General Chemistry I
23011

Ali Nassimi
a.nassimi@sharif.edu
Chemistry Department
Sharif University of Technology

May 22, 2021

- Your most valuable asset is your learning ability.
- This course is a practice in learning and specially improves your deduction skills.
- This course provides you with tools applicable in understanding many natural phenomena.
- End of semester goal: Be able to explain properties of a material sample based on, 1- Atomic structure and properties, 2- chemical bonding, 3- molecular interactions, 4-symmetries and asymmetries of the samples crystals, 5- energy content of that sample.

References

- General Chemistry Molecular Approach (vol. 1) by G. A. Parsafar, M. Bagherzadeh and M. Tafazzoli (In Farsi), accessible from `http://ch.sharif.ir/~laboratory/`
- University Chemistry by B. Mahan and R. Myers
- General Chemistry for Engineering. by G. Parsafar, M. Jalali-heravi, M. Saidi and M. Ghiaci
- Chemistry: The Central Science. By T. Brown, H. LeMay, B. Bursten, C. Murphy, P. Woodward, M. Stoltzfus
- Chemistry: The Molecular Nature of Matter and Change. by Martin Silberberg
- General Chemistry by P. W. Atkins and J. A. Beran
- Not less important from any of the above are course slides accessible from: `http://sina.sharif.edu/~a.nassimi/`

Course Information

Midterm exam	Chapters 0-3	19 Azar 5 pm	45%
Final exam	Chapters 4-7	12 Bahman 3 pm	45%
Tutorials	`vc.sharif.edu/` `ch/a.nassimi-ta`	Every week	10%

- Class location: `https://vc.sharif.edu/ch/a.nassimi`
- Office hours: Due to special situation of corona pandemic office hour is not set, email for an appointment instead.
- Exams are of equal weight, material of each exam to be excluded from the next exam but no exam mark can make up for another exam's mark.

Changes in TA hours

Group #	Initial time	TA	New time
6	9-10 am	Mr. Weisi	5-6 pm
7	10-11 am	Mr. Weisi	4-5 pm
8	11-12 am	Mr. Daneshgar	2-3 pm
9	12-1 pm	Mr. Daneshgar	3-4 pm
10	1-2 pm	Mr. Daneshgar	1-2 pm

Content of the course

- Preamble
- Structure and properties of atoms
- Chemical bonding
- Solids and liquids
- Gases
- Thermodynamics
- Solutions
- Environmental chemistry

Significant figures

- The significant figures of a number are digits that carry meaning contributing to its measurement resolution. This includes all digits except: All leading zeros; Trailing zeros when they are merely placeholders to indicate the scale of the number; and spurious digits introduced, for example, by calculations carried out to greater precision than the original data, or measurements reported to a greater precision than the equipment supports.

- Significance arithmetic are approximate rules for roughly maintaining significance throughout a computation. The more sophisticated scientific rules are known as propagation of uncertainty.

Significant figures

- All non-zero digits are significant: 1, 2, 3, 4, 5, 6, 7, 8, 9. Zeros between non-zero digits are significant: 102, 2005, 50009. Leading zeros are never significant: 0.02. In a number with a decimal point, trailing zeros are significant. 2.02000, 5.400, 57.5400. In a number without a decimal point, trailing zeros may or may not be significant.

- In the normalized form of scientific notation, placeholder leading and trailing digits do not occur, so all digits are significant. For example, 0.00012 (two significant figures) becomes 1.2×10^{-4}, and 0.00122300 (six significant figures) becomes 1.22300×10^{-3}.

- 1300 to four significant figures is written as 1.300×10^3, while 1300 to two significant figures is written as 1.3×10^3.

- A number is normalized when it is written in scientific notation with one nonzero decimal digit before the decimal point.

Significant figures

- The part of the representation that contains the significant figures (as opposed to the base or the exponent) is known as the significand or mantissa.

- Rounding to significant figures is a more general-purpose technique than rounding to n decimal places, since it handles numbers of different scales in a uniform way.

- Only measured quantities figure into the determination of the number of significant figures in calculated quantities. Exact mathematical quantities like the π in the formula for the area of a circle with radius r, πr^2 has no effect on the number of significant figures in the final calculated area.

- For quantities created from measured quantities by multiplication and division, the calculated result should have as many significant figures as the measured number with the least number of significant figures.

Significant figures

- For quantities created from measured quantities by addition and subtraction, the last significant decimal place (hundreds, tens, ones, tenths, and so forth) in the calculated result should be the same as the leftmost or largest decimal place of the last significant figure out of all the measured quantities in the terms of the sum.
- In a base 10 logarithm of a normalized number, the result should be rounded to the number of significant figures in the normalized number. For example, $\log_{10}(3.000 \times 10^4) = \log_{10}(10^4) + \log_{10}(3.000) \approx 4 + 0.47712125472$, should be rounded to 4.4771.
- When taking antilogarithms, the resulting number should have as many significant figures as the mantissa in the logarithm.
- Do not follow these guidelines for intermediate results; keep as many digits as is practical (at least 1 more than implied by the precision of the final result) until the end of calculation to avoid cumulative rounding errors.

SI system of units

Quantity	Unit	Unit symbol
Length (l)	Meter	m
Mass (m)	Kilogram	kg
Time (t)	Second	s
Electric current (I)	Ampere	A
Temperature (T)	Kelvin	K
Light intensity (I_v)	Candella	cd
quantity of matter	mol	mol

- Units for other quantities can be deduced from their relation with the quantities possessing a main SI unit.

SI system of units

Prefix	Prefix symbol	Prefix multiple
Exa	E	10^{18}
Peta	P	10^{15}
Tera	T	10^{12}
Giga	G	10^{9}
Mega	M	10^{6}
Kilo	k	10^{3}
Hecto	h	10^{2}
Deca	da	10^{1}
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}
atto	a	10^{-18}

SI system of units

- Never neglect units when performing mathematical manipulations.
- Use conversion factors from the back of your book.
- Temperature units. $T(K) = t(^\circ C)(\frac{1K}{1^\circ C}) + 273.15K$
- Fahrenheit scale. Lowest salt/ice temperature is 0°F. Highest animal body temperature is 100°F. Water freezes and boils at 32°F and 212°F.
- $t(^\circ C) = \frac{5^\circ C}{9^\circ F}[t(^\circ F) - 32(^\circ F)]$

Mole and molar mass

- Experimentally we measure the relation between masses of reactants and products.
- Theoretically we understand the relation between the number of atoms and molecules.
- Since mass of atoms are inconveniently small to deal with, we define a mole of (electron, atom, molecule, ion, etc) as Avogadro's number (6.022141×10^{23}) of (electron, atom, molecule, ion, etc).
- Mass of Avogadro's number (6.022141×10^{23}) of (electron, atom, molecule, ion, etc) is called molar mass of that particle.
- Atomic mass unit (amu) is defined as $1/12$ of the mass of a ^{12}C atom. Numerically amu's are equal to molar masses.
- Isotopes $A = \sum_i \frac{A_i P_i}{100} \qquad \sum_i P_i = 100$.

Stoichiometry and chemical reactions

- Stoichiometry is the calculation of reactants and products in chemical reactions.
- Stoichiometry is founded on the law of conservation of mass where the total mass of the reactants equals the total mass of the products.
- The relations among quantities of reactants and products typically form a ratio of positive integers.
- Stoichiometric coefficient (stoichiometric number), ν_i of any given component is the number of molecules that participate in the reaction as written.
- The extent of reaction ξ is defined as $\Delta N_i = \nu_i \Delta \xi$.

Stoichiometry and chemical reactions

- ξ is the extensive quantity describing the progress of a chemical reaction equal to the number of chemical transformations, as indicated by the reaction equation on a molecular scale, divided by the Avogadro constant.

- In a system of chemical equations: $\nu_{ik} = \frac{\partial N_i}{\partial \xi_k}$ so that the total (differential) change in the amount of the ith component is $dN_i = \sum_k \nu_{ik} d\xi_k$.

- It is useful to consider both the representation of a reaction system in terms of the amounts of the chemicals present $\{N_i\}$ (state variables), and the representation in terms of the extents of reaction $\{\xi_k\}$.

- The transformation from a vector expressing the extents to a vector expressing the amounts uses a rectangular matrix whose elements are the stoichiometric coefficients $[\nu_{ik}]$.

Stoichiometry and chemical reactions

- Moles of reaction method, $aA + bB \rightarrow cC + dD$
- Reaction moles $= \xi =$
  $\frac{\text{\# of moles of each reactant consumed or product produced}}{\text{coefficient of that reactant or product in reaction equation}}$
- $\frac{\Delta n_A}{a} = \frac{\Delta n_B}{b} = \frac{\Delta n_C}{c} = \frac{\Delta n_D}{d}$, $\Delta n_i = \frac{\Delta m_i}{M_i}$
- Conversion factor or factor-label method.
- E.g., How many grams of air is required to produce 2 pounds of ammonia according to the equation $3H_2 + N_2 \rightarrow 2NH_3$? Noting that air is compose of 0.78 N_2, 0.21 O_2 and 0.01 Ar.
- Limiting reagent.
- How many grs of DDT can be produced from 100 lbs of chloral and 100 lbs of chlorobenzene according to the equation $CCl_3CHO + C_6H_5Cl \rightarrow (ClC_6H_4)_2CHCCl_3 + H_2O$

- The law of constant ratios or the law of constant composition: in any particular chemical compound, all samples of that compound are made up of the same elements in the same proportion.
- The law of multiple ratios or law of multiple proportions: when two elements combine with each other to form more than one compound, the weights of one element that combine with a fixed weight of the other are in a ratio of small whole numbers.
- There are five distinct oxides of nitrogen, and the weights of oxygen in combination with 14 grams of nitrogen are, in increasing order, 8, 16, 24, 32, and 40 grams, or in a ratio of 1, 2, 3, 4, 5.

Stoichiometry

- The law of equivalence ratios or the law of reciprocal proportions, or law of permanent ratios: If element A combines with element B and also with C, then, if B and C combine together, the proportion by weight in which they do so will be simply related to the weights of B and C which separately combine with a constant weight of A.

- E.g., 1 gram of sodium ($Na = A$) is observed to combine with either 1.54 grams of chlorine ($Cl = B$) or 5.52 grams of iodine ($I = C$). (These ratios correspond to the modern formulas $NaCl$ and NaI). The ratio of these two weights is $5.52/1.54 = 3.58$. It is also observed that 1 gram of chlorine reacts with 1.19 g of iodine. This ratio of 1.19 obeys the law because it is a simple fraction ($1/3$) of 3.58. (This is because it corresponds to the formula ICl_3.)

