steps

$$\text{pI} = \frac{\text{pK}_{a1} + \text{pK}_{a2}}{2}. \quad (2)$$

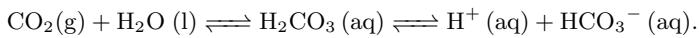
(b) $2.0 \times 10^{-4} \text{ mol HCl}$ adds to the original H^+ and gives $2.018 \times 10^{-4} \text{ mol H}^+$.

$$[\text{H}^+] = \frac{2.018 \times 10^{-4}}{0.102} = 1.98 \times 10^{-3} \text{ M}$$

$$\text{pH} = 2.7.$$

3 ACID-BASE HOMEOSTASIS

Acid-base homeostasis is the regulation of pH inside the living body in order to maintain normal physiological activities, often achieved by buffers, for instance, the carbonic acid-bicarbonate buffer system¹



In medicine, the pH of a $\text{CO}_2 / \text{HCO}_3^-$ buffered solution is given by the Henderson-Hasselbalch equation

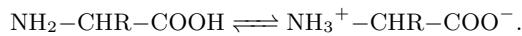
$$\text{pH} = 6.1 + \log \frac{[\text{HCO}_3^-]}{0.03 \times P_{\text{CO}_2}}$$

where $[\text{HCO}_3^-]$ is in milliequivalents per liter (mEq/L, here 1 mEq/L = 1 m mol /L = 10^{-3} M) and P_{CO_2} is in millimeters of mercury (mmHg). In normal blood plasma, $[\text{HCO}_3^-] = 24 \text{ mEq/L}$ and $P_{\text{CO}_2} = 40 \text{ mmHg}$, thus $\text{pH} = 6.1 + \log \frac{24}{0.03 \times 40} = 7.4$.

Respiratory alkalosis after intense exercise.

4 ISOELECTRIC POINT

α -amino acids are *amphoteric*, that is being able to react with both acids and bases, due to the existence of acidic –COOH group and basic –NH₂ group in the same molecule. When these two groups interact within one molecule in neutral aqueous solution, amino acids become *zwitterions* (两性离子),



One such zwitterion $\text{NH}_3^+ - \text{CHR} - \text{COO}^-$ can further react with H^+ or OH^- ²,

$$\text{AH}_2^+ \xrightleftharpoons{\text{K}_{a1}} \text{AH} + \text{H}^+, \quad \text{K}_{a1} = \frac{[\text{AH}][\text{H}^+]}{[\text{AH}_2^+]}$$

$$\text{AH} \xrightleftharpoons{\text{K}_{a2}} \text{A}^- + \text{H}^+, \quad \text{K}_{a2} = \frac{[\text{A}^-][\text{H}^+]}{[\text{AH}]}$$

So

$$\text{K}_{a1} \text{K}_{a2} = \frac{[\text{AH}][\text{H}^+]}{[\text{AH}_2^+]} \frac{[\text{A}^-][\text{H}^+]}{[\text{AH}]} = \frac{[\text{A}^-]}{[\text{AH}_2^+]} [\text{H}^+]^2.$$

At pl, $[\text{A}^-] = [\text{AH}_2^+]$, so $\text{K}_{a1} \text{K}_{a2} = [\text{H}^+]^2$ and $\text{pK}_{a1} + \text{pK}_{a2} = 2 \text{ pH}$.

If -R is neutral, e.g. alanine, the pl of the amino acid is close to

7. Or at $\text{pH} \approx 7$, the amino acid is charge neutral.

If -R is acidic, e.g. aspartic acid, the pl of the amino acid is much lower than 7. Or at $\text{pH} \approx 7$, the amino acid is negatively charged.

¹Hamm, L. Lee, Nazih Nakhoul, and Kathleen S. Hering-Smith. "Acid-base homeostasis." Clinical Journal of the American Society of Nephrology 10, no. 12 (2015): 2232-2242.

²Here we only consider amino acids that have only one COOH and one NH₂ in each molecule, while some amino acids have one extra COOH or NH₂ in the R group.

If $-R$ is basic, e.g. lysine, the pI of the amino acid is much higher than 7. Or at $pH \approx 7$, the amino acid is positively charged.

5 SICKLE CELL ANEMIA

Three phenotypes of red blood cells (erythrocytes)

- normal: biconcave disk
- sickle cell trait (sicklemia): sickle at extremely low pO_2
- sickle cell anemia: sickle at low pO_2

Phenotypes of hemoglobins and corresponding genotypes (autosomal recessive inheritance 常染色体隐性遗传) among people (Page 782 [Pauling])

- normal people: 100% normal hemoglobin, RR
- sickle cell trait (sicklemia) people: 60% normal hemoglobin + 40% defective hemoglobin, Rr
- sickle cell anemia patients: 100% defective hemoglobin, rr

A red blood cell has $\sim 10^8$ hemoglobins.

Defective hemoglobins can polymerize to form long fibers at low pO_2 , causing red blood cells to break.

Electrophoresis finds that the $pI = 7.09$ of defective hemoglobin is about 0.22 higher than the $pI = 6.87$ of normal hemoglobin. The former has more positive charges than the latter at the same pH. Changing pH by 1 causes the change of net charge by 13. So, defective hemoglobin has about $0.22 \times 13 \approx 2.86$, after considering errors in measurement, 2–4 more net positive charge per molecule than normal hemoglobin (Pauling et al, Sickle cell anemia, a molecular disease, Science, 1949).

Net positive charge = number of cation groups minus total number of anion groups in each protein molecule.

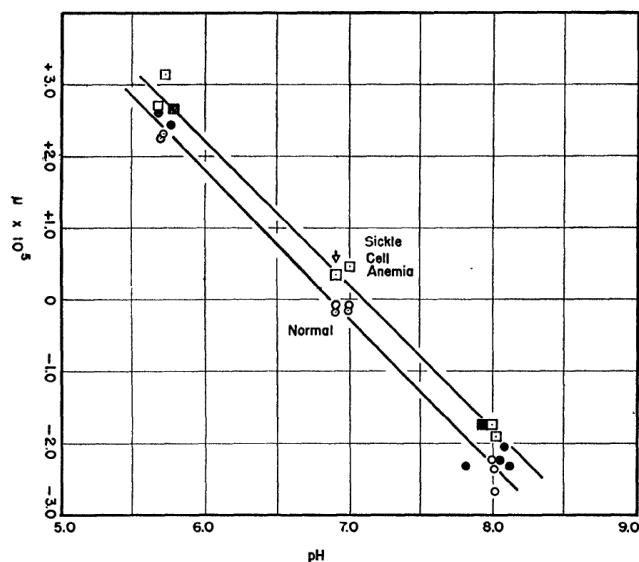


Figure 1: Electrophoresis of normal and defective hemoglobin (bind to CO). Mobility μ under electric field (> 0 means to carry + charge) v.s. pH. (Pauling et al, Sickle cell anemia, a molecular disease, Science, 1949)

There 146 amino acids in the β subunit of hemoglobin (Page 777 [Pauling]). On the 6th position, it is Glu for normal hemoglobin (HbA) but Val for defective hemoglobin (HbS).

Table 1: Genetics of normal and defective hemoglobins.

	normal hemoglobin	defective hemoglobin
β subunit	HbA	HbS
allele (gene)	R (A)	r (S)
DNA	-CTT-	-CAT-
mRNA ³	-GAA-	-GUA-
amino acid	glutamic acid (Glu)	valine (Val)
-R group ⁴	$-\text{CH}_2\text{CH}_2\text{COO}^-$	$-\text{CH}(\text{CH}_3)_2$

⁴See genetic code on Page 788 [Pauling]

⁴See amino acids table on Page 772 [Pauling]

Chapter 7 Chemical Kinetics

Lecture 21 Rate Laws

1 RATE OF CHEMICAL REACTIONS

Consider a simple chemical reaction



for which the concentration of product C changes from $[C]_1$ at time t_1 to $[C]_2$ at time t_2 . The *average rate* of the reaction during this time interval $\Delta t = t_2 - t_1$ is

$$\bar{r} = \frac{[C]_2 - [C]_1}{t_2 - t_1} = \frac{\Delta[C]}{\Delta t}.$$

The *instantaneous rate*

$$r = \lim_{\Delta t \rightarrow 0} \frac{\Delta[C]}{\Delta t} = \frac{d[C]}{dt}.$$

For a general chemical reaction



define the *rate of reaction*

$$r = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt}. \quad (2)$$

Note that, under this definition, $r > 0$ and is in units of M / s.

2 RATE LAW

A *rate law* describes the relationship between rate r and the concentrations of reactants. For instance, for the reaction

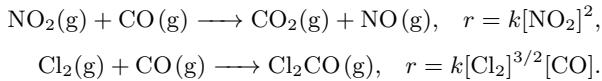


k is called the *rate constant* of the reaction, whose unit is determined by the dimensions of the rate law. Generally,

$$r = k[A]^{m_A} [B]^{m_B} \dots, \quad (3)$$

the exponents m_A, m_B, \dots of the concentrations of reactants are *orders*, the overall order of the reaction is $m_A + m_B + \dots$. This form of relationship between rate and concentration is often given the name, **law of mass action**.

In the above example and many reactions, the order of each reactant is the same as its stoichiometric coefficient, i.e. $m_A = a, m_B = b, \dots$, but generally, the order of a reaction has nothing to do with the stoichiometric coefficients and can even be zero or a fractional number, which should be determined experimentally¹. For instance,



The reason is that, generally, a stoichiometric equation does not reflect how the (complex) reaction occurs and the actual *mechanism* may involve multiple steps (elementary reactions).

To determine reaction order and the rate law,

2.1 Method of isolation

To have all but one reactant in large excess amounts such that their concentrations effectively remain constant during the measurement. For instance, if $k[A]^{m_A} = k'$ is constant, then the rate law (3) becomes $r = k'[B]^{m_B}$ and m_B can be determined by measuring r as a function of $[B]$.

2.2 Method of initial rates

To fix the initial concentrations of all but one reactant, for instance,

$$\begin{aligned} r_1 &= k[A]_0^{m_A} [B]_1^{m_B} \dots \\ r_2 &= k[A]_0^{m_A} [B]_2^{m_B} \dots \end{aligned}$$

then

$$\frac{r_1}{r_2} = \frac{[B]_1^{m_B}}{[B]_2^{m_B}}$$

thus

$$m_B = \frac{\ln \frac{r_1}{r_2}}{\ln \frac{[B]_1}{[B]_2}}$$

2.3 First-order reaction

$$r = -\frac{d[A]}{dt} = k[A], \quad [A] = [A]_0 e^{-kt} \text{ or } \ln[A] = \ln[A]_0 - kt \quad (4)$$

$[A]$ v.s. t on a semi-log plot is a straight line with slope $-k$.

The *half-life* ($\tau_{\frac{1}{2}}$) of the reaction or a reactant is the time required for half of the reactant to decompose. For first-order reactions,

$$\tau_{\frac{1}{2}} = \frac{\ln 2}{k} = \frac{0.693}{k}, \quad (5)$$

which is independent of the initial concentration $[A]_0$, i.e. the reaction is memoryless about its history.

2.4 Second-order reaction

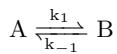
$$r = -\frac{d[A]}{dt} = k[A]^2, \quad \frac{1}{[A]} = \frac{1}{[A]_0} + kt \quad (6)$$

$\frac{1}{[A]}$ v.s. t on a linear plot is a straight line with slope k .

¹For elementary reactions, the relationship $m_A = a, m_B = b, \dots$ is true.

3 REVERSIBLE REACTION AND CHEMICAL EQUILIBRIUM

Reactions mentioned above are predominantly in the forward direction, or irreversible, for which we use \longrightarrow . For *reversible* reactions, e.g.



the net forward rate is

$$r = -\frac{d[A]}{dt} = k_1[A] - k_{-1}[B]$$

At steady state, or chemical equilibrium, $\frac{d[A]}{dt} = 0$, so

$$k_1[A]_{\text{eq}} = k_{-1}[B]_{\text{eq}}.$$

Thus the chemical equilibrium constant can be expressed as

$$K = \frac{[B]_{\text{eq}}}{[A]_{\text{eq}}} = \frac{k_1}{k_{-1}}.$$

Chapter 7 Chemical Kinetics

Lecture 22 Reaction Mechanisms

1 ELEMENTARY REACTION

Generally, an overall reaction is a *complex reaction*, which occurs through a sequence of *elementary reactions* or *elementary steps*. The *mechanism* of a chemical reaction reveals how it occurs in consecutive elementary steps. *Intermediates* are chemicals that exist temporarily during reaction but cancel out on two sides of intermediate reaction steps. Depending on the number of molecules involved, an elementary reaction may be *unimolecular*, *bimolecular* or *termolecular*. For an elementary reaction, the stoichiometry does determine its rate law. The rate law of a complex reaction can be derived from the mechanism and rate laws of its elementary steps.