Dalton's atomic theory

- All material are composed of small particles called atoms.
- Atoms are indivisible and atoms of one element cannot transform into atoms of another element.
- Atoms cannot be produced or consumed.
- All atoms of each element have the same properties.
- Atoms of one element have mass and other properties different from other elements.
- In chemical compounds composed of different elements, constituting elements have specified ratios.

Atomic structure: electric nature of matter

- Faraday placed two opposite electrodes in a solution of water containing a dissolved salt. He observed that one of the elements of the dissolved compound accumulated on one electrode, and the other element was deposited on the opposite electrode. It suggests that electrical forces were responsible for the joining of atoms in compounds.

- In 1832 Michael Faraday Studied the effect of electricity on solutions, coined term "electrolysis" as a splitting of molecules with electricity and developed laws of electrolysis.

Atomic structure: electric nature of matter

- Faraday's laws can be summarized by $m = \left(\frac{Q}{F}\right)\left(\frac{M}{z}\right)$
- m is the mass of the substance liberated at an electrode in gr; Q is the total electric charge passed through the substance in coulombs; $F = 96500$ C mol^{-1} is the Faraday constant; M is the molar mass of the substance in grams per mol; z is the valency number of ions of the substance (electrons transferred per ion). Note that M/z is the same as the equivalent weight of the substance altered.
- In 1879, Crookes studied the effects of sending an electric current through a gas in a sealed tube. The tube had electrodes at either end and a flow of electrically charged particles moved from one of electrodes. This electrode was called the cathode, and the particles were known as cathode rays.
- The Crookes tubes require a small amount of air in them to function, from about 10^{-6} to 5×10^{-8} atmosphere.
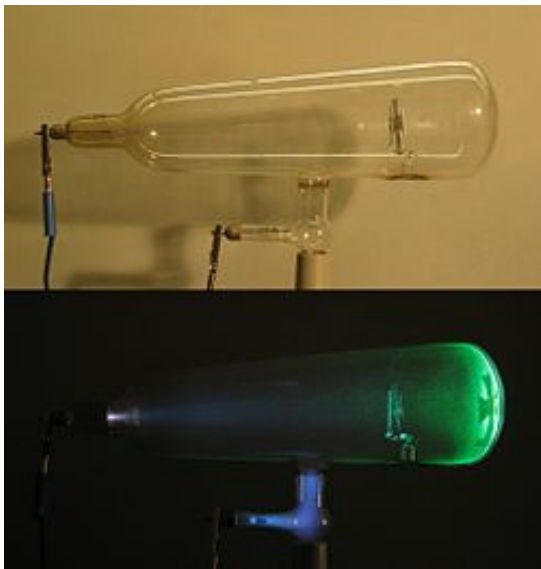
Figure: Crooks tube taken from
https://en.wikipedia.org/wiki/Crookes_tube

Atomic structure: electric nature of matter

- Cathode rays are so named because they are emitted by the negative electrode, or cathode, in a vacuum tube.
- Cathode rays were first believed to be negatively charged atoms or molecules. Cathode rays could penetrate thin sheets of material which would not be possible if the particles were as large as atoms or molecules.
- Cathode rays have the following properties: travel in straight lines from the cathode; cause glass to fluoresce; impart a negative charge to objects they strike; are deflected by electric fields and magnets to suggest a negative charge; cause pinwheels in their path to spin indicating they have mass.
- In 1886, E. Goldstein Used a cathode ray tube (CRT) to study anode (canal) rays which had electrical and magnetic properties opposite of cathode ray.

Atomic structure: electric nature of matter

- In 1894, G.J. Stoney proposed that electricity was made of discrete negative particles he called electrons.

  -
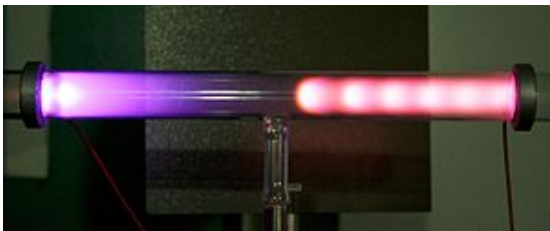
Figure: a pattern of glowing regions of gas called a glow discharge taken from https://en.wikipedia.org/wiki/Crookes_tube

Atomic structure: electric nature of matter

- In 1895 Wilhelm Roentgen using a CRT observed that nearby chemicals glowed. Further experiments found very penetrating rays coming from the CRT that were not deflected by a magnetic field. He named them "X-rays".
- In 1896 Henri Becquerel while studying the effect of x-rays on photographic film, discovered some chemicals spontaneously decompose and give off very penetrating rays.
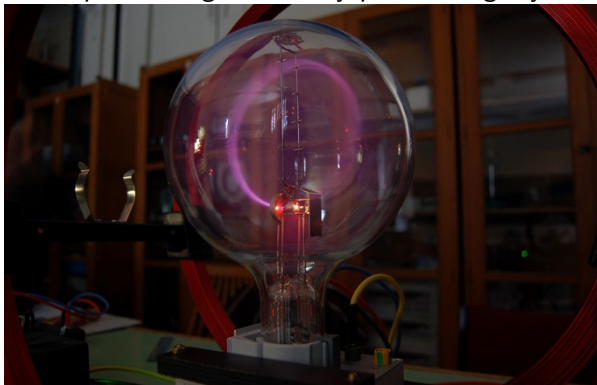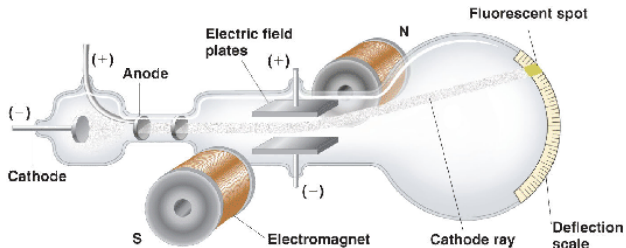
-
- $F_E = Ee \qquad F_H = Hev$
- When forces balance, $v_x = \frac{E}{H}$
- In the absence of magnetic field, $y(t) = \frac{1}{2}a_y t^2$, $\quad ma_y = F_E = eE$, $\quad y(t) = \frac{eE}{2m}t^2$ $\quad l = v_x t \rightarrow \frac{e}{m} = \frac{2SE}{l^2 H^2}$
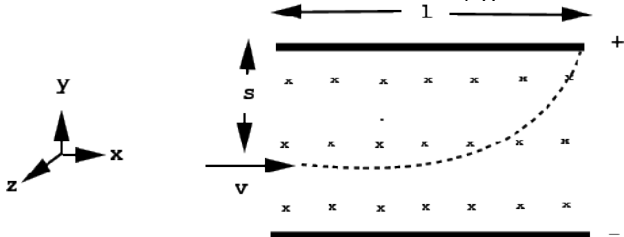
Millikan experiment, electron charge measurement

- The oil drop experiment was performed by Robert Millikan and Harvey Fletcher in 1909 to measure the elementary electric charge (the charge of the electron).

- The experiment entailed observing tiny electrically charged droplets of oil located between two parallel metal surfaces, forming the plates of a capacitor.

- The plates were oriented horizontally, with one plate above the other. A mist of atomized oil drops was introduced through a small hole in the top plate and was ionized by an x-ray, making them negatively charged.

- With zero applied electric field, the velocity of a falling droplet was measured. At terminal velocity, the drag force equals the gravitational force.

- As both forces depend on the radius in different ways, the radius of the droplet, and therefore the mass and gravitational force, could be determined (using the known density of the oil).

Figure: Schematic of the Millikan experiment taken from
https://en.wikipedia.org/wiki/Oil_drop_experiment

- A voltage was applied between the plates and adjusted until the drops were suspended in mechanical equilibrium, indicating that the electrical force and the gravitational force were in balance.
- Fine spray of ionized oil droplets,
  $M = \frac{4}{3}\pi r^3 \rho, \quad w_{apa} = \frac{4\pi}{3} r^3 (\rho - \rho_{\mathrm{air}}) \boldsymbol{g}$
- In the absence of electric field:
  $F = w_{apa} - \gamma v_{lim} = w_{apa} - 6\pi r\eta v_{lim} = 0.$
- At suspension $w_{apa} = qE$.
- $q = n(-1.60 \times 10^{-19})C, \quad \frac{e}{m} =$
  $-1.75882 \times 10^{11} C/Kg, \qquad m = 9.10 \times 10^{-31} Kg$
- The oil was of a type usually used in vacuum apparatus and was chosen because it had an extremely low vapor pressure.

The Thomson Model

- J. Thomson, who discovered the electron in 1897, proposed the plum pudding model of the atom in 1904 before the discovery of the atomic nucleus in order to include the electron in the atomic model.
- In Thomson's model, the atom is composed of electrons surrounded by a soup of positive charge to balance the electrons negative charges.
- The 1904 Thomson model was disproved by Hans Geiger's and Ernest Marsden's 1909 gold foil experiment.
- α- particle: A positively charged nucleus of a helium-4 atom, emitted as a consequence of radioactivity.
- Geiger and Marsden shot alpha particles with large kinetic energies toward a thin foil of gold.

Rutherford experiment or Geiger—Marsden experiment

- Measuring the pattern of scattered particles was expected to provide information about the distribution of charge within the atom.

- Under the prevailing plum pudding model, the alpha particles should all have been deflected by, at most, a few degrees. However, the actual results surprised Rutherford.

- Although many of the alpha particles did pass through as expected, many others were deflected at small angles while others were reflected back to the alpha source.

- Gold foil experiment was interpreted by Ernest Rutherford in 1911 to suggest that there is a very small nucleus of the atom that contains a very high positive charge. His conclusions led him to propose the Rutherford model of the atom.

- This highly concentrated, positively charged region is named the nucleus of the atom.

The alpha particles propagated on the atomic nucleuses of the gold foil.

- Rutherford estimated the "diameter" of an atom to be approximately 10^{-8} cm and that of the nucleus to be approximately 10^{-13} cm. He proposed a model of the atom as consisting of a small, dense nucleus surrounded by enough electrons to yield an overall charge-neutral aggregate.