Usually, among multiple elementary steps, there is a slowest step, called **rate-determining step** (RDS), which is the bottleneck of the overall process and sets the overall reaction rate.

2 FULL SOLUTION*

Example 1

Consider an overall reaction $A \xrightarrow{k} C$, occurring via two elementary steps



work out the time evolution of concentrations of [A], [B] and [C] under initial conditions $[A]_0, 0, 0$. What is the overall rate law $r = kf([A])$?

Solution

Need to solve the coupled ODEs

$$\begin{cases} \frac{d[A]}{dt} = -k_1[A] \\ \frac{d[B]}{dt} = k_1[A] - k_2[B] \\ \frac{d[C]}{dt} = k_2[B] \end{cases}$$

which gives¹

$$\begin{cases} [A] = [A]_0 e^{-k_1 t} \\ [B] = \frac{k_1 [A]_0}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) \quad (k_2 \neq k_1) \\ [C] = [A]_0 - [A] - [B] \end{cases}$$

When $k_1 \ll k_2$, step 1 is the RDS. So overall rate $r = k_1[A] = k[A]$ ($k = k_1, m_A = 1$). In this case, B is consumed so fast in step

¹ $y'(x) + ay(x) = f(x)$, $\frac{dy}{dx} e^{ax} y(x) = e^{ax} y' + aye^{ax} = e^{ax} f(x) \Rightarrow e^{ax} y(x) = \int e^{ax} f(x) dx + C$. So, $e^{k_2 t} [B] = \int k_1 [A] e^{k_2 t} dt + C = \frac{k_1 [A]_0}{k_2 - k_1} e^{(k_2 - k_1)t} + C$ ($k_2 \neq k_1$) or $k_1 [A]_0 t + C$ ($k_2 = k_1$).

2 such that its concentration remains effectively zero $[B] \approx 0$ after a short initialization period. Also, it is hard to distinguish whether the reaction occurs by one step or two steps.

When $k_1 \gg k_2$, step 2 is the RDS. So overall rate $r = k_2[B] = k_2 \frac{k_1}{k_2 - k_1} [A] - k_2 \frac{k_1}{k_2 - k_1} [A]_0 \left(\frac{[A]}{[A]_0} \right)^{\frac{k_2}{k_1}} = \frac{k_1 k_2}{k_2 - k_1} \left[[A] - [A]_0 \left(\frac{[A]}{[A]_0} \right)^{\frac{k_2}{k_1}} \right]$ (not a power rate law). In this case, the reactant A quickly degrades into the long-lived intermediate B. The reaction is then effectively going from B to C.

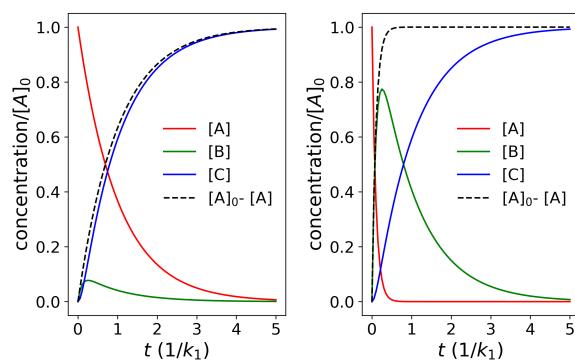


Figure 1: Left: $k_1 = 1$ and $k_2 = 10$ and step 1 is RDS. Right: $k_1 = 10$ and $k_2 = 1$ and step 2 is RDS.

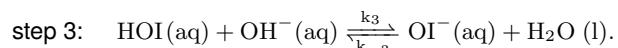
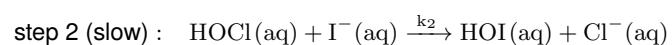
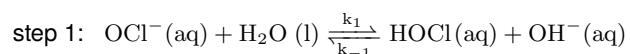
3 APPROXIMATE SOLUTION

Example 2

An overall reaction $I^- (\text{aq}) + \text{OCl}^- (\text{aq}) \xrightarrow{k} \text{OI}^- (\text{aq}) + \text{Cl}^- (\text{aq})$ is observed to obey the rate law

$$r = k \frac{[\text{I}^-][\text{OCl}^-]}{[\text{OH}^-]}.$$

Prove that the following mechanism reproduces the rate law above.



Solution

Because the step 2 is RDS,

$$r = k_2 [\text{HOCl}] [\text{I}^-]$$

Chemical equilibrium of step 1

$$k_1 [\text{OCl}^-] [\text{H}_2\text{O}] = k_{-1} [\text{HOCl}] [\text{OH}^-]$$

so

$$[\text{HOCl}] = \frac{k_1 [\text{OCl}^-] [\text{H}_2\text{O}]}{k_{-1} [\text{OH}^-]}$$

Substitute into the rate law of step 2

$$r = k_2 \frac{k_1 [\text{OCl}^-] [\text{H}_2\text{O}]}{k_{-1} [\text{OH}^-]} [\text{I}^-] = k_2 \frac{k_1}{k_{-1}} [\text{H}_2\text{O}] \frac{[\text{I}^-][\text{OCl}^-]}{[\text{OH}^-]}$$

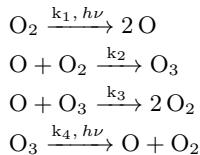
In aqueous solution, the concentration of solvent water $[\text{H}_2\text{O}]$ is effectively constant, so $k = k_2 \frac{k_1}{k_{-1}} [\text{H}_2\text{O}]$.

4 OZONE DEPLETION

A *radical* (自由基) is an atom, molecule or ion that has an unpaired valence electron (often denoted explicitly as $\cdot\text{X}$), thus is highly reactive.

4.1 Photochemical equilibrium in ozone layer

About 24 km above the Earth surface, the photochemical equilibrium between O_2 , O and O_3 maintain a small concentration of ozone and forms the ozone layer, which strongly absorbs ultraviolet light and protects life on Earth from being damaged.



$$\left\{ \begin{array}{l} \frac{d[\text{O}_2]}{dt} = -k_1[\text{O}_2] - k_2[\text{O}][\text{O}_2] + 2k_3[\text{O}][\text{O}_3] + k_4[\text{O}_3] \\ \frac{d[\text{O}]}{dt} = 2k_1[\text{O}_2] - k_2[\text{O}][\text{O}_2] - k_3[\text{O}][\text{O}_3] + k_4[\text{O}_3] \\ \frac{d[\text{O}_3]}{dt} = k_2[\text{O}][\text{O}_2] - k_3[\text{O}][\text{O}_3] - k_4[\text{O}_3] \end{array} \right.$$

Solution*

Solve the ODEs under the condition of *steady-state* $\frac{d[\text{O}_2]}{dt} = \frac{d[\text{O}]}{dt} = \frac{d[\text{O}_3]}{dt} = 0$ and conservation of oxygen $2[\text{O}_2] + [\text{O}] + 3[\text{O}_3] = 2[\text{O}_2]_0$. Let $[\text{O}_2] = x$, $[\text{O}] = y$, $[\text{O}_3] = z$ and $[\text{O}_2]_0 = C_0$.

$$\left\{ \begin{array}{l} \textcircled{1} \quad -k_1x - k_2xy + 2k_3yz + k_4z = 0 \\ \textcircled{2} \quad 2k_1x - k_2xy - k_3yz + k_4z = 0 \\ \textcircled{3} \quad k_2xy - k_3yz - k_4z = 0 \\ \textcircled{4} \quad 2x + y + 3z = 2C_0 \end{array} \right.$$

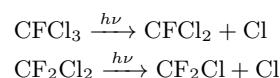
Because $\textcircled{3} = \textcircled{1} \times 2 + \textcircled{2}$, only two of $\textcircled{1}, \textcircled{2}, \textcircled{3}$ are independent and useful. Solve say $\textcircled{2}, \textcircled{3}, \textcircled{4}$ gives $\textcircled{2} - \textcircled{3} = k_1x - k_2xy + k_4z = 0$ and $y = 2C_0 - 2x - 3z$ leads to $z = \frac{-2k_2x^2 + (2k_2C_0 - k_1)x}{3k_2x + k_4}$. After substitution into $\textcircled{3}$, we arrive at a 4th order equation for x , which in turn can be reduced into a 2nd order equation for nonzero x :

$$(4k_2k_3k_4 - 6k_1k_2k_3 - 9k_1k_2^2)x^2 + (6C_0k_1k_2k_3 - 8C_0k_2k_3k_4 - 3k_1^2k_3 - 6k_1k_2k_4 + 2k_1k_3k_4)x + 4k_2k_3k_4C_0^2 - 2C_0k_1k_3k_4 - k_1k_4^2 = 0.$$

For a particular set of (k_1, k_2, k_3, k_4) , say $(1, 100, 100, 1)$, we find $[\text{O}_2] = 0.515[\text{O}_2]_0$, $[\text{O}] = 0.016[\text{O}_2]_0$ and $[\text{O}_3] = 0.318[\text{O}_2]_0$.

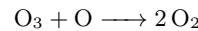
4.2 Photolysis of Freon

Chlorofluoromethanes (commercial name Freon), CF_2Cl_2 and CFCl_3 , produced by industry accumulate in atmosphere and dissociate into radicals under radiation

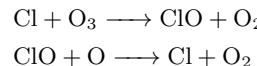


4.3 Chlorine-catalyzed depletion of ozone²

The originally slow overall reaction



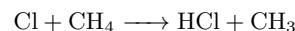
can be accelerated by chlorine radicals via two elementary steps



ClO is an *intermediate* first being produced then consumed; Cl is a *catalyst* first being consumed then produced, which increases the rate of the reaction.

4.4 Termination and removal of chlorine

Possible termination of chlorine radicals



HCl and ClO are eventually removed from atmosphere by downward diffusion and tropospheric process.

²Molina, Mario J., and F. Sherwood Rowland. "Stratospheric sink for chlorofluoromethanes: chlorine atom-catalysed destruction of ozone." Nature 249.5460 (1974): 810.

Chapter 7 Chemical Kinetics

Lecture 23 Activation and Catalysis

The rate r of chemical reactions changes not only with concentrations of reactants but also with temperature T , because the rate constant $k(T)$ is a function of T .

1 ACTIVATION PROCESS

The temperature dependence of $k(T)$ can be explained by Arrhenius's activation theory. The reaction process involves a barrier-crossing process, called *activation*, during which reactants form *activated complex* (Figure 1). The energy difference between activated complex and reactants is the *activation energy* E_a ¹. The barrier crossing is slow and determines the reaction rate. Once activated complex is formed, its decomposition into products is spontaneous and fast.

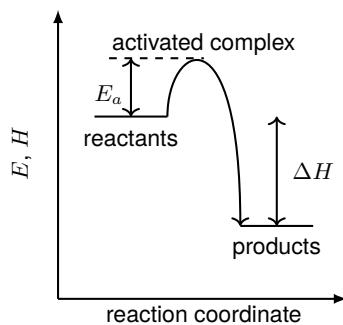


Figure 1: Enthalpy change ΔH of endothermic and exothermic reactions.

Quantitatively, $k(T)$ is determined by $E_a (> 0)$ through the **Arrhenius equation**

$$k = Ae^{-\frac{E_a}{RT}} \quad (1)$$

or equivalently

$$\ln k = -\frac{E_a}{RT} + \ln A \quad (2)$$

where E_a is the molar activation energy and A is a kinetic factor depending on the collision number. Note the Boltzmann factor form of the equation. In fact, the Arrhenius equation can be derived from a statistical mechanics treatment.

Increasing T will increase k . That is why the rate of reaction can be enhanced by heating. Some reactions have very high E_a thus need high-energy input like radiation $h\nu$ or ignition to initiate.