Electromagnetic radiation

- Wave is a disturbance in a medium.
- Electromagnetic wave consists of orthogonal electric and magnetic components: $E(x, t) = E_{max} \cos[2\pi(\frac{x}{\lambda} + \nu t)], \qquad B(x, t) = B_{max} \cos[2\pi(\frac{x}{\lambda} + \nu t)]$

Electromagnetic Wave
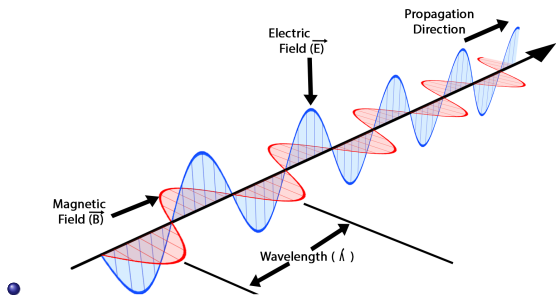
-
- $c = \lambda\nu, \qquad Energy \propto Intensity \propto E_{max}^2$
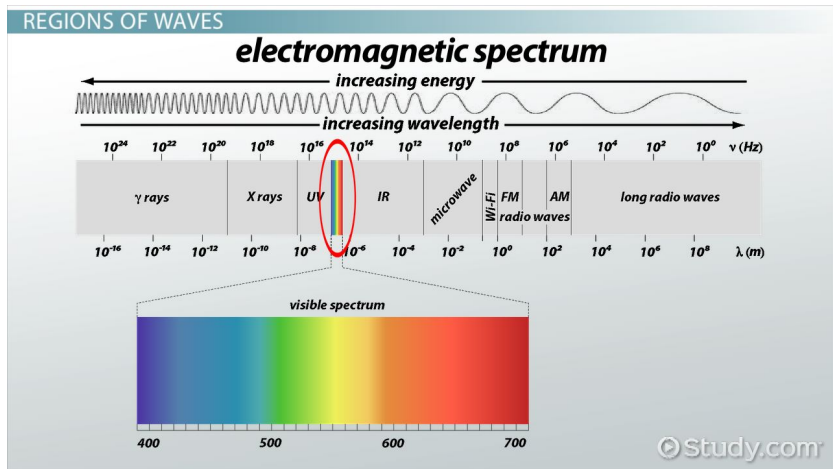
Black body radiation

- A body which absorbs all the incident radiation and reflects none of it.
- This is an idealization best approximated by a small entrance to a cavity.
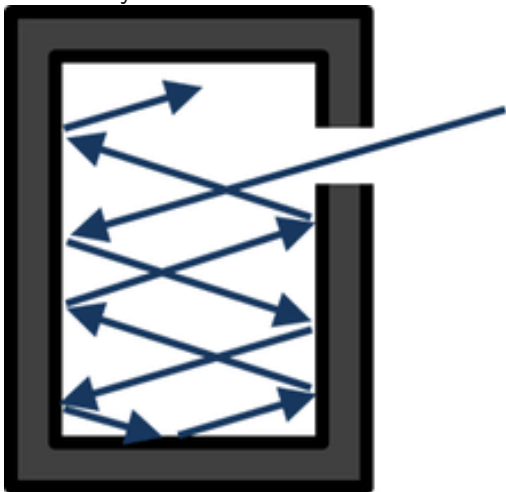
Black body radiation

- A materially isolated body reaches an equilibrium temperature where the energy of the incident and radiated electromagnetic radiation are equal.
- Classical physics predicts $E(\lambda) \propto \frac{kT}{\lambda^4}$, i.e., ultraviolet catastrophe.

Plank quantum theory
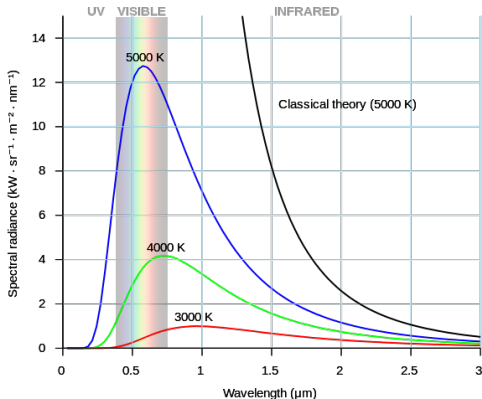
- Suggested the concept of photons carrying electromagnetic energy and derived the correct relation for energy radiation from a black-body.
- $E = nh\nu, \quad h = 6.626 \times 10^{-34}\,\text{Js}.$
- $\rho(\omega, T)d\omega = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\beta\hbar\omega}-1} d\omega$

Photoelectric effect

- Metals exist as lattice of positive ions immersed in a sea of electrons.
- Electromagnetic radiation might be able to separate electrons from a metal surface.
- This occurs at frequencies greater than a threshold frequency. Radiation intensity determines the number of separated
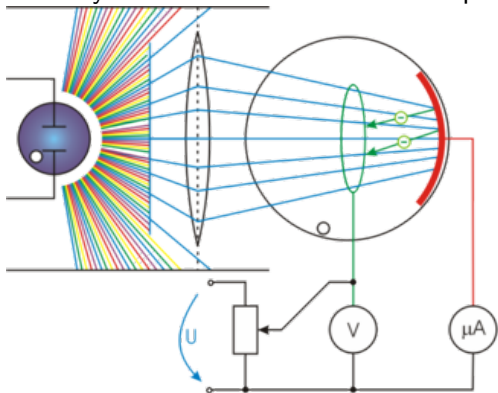
electrons.

Wave-particle duality

- In photoelectric experiment light shows corpuscular nature while in interference experiments (e.g., double slit experiment) it shows a wave nature.
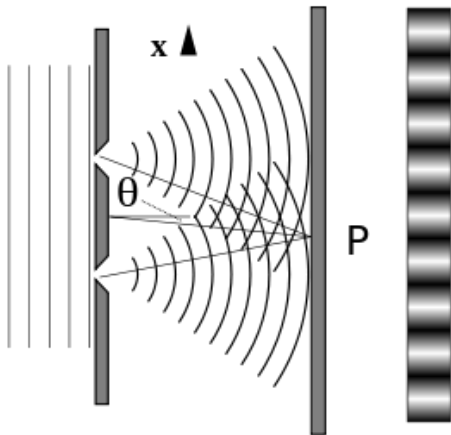
Figure: Two slits are illuminated by a plane wave. Taken from
en.wikipedia.org/wiki/Double_slit_experiment

Wave-particle duality

- De Brogli relation: If particle $E = mc^2$, if wave $E = h\frac{c}{\lambda}$, when both $\lambda = \frac{h}{P}$ and $P = \frac{h}{\lambda}$.
- What about fundamental particles?
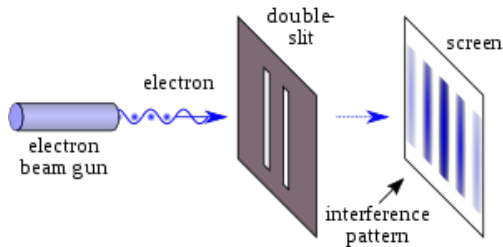
Figure: Photons or particles of matter produce a wave pattern. Taken from en.wikipedia.org/wiki/Double-slit_experiment

Elemental spectra for hydrogen

- The emission spectrum of atomic hydrogen has been divided into a number of spectral series, with wavelengths given by the Rydberg formula.
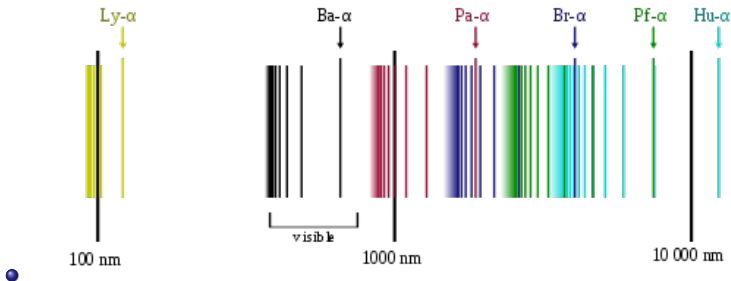
Figure: The spectral series of hydrogen, on a logarithmic scale.
Taken from en.wikipedia.org/wiki/Double-slit_experiment

- $\bar{\nu} = \dfrac{1}{\lambda} = R_y Z^2 \left(\dfrac{1}{n'^2} - \dfrac{1}{n^2} \right)$ where Z is the atomic number, i.e. the number of protons in the atomic nucleus of this element; n is the upper energy level; n' is the lower energy level; and R is the Rydberg constant $(1.09737 \times 10^7\, m^{-1})$

- Hydrogen spectrum includes: Lyman (UV, n'=1), Balmer (vis, n'=2), Paschen (IR, n'=3), Brackett (n'=4) and Pfund (n'=5) series, Humphreys series (n' = 6).

Classical Mechanics-Newton formalism

- In the absence of external forces motion will continue with a constant speed.
- $F = ma$.
- If body A exert a force on body B, then B exerts the same force in the opposite direction on A.
- Two dimensional motion under coulomb attraction to a fixed center.
- $F = -k\vec{r}/r^3$, break down into components to derive
- $m\ddot{x} = F_x = -\frac{Kx}{(x^2+y^2)^{3/2}}$ and $m\ddot{y} = F_y = -\frac{Ky}{(x^2+y^2)^{3/2}}$
- Use polar coordinate system $x = r\cos\theta$ and $y = r\sin\theta$ to derive
- $mr^2\dot{\theta} = $ constant and $m\ddot{r} = -\frac{k}{r^2} + \frac{l^2}{mr^3}$

Classical Mechanics-Lagrangian

- Lagrange's treatise on analytical mechanics offered the most comprehensive treatment of classical mechanics since Newton and formed a basis for the development of mathematical physics in the nineteenth century.
- Lagrangian, $L \equiv K - U$, where $K = \sum_i \frac{m_i}{2} \dot{x}_i^2$
- Lagrangian dynamics: $\frac{d}{dt} \frac{\partial L}{\partial \dot{q}_j} = \frac{\partial L}{\partial q_j}$, the form of this equation is invariant under the change of coordinates.
- Two dimensional motion under coulomb attraction to a fixed center.

Classical Mechanics-Hamiltonian

- William Hamilton's Hamiltonian mechanics has proven central to the modern study of classical field theories such as electromagnetism, and to the development of quantum mechanics.

- Momentum, $p_j = \frac{\partial L}{\partial \dot{q}_j}$.

- Hamiltonian, $H = \sum_j p_j \dot{q}_j - L$.

- Kinetic energy, $K = \sum_j a_j(q) \dot{q}_j^2$. Total energy of the system, $H = K + V$.

- Hamilton's equations of motion, $\frac{\partial H}{\partial p_j} = \dot{q}_j$, $\qquad \frac{\partial H}{\partial q_j} = -\dot{p}_j$.