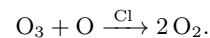
Catalysts do NOT change the reaction enthalpy ΔH nor the chemical equilibrium nor the thermodynamic spontaneity.

2 CATALYST

A catalyst is a substance that accelerates a chemical reaction without being permanently used up. Catalysts increase the rate con-

stant k by lowering the activation barrier (by changing reaction mechanism or path). Usually, catalysts first participate in the reaction then is regenerated and recovered at a later step.

In the example of ozone depletion, chlorine radical works as a catalyst. The overall catalyzed reaction can be written as

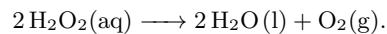


2.1 Homogeneous catalysis

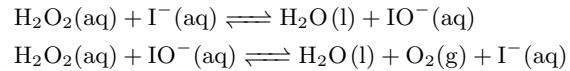
In this case, the catalyst is well-mixed with other reaction substances in the same phase (gaseous or solution).

Example

The originally slow decomposition hydrogen peroxide



can be catalyzed by, e.g. $\text{I}^-(\text{aq})$

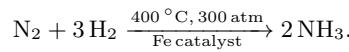


2.2 Heterogeneous catalysis and surface reaction

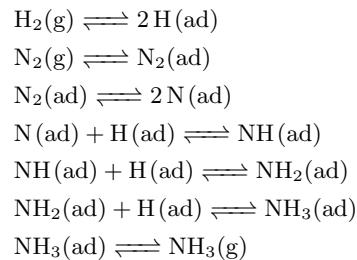
Heterogeneous catalysts are solids, often substances containing metallic elements such as platinum (Pt), nickel (Ni), copper (Cu) and iron (Fe)², upon whose surfaces reactants become adsorbed and react at a faster rate.

Example

The Haber-Bosch process of ammonia production (nitrogen fixation), with an overall reaction



The 2007 Nobel laureate Gerhard Ertl examined and mapped out the details of the elementary steps (Figure 2)³



¹More exactly, it should be an activation free energy F_a , but usually the entropy contribution is small. Also, the pV work is negligible, so we use H and E indistinguishably.

²In the case of well-dissolved metallic cations catalyzing solution reactions, it is a common homogeneous catalysis.

³See the Nobel lecture (lecture note, slides and video) of Prof. Gerhard Ertl at <https://www.nobelprize.org/prizes/chemistry/2007/ertl/lecture/>. The second half of the talk is about chemical oscillation and reaction diffusion of CO oxidation, which can be watched later.

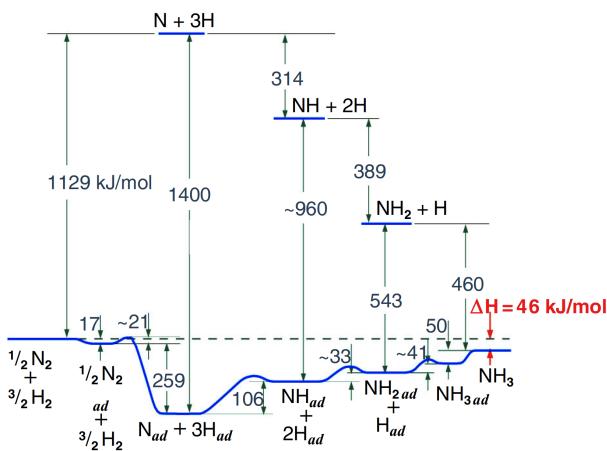
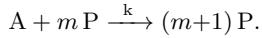


Figure 2: Reduction of activation barrier in the Haber-Bosch process of ammonia production. Adapted from the Nobel lecture note of Gerhard Ertl.

2.3 Autocatalysis

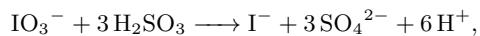
If a reaction is catalyzed by one of its own products, it is *autocatalytic* and generally takes the form of



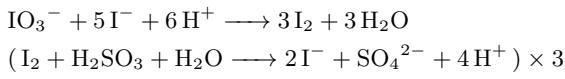
Namely, when the extra moles of products are not cancelled in the stoichiometric reaction, it indicates that the product is used as a catalyst.

Example

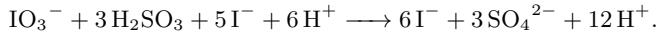
Consider an overall aqueous reaction



which turns out to be catalyzed by I^- and H^+ through two elementary steps

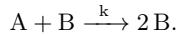


To recognize autocatalysis, the overall reaction is written as



Example*

Consider an autocatalytic reaction



The ODEs for reaction rates are

$$\begin{cases} \frac{d[A]}{dt} = -k[A][B] \\ \frac{d[B]}{dt} = k[A][B] \end{cases}$$

Under the initial conditions at $t = 0$, $[A]_0$ and $[B]_0$, and the conservation of matter $[A] + [B] = [A]_0 + [B]_0$, the first ODE becomes

$$\frac{d[A]}{dt} = -k[A]([A]_0 + [B]_0 - [A])$$

or $\frac{d[A]}{[A]([A]_0 + [B]_0 - [A])} = kdt$, namely $\frac{d[A]}{[A] - ([A]_0 + [B]_0)} = \frac{d[A]}{[A]} = k([A]_0 + [B]_0) dt$. The solution is a logistic curve (Figure 3)

$$\begin{cases} [A] = \frac{[A]_0 + [B]_0}{1 + \frac{[B]_0}{[A]_0} e^{([A]_0 + [B]_0)kt}} \\ [B] = \frac{[A]_0 + [B]_0}{1 + \frac{[A]_0}{[B]_0} e^{-([A]_0 + [B]_0)kt}} \end{cases}$$

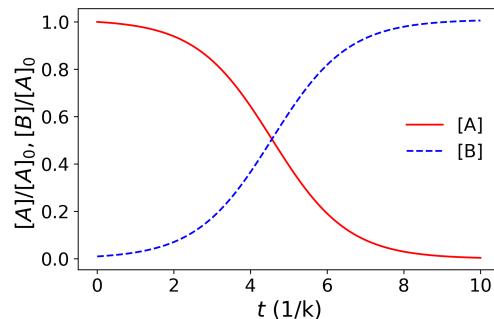
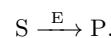


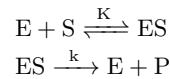
Figure 3: Concentration change in the autocatalytic reaction $A + B \xrightarrow{k} 2B$ at initial condition $[B]_0 = 0.01[A]_0$.

3 ENZYME

An enzyme E, often a protein molecule, is a biological catalyst in living organisms. An overall enzyme-catalyzed reaction from substrate S to product P



assumes two elementary steps



Step 1 is a fast chemical equilibrium with equilibrium constant K

$$\frac{[ES]}{[E][S]} = K.$$

Step 2 is a slow RDS $r = k[ES] = kK[E][S]$.

The total enzyme concentration is conserved $[E]_0 = [ES] + [E]$.

So

$$\frac{[E]_0 - [E]}{[E][S]} = K \Rightarrow [E] = \frac{[E]_0}{K[S] + 1}.$$

Substitute above relationship into the rate law

$$r = kK \frac{[E]_0}{K[S] + 1} [S]$$

arriving at the **Michaelis-Menten equation**

$$r = -\frac{d[S]}{dt} = \frac{k[S][E]_0}{[S] + 1/K}. \quad (3)$$

When $[S] \ll 1/K$, $r \approx kK[S][E]_0 \propto [S]$.

When $[S] \gg 1/K$, $r \approx k[E]_0 = \text{constant}$.

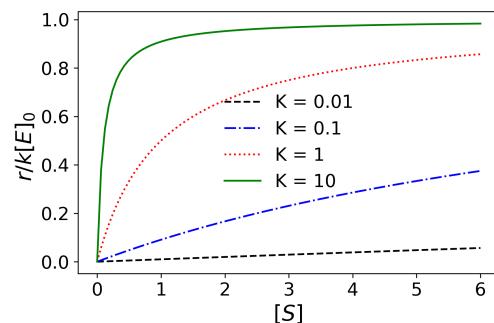


Figure 4: Rate of enzyme-catalyzed reaction from the Michaelis-Menten model.

Chapter 7 Chemical Kinetics

Lecture 24 Mathematical Modeling of Infectious Diseases

1 SIR MODEL OF EPIDEMICS

In the Susceptibles–Infectives–Recovered (SIR) model, the total population $N = S + I + R$ is divided into three classes (or compartments), where, as a function of time t ,

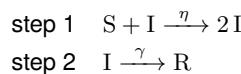
$S(t)$ is the number of susceptibles who are still able to be, but not yet, infected by the disease;

$I(t)$ is the number of infectives who currently have the disease and can transmit it to susceptibles;

$R(t)$ is the number of recovered (or removed) who, after being infected, have recovered and become immune to the disease.

They cannot transmit the disease to others. If total N is held constant, dead people should also be grouped into this class.

In analogy to chemical reactions, the SIR model describes two elementary steps



which are modeled by the ordinary differential equations (ODEs)

$$\left\{ \begin{array}{ll} \text{susceptibles} & \frac{dS}{dt} = -\eta SI \\ \text{infectives} & \frac{dI}{dt} = \eta SI - \gamma I \\ \text{recovered} & \frac{dR}{dt} = \gamma I \end{array} \right.$$

with initial conditions, e.g. $S(0) > 0$, $I(0) > 0$ and $R(0) = 0$.

It is sometimes convenient to express the ODE with number fraction of each class

$$\left\{ \begin{array}{ll} \text{susceptibles} & \frac{ds}{dt} = -\eta N si = -\beta si \\ \text{infectives} & \frac{di}{dt} = \eta N si - \gamma i = \beta si - \gamma i \\ \text{recovered} & \frac{dr}{dt} = \gamma i \end{array} \right.$$

where $s(t) = S(t)/N$, $i(t) = I(t)/N$, $r(t) = R(t)/N$ and $s(t) + i(t) + r(t) = 1$. The initial conditions are $s_0 = S(0)/N$, $i_0 = I(0)/N$ and $r_0 = R(0)/N = 0$.

2 PARAMETERS OF SIR MODEL

An *adequate contact* is a close contact between two people that is sufficient enough for transmission of the disease if the contact is between a susceptible and an infective. $-\frac{dS}{dt}$ should equal the number of adequate contacts between susceptibles and infectives per unit time, which is written as ηSI according to law of mass action.

Define

$$\beta = \eta N,$$

$$\text{then } \eta SI = \beta \frac{I}{N} S = \beta iS.$$

β is contact rate or infection rate, which is the number of adequate contacts per person (can be any class) per unit time.

βi is the number of adequate contacts with infectives per person per unit time, considering there is i fraction of infectives in the population.

βiS is the number of adequate contacts with infectives by S susceptibles per unit time, thus the number of new disease cases per unit time.

γ is the removal rate of infectives, that is, the probability or the extent (percentage) of recovery for an infective per unit time. For example, $\gamma = 0.05$ per day = $\frac{1}{20}$ days means that an infective recovers 5% each day or it takes 20 days for an infective to fully recover. If there are $I = 100$ infectives currently, there will be $\gamma I = 0.05 \times 100 = 5$ infectives to recover that day (we assume the percentage of recovery of different infectives can add up together to indicate full recovery of certain infectives).

$\tau = 1/\gamma$ is the average infectious period, that is, the average time that an infective spends before full recovery.

$\sigma = \frac{\beta}{\gamma} = \beta\tau$, contact number, is the average number of adequate contacts of an infective during the infectious period.

R_0^1 , basic reproduction rate (or basic reproduction number, basic reproduction ratio), is the average number of (secondary) infectives produced when an (primary) infective is introduced into a host population where everyone is susceptible. In this SIR model, we consider

$$R_0 = \frac{\eta N}{\gamma} = \frac{\beta}{\gamma} = \sigma. \quad (1)$$

If $R_0 < 1$, an infective transmits the disease to less than one susceptible before himself/herself is recovered. The epidemic can break out only if $R_0 > 1$.