- Show the equivalence of both Lagrangian and Hamiltonian dynamics to Newtonian dynamics.

Standing waves

- Contradiction in motion of electron around the nucleus.
- A stationary wave is a wave which oscillates in time but whose peak amplitude profile does not move in space.
- The peak amplitude of the wave oscillations at any point in space is constant with time, and the oscillations at different points throughout the wave are in phase.
- The locations at which the amplitude is minimum are called nodes, and the locations where the amplitude is maximum are called anti-nodes.
- This phenomenon can occur because the medium is moving in the opposite direction to the wave, or it can arise in a stationary medium as a result of interference between two waves traveling in opposite directions.

Bohr atomic theory
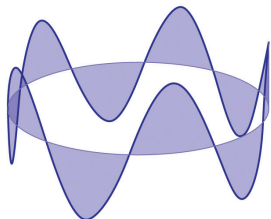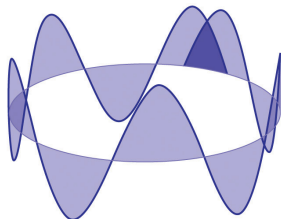
(a) Standing wave **(b) Destructive Interference**

- Standing wave requirement of a circular electron path.
- Circumference equals some multiple of wavelength, thus,
  $2\pi r = n\lambda \rightarrow l = mvr = n\hbar$
- Coulomb force = centrifugal force, $\frac{Ze^2}{4\pi\epsilon_0 r^2} = \frac{mv^2}{r}$
- $r = \frac{\epsilon_0 h^2 n^2}{Ze^2 \pi m} = a_0 \frac{n^2}{Z}, \quad v = \frac{e^2}{2\epsilon_0 h} \frac{Z}{n}$
- $E = \frac{1}{2}mv^2 - \frac{Ze^2}{4\pi\epsilon_0 r} = -\frac{e^4 m Z^2}{8\epsilon_0^2 n^2 h^2} = -13.6 eV(\frac{Z^2}{n^2})$

Proton

- In 1815, based on early values of atomic weights Prout proposed that all atoms are composed of hydrogen atoms.
- In 1898, Wien identifies H^+ as particle with highest charge to mass ratio in canal rays.
- It was proposed that the place of each element in the periodic table is equal to its nuclear charge.
- In 1917, Rutherford proved that hydrogen nucleus is present in other nuclei.

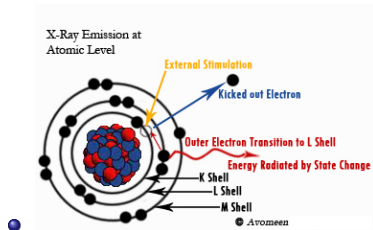- In 1912, Moseley showed that bombarding a metal with β rays causes emission of X-rays.

Figure: Taken from www.avomeen.com

Moseley law

- Using x-ray diffraction techniques in 1913-1914, Moseley found that the most intense short-wavelength line in the x-ray spectrum of a particular element was indeed related to the element's periodic table atomic number, Z.
- Following Bohr's lead, Moseley found that for more general lines, this relationship could be expressed by a simple formula, later called Moseley's Law. $\sqrt{\nu} = k_1 \cdot (Z - k_2)$
- Moseley derived his formula empirically by plotting the square root of X-ray frequencies against a line representing atomic number.

- Difference between atomic mass and Zm_p suggested the existence of neutral particles in nuclei.
- In 1932 Chudwick produced a flux of neutrons by bombarding beryllium atoms ($^9_4$Be) with alpha particles ($^4_2$He^{2+}).
- Protons and neutrons are made of even smaller units called quarks.

Microscopic world and quantum mechanics

- From the late 19th century people started to patch classical physics to justify some observations including photoelectric effect and black body radiation.
- Quantum mechanics was formally formulated in the 1920s.
- All information that can be known about a system is contained in a wavefunction, ψ, which in general is a complex valued function of space coordinate.
- Every observable in quantum mechanics is represented by an operator.
- An operator is generally a mapping that acts on elements of a space to produce other elements of the same space. The most common operators are linear maps, which act on vector spaces.

Microscopic world and quantum mechanics

- Differentiation and indefinite integration are linear operators; operators that are built from them are called differential operators, integral operators or integro-differential operators.
- Let U and V be vector spaces over a field K. A mapping $A : U \rightarrow V$ is linear if $A(\alpha\mathbf{x} + \beta\mathbf{y}) = \alpha A\mathbf{x} + \beta A\mathbf{y}$ for all x, y in U and for all α, β in K.
- In finite-dimensional cases linear operators can be represented by matrices
- Expectation value (average value) of observable A is given by $\langle \hat{A} \rangle = \int \psi^* \hat{A} \psi d\tau$.
- Time independent Schrodinger equation $\hat{H}\psi = E\psi$ determines the stationary states of a system.

Quantum Mechanics-operators

Observable Name	Observable Symbol	Operator Symbol	Operator Operation
Position	$\mathbf{r}$	$\hat{\mathbf{r}}$	Multiply by $\mathbf{r}$
Momentum	$\mathbf{p}$	$\hat{\mathbf{p}}$	$-i\hbar\left(\hat{i}\frac{\partial}{\partial x} + \hat{j}\frac{\partial}{\partial y} + \hat{k}\frac{\partial}{\partial z}\right)$
Kinetic energy	T	$\hat{T}$	$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$
Potential energy	$V(\mathbf{r})$	$\hat{V}(\mathbf{r})$	Multiply by $V(\mathbf{r})$
Total energy	E	$\hat{H}$	$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V(\mathbf{r})$
Angular	l_x	$\hat{l}_x$	$-i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$
momentum	l_y	$\hat{l}_y$	$-i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$
	l_z	$\hat{l}_z$	$-i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$

Quantum mechanics

- Wave function or state function, has the important property that $\Psi^*(\mathbf{r}, t)\Psi(\mathbf{r}, t)d\tau$ is the probability that the particle lies in the volume element $d\tau$ located at $\mathbf{r}$ at time t.

- For the case of a single particle, the probability of finding it somewhere is 1, we have the normalization condition $\int_{-\infty}^{\infty} \Psi^*(\mathbf{r}, t)\Psi(\mathbf{r}, t)d\tau = 1$.

- The wavefunction must also be single-valued, continuous, and finite.

- In any measurement of the observable associated with operator $\hat{A}$, the only values that will ever be observed are the eigenvalues a, which satisfy the eigenvalue equation $\hat{A}\Psi = a\Psi$.

- The values of dynamical variables can be quantized (although it is still possible to have a continuum of eigenvalues).

- If the system is in an eigenstate of $\hat{A}$ with eigenvalue a, then any measurement of the quantity A will yield a.

- Magnetic moment is a quantity that represents the magnetic strength and orientation of a magnet.
- Loops of electric current (such as electromagnets), permanent magnets, elementary particles (such as electrons), various molecules, and many astronomical objects poses magnetic dipole moment.
- The magnetic dipole moment of an object is readily defined in terms of the torque that object experiences in a given magnetic field. $\boldsymbol{\tau} = \mathbf{m} \times \mathbf{B}$
- The direction of the magnetic moment points from the south to north pole of the magnet (inside the magnet).
- A magnetic moment in an externally produced magnetic field has a potential energy $U = -\mathbf{m} \cdot \mathbf{B}$.

- $\mathbf{m} = -\hat{\mathbf{x}}\frac{\partial U_{\mathrm{int}}}{\partial B_x} - \hat{\mathbf{y}}\frac{\partial U_{\mathrm{int}}}{\partial B_y} - \hat{\mathbf{z}}\frac{\partial U_{\mathrm{int}}}{\partial B_z}$.
- $\mathbf{m} = I\mathbf{S}$, $\mathbf{m} = NI\mathbf{S}$.
- $\mathbf{m} = \frac{1}{2}\iiint_V \mathbf{r} \times \mathbf{j}\,\mathrm{d}V$,
- Since the particles creating the current (by rotating around the loop) have charge and mass, both the magnetic moment and the angular momentum increase with the rate of rotation. The ratio of the two is called the gyromagnetic ratio or γ so that: $\mathbf{m} = \gamma\mathbf{L}$

Stern-Gerlach experiment and Spin
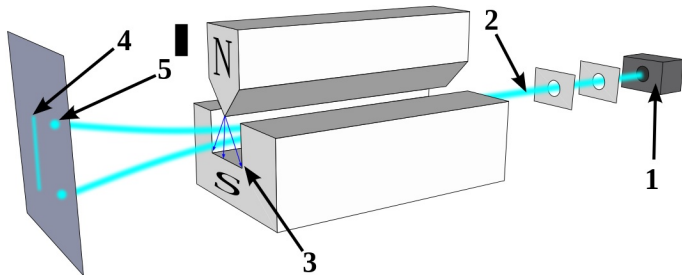
-
- The Stern–Gerlach experiment demonstrated that the spatial orientation of angular momentum is quantized.
- Silver atoms were sent through a spatially varying magnetic field, which deflected them before they struck a detector screen, such as a glass slide.

Stern-Gerlach experiment and Spin

- Particles with non-zero magnetic moment are deflected, due to the magnetic field gradient, from a straight path.
- The screen reveals discrete points of accumulation, rather than a continuous distribution, owing to their quantized spin.
- Spin is an intrinsic angular momentum of subatomic particles that is closely analogous to the angular momentum of a classically spinning object, but that takes only certain quantized values. $\hat{S}_z \psi_{z+} = \frac{\hbar}{2} \psi_{z+}$ $\hat{S}_z \psi_{z-} = -\frac{\hbar}{2} \psi_{z-}$
- Only one component of a particle's spin can be measured at one time, meaning that the measurement of the spin along the z-axis destroys information about a particle's spin along the x and y axis.
- Particles with a half integral spin are called Fermions while those with integral spin are called Bosons.

- Average value show the mean of experimental results while variance shows its dispersion.
$$\bar{X} = \frac{\sum_i X_i}{N}, \qquad \Delta X = \sigma_X = \sqrt{\frac{\sum_i (X_i - \bar{X})^2}{N}}$$

- The uncertainty principle $\Delta X \Delta P \geq \frac{h}{4\pi}$ results from the Cauchy-Schwartz inequality.

- The precision of observing an object is of the order of detecting light's wavelength $\Delta X = \lambda$

- Incidence of a photon might change the objects momentum by the incident photons momentum $\Delta P = \frac{h}{\lambda}$.

Simple models

- Particle in a 1-D box: $\begin{cases} U(x) = 0 & 0 < x < a, \\ U(x) = \infty & \text{otherwise.} \end{cases}$

- The particle is inside the box, thus for $x < 0$ and $x > a$,
  $|\psi(x)|^2 = 0 \rightarrow \psi(x) = 0$.

- For $0 < x < a$, $-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi = E\psi \rightarrow \frac{d^2}{dx^2}\psi = -\frac{2mE}{\hbar^2}\psi = -k^2\psi$

- $\psi(x) = A\sin kx + B\cos kx$

- Apply the boundary condition,
  $\psi(0) = 0 \rightarrow B = 0 \qquad \psi(a) = 0 \rightarrow ka = n\pi \rightarrow \frac{2mE}{\hbar^2}a^2 = n^2\pi^2$

- $E_n = \frac{h^2}{8ma^2}n^2$,

- Normalization condition:
  $\int_{-\infty}^{\infty} \psi(x)^2 dx = 1 = \int_0^a \psi(x)^2 dx \rightarrow A^2 \int_0^a \sin^2 kx dx = 1 = A^2 \int_0^a \frac{1-\cos 2kx}{2} dx \qquad \psi(x) = \sqrt{\frac{2}{a}}\sin(\frac{n\pi}{a}x)$.

Simple models
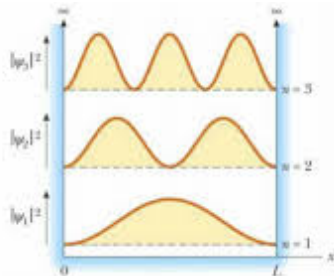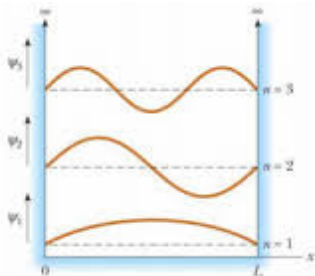
-
- Quantized energy levels appeared when the particle was confined with a potential barrier.
- Spacing of energy levels is inversely proportional to particles mass and its confinement.
- A node is where the wavefunction become zero. Energy corresponding to wavefunction increases with number of its nodes.
- For a particle in a box energy levels and the wavefunction could be derived using wave-particle duality.

Simple models

- Theorem: If
  $H(x_1, x_2, \cdots, y_1, y_2, \cdots) = H_1(x_1, x_2, \cdots) + H_2(y_1, y_2, \cdots)$
  then $\psi = \psi_1 \psi_2$ and $E = E_1 + E_2$.

- Harmonic oscillator:
  $U(x) = \frac{1}{2}kx^2$, $\qquad \epsilon_n = (n + \frac{1}{2})\hbar\omega$, $\qquad \omega = \sqrt{k/m}$.

- Because an arbitrary potential can usually be approximated as a harmonic potential at the vicinity of a stable equilibrium point, it is one of the most important model systems in quantum mechanics.

- $\hat{H} = \dfrac{\hat{p}^2}{2m} + \dfrac{1}{2}k\hat{x}^2 = \dfrac{\hat{p}^2}{2m} + \dfrac{1}{2}m\omega^2\hat{x}^2$.

- $\psi_n(x) = \dfrac{1}{\sqrt{2^n\, n!}} \cdot \left(\dfrac{m\omega}{\pi\hbar}\right)^{1/4} \cdot e^{-\frac{m\omega x^2}{2\hbar}} \cdot H_n\left(\sqrt{\dfrac{m\omega}{\hbar}}x\right)$, $\qquad n = 0, 1, 2, \ldots$.

- $H_n(z) = (-1)^n\, e^{z^2} \dfrac{d^n}{dz^n}\left(e^{-z^2}\right)$.

Hydrogen atom

- $\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) - \frac{Ze^2}{4\pi\epsilon_0 r}$
- There is an spherical symmetry in the potential.
- $x, y, z \rightarrow r, \theta, \phi$

-

Hydrogen atom
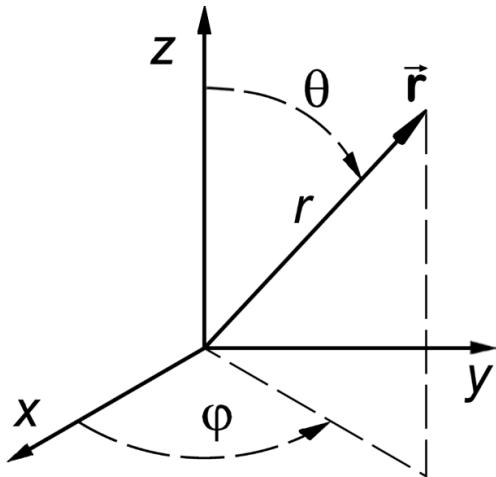
- $\hat{H}\psi(r,\theta,\phi) = E\psi(r,\theta,\phi)$
- $\psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$
- The principle quantum number n determines energy
  $E_n = -\frac{2\pi^2 me^4 Z^2}{h^2 n^2}$, n takes on any natural number, $n = 1, 2, \cdots$
- The angular momentum quantum number l determines the angular momentum of electron, since angular kinetic energy of electrons is limited to total energy of the electron,
  $l = 0, 1, \cdots, n-1$.

Hydrogen atom

- n and l determine the radial component of the wavefunction, $R_{n,l}(r)$.
- The magnetic quantum number, m_l, determines the strength of the dipole moment created due to charged electrons angular momentum. Values of m_l are confined by the electrons angular momentum, $m_l = -l, -l + 1, \cdots, l$.
- l and m_l determine the angular component of the wavefunction, $Y_{l,m_l}(\theta, \phi)$.
- Geometric location of the set of points where electron is most likely to be found is called an orbital.
- Each orbital corresponds to a possible combination of quantum numbers.

Shape and size of orbitals

- $\sigma = \frac{Zr}{a_0}$ and $a_0 = \frac{\epsilon_0 h^2}{\pi e^2 m_e} = 0.529 \times 10^{-10} m$
- $R_{1,0}(r) = 2(\frac{Z}{a_0})^{3/2} \exp(-\sigma)$
  $R_{2,0}(r) = \frac{1}{2\sqrt{2}}(\frac{Z}{a_0})^{3/2}(2 - \sigma) \exp(-\sigma/2)$
  $R_{3,0}(r) = \frac{2}{81\sqrt{3}}(\frac{Z}{a_0})^{3/2}(27 - 18\sigma - 2\sigma^2) \exp(-\sigma/3)$
  $R_{2,1}(r) = \frac{1}{2\sqrt{6}}(\frac{Z}{a_0})^{3/2}(\sigma) \exp(-\sigma/2)$
  $R_{3,1}(r) = \frac{4}{81\sqrt{6}}(\frac{Z}{a_0})^{3/2}(6\sigma - \sigma^2) \exp(-\sigma/3)$
  $R_{3,2}(r) = \frac{4}{81\sqrt{30}}(\frac{Z}{a_0})^{3/2}(\sigma^2) \exp(-\sigma/3)$

Shape and size of orbitals

- $l = 0 \rightarrow Y_{0,0} = \frac{1}{\sqrt{4\pi}}$

- $l = 1 \rightarrow \begin{cases} Y_{P_x} = (\frac{3}{4\pi})^{1/2} \sin\theta \cos\phi \\ Y_{P_y} = (\frac{3}{4\pi})^{1/2} \sin\theta \sin\phi \\ Y_{P_z} = (\frac{3}{4\pi})^{1/2} \cos\theta \end{cases}$

- $l = 2 \rightarrow \begin{cases} Y_{d_{z^2}} = (\frac{5}{16\pi})^{1/2}(3\cos^2\theta - 1) \\ Y_{d_{xz}} = (\frac{15}{4\pi})^{1/2}(\sin\theta \cos\theta \cos\phi) \\ Y_{d_{yz}} = (\frac{15}{4\pi})^{1/2}(\sin\theta \cos\theta \sin\phi) \\ Y_{d_{xy}} = (\frac{15}{16\pi})^{1/2}(\sin\theta \sin 2\phi) \\ Y_{d_{x^2-y^2}} = (\frac{15}{16\pi})^{1/2}(\sin\theta \cos 2\phi) \end{cases}$

Figure: Wavefunction density for a 2p$_z$ orbital taken from
`chem.libretexts.org`

Figure: 1s, 2p, 3d and 4f orbitals taken from `chem.libretexts.org`

- The probability of finding electron in the volume element $d\tau$ around the point (r, θ, ϕ) is
  $\psi^*\psi d\tau = R_{n,l}(r)^2 Y_{l,m_l}(\theta, \phi)^2 r^2 \sin\theta dr d\theta d\phi.$

Electron presence probability

- Normalization condition:
  $\int_0^\infty dr \int_0^{2\pi} d\phi \int_0^\pi d\theta R_{n,l}(r)^2 Y_{l,m_l}(\theta,\phi)^2 r^2 \sin\theta = 1 =$
  $(\int_0^\infty dr R_{n,l}(r)^2 r^2)(\int_0^{2\pi} d\phi \int_0^\pi d\theta Y_{l,m_l}(\theta,\phi)^2 \sin\theta) = 1$

- Radial normalization condition: $\int_0^\infty dr r^2 R_{n,l}(r)^2 = 1$ and angular normalization condition:
  $\int_0^{2\pi} d\phi \int_0^\pi d\theta Y_{l,m_l}(\theta,\phi)^2 \sin\theta = 1$.

- The probability density of finding the electron at a radius r is
  $\int_0^\pi d\theta \int_0^{2\pi} d\phi R_{n,l}(r)^2 Y_{l,m_l}(\theta,\phi)^2 r^2 \sin\theta =$
  $R_{n,l}(r)^2 r^2 \int_0^\pi d\theta \int_0^{2\pi} d\phi Y_{l,m_l}(\theta,\phi)^2 \sin\theta = R_{n,l}(r)^2 r^2$

- Use a software like Mathematica or Maple to plot these curves and compare them.

- Three quantum numbers n, l, m_l arise from solving the Schrodinger equation and m_s arise from the Stern-Gerlach experiment. Together they completely specify the state of an electron.