R_t , replacement number or effective reproduction number, is the average number of (secondary) infectives produced by an (primary) infective at time t during the outbreak of the disease when there are $s(t) = S(t)/N$ fraction of susceptibles in the population.

$$R_t = \frac{\eta S(t)}{\gamma} = \frac{\beta s(t)}{\gamma} = \sigma s(t). \quad (2)$$

Note that $R_t = R_0$ when $S = N$ or $s = 1$.

p_c , herd immunity threshold, is the critical fraction of immune population (either by recovering from an earlier infection or by vaccination) needed to stop the epidemic. This threshold is found by $1 = R_t = R_0 s(t) = R_0 (1 - p_c)$, i.e.

$$p_c = 1 - \frac{1}{R_0}. \quad (3)$$

¹not to be confused with the initial condition of $R(0)$

So $R_0 = 2$ needs $p_c = 50\%$ and $R_0 = 3$ needs $p_c = 66.7\%$ immune population to stop the epidemic.

Table 1: Examples of R_0 of p_c for various infectious diseases.

disease	R_0	p_c
Measles	12-18	92-95%
Smallpox, Polio	5-7	80-86%
SARS (2003)	2-5	50-80%
Ebola	1.5-2.5	33-60%
COVID-19	2.5-4	60-75 % ²

3 TRAJECTORY AND PHASE PORTRAIT OF SIR MODEL

The trajectory of $S(t)$, $I(t)$, $R(t)$ (or $s(t)$, $i(t)$, $r(t)$) as a function of time t typically looks like

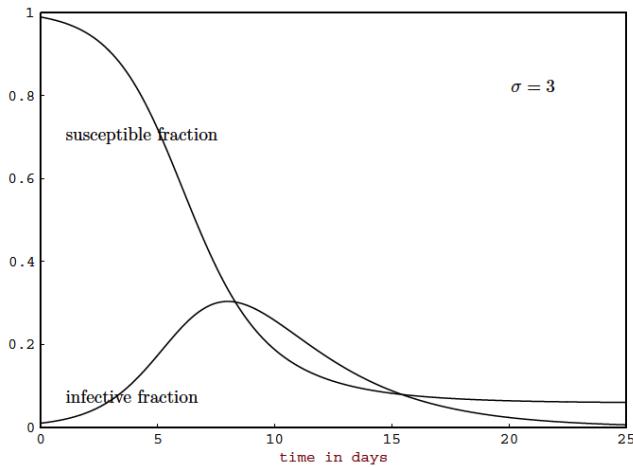


Figure 1: Trajectories of $i(t)$, $s(t)$ as a function of time t for the SIR model with $\sigma = 3$ and $1/\gamma = 3$ days. (Hethcote, Herbert W. "The mathematics of infectious diseases." SIAM Review 42.4 (2000): 599-653.)

There is no easy analytical solution to the trajectories, but they can be obtained numerically.

The phase portrait depicts $I(t)$ v.s. $S(t)$ (or $i(t)$ v.s. $s(t)$) and obeys implicit equation

$$i(t) + s(t) - \frac{1}{\sigma} \ln s(t) = i_0 + s_0 - \frac{1}{\sigma} \ln s_0 = 1 - \frac{1}{\sigma} \ln s_0 \quad (4)$$

Proof:

$$\frac{di}{ds} = \frac{\beta si - \gamma i}{-\beta si} = -1 + \frac{\gamma}{\beta} \frac{1}{s} = -1 + \sigma^{-1} s^{-1}$$

$$di = -ds + \sigma^{-1} s^{-1} ds$$

$$\int_{i_0}^{i(t)} di = - \int_{s_0}^{s(t)} ds + \sigma^{-1} \int_{s_0}^{s(t)} s^{-1} ds$$

$$i(t) - i_0 = s_0 - s(t) + \sigma^{-1} (\ln s(t) - \ln s_0)$$

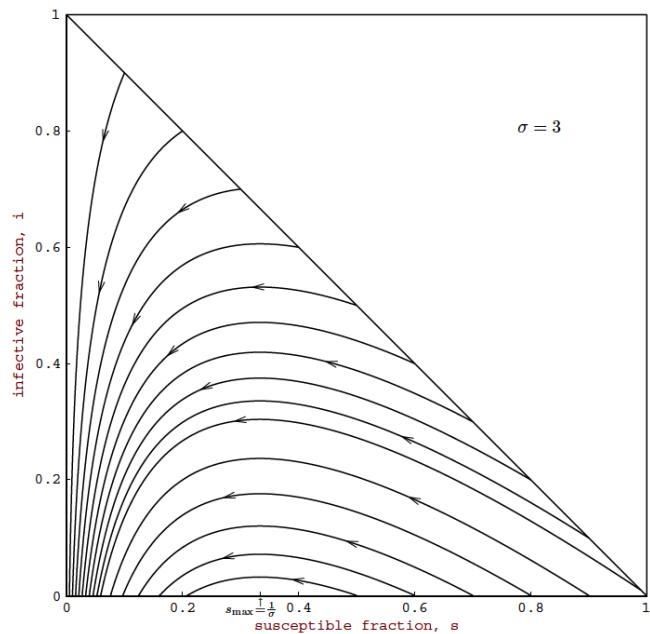


Figure 2: Phase portrait $i(t)$ v.s. $s(t)$ of the SIR model with $\sigma = 3$. Arrows point to the direction of increasing time t . (Hethcote, Herbert W. "The mathematics of infectious diseases." SIAM Review 42.4 (2000): 599-653.)

The peak position value of s and i are

$$s_{\text{peak}} = \sigma^{-1} \quad (5)$$

Proof:

$$\frac{di}{dt} = 0 \Rightarrow \beta si - \gamma i = 0$$

$$\beta s - \gamma = 0$$

and

$$i_{\text{peak}} = 1 - \sigma^{-1} - \sigma^{-1} \ln(\sigma s_0) \quad (6)$$

Proof: Substitute Eq. (5) into Eq. (4).

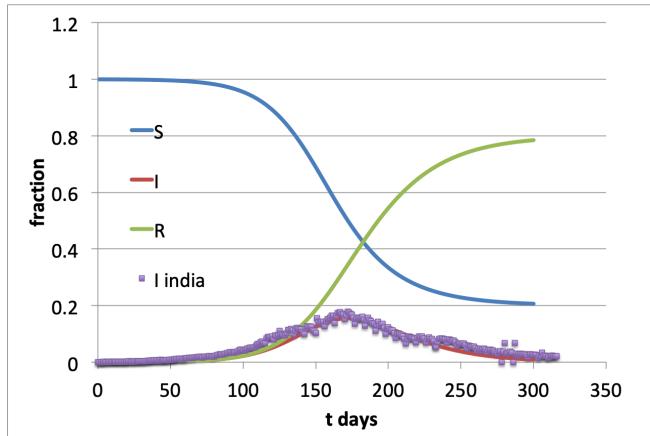


Figure 3: SIR model fits to the COVID-19 data of India.

4 COVID-19

We can fit SIR model to COVID-19 data³ and try to estimate R_0 . Taking the data from India as an example⁴, we can roughly use it in the fitting

²Fontanet, Arnaud, and Simon Cauchemez. "COVID-19 herd immunity: where are we?." Nature Reviews Immunology 20.10 (2020): 583-584. Randolph, Haley E., and Luis B. Barreiro. "Herd immunity: understanding COVID-19." Immunity 52.5 (2020): 737-741.

³<https://ourworldindata.org/coronavirus>

⁴<https://ourworldindata.org/coronavirus/country/india?country=~IND>

$\gamma \approx 0.05$ per day

$\beta \approx 0.1$ adequate contacts per person per day

$s_{\text{peak}} = 0.5$

$i(0) \approx 100/550000 = 0.00018182$

$i_{\text{peak}} \approx 0.1535$

$R_0 = \sigma \approx 2$

- natural birth and death rate

- demography (age, gender, etc)

- other classes, e.g. passive immunity, exposed but not infectious, etc.

- spatial inhomogeneity

- human contact network structure

- random noise

Be careful that predictions from mathematical modeling could be quite off.⁵

5 LIMITATIONS AND MODIFICATIONS OF SIR MODEL

SIR model assumes that people are well mixed in the population, but neglects many other realistic factors.

⁵The Hard Lessons of Modeling the Coronavirus Pandemic, <https://www.quantamagazine.org/the-hard-lessons-of-modeling-the-coronavirus-pandemic-20210128/>

Chapter 7 Chemical Kinetics

Lecture 25 Chemical Oscillation

So far, in all the reaction systems we considered, the concentration of substances goes to steady-state value or zero in the long run $t \rightarrow 0$. Here we will show that, in certain systems, the concentration of reaction substances can oscillate periodically between two values. We begin with an analogous problem in evolutionary dynamics.

1 PREDATOR-PREY MODEL

In an ecosystem where preys N (e.g. hare) feed on abundant food and predators P (e.g. lynx) hunt the preys for food, the time evolution of their population oscillate roughly periodically (Figure 1).

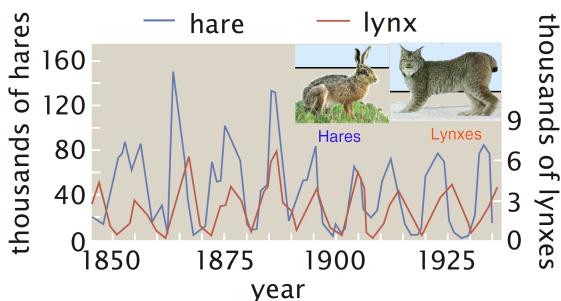


Figure 1: Population of hare and lynx as a function of time. Adapted from *Physical Biology of the Cell* by Rob Phillips et al.

A possible theory for this dynamic system is the **Lotka–Volterra equations**¹

$$\begin{cases} \text{prey} & \frac{dN}{dt} = \alpha N - \beta NP \\ \text{predator} & \frac{dP}{dt} = \gamma NP - \delta P \end{cases}$$

with $\alpha, \beta, \gamma, \delta > 0$. In absence of interaction (βNP or γNP), $N(t)$ grows exponentially (because of the abundance of food) but $P(t)$ decays exponentially.

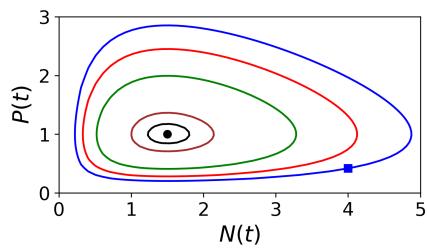


Figure 2: $P(t)$ vs $N(t)$ at $\alpha = \beta = 2$, $\gamma = 1$ and $\delta = 1.5$. From outer to inner contours, $V = 4.5, 4.0, 3.5, 3.0, 2.92$. Black circle marks the fixed point at $(1.5, 1.0)$. Blue square is at initial condition $(4.0, 0.41839)$.

¹ Lotka, A J. "Analytical Note on Certain Rhythmic Relations in Organic Systems." Proceedings of the National Academy of Sciences of the United States of America vol. 6,7 (1920): 410-5. doi:10.1073/pnas.6.7.410

² Alfred J. Lotka, "Contribution to the Theory of Periodic Reactions", J. Phys. Chem. 1910, 14, 3, 271-274. "UNDAMPED OSCILLATIONS DERIVED FROM THE LAW OF MASS ACTION.", J. Am. Chem. Soc. 1920, 4, 28, 1595-1599

The general solution $N(t)$ and $P(t)$ is implicitly related by

$$\gamma N - \delta \ln N + \beta P - \alpha \ln P = V$$

where V is a constant depending on the initial condition $N(0) = N_0$ and $P(0) = P_0$. We can plot the contours of $P(t)$ vs $N(t)$ at different V 's (Figure 2). Picking up one initial condition (N_0, P_0) determines V and we can plot the corresponding population evolution over time using numerical solution to the ODEs (Figure 3).

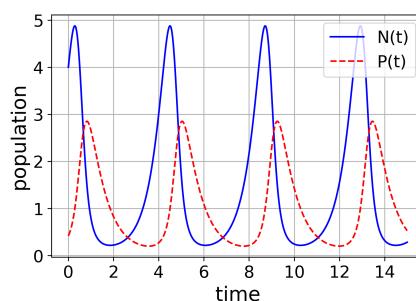
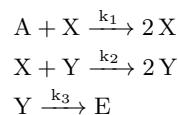


Figure 3: Time evolution of $N(t)$ (prey) and $P(t)$ (predator) at $\alpha = \beta = 2$, $\gamma = 1$ and $\delta = 1.5$. Initial condition $(4.0, 0.41839)$ corresponds to $V = 4.5$.