Multi-electron atoms (Effective charge)

- Schrodinger equation for a multi-electron atom cannot be solved analytically just as the classical mechanical solution to the three body problem cannot be expressed analytically.
- To derive a solution we substitute the interelectronic repulsion with an screening effect, σ and the atomic number with an effective atomic number.
- $Z_{eff} = Z - \sigma$.
- Slater rules for Screening effect, σ, determination:
- Electrons are arranged into a sequence of groups in order of increasing principal quantum number n, and for equal n in order of increasing azimuthal quantum number l, except that s- and p- orbitals are kept together:
  (1s)(2s,2p)(3s,3p)(3d)(4s,4p)(4d)(4f)(5s,5p)(5d)(5f)(6s,6p)(6d)...
- The shielding constant for each group is formed as the sum of the following contributions:

Multi-electron atoms (Effective charge)

- An amount of 0.35 from each other electron within the same group except for the [1s] group, where the other electron contributes only 0.30.
- If the group is of the [ns, np] type, an amount of 0.85 from each electron with principal quantum number (n-1), and an amount of 1.00 for each electron with principal quantum number (n-2) or less.
- If the group is of the [d] or [f] type, an amount of 1.00 for each electron "closer" to the atom than the group. This includes both i) electrons with a smaller principal quantum number than n and ii) electrons with principal quantum number n and a smaller azimuth quantum number l.

Multi-electron atoms (Effective charge)

- Example for Iron:

  $4s$: $0.35 \times 1 + 0.85 \times 14 + 1.00 \times 10 = 22.25$

  $\Rightarrow \quad Z_{\text{eff}}(4s) = 26.00 - 22.25 = 3.75$

  $3d$: $0.35 \times 5 + 1.00 \times 18 = 19.75$

  $\Rightarrow \quad Z_{\text{eff}}(3d) = 26.00 - 19.75 = 6.25$

  $3s, 3p$: $0.35 \times 7 + 0.85 \times 8 + 1.00 \times 2 = 11.25$

  $\Rightarrow \quad Z_{\text{eff}}(3s, 3p) = 26.00 - 11.25 = 14.75$

  $2s, 2p$: $0.35 \times 7 + 0.85 \times 2 = 4.15$

  $\Rightarrow \quad Z_{\text{eff}}(2s, 2p) = 26.00 - 4.15 = 21.85$

  $1s$: $0.30 \times 1 = 0.30 \Rightarrow Z_{\text{eff}}(1s) = 26.00 - 0.30 = 25.70$

- Thus in a multi electron atom energy depends on the quantum number l in addition to the quantum number n. Further in the presence of an external magnetic field electronic energy depends on m_l and m_s as well.

Pauli exclusion principle and Hund's rule

- Pauli exclusion principle states that no two identical Fermionic particles can have identical quantum numbers.
- Total spin quantum number of a system of electrons $S = |\sum_i s_i|$ where s_i is the spin quantum number of the electron i.
- Spin multiplicity is defined as $2S+1$.
- Hund's rule of maximum multiplicity states that the electron configuration maximizing spin multiplicity is more stable.
- Aufbau principle: in the ground state of an atom or ion, electrons fill atomic orbitals of the lowest available energy levels before occupying higher levels.
- Chelchekowski rule states that energy of states is determined by their $n + l$. For states with equal $n + l$, n is more important.
- Madelung (n+l) rule is essentially an approximate empirical rule although with some theoretical justification.

1s
2s 2p
3s 3p 3d
4s 4p 4d 4f
5s 5p 5d 5f ...
6s 6p 6d ... ...

Direction of increasing $n + l$ value
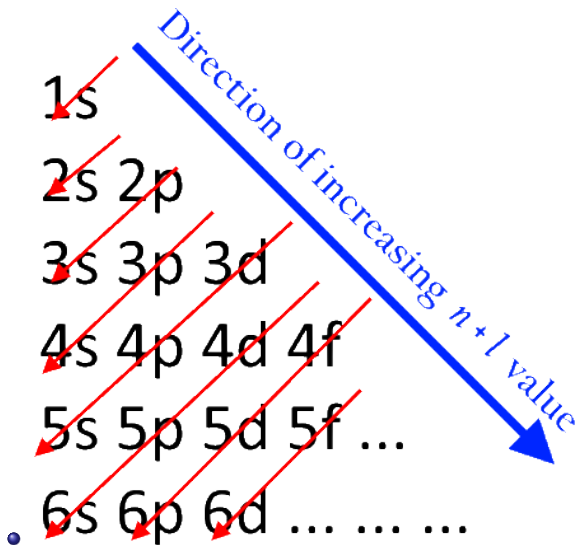
- Use symmetry and stability of filled and half filled electronic sub-levels to justify 19 deviations from Aufbau principle.

Magnetic properties

- Diamagnetic vs. paramagnetic.
- Spin magnetic moment is dominant over orbital magnetic moment and when spin magnetic moment is nonzero it determines atomic magnetic moment.
- Curie's law, $\mathbf{M} = \chi \mathbf{H} = \dfrac{C}{T}\mathbf{H}$, $C = \dfrac{n}{3k_{\mathrm{B}}}\mu_s^2$.
- $\mu_s = \sqrt{n(n+2)}BM$ where $BM = \frac{e\hbar}{2m_e}$ The parameter μ_s is interpreted as the effective magnetic moment per paramagnetic ion.
- Elemental properties are due to interactions of the valence shell (highest in energy or farthest from nuclei in space) electrons of an atom with the external world.
- Since valence shell configuration repeat itself with increasing atomic number, repeat of atomic properties for atoms ordered by atomic number is expected.

The Periodic Table of the Elements

by Robert Claracene version 1.2

Legend:
- alkali metals
- alkaline earth metals
- other metals
- transition metals
- lanthanoids
- actinoids
- metalloids
- nonmetals
- halogens
- noble gases
- unknown elements

☢ radioactive elements have masses in parentheses

atomic mass / or most stable mass number
1st ionization energy in kJ/mol
chemical symbol
name
electron configuration
atomic number
electronegativity
oxidation states most common in bold

notes
- as of yet, elements 113,115,117 and 118 have no official name designated by the IUPAC.
- 1 kJ/mol = 96.485 eV
- all elements are implied to have an oxidation state of zero.

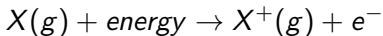electron configuration blocks

Atomic radius

- Van der Waals radius: half the minimum distance between the nuclei of two atoms of the element that are not bound to the same molecule.
- Ionic radius: the spacing between two adjacent oppositely charged ions (the length of the ionic bond between them) should equal the sum of their ionic radii.
- Covalent radius: the distance between two atoms that are bound to each other in a molecule (the length of that covalent bond) should equal the sum of their covalent radii.
- Metallic radius: the nominal radius of atoms of an element when joined to other atoms by metallic bonds.
- For hydrogen like atoms $r \propto \frac{n^2}{Z}$, for any atom $r \propto \frac{n^2}{Z_{eff}}$
- Periodic trend and Lanthanide contraction.

Ionization energy

- Minimum amount of energy required to remove the most loosely bound electron, the valence electron, of an isolated neutral gaseous atom or molecule.
  $X(g) + energy \rightarrow X^+(g) + e^-$
- E_i generally increases as one moves from left to right within a given period (that is, row). E_i generally decreases as one moves from top to bottom in a given group (that is, column).
- 1st ionization energy $X \rightarrow X^+ + e^-$, 2nd ionization energy $X^+ \rightarrow X^{2+} + e^-$, 3rd ionization energy, $X^{2+} \rightarrow X^{3+} + e^-$.
- Nuclear charge, number of shells, effective charge, type of orbital, occupancy of orbital.
- Bohr energy together with the Slater screening suggest the approximation: $I = 13.6 eV \frac{Z_{eff}^2}{n^2}$.

Ionization energy in eV

Element	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
H	13.598											
He	24.587	54.418										
Li	5.392	75.640	122.454									
Be	9.323	18.211	153.897	217.719								
B	8.298	25.155	37.931	259.375	340.226							
C	11.260	24.383	47.888	64.494	392.087	489.993						
N	14.534	29.601	47.449	77.473	97.890	552.072	667.046					
O	13.618	35.117	54.935	77.413	113.899	138.120	739.29	871.410				
F	17.423	34.971	62.708	87.140	114.243	157.165	185.186	953.911	1103.12			
Ne	21.565	40.963	63.45	97.12	126.21	157.93	207.276	239.099	1195.83	1362.20		
Na	5.139	47.286	71.620	98.91	138.40	172.18	208.50	264.25	299.86	1465.12	1648.70	
Mg	7.646	15.035	80.144	109.265	141.27	186.76	225.02	265.96	328.06	367.50	1761.80	1962.66

Ionization energy in eV

Al	5.986	18.829	28.448	119.992	153.825	190.49
	241.76	284.66	330.13	398.75	442.00	2085.98
Si	8.152	16.346	33.493	45.142	166.767	205.27
	246.5	303.54	351.12	401.37	476.36	523.42
P	10.487	19.769	30.203	51.444	65.025	220.421
	263.57	309.60	372.13	424.4	479.46	560.8
S	10.360	23.338	34.79	47.222	72.594	88.053
	280.948	328.75	379.55	447.5	504.8	564.44
Cl	12.968	23.814	39.61	53.465	67.8	97.03
	114.196	348.28	400.06	455.63	529.28	591.99
Ar	15.760	27.630	40.74	59.81	75.02	91.009
	124.323	143.460	422.45	478.69	538.96	618.26
K	4.341	31.63	45.806	60.91	82.66	99.4
	117.56	154.88	175.8174	503.8	564.7	629.4
Ca	6.113	11.871	50.913	67.27	84.50	108.78
	127.2	147.24	188.54	211.27	591.9	657.2

Electron affinity

Electron affinity, EA, is the amount of energy released or spent when an electron is added to an atom or molecule in the gaseous state. $A(g) + e^- \rightarrow A(g)^- \quad \Delta E = -EA$.

H 73																	He (−50)
Li 60	Be (−50)											B 27	C 122	N −0.07	O 141	F 328	Ne (−120)
Na 53	Mg (−40)											Al 42	Si 134	P 72	S 200	Cl 349	Ar (−96)
K 48	Ca 2	Sc 18	Ti 8	V 51	Cr 65	Mn (−50)	Fe 15	Co 64	Ni 112	Cu 119	Zn (−60)	Ga 41	Ge 119	As 78	Se 195	Br 325	Kr (−60)
Rb 47	Sr 5	Y 30	Zr 41	Nb 89	Mo 72	Tc (53)	Ru (101)	Rh 110	Pd 54	Ag 126	Cd (−70)	In 29	Sn 107	Sb 101	Te 190	I 295	Xe (−80)
Cs 46	Ba 14	*	Hf (2)	Ta 31	W 79	Re (14)	Os (106)	Ir 151	Pt 205	Au 223	Hg (−50)	Tl 36	Pb 34	Bi 91	Po (183)	At (222)	Rn (−70)
Fr (47)	Ra (10)	**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg (151)	Cn (<0)	Nh (67)	Fl (<0)	Mc (35)	Lv (75)	Ts (212)	Og (5)

*	La 45	Ce 63	Pr 93	Nd (>185)	Pm (12)	Sm (16)	Eu 83	Gd (13)	Tb (>112)	Dy (>34)	Ho (33)	Er (30)	Tm 99	Yb (−2)	Lu 33
**	Ac (34)	Th (113)	Pa (53)	U (51)	Np (46)	Pu (−48)	Am (10)	Cm (27)	Bk (−165)	Cf (−97)	Es (−29)	Fm (34)	Md (94)	No (−223)	Lr (−30)

Figure: Electron affinity in kJ/mol

- Electronegativity is a measure of an atoms ability or tendency to attract and bring shared electrons toward itself.
- Robert Mulliken developed an electronegativity scale for atoms, equal to the average of the electron affinity and ionization potential.