2 CHEMICAL OSCILLATION

It can be recognized that the predator-prey system is equivalent to an autocatalytic reaction system in which the concentration of chemicals oscillate. In fact, Lotka was originally a chemist and started to investigate the problem in the context of chemical oscillation first, before realizing its relationship to biological systems².

Consider a model overall reaction $A \longrightarrow E$ consisting of three elementary steps, two of which are autocatalytic



The rate laws for X and Y are

$$\begin{cases} \frac{d[X]}{dt} = k_1[A][X] - k_2[X][Y] \\ \frac{d[Y]}{dt} = k_2[X][Y] - k_3[Y] \end{cases}$$

In excessive amount of A , $[A]$ is a constant. If we set $\alpha = k_1[A]$, $\beta = \gamma = k_2$ and $\delta = k_3$, the equations become equivalent to the ecological Lotka–Volterra equations. We may view A as the food of preys, like grass, and E as dead predators.

3 EXAMPLES

Many reaction systems are found to exhibit chemical oscillation, such as oxidation of iodine (I_2) by H_2O_2 ³, iodine clock⁴, Pt-catalyzed surface oxidation of CO⁵ and many others⁶. The best-known example is the Belousov-Zhabotinsky reaction (BZ reaction), created in a mixture of potassium bromate ($KBrO_3$), malonic acid ($CH_2(COOH)_2$), and manganese sulfate ($MnSO_4$) prepared in a heated solution with sulfuric acid (H_2SO_4) as solvent⁷. The mechanism for these reactions can be very complex, sometimes involving dozens of elementary steps. Many details are still unknown, but they all include some types of autocatalytic reactions responsible for the interacting term (xy) in the ODEs and nonlinear dynamics. Certain simplified and idealized theoretical models have been proposed to explain the mechanism, such as the brusselator⁸ and the oregonator⁹.

³William C. Bray, "A PERIODIC REACTION IN HOMOGENEOUS SOLUTION AND ITS RELATION TO CATALYSIS.", J. Am. Chem. Soc. 1921, 43, 6, 1262-1267; William C. BrayHerman A. Liebhafsky, "REACTIONS INVOLVING HYDROGEN PEROXIDE, IODINE AND IODATE ION. I. INTRODUCTION", J. Am. Chem. Soc. 1931, 53, 1, 38-44

⁴Thomas S. Briggs and Warren C. Rauscher, "An oscillating iodine clock", J. Chem. Educ. 1973, 50, 7, 496

⁵K. Krischer, M. Eisworth, and G. Ertl, "Oscillatory CO oxidation on Pt(110): Modeling of temporal self-organization", J. Chem. Phys. 96, 9161 (1992)

⁶Hans Degn, "Oscillating chemical reactions in homogeneous phase", Journal of Chemical Education 1972, 49, 5, 302

⁷Belousov B. P., "A periodic reaction and its mechanism", in Collection of short papers on radiation medicine for 1958, Med. Publ., Moscow, 1959.

⁸Invented by researchers from Brussel including Ilya Prigogine.

⁹Field, Richard J.; Noyes, Richard M. (1974). "Oscillations in chemical systems. IV. Limit cycle behavior in a model of a real chemical reaction". J. Chem. Phys. 60 (5): 1877–1884.

Chapter 7 Chemical Kinetics

Lecture 26 Reaction-Diffusion Model

So far, for all reactions discussed before, we assume spatial homogeneity, i.e. substances are well-mixed such that their concentration is only a function of time $[A](t)$. In physics term, this is called *mean-field* picture.

In this lecture, we will introduce a special type of reaction, in which the concentration is a function of both time and position, $[A](t, \mathbf{r})$ (or $[A](t, x)$ in one-dimensional systems, $[A](t, x, y)$ in two-dimensional systems). In this case, the spatial distribution of chemicals is non-uniform, because the diffusion time scale τ_D is slightly larger than or comparable with reaction time scale τ_R , $\tau_D \gtrsim \tau_R$ ¹. Such *reaction-diffusion* systems may give rise to interesting spatial-temporal patterns, *Turing patterns*, that provide the chemical basis of biological *morphogenesis*. While chemical oscillations are described by ODEs, reaction-diffusion models are embodied in partial differential equations (PDEs).

Diffusion*

Diffusion is the net motion of particles due to random walks or Brownian motion. Macroscopic diffusion of particles is from high concentration to low concentration region.

Diffusion constant D , which has the dimension of $\frac{L^2}{T}$, characterizes how fast particles diffuse.

Diffusion equation describes the spatial-temporal evolution of concentration $c(t, \mathbf{r})$

$$\frac{\partial c}{\partial t} = D \nabla^2 c = D \left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2} \right). \quad (1)$$

Derivation (in 1D):

By *Fick's law*, the flux J of materials through a unit area per unit time, is proportional to the gradient of the concentration of the material

$$J = -D \frac{\partial c}{\partial x}. \quad (2)$$

The rate of change of the total amount of materials in the small interval $x_0 < x < x_0 + \Delta x$ is equal to the rate of flow across the boundary

$$\frac{\partial}{\partial t} \int_{x_0}^{x_0 + \Delta x} c(x, t) dx = J(x_0, t) - J(x_0 + \Delta x, t) \quad (3)$$

$$\frac{\partial}{\partial t} \frac{\int_{x_0}^{x_0 + \Delta x} c(x, t) dx}{\Delta x} = - \frac{J(x_0 + \Delta x, t) - J(x_0, t)}{\Delta x}$$

In the limit of $\Delta x \rightarrow 0$,

$$\frac{\partial}{\partial t} c(x, t) = - \frac{\partial J}{\partial x} = D \frac{\partial^2 c}{\partial x^2}.$$

Starting from a point source at $x = 0$ and $t = 0$, $c(x, 0) = Q\delta(x)$, where $\delta(x)$ is the Dirac delta function with the property $\int \delta(x) dx = 1$, the concentration profile at later time $t > 0$ is a Gaussian distribution

$$c(x, t) = \frac{Q}{\sqrt{4\pi Dt}} e^{-\frac{x^2}{4Dt}}, \quad t > 0. \quad (4)$$

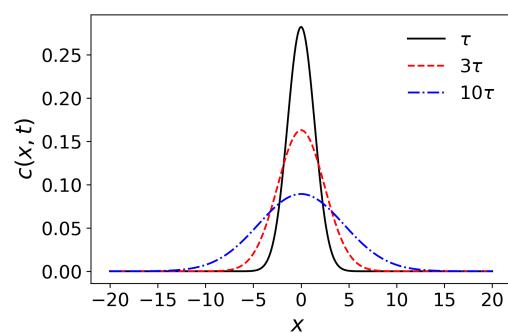


Figure 1: Gaussian density profile $c(x, t)$ at time $t = \tau$, $t = 3\tau$ and $t = 10\tau$.

1 MORPHOGENESIS

Morphogenesis, “beginning of the shape”, is the biological process that causes organisms to develop shapes, such as the development of embryonic cells and skin patterns of animals.

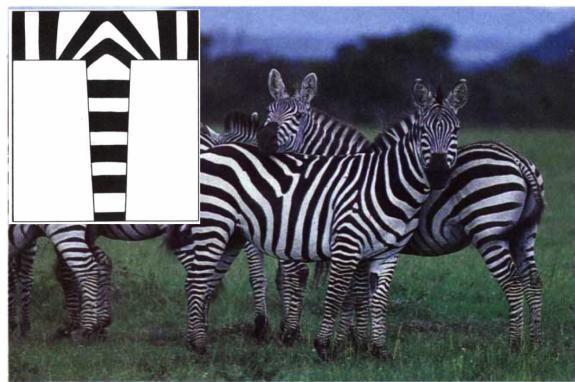


Figure 2: Zebra stripes and a theoretical pattern produced by a reaction-diffusion model. (Adapted from Ref.²)

Alan Turing is the first scientist who realized that such patterns

¹In most reactions, $\tau_D \ll \tau_R$ such that substances are always well-mixed or $\tau_D \gg \tau_R$ such that the reaction is completely finished locally.

²Murray, James D. "How the leopard gets its spots." *Scientific American* 258, no. 3 (1988): 80-87.

³A media coverage of the history and background is at <https://www.chemistryworld.com/feature/turing-patterns/4991.article>. A review by the same author, Ball, Philip.

"Forging patterns and making waves from biology to geology: a commentary on Turing (1952)'The chemical basis of morphogenesis'." *Philosophical Transactions of the Royal Society B: Biological Sciences* 370, no. 1666 (2015): 20140218.

can be explained by spatial-temporal modulation of chemical signals in reaction-diffusion systems³.

2 TURING PATTERN

In Turing's reaction-diffusion model⁴, the formation of patterns is caused by reaction between diffusing *morphogens*, "shape-formers", i.e. chemical agents that cause morphogenesis.

A simplest version involves an *activator* U and an *inhibitor* V in 1D⁵.

$$\begin{cases} \frac{\partial u}{\partial t} = a_u u + b_u v + c_u + D_u \frac{\partial^2 u}{\partial x^2} \\ \frac{\partial v}{\partial t} = a_v u + b_v v + c_v + D_v \frac{\partial^2 v}{\partial x^2} \end{cases}.$$

$$\begin{cases} u_i(t + \Delta t) = u_i(t) + \Delta t \left(a_u u_i(t) + b_u v_i(t) + c_u + D_u \frac{u_{i+1}(t) + u_{i-1}(t) - 2u_i(t)}{\Delta x^2} \right) \\ v_i(t + \Delta t) = v_i(t) + \Delta t \left(a_v u_i(t) + b_v v_i(t) + c_v + D_v \frac{v_{i+1}(t) + v_{i-1}(t) - 2v_i(t)}{\Delta x^2} \right) \end{cases},$$

where partial derivatives are approximated by finite differences. Periodic boundary condition is used, for which $u_N = u_0$ and $u_{-1} = u_{N-1}$ etc.

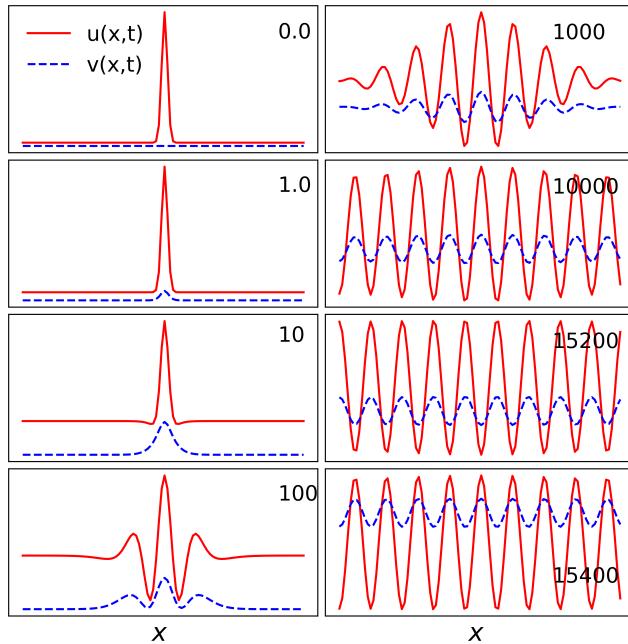


Figure 3: Time evolution of relative⁶ concentration profile of activator u and inhibitor v at time moment $t = 0, 1, 10, 100, 1000, 10000, 15200, 15400$.

We solve the above numerical equations for $(a_u, b_u, c_u) = (0.08, -0.08, 0.04)$ and $(a_v, b_v, c_v) = (0.1, 0.0, -0.15)$. $(D_u, D_v) =$

where $u(x, t)$ and $v(x, t)$ are local concentrations of the activator and inhibitor. Different choices of parameters and coefficients lead to different solutions. To develop Turing pattern, the diffusion of inhibitor is much faster than that of activator, i.e. $D_v \gg D_u$. $a_u, a_v > 0$ indicates the activator promotes the production of both U and V . $b_u < 0$ means the inhibitor reduces the production of U . c_u, c_v together set the steady-state concentration of U and V averaged over space. We can solve the 1D PDEs using numerical forward integration method.

Solution*

We divide the 1D box of length L into N parts, each of length $\Delta x = \frac{L}{N}$. At a given moment t , u and v then has discrete values $u_i(t)$ and $v_i(t)$ with $i = 0, 1, 2, \dots, N - 1$. The concentration at $t + \Delta t$ is

$$\begin{cases} u_i(t + \Delta t) = u_i(t) + \Delta t \left(a_u u_i(t) + b_u v_i(t) + c_u + D_u \frac{u_{i+1}(t) + u_{i-1}(t) - 2u_i(t)}{\Delta x^2} \right) \\ v_i(t + \Delta t) = v_i(t) + \Delta t \left(a_v u_i(t) + b_v v_i(t) + c_v + D_v \frac{v_{i+1}(t) + v_{i-1}(t) - 2v_i(t)}{\Delta x^2} \right) \end{cases},$$

(0.02, 0.5). $L = 60$ and $N = 100$ such that $\Delta x = 0.6$. $\Delta t = 0.1$. Initial condition is set for constant $v_i(0) = 0.4$ and a Gaussian source of $u_i(0)$

$$u_i(0) = \frac{10}{2\pi} e^{-\frac{(i-50)^2}{2}} + 0.5, \quad i = 0, 1, 2, \dots, 99.$$

The solution up to time $t = 16000$ (1.6×10^5 time steps) is summarized in Figure 3. A standing wave Turing pattern is developed.

See Ref.⁷ for more examples of Turing patterns.

3 CHEMICAL EXAMPLES

The chemical oscillation systems introduced earlier, such as the BZ reaction, can exhibit Turing patterns⁸, if the diffusion of chemicals is slowed down, for instance, by laying the system in shallow 2D disks or placing chemicals in gels^{9 10}.

4 SELF-ORGANIZATION AND NON-EQUILIBRIUM THERMODYNAMICS

Questions: is the reaction-diffusion system at equilibrium or not? Does the entropy, if defined for non-equilibrium macrostates, increase or decrease? What drives self-organization of the system from disordered to ordered state? Where does the order in living organisms come from?

⁴Turing, Alan M. "THE CHEMICAL BASIS OF MORPHOGENESIS." Philosophical Transactions of the Royal Society of London. Series B, Biological Sciences 237.641 (1952): 37-72.

⁵Kondo, Shigeru, and Takashi Miura. "Reaction-diffusion model as a framework for understanding biological pattern formation." Science 329.5999 (2010): 1616-1620. Need to see its supplemental information for mathematical details. Also, see its simulation code to visualize the results of the model.

⁶It can be seen that, if u, v is a solution to the PDEs above, then a linear transform $(ku + m, kv + m)$ is also a solution to the same PDE. In this figure, we shift and normalize u, v such that u is bounded between $[0, 1]$ (In this case, v may be negative).

⁷A useful graphic visualization tool is at <https://github.com/GollyGang/ready>

⁸See videos at Envisioning Chemistry <https://www.envisioningchemistry.com/chemical-patterns>

⁹Field, Richard J. "A reaction periodic in time and space. A lecture demonstration." Journal of Chemical Education 49, no. 5 (1972): 308.

¹⁰Nettesheim, S., A. Von Oertzen, H. H. Rotermund, and G. Ertl. "Reaction diffusion patterns in the catalytic CO-oxidation on Pt (110): Front propagation and spiral waves." The Journal of chemical physics 98, no. 12 (1993): 9977-9985.

Supplement: Glossary of Mechanics*

A

Acceleration ($\vec{a} = \frac{d\vec{v}}{dt} = \frac{d^2\vec{r}}{dt^2}$ or $\vec{a} = \dot{\vec{v}} = \ddot{\vec{r}}$ in Newton's fluxion notation) is the rate of change of velocity of an object with respect to time. Mathematically, it is the first order derivative of velocity and the second order derivative of position with respect to time.

Amplitude (see Wave)

Angular frequency (angular speed) ($\omega = \frac{d\theta}{dt}$) is the rate of change of phase (angle) θ with respect to time t during rotation. It has a unit of radian/s. For a uniform circular motion with radius r , frequency f and period T , $\omega = \frac{2\pi}{T} = 2\pi f$ and is related to the linear speed v by $v = \omega r$.

Angular velocity $\vec{\omega}$ is a vector whose magnitude is the angular speed ω and whose direction is perpendicular to the rotation plane and determined by the right-hand rule.

Angular momentum ($\vec{L} = \vec{r} \times \vec{p}$) of a rotating body is a vector, which is perpendicular to the linear momentum \vec{p} and the position \vec{r} about the center of rotation.

C

Cartesian coordinates are two- or three-dimensional coordinates in which all the axes, conventionally denoted the x- and y-axes (and z-axis), are chosen to be linear and mutually perpendicular (orthogonal).

Centripetal force A force which keeps a body moving along a circular path and is directed along the radius towards the center. For an object of mass m moving at linear speed v along a path with radius of curvature r , its magnitude is $F_c = \frac{mv^2}{r}$.

Circular motion is a movement of an object along the circumference of a circle or rotation along a circular path.

Classical mechanics (Newtonian mechanics) describes the motion of macroscopic objects in terms of deterministic trajectories using Newton's laws, which break down in the limit of either high speed or microscopic length scale.

Conservation law In physics, a conservation law states that a particular measurable physical quantity of an isolated physical system does not change as the system evolves over time. Examples are:

- Conservation of energy
- Conservation of momentum, if there are no external forces acting on the system.

- Conservation of angular momentum, if there are no external torques acting on the system.

Conservative force (see Force)

Cross product (vector product) $\vec{a} \times \vec{b}$ of two vectors \vec{a} and \vec{b} is a vector with the magnitude $ab \sin \theta$, where θ is the angle between \vec{a} and \vec{b} , and in the direction perpendicular to the plane spanned by \vec{a} and \vec{b} satisfying the right-hand rule. In three-dimensional Cartesian coordinate system, $\vec{a} \times \vec{b} = (a_y b_z - a_z b_y, a_z b_x - a_x b_z, a_x b_y - a_y b_x)$.

D

de Broglie wave (matter wave) In quantum mechanics point of view, any body moving with momentum of magnitude p , at the same time, behaves like a wave with wavelength $\lambda_B = \frac{h}{p}$.

Degrees of freedom is the number of parameters of the system that may vary independently.

Density (mass density) (ρ) is the amount of matter per unit volume. For homogeneous bodies, the density is constant everywhere. For inhomogeneous bodies, the density profile $\rho(\vec{r})$ is a function of position \vec{r} .

Dimension (of physical quantities) The dimension of a physical quantity A is written as $[A]$ and does not change with the unit in which A is measured. By convention, the dimension of mass, time and length is written as $[M]$, $[T]$ and $[L]$. A quantity without unit, e.g. number of particles, is said to be *dimensionless* or to have the dimension of 1.

Dimension (of space or object) A dimension is a measurable extent. Number of dimensions is the number of independent parameters or coordinates (or degrees of freedom) that are needed for defining the space or object. The shorthand for n -dimensional is nD or nd .

Dot product (scalar product, inner product) $\vec{a} \cdot \vec{b}$ of two vectors \vec{a} and \vec{b} is a scalar with magnitude $ab \cos \theta$, where θ is the angle between \vec{a} and \vec{b} . In three-dimensional Cartesian coordinate system, $\vec{a} \cdot \vec{b} = a_x b_x + a_y b_y + a_z b_z$.

E

Energy A calculable scalar quantity that comes in many different forms whose total amount is always conserved. Loosely speaking, energy is the ability to do work. Examples are:

- Chemical energy is the energy stored in chemical bonds, which can be released during chemical reaction (rearrangement of atoms in reacting molecules).

- Electrical energy is the energy due to the ability of electric field to move electric charges.
- Kinetic energy is the energy of motion. For a moving body of mass m and speed v , it is $K = \frac{1}{2}mv^2$.
- Mechanical energy is the sum of potential energy and kinetic energy that can be used to do work.
- Nuclear energy is the energy stored in nucleus of atoms bonded by strong force, which can be released during nuclear reaction (change and rearrangement of protons and neutrons).
- Potential energy is the energy resulted from the location relative to a reference within a force field. In the gravitational field, $U = mgh$, where h is the height with respect to the reference.
- Radiant energy is the energy of electromagnetic waves that can be received by shining the waves upon objects.
- Thermal energy (internal energy) is due to random thermal motion of constituent atoms or molecules at finite temperatures, which can be used to do work or release heat.

F

Field is a continuous spatial distribution (can be time-dependent too) of a physical quantity, which can be either a scalar or a vector. For instance, the potential energy field $U(\vec{r})$ and the velocity field $\vec{v}(\vec{r}, t)$.

Frequency (see Wave)

Force is the interaction, intuitively, a push or a pull, that will change the motion of an object by causing it to accelerate.

- *Conservative force* is a force which does path-independent work when moving an object between two positions. Conservative force can be expressed as the negative derivative $-\frac{dU}{dx}$ (or gradient $-\nabla U$ in higher dimensions) of some potential energy field U . The mechanical energy of a system under conservative forces is conserved.
- *Non-conservative force* The work done by a non-conservative force depends on the path, for instance, friction.

G

Gravity (gravitation, gravitational force) is the attraction among all things with mass or energy.

Gravitational acceleration (acceleration of free fall) (\vec{g}) is the acceleration due to gravity, in particular, at the surface of Earth, with magnitude $g = 9.8\text{m/s}^2$.

Gravitational constant $G = 6.67 \times 10^{-11}\text{Nm}^2\text{kg}^{-2}$ is the coefficient of proportionality in the law of universal gravitation, which was first measured by Henry Cavendish in 1798.

Hamiltonian \mathcal{H} is the total energy (kinetic plus potential) of a system, viewed as a function of its degrees of freedom. For a system of N particles, \mathcal{H} is a function of their positions and momenta, i.e. $\mathcal{H}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, \mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_N)$.

Harmonic oscillator (see Simple harmonic oscillator)

Hertz ($\text{Hz} = \text{s}^{-1}$) is the unit of frequency.

Hooke's law states that the restoring force $F = -kx$ trying to bring a spring back to equilibrium position, when it is extended or compressed by a distance x , is proportional to x with coefficient k , called *stiffness* of the spring.

I

Inertia (of an object) is the tendency to preserve its present state or the resistance to change its velocity, due to the existence of its mass.

Inner product (see Dot product)

J

Joule ($\text{J} = \text{N}\cdot\text{m} = \text{Pa}\cdot\text{m}^3$) is the unit of energy and work.

K

Kinetic energy (see Energy)

L

Light is electromagnetic radiation (electromagnetic wave) with wavelengths visible to human eyes, roughly in the range of 400-700 nm (corresponding to colors violet-red). Immediately outside the visible range is the infrared (wavelength longer than red) and ultraviolet (wavelength shorter than violet) zone.

M

Mass (m) measures the amount of matter inside a body. It is the source of inertia and gravity. In relativistic view, it is equivalent to energy (up to a unit change due to the factor c^2).

Mechanical energy (see Energy)

Mechanics studies the principles and mechanisms of motion.

Momentum (linear momentum) ($\vec{p} = m\vec{v}$) is a measure of motion that arises from the velocity and the mass jointly.

Motion is the change of position of a body from one place to another, and is either absolute or relative, depending on the place.

N

Newtonian mechanics (see Classical mechanics)

Newton's equation of motion describes the evolution of a physical system and its dynamical quantities, such as position, velocity and acceleration, as a function of time based on Newton's second law.

Newton's laws of motion are three physical laws published by Sir Isaac Newton in his book *Mathematical Principles of Natural Philosophy* in 1687, which laid the foundation for classical mechanics.

- First law (law of inertia): every body perseveres in its state of being at rest or of moving uniformly straight forward, unless being compelled to change such a state by forces.
- Second law ($\vec{F} = m\vec{a} = \frac{d\vec{p}}{dt}$): a change in momentum is proportional to the force impressed and takes place in the direction of the force.
- Third law ($\vec{F}_{ij} = -\vec{F}_{ji}$): to any action there is always an opposite and equal reaction.

Newton's law of universal gravity ($G \frac{m_1 m_2}{r^2}$) Gravity exists in all bodies universally and is proportional to the mass of each body and inversely proportional to the square of the distance between them (when the matter is symmetrically and uniformly distributed within the bodies).

Non-conservative force (see Force)

Normal (force, velocity, direction, etc.) refers to the direction perpendicular to a surface or a curve. Correspondingly, the direction perpendicular to the normal one is called tangential.