Chemical bonding

- Valence is the combining capacity of an element; the number of atoms of hydrogen or chlorine with which one atom of the element combines.
- A bonding theory should relate molecular formulas to the atomic structure of the constituting elements.
- The reason for bond formation?
- In 1916, Lewis developed the concept of the electron-pair bond, in which two atoms may share one to six electrons, thus forming a single electron bond, a single bond, a double bond, or a triple bond.
- Niels Bohr proposed a model of the atom and a model of the chemical bond.

Chemical bonding

- The electrons of the atoms of the molecule form a rotating ring whose plane is perpendicular to the axis of the molecule and equidistant from the atomic nuclei.

- The dynamic equilibrium of the molecular system is achieved through the balance of forces between the forces of attraction of nuclei to the plane of the ring of electrons and the forces of mutual repulsion of the nuclei.

- In 1927, the first mathematically complete quantum description of a simple chemical bond, i.e. that produced by one electron in the hydrogen molecular ion, H_2^+, was derived by Burrau.

- Electro-negativity and bonding type: $\Delta\chi > 1.7 \rightarrow$ ionic bond while $\Delta\chi < 1.7 \rightarrow$ covalent bond.

- Octet rule results from the tendency of atoms to reach electronic structure of nearest noble gas.

Oxidation number

- In determining oxidation number it is assumed that shared electrons belong to the more electronegative atom. Except in catenation where electrons are divided equally.
- Total oxidation number of each ion equals the charge on that ion. Sum of oxidation numbers in a neutral species equal zero.
- Fluorine is the most electronegative element and its oxidation number is -1 except in F_2.
- Oxygen is the next most electronegative element with oxidation state -2 in most of its compounds, except for -1 in peroxides (O_2^{2-}), -1/2 in superoxides (O_2^{1-}) and +2 in OF_2.
- Hydrogen has oxidation number +1 except in metal hydrides where its oxidation number is -1.

Formal charge

- Each bond with a more electronegative element increases the oxidation number by one and each bond with the more electropositive element reduces the oxidation number by one.
- $ON = n_v - (n_B + n_N)$
- Formal charge determines the valence of an atom obeying octet.
- Electrons are divided equally in formal charge determination.
- $FC = n_v - (n_B/2 + n_N)$
- E.g., $BeCl_2$, $BeCl_3^-$ $BeCl_4^{2-}$
- Valence = n_v - FC

Lewis structure determination

- Larger electro-positive atoms tend to become central atoms while smaller electronegative atoms tend to be terminal atoms.
- Oxygen, hydrogen and halogens tend to adopt a symmetric configuration around the central atom.
- Carbon atoms tend to bond with other carbon atoms.
- Oxygens rarely bond each other except in peroxides or super-oxides.
- Oxygen and hydrogen tend to bond with each other.
- Only consider stable Lewis structures.

Lewis structure determination

- Add all the valence shell electrons.
- Determine the spacial configuration of atoms.
- Draw the sigma bond backbone and determine number of remaining electrons.
- Use the remaining electrons to complete the octet of atoms by adding non-bonding pairs of electrons from the most electronegative atom to the most electropositive atom.
- Try completing the octet of all atoms by changing nonbonding pairs into π bonds.
- Does the following compounds follow Lewis rules? Draw their structures. $BF_3, PCl_2, CH_2Cl, BF_4^-$

Resonance structures

- In NO_3^- three possible structures are equivalent, correct wave-function is $\psi_{hyb} = a\psi_I + b\psi_{II} + c\psi_{III}$.
- Resonance structures should all have the same atomic arrangement.
- Number of Valence electrons in all structures should be the same.
- The number of bonding electron pairs and the number of non-bonding electron pairs should stay the same.
- Octet should be obeyed.
- Formal charges should be minimized. Positive formal charge on the more electronegative atom and negative formal charge on the more electro-positive atom should be avoided as much as possible.
- The same sign of formal charge should not be placed on neighboring atoms.

Covalent bond energy and bond length

Potential Energy vs. Internuclear Distance
Design & Animation : Dr. Amal K Kumar
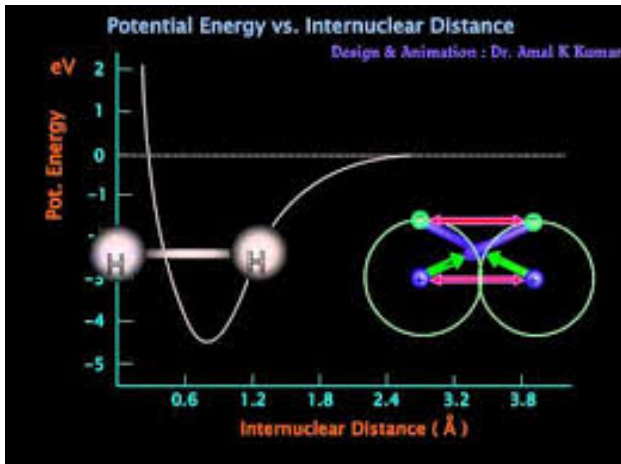
-
- Potential well
- Bond equilibrium energy: D_e
- Equilibrium bond distance: r_e
- Bond energy: $D_0 = D_e + \frac{1}{2}h\nu$ $\qquad \nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$ $\qquad \mu = \frac{m_1 m_2}{m_1 + m_2}$

Bond dissociation

- Homolysis, homolytic fission or homolytic cleavage:
  $$AB(g) \to A(g) + B(g) \qquad \Delta E = D$$
- Heterolysis, heterolytic fission or heterolytic cleavage:
  $$AB(g) \to A^+(g) + B^-(g) \qquad \Delta E = D + IE_A + EA_B$$
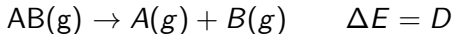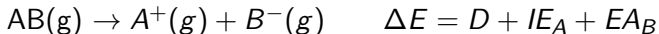
Bond polarization and electric dipole moment

- Presence of partial charges on atoms result in a dipole moment, $\mu = qr$ more generally, $\vec{\mu} = \sum_i q_i \vec{r_i}$.
- Interaction of the dipole moment with an electric field give rise to the torque $\vec{\tau} = \vec{\mu} \times \vec{E}$ and changes the potential energy by $U = -\vec{\mu} \cdot \vec{E}$.
- $1D = 3.336 \times 10^{-30}$ Cm
- $\mu_{cal} = er, \quad \mu_{exp} = \delta er, \quad \delta = \frac{\mu_{exp}}{\mu_{cal}}$.
- Molecular symmetry may set $\mu = 0$ in spite of the presence of polar bonds.
- Axis of symmetry
- Plane of symmetry
- Improper axis of symmetry

Bond energy and electronegativity

- Pauling electronegativity scale.
- $E_{AB}(cal) = \frac{E_{AA} + E_{BB}}{2}$,
- Ionic resonance energy $\Delta = E_{AB}(exp) - E_{AB}(cal)$
- $\Delta \chi = \sqrt{\frac{\Delta}{96.39 kJmol^{-1}}}$
- $|\chi_A - \chi_B| = (eV)^{-1/2}\sqrt{\Delta}$

H 2.1																	He ---
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne ---
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.2	S 2.5	Cl 3.0	Ar ---
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr 3.0
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe 2.6
Cs 0.7	Ba 0.9	La-Lu 1.1-1.2	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	Rn ---
Fr 0.7	Ra 0.9	Ac-No 1.1-1.7															

-

Simplest molecule

- H_2^+ is the simplest molecule and the only molecule for which Schrodinger equation can be solved analytically.
- For H_2^+: D=64 kcal/mol and r=1.07 $\mathring{A}$.
- $U_{H_2^+} = -e^2(\frac{1}{r_A} + \frac{1}{r_B})$
- Consider the locus of points where electrons presence pulls the nuclei towards each other.
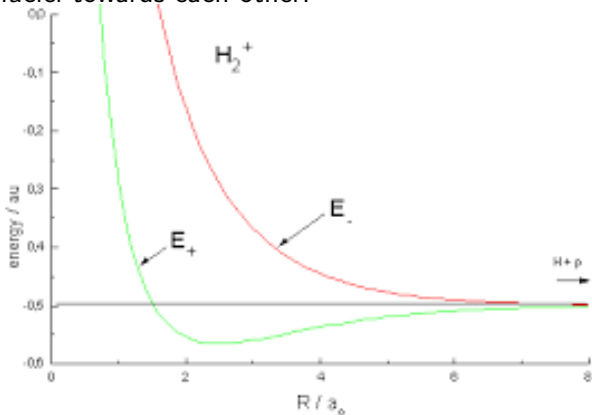
Valence Bond theory

- For H_2: D=104 kcal/mol and r=0.74 Å.
- Proposed by Heitler and London in 1927 combines atomic orbitals to construct molecular orbitals.
- Energy of the constructed orbitals is used to judge how well they resemble the correct orbitals.
- $H_A + H_B \rightarrow H_A - H_B$,

(a) Wave functions combined for σ_{1s}

(b) Bonding probability density

(c) Wave functions combined for σ_{1s}^*
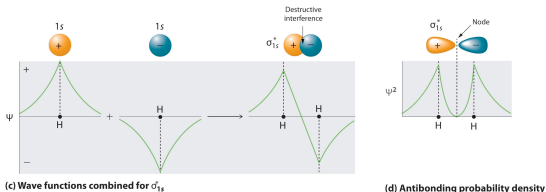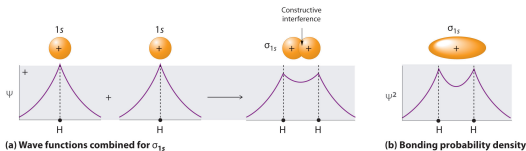
(d) Antibonding probability density

Suggest $\psi_c = \phi_{1s(A)}(1)\phi_{1s(B)}(2)$ but correct it for indistinguishability of electrons (and nuclei) to $\psi_c = N[\phi_{1s(A)}(1)\phi_{1s(B)}(2) + \phi_{1s(A)}(2)\phi_{1s(B)}(1)]$.
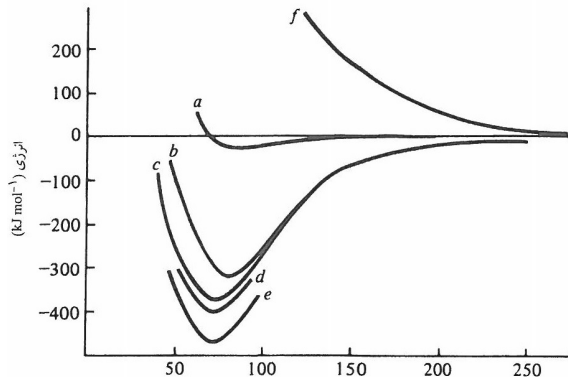
شکل ۳-۵ تغییرات انرژی و طول پیوند در مولکول H_2 در اثر اعمال تصحیحات مختلف
در تابع موج مولکول H_2 (a) برای دو اتم هیدروژن مجزا، (b) برای ψ_c (c)
پس از جایگزین کردن z با بار مؤثر هسته‌ها در ψ_c (d) پس از منظور کردن سهم

Valence Bond theory

- Variation principle: $E_g \leq \langle \psi | \hat{H} | \psi \rangle$.
- Then substitute effective charge for nuclear charge.
- Pauling introduced ionic contribution and other corrections.
- $H_A - H_B \leftrightarrow H_A^+ H_B^- \leftrightarrows H_A^- H_B^+$ where
  $\psi_i = N[\phi_{1s(A)}(1)\phi_{1s(A)}(2) + \phi_{1s(B)}(2)\phi_{1s(B)}(1)]$.
- $\psi = a\psi_c + b\psi_i$
- Bonds are classified by their symmetry, σ bonds have full cylindrical symmetry about the bond axis. σ bonds result from head to head overlap of AO.
- π bonds have one nodal plane and change sign after rotating by π radians. π bonds result from side by side overlap of AO.
- δ bonds change sign after rotating by $\pi/2$ radians.

Molecular energy
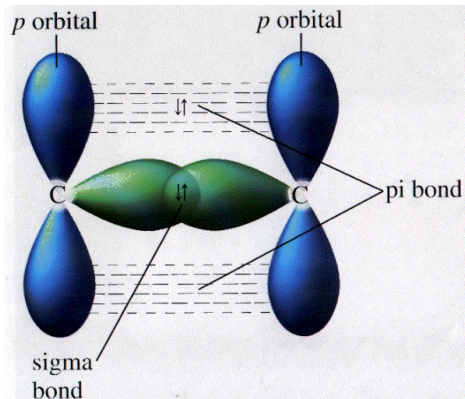
- Adiabatic approximation $H = H_{elec} + H_{Nucl}$
- $H_{Nucl} = H_{trns} + H_{rot} + H_{vib}$,
- Degrees of freedom
- Calculate the energy required for first translational excitation of H_2 and its first vibrational excitation given that $h\nu_{H_2} = 6215 \times k_B$

VSEPR and hybridization

- Molecular shape is determined by σ bonding and non-bonding electrons.
- Valence Shell Electron Pair Repulsion (VSEPR) assumes each shape determining electron pair as a charged balloon and determines molecular shape based on maximum balloon separation.
- Valence bond (VB) theory uses experimental evidence on bond equivalence to deduce the necessity of hybridization.
- Mathematical form of hybrid orbitals determines their orientation in space which in turn determines molecular shape.

VSEPR and hybridization

- sp hybridization, e.g., chemical bonding in acetylene (ethyne) (C_2H_2), $Ag(NH_3)_2^+$ and CO_2 result in linear molecules with π radian bond angles.

s orbital   p orbital

Hybridize

180

linear, 180°

Two sp hybrid orbitals   sp hybrid orbitals shown together
(large lobes only)

-
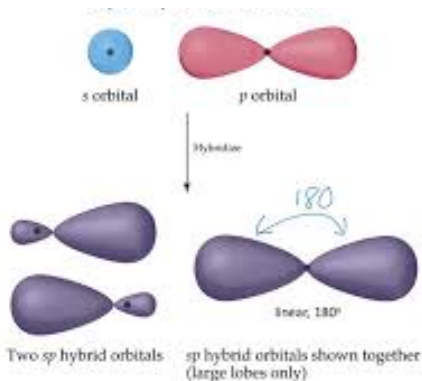
VSEPR and hybridization

- sp^2 hybridization, e.g., BF_3 and BH_3 and $Cu(CN)_3^{2-}$.
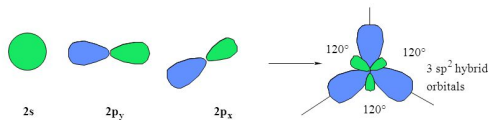
-
- sp^3 hybridization, e.g., CH_4, NH_3 and H_2O and $Ni(CO)_4$.
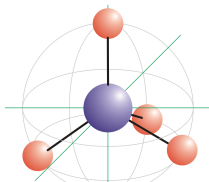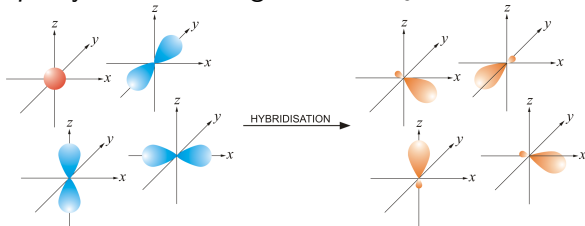
VSEPR and hybridization

- sp^3d hybridization, consists of equatorial sp^2 and axial pd hybridization, e.g., PF_5, PCl_5, SF_4 and PF_3Cl_2. Resulting full structure is trigonal bi-pyramid (TBP).

-
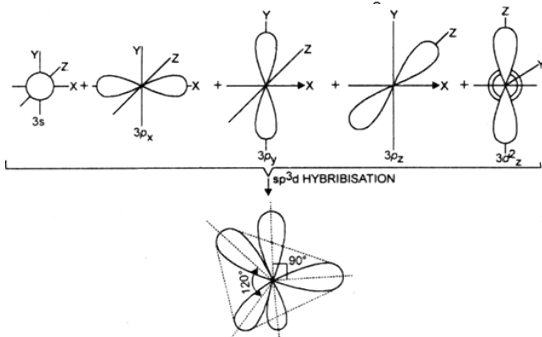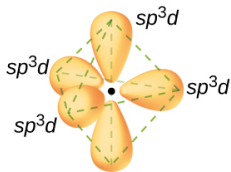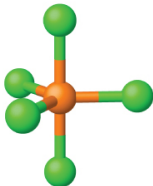
VSEPR and hybridization

- Bent rule suggests that more electronegative atoms engage with more electropositive orbitals.
- sp^3d^2 or d^2sp^3 hybridization, e.g., SF_6, and $Mo(CO)_6$. Resulting full structure is octahedral. This hybridization is most common among metal complexes.

sp^3d^2

sp^3d^2 sp^3d^2

sp^3d^2 sp^3d^2
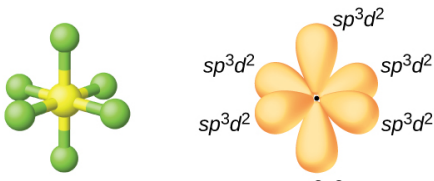
-
- sp^2d or dsp^2 built of s, p_x, p_y, $d_{x^2-y^2}$ produces a square shaped molecule. E.g., $[NiCl_4]^{2-}$ and $[Ni(CN)_4]^{2-}$ and $[Pt(Cl)_4]^{2-}$.

- Atoms which access d-orbitals can go beyond octet in order to avoid having large formal charges. E.g., $HClO_4$, ClO_4^-, SO_4^{2-}
- Maximum number of half-filled orbitals of an atom determines the maximum number of bonds of that atom.

Complexes

- Lewis acid/base definition.
- Complexes are made of a central atom (called nuclear atom) acting as a Lewis acid and a number of non-metal ligands acting as Lewis bases (called coordinating group or ligand). E.g., $Ag(NH_3)_2^+$, $Fe(CN)_6^{3-}$
- In complexes both the nuclear atom and ligands are stable species, BF_4^-.
- Stereochemistry:
- Two fold coordination in Cu(I), Ag(I), Au(I) and some Hg(II), Eg, $Cu(CN)_2^-$, $Ag(NH_3)_2^+$, $Au(CN)_2^-$ and $Hg(NH_3)_2^{2+}$.
- Fourfold coordination with tetrahedral geometry, e.g., $ZnCl_4^{2-}$, $Zn(CN)_4^{2-}$, $Cd(CN)_4^{2-}$ and $Hg(CN)_4^{2-}$
- Fourfold coordination with square planer geometry in complexes of Pd(II), Pt(II), Ni(II), Cu(II) and Au(III).
- Unidentate ligands like F⁻, Cl⁻, OH⁻, H_2O, NH_3, and CN⁻.
- Bidentate ligand ethylene diamine, $NH_2CH_2CH_2NH_2$ and oxalate ion $[O_2CCO_2]^{2-}$.

Molecular orbital theory

- Molecular orbitals (MOs) are made of linear combination of atomic orbitals (LCAO).
- Combining atomic orbitals are required to have the same symmetry and similar energy levels.
- Upon composition of a bonding MO electron density between bonding atoms increases while upon composition of an anti-bonding MO electron density between bonding atoms decreases.
- Electron in a bonding MO strengthens the bond while an electron in an anti-bonding MO weakens the bond.
- $\psi_{MO} = a\psi_A + b\psi_B \quad \psi_{MO}^* = c\psi_A - d\psi_B$
- $\psi_{MO}^2 \propto (\psi_A + \psi_B)^2 = \psi_A^2 + \psi_B^2 + 2\psi_A\psi_B$.
  $\psi_{MO}^{*2} \propto (\psi_A - \psi_B)^2 = \psi_A^2 + \psi_B^2 - 2\psi_A\psi_B$.
- $s = \int \psi_A\psi_B d\tau$ is the overlap integral.

Molecular orbital theory

- The dimension of orbital space is conserved, so AOs combine to make the same number of MOs.
- Each bonding MO