O

Order of magnitude is the number of digits of a decimal number. That is n (or sometimes loosely spoken as 10^n), if a number N can be written in scientific notation as $N = m \times 10^n$ with $1 \leq |m| < 10$. Frequently used prefix symbols for order of magnitude:

- tera (T) 10^{12}
- giga (G) 10^9
- mega (M) 10^6
- kilo (k) 10^3
- deci (d) 10^{-1}
- centi (c) 10^{-2}
- milli (m) 10^{-3}
- micro (μ) 10^{-6}
- nano (n) 10^{-9}
- pico (p) 10^{-12}

- femto (f) 10^{-15}

Oscillation is a motion in which a system or a physical quantity repeats itself over time, often periodically, due to a force trying to restore it back to equilibrium.

P

Parallelogram law (of forces) ($\vec{F} = \vec{F}_1 + \vec{F}_2$) A body acted on by two forces \vec{F}_1, \vec{F}_2 separately, which form two sides of a parallelogram, behaves as if it were acted on by a total force \vec{F} that is the diagonal of the parallelogram.

Particle can either refer to an abstract constituent unit or to a fundamental physical object, such as proton and electron, depending on the context.

Pascal (Pa) is the unit of pressure with dimension [force]/[area] or [energy]/[volume].

Period (see Wave)

Periodic is the property of repeating the same state, strictly speaking, during the same time interval or over the same spatial distance.

Phase (see Wave)

Photon is the quantum of light. Each photon carries the energy of $h\nu$, where ν is the frequency of the light.

Planck constant ($h = 6.626 \times 10^{-34} \text{ m}^2 \text{ kg/s}$) is the quantum of action (the definition of action is out of the scope of this course, it is the integral of an energy-like quantity over time), which is related to the smallest energy scale in quantum mechanics. It has the dimension of [energy][time] or [momentum][length] or [angular momentum]. The reduced version $\hbar = \frac{h}{2\pi}$ is also frequently used.

Point particle (point mass) is an idealization of a particle whose mass is concentrated at a geometric point without spatial extension, in another word, being zero-dimensional. It serves as a good approximate model for real particles when the size of particles is negligible compared to the length scale of the problem concerned.

Position vector (\vec{r}) is a vector from the origin or the reference point to the position where a body resides.

Potential energy (see Energy)

Pressure ($p = \frac{F}{A}$) is the magnitude of the normal force per unit area applied to a surface.

Q

Quantization is the process of transition from classical mechanics to quantum mechanics, usually starting from discretizing continuous physical quantities.

Quantum (plural: quanta) is the minimum amount of physical quantities, such as energy, angular momentum, etc. Under quantization, physical quantities can only take on discrete values that are integer multiples of one quantum.

Quantum mechanics is an alternative mechanical viewpoint which abandons the classical mechanics ideas of describing motions as deterministic trajectories and of treating physical quantities as continuous variables. In quantum mechanics, the state of the system is described by a (probability) wave function and physical quantities can only take on discrete values.

Quantum number is a number, usually an integer, used to characterize the quantum state of a system or to describe the values of a physical quantity. For instance, the state of electrons inside an atom is characterized by four quantum numbers (n, l, m, s).

R

Right hand rule is a convention used in several physical situations to choose between one of the two possible symmetries, left hand and right hand. It specifies the direction in which the thumb points, when the curling direction of other four fingers is given, and vice versa.

Rotation (rotational motion) is a type of motion by which a body rotates or revolves around a fixed axis or a center.

S

Scalar is a quantity with only magnitude but no direction.

Schrödinger equation $i\hbar \frac{\partial \psi(\vec{r}, t)}{\partial t} = \left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}, t) \right] \psi(\vec{r}, t)$ is a wave equation and the equation of motion in quantum mechanics that describes the evolution of wave function with time.

Simple harmonic motion (harmonic oscillation) is the periodic motion of a harmonic oscillator described by a sinusoidal function.

Simple harmonic oscillator (harmonic oscillator) is a system under a restoring force satisfying Hooke's law, which undergoes sinusoidal oscillations about the equilibrium position.

Speed (v) is the magnitude of velocity \vec{v} .

Speed of light (in vacuum) $c = 2.99792458 \times 10^8$ m/s.

T

Torque ($\vec{\tau} = \vec{r} \times \vec{F}$) is a vector that causes rotation and is resulted from a force \vec{F} applied at a non-zero position \vec{r} from a fulcrum. The component of \vec{r} perpendicular to \vec{F} defines the *moment arm*. Torque can also be defined as the rate of change of angular momentum $\vec{\tau} = \frac{d\vec{L}}{dt}$.

Trajectory (of a body) is its motion path and mathematically described by its position vector $\vec{r}(t)$ as a function of time.

Translation (translational motion) is the type of motion by which a body shifts from one position to another.

U

Uncertainty principle (Heisenberg uncertainty principle) asserts that the precision, with which certain pairs of physical quantities can be known, cannot exceed a fundamental limit set by Planck constant. For instance, the uncertainty of position Δx and of momentum Δp_x satisfies $\Delta x \Delta p_x \geq \frac{\hbar}{2}$.

Uniform circular motion is a motion around a circle with constant angular speed ($\omega = \text{constant}$).

Uniform motion (uniform linear motion, uniform rectilinear motion) is a motion in a straight line with constant speed ($\vec{v} = \text{constant}$).

Unit (of physical quantities) is a quantity chosen as a standard in terms of which physical quantities can be measured. The numerical result of the measurement is then expressed as multiple of that unit.

Unit vector \hat{u} is a vector with magnitude one. Any vector \vec{a} can be normalized to form a unit vector as $\hat{a} = \frac{\vec{a}}{a}$.

V

Vector \vec{a} is a quantity with both magnitude (length) ($|\vec{a}| = a$) and direction. A vector in three-dimensional Cartesian coordinate system can be decomposed as $\vec{a} = (a_x, a_y, a_z) = a_x \hat{x} + a_y \hat{y} + a_z \hat{z}$, where a_x, a_y, a_z are the coordinates or components. The magnitude a is given by the Pythagorean theorem $a^2 = a_x^2 + a_y^2 + a_z^2$.

Velocity (instantaneous velocity, or linear velocity in the context of rotation) ($\vec{v} = \frac{d\vec{r}}{dt}$) is the rate of change of position with respect to time.

W

Wave is the periodic distribution of matter or energy over space resulted from spatiotemporal oscillations of physical medium or field. Waves can be classified into different types based on

whether physical medium is involved

- *Mechanical wave*
- *Electromagnetic wave*

whether the peak amplitude profile travels in space

- *Traveling wave*
- *Standing wave*, e.g. drumhead, guitar string.

whether the oscillation direction is perpendicular to the propagation direction

- *Transverse wave* (perpendicular), e.g. electromagnetic wave, water wave, earthquake S-wave (secondary shear wave).
- *Longitudinal wave* (parallel), e.g. sound wave, earthquake P-wave (primary pressure wave).

Generally, a wave can be described by a sinusoidal function, e.g. a 3D wave $u(\vec{r}, t) = A \cos(\vec{k} \cdot \vec{r} - \omega t + \phi_0)$ where

- *Amplitude* (A) is the maximum magnitude of oscillation.
- *Wave vector* (\vec{k}) points to the direction of propagation, whose magnitude, *wave number* k , describes the periodicity over space.
- *Angular frequency* (ω) reflects the periodicity over time.
- (Initial) *phase* (ϕ_0) is the phase angle at $\vec{r} = 0$ and $t = 0$.
- *Phase (angle)* (ϕ) is $\vec{k} \cdot \vec{r} - \omega t + \phi_0$.

- *Wavelength* ($\lambda = \frac{2\pi}{k}$) is the distance between two successive peaks or valleys of the wave.
- *Frequency* (f) is the number of oscillating cycles per unit time. $\omega = 2\pi f$.
- *Period* (T) is the time duration of one oscillating cycle. $T = \frac{1}{f}$.
- *Speed* (v) of propagation equals $v = \lambda f$.

Wave equation is a partial differential equation, $\frac{\partial^2 u}{\partial t^2} = c^2 \nabla^2 u$, whose solution describes a wave $u(\vec{r}, t)$ with propagation speed c .

Wave function ($\psi(\vec{r}, t)$) is the probability amplitude (whose square $|\psi(\vec{r}, t)|^2$ gives the probability or probability density) that a system is at a specific state, in this case, at position \vec{r} at time t .

Work ($W = \vec{F} \cdot \vec{s}$) A force \vec{F} acting on an object does work upon it when there is a displacement \vec{s} of the object in the direction of the force.

Z

Zero point (of potential energy) is the position at which the potential energy is set zero, which can be chosen arbitrarily.

Supplement: Calculus*

1 FUNCTION

A (real-valued) *function* $y = f(x)$ maps the input, or *independent variable* x , to the *dependent variable* y . The symbol $f(x)$ represents some types of mathematical operations or manipulations upon x , for instance, $x^2, \cos(x), \log x$ etc.

In the above notation, the function is a *single-variable* or *one-variable* function, because y only depends on one input x .

For a *multi-variable* function, the relationship becomes, e.g. $z = f(x, y)$, $u = f(x, t)$, or $y = f(x_1, x_2, x_3)$ etc.

2 DERIVATIVE AND DIFFERENTIATION

An infinitesimal change of the dependent variable can be expressed as dy or sometimes df , which is resulted from the infinitesimal change of the independent variable dx or variables dx_1, dx_2, \dots .

The (first order) *derivative* is the ratio of dy to dx with notations

$$f'(x) = \frac{df}{dx} = \frac{dy}{dx} = \dot{y}, \quad (1)$$

which quantifies how fast y changes with x . Note that the derivative $f'(x)$ of a function $f(x)$ is also a function that changes with x . The process to find derivatives is called (*differentiation*). In the case of single-variable functions, it is *ordinary differentiation*.

The second order derivative of $f(x)$ is the derivative of the derivative $f'(x)$,

$$f''(x) = \frac{d^2f}{dx^2} = \frac{d}{dx} \frac{df}{dx}. \quad (2)$$

For multivariable functions $z = f(x, y)$, the *partial derivative* can be defined with respect to each independent variable while holding others at constant, i.e.

$$\frac{\partial z}{\partial x} = \frac{\partial f(x, y)}{\partial x}, \quad \frac{\partial z}{\partial y} = \frac{\partial f(x, y)}{\partial y}. \quad (3)$$

The differential (a small amount of change) of z (or $f(x, y)$) can be expanded as the sum of two contributions from the change of x nad y

$$dz = df(x, y) = \frac{\partial f(x, y)}{\partial x} dx + \frac{\partial f(x, y)}{\partial y} dy. \quad (4)$$

Derivative Formulas*

$$\frac{d(cx^n)}{dx} = cnx^{n-1} \quad (5)$$

$$\frac{de^x}{dx} = e^x \quad \frac{d \ln x}{dx} = \frac{1}{x} \quad (6)$$

$$\frac{d \sin x}{dx} = \cos x \quad \frac{d \cos x}{dx} = -\sin x \quad (7)$$

$$\frac{df(y(x))}{dx} = \frac{df}{dy} \frac{dy}{dx} \quad (\text{chain rule}) \quad (8)$$

3 INTEGRAL AND INTEGRATION

An *indefinite integral* (or antiderivative) of a function $f(x)$ is a function $F(x)$ (called primitive function), denoted by $\int f(x)dx$, whose derivative equals to $f(x)$. Generally, if $F(x)$ is one primitive function of $f(x)$, then the whole family of $F(x) + C$, where C is a constant, are primitive functions of $f(x)$.

Indefinite Integral Formulas*

$$\int ax^n dx = a \frac{x^{n+1}}{n+1} + C \quad (9)$$

$$\int e^x dx = e^x + C \quad \int \frac{1}{x} dx = \ln x + C \quad (10)$$

$$\int \sin x dx = -\cos x + C \quad \int \cos x dx = \sin x + C \quad (11)$$

A *definite integral* $I(x) = \int_{x_1}^{x_2} f(x)dx$ specifies the integration limits x_1, x_2 , and sums the product of $f(x)$ (called integrand) and the infinitesimal dx over the interval $[x_1, x_2]$. Geometrically, $I(x) = \int_{x_1}^{x_2} f(x)dx$ can be understood as the total area covered by the curve $f(x)$ along the x -axis between $[x_1, x_2]$.

For multi-variable functions, the integration can be performed on each independent variables.

Definite Integration*

The area of a rectangle with length a and width b can be expressed by an integral

$$A = \int_0^a dx \int_0^b dy = ab, \quad (12)$$

if the rectangle is placed in a Cartesian coordinate system with x running from 0 to a and y from 0 to b . Here “ dx ” means a small segment of x .

Supplement: Probability*

1 RANDOM VARIABLE

A *random variable* X is a real-valued function defined on the sample space of a random experiment, which represents the outcome of the random experiment. For instance, the outcome of a dice is a *discrete* random variable, $X = 1, 2, 3, 4, 5, 6$. The height (in unit of meter) of a random person in the population is a *continuous* random variable, $X = 1.78, 1.65, 1.83$, etc.

2 PROBABILITY

The *probability* for an event A to occur, $P(A)$, or for a random variable to adopt a specific value x_0 , $P(X = x_0)$, is the chance for this to be true, which is a number bounded between 0 and 1.

For discrete random variables, like the example of a fair dice, $P(X = 1) = P(X = 2) = P(X = 3) = P(X = 4) = P(X = 5) = P(X = 6) = \frac{1}{6}$. Generally, we can denote $p_i = P(X = x_i)$.

For continuous random variables, $P(X = x_0) = 0$ for any fixed x_0 . It is useful to define $P(X \leq x_0) = \int_{-\infty}^{x_0} f(x)dx$, where $f(x)$ is the *probability density* or *distribution function*. That is, for continuous random variables, it is more meaningful to talk about probability over a finite interval, e.g. $P(a \leq X \leq b) = \int_a^b f(x)dx$.

The probability *distribution* specifies probabilities of all events or all values of the random variable. That is, all p_i 's in the discrete case and $f(x)$ over the entire range of X , $(-\infty, \infty)$, in the continuous case.

Generally, probability should be normalized. That is,

$$\sum_i P(X = x_i) = \sum_i p_i = 1 \text{ in the discrete case,}$$

$$\int_{-\infty}^{\infty} f(x)dx = 1 \text{ in the continuous case.}$$

If *relative* probabilities are given, whose sum is not unity, one

can follow a normalization procedure to find the *absolute* probabilities. For example, a randomly tossed coin lands 380 times on head (H) and 620 times on tail (T) out of one thousand trials. The estimated probabilities after normalization are $P(H) = 380/1000 = 0.38$ and $P(T) = 620/1000 = 0.62$.

3 EXPECTATION AND VARIANCE

The *expectation* $E[X] = \langle X \rangle = \mu$ of a random variable is its average, also called mean, i.e.

$$E[X] = \sum_i x_i p_i \text{ in the discrete case,}$$

$$E[X] = \int_{-\infty}^{\infty} x f(x)dx \text{ in the continuous case.}$$

The mean square $E[X^2] = \langle X^2 \rangle$ of a random variable is the average of its square, i.e.

$$E[X^2] = \sum_i x_i^2 p_i \text{ in the discrete case,}$$

$$E[X^2] = \int_{-\infty}^{\infty} x^2 f(x)dx \text{ in the continuous case.}$$

The *variance* of a random variable

$$\text{Var}[X] = E[X^2] - E[X]^2 = E[(X - \mu)^2] = \sigma^2$$

where σ is called the *standard deviation*.

4 GAUSSIAN DISTRIBUTION

A Gaussian random variable $X \sim \mathcal{N}(\mu, \sigma^2)$ has a probability density function

$$f(x) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{(x-\mu)^2}{2\sigma^2}}, \quad -\infty < x < \infty. \quad (1)$$

It can be verified that, the mean and variance of the Gaussian distribution is μ and the σ^2 , respectively.

Supplement: Ordinary Differential Equations*

1 CONCEPTS

Function $y = f(x)$, or sometimes written as $y = y(x)$. We say y is a function of x .

Dependent and Independent Variables In a function relationship $y = f(x)$, y is the dependent variable (因变量) and x is the independent variable (自变量). The nature of the variable is set by its role in the function relationship, not by its name or symbol. For instance, we can have $x(t)$ with x being the dependent variable.

n th (Order) Derivative $y^{(n)}(x) = \frac{d^n y}{dx^n}$, which is generally still a function of x (not to be confused with y to the n th power y^n). For small n , we often write $y^{(2)} = y'' = \frac{d^2 y}{dx^2}$ and $y^{(1)} = y' = \frac{dy}{dx}$ with prime notation.

Differential Equations Equations involving one dependent variable and its derivatives with respect to one or multiple independent variables.

- *Ordinary Differential Equations (ODEs)* have only ONE independent variable. For example,

(harmonic oscillator)

$$m \frac{d^2 x}{dt^2} = -kx \quad (1)$$

(logistic equation of population growth)

$$\frac{dN}{dt} = rN \left(1 - \frac{N}{K}\right) \quad (2)$$

- *Partial Differential Equations (PDEs)* involve more than one independent variables. For example,

(1D wave equation)

$$\frac{1}{v^2} \frac{\partial^2 u(x, t)}{\partial t^2} = \frac{\partial^2 u(x, t)}{\partial x^2} \quad (3)$$

(time-dependent Schrödinger equation)

$$i\hbar \frac{\partial \psi(x, t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x, t)}{\partial x^2} + V(x)\psi(x, t) \quad (4)$$

Order 阶 (of differential equations) is the order of the highest derivative. For example, Equation (2) is a 1st order ODE and Equation (4) is a 2nd order PDE.

Initial Condition(s) (ICs) set the values of the dependent variable and its derivatives, when the independent variable (often to be interpreted as time) is at zero. For example, $y(0) = y_0$ and $y'(0) = 0$.

Boundary Condition(s) (BCs) set the values of the dependent variable and its derivatives at the boundaries of the domain of the independent variables. For example, $y(a) = y_1$ and $y(b) = y_2$; periodic boundary condition (PBC), $y(x) = y(x + L)$.

Solution (to a differential equation) is a function that satisfy the differential equation after substituting the function and all its derivatives into the equation.

- *General Solution* is the family of all functions that are solutions to the differential equation, which are often related by undetermined coefficients or constants (to be determined by ICs and BCs). The number of coefficients in the general solution equals to the order of the differential equation.
- *Particular Solution* is one of the solutions from the family of general solution, after its coefficients are determined, that satisfies a particular set of ICs or BCs.

2 SEPARABLE FIRST ORDER ODEs

2.1 A Simple ODE

The general solution of

$$\frac{dy}{dx} = u(x) \quad (5)$$

is

$$y(x) = \int u(x)dx + C, \quad (6)$$

where C is a constant and the indefinite integral $\int u(x)dx$ is to be understood as a function (any function) with derivative $u(x)$. Let us give this function a symbol $U(x) = \int u(x)dx$.

If the IC $y(0) = y_0$ is given, then the particular solution of Equation (5) is $y(x) = U(x) + y_0 - U(0)$.

2.2 Separable ODEs

$$\frac{dy}{dx} = u(x)v(y) \quad (7)$$

$$\frac{dy}{v(y)} = u(x)dx$$

$$\int \frac{dy}{v(y)} = \int u(x)dx + C$$

which leads to the explicit form of the general solution of Equation (7), if the integral $\int \frac{dy}{v(y)}$ can be solved.

2.3 Raw Laws of Chemical Reactions

2.3.1 0th order

$$-\frac{dc(t)}{dt} = k \text{ with } c(0) = c_0 \quad (8)$$

Solution: $c(t) = -kt + c_0$.

2.3.2 1st order

$$-\frac{dc(t)}{dt} = kc \text{ with } c(0) = c_0 \quad (9)$$

$$\frac{dc}{c} = -kdt$$

$$\ln c = -kt + C$$

$$c(t) = e^C e^{-kt} = \tilde{C} e^{-kt}$$

Solution: $c(t) = c_0 e^{-kt}$.

2.3.3 2nd order

$$-\frac{dc(t)}{dt} = kc^2 \text{ with } c(0) = c_0 \quad (10)$$

$$\begin{aligned} -\frac{dc}{c^2} &= kdt \\ \frac{1}{c} &= kt + C \end{aligned}$$

Solution: $\frac{1}{c} = kt + \frac{1}{c_0}$.

IC $v(0) = 0$ implies $\tilde{C} = g$.

So the particular solution is $v(t) = \frac{g}{\zeta}(1 - e^{-\zeta t})$.

3.3 Exponential Growth/Decay

A lot of processes in nature follow the similar law as the 1st order chemical reaction, i.e. the rate of change of some quantity is proportional to the current value of that quantity, which leads to exponential growth or decay. For example,

Population growth with rate r , $\frac{dN}{dt} = rN$.

Decay of radioactive elements $\frac{dx}{dt} = kx$, whose half-life $\tau_{1/2} = \frac{\ln 2}{k}$ is used in radiocarbon dating (C-14 dating).

Newton's law of cooling $\frac{dT}{dt} = -r(T - T_{\text{env}})$ describes how the temperature $T(t)$ of a hot object drops when it is immersed in the environment with temperature T_{env} .

3.4 Logistic Equation*

In ecology, the rate of population growth is also constrained by the *carrying capacity* K of the environment and thus described by the logistic equation (2)

$$\frac{dN}{dt} = rN \left(1 - \frac{N}{K}\right)$$

Show that the particular solution to Equation (2) under IC $N(0) = N_0$ is

$$N(t) = \frac{KN_0 e^{rt}}{K - N_0 + N_0 e^{rt}} \quad (12)$$

Hint: $\frac{1}{x(a-x)} = \frac{1}{a} \left(\frac{1}{x} + \frac{1}{a-x}\right)$.

Comment: the resulted *logistic function* $f(x) = \frac{e^x}{1+e^x} = \frac{1}{1+e^{-x}} = \frac{1}{2} + \frac{1}{2} \tanh(\frac{x}{2})$, where the hyperbolic tangent function $\tanh(x) = \frac{e^x - e^{-x}}{e^x + e^{-x}}$, describes a S-curve and captures many natural processes that change between two states. It is also one of most popular "activation function" used in computational neural network and machine learning. The discrete version of the logistic equation, the logistic map $x_{n+1} = rx_n(1 - x_n)$, gives rise to the interesting phenomenon of chaos.

3 EXERCISES

3.1 Harmonic Oscillator

Verify that

- (a) $\cos \omega t$ and $\sin \omega t$
- (b) $e^{i\omega t}$ and $e^{-i\omega t}$

can solve Equation (1) $\frac{d^2x}{dt^2} = -\omega^2 x$, such that the general solution can be expressed as

$$c_1 \cos \omega t + c_2 \sin \omega t \text{ or}$$

$$d_1 e^{i\omega t} + d_2 e^{-i\omega t} \text{ or}$$

$$A \cos(\omega t + \delta).$$

Find the solution under the ICs

$$x(0) = x_0 \text{ and } \frac{dx}{dt} \Big|_{t=0} = v(0) = 0.$$

Comment: for a 2nd order ODE, we need two orthogonal (perpendicular, independent) solutions to express the general solution as their linear combination/expansion. Two BCs or ICs are needed to determine the value of the two coefficients, in order to pin down a particular solution.

3.2 Retarded Fall

A falling body under gravity through a viscous medium satisfies Newton's equation of motion

$$m \frac{d^2y}{dt^2} = mg - \xi \frac{dy}{dt} \quad (11)$$

where the drag force $-\xi \frac{dy}{dt}$ is proportional to the velocity $v = \frac{dy}{dt}$, but in the opposite direction. Find $v(t)$ under IC $v(0) = 0$.

$$\begin{aligned} \frac{d^2y}{dt^2} &= g - \frac{\xi}{m} \frac{dy}{dt} \\ \frac{dv}{dt} &= g - \zeta v \quad (\zeta = \xi/m) \\ \frac{dv}{g - \zeta v} &= dt \\ -\frac{1}{\zeta} \frac{d(g - \zeta v)}{g - \zeta v} &= dt \\ -\frac{1}{\zeta} \ln(g - \zeta v) &= t + C \\ g - \zeta v &= \tilde{C} e^{-\zeta t} \end{aligned}$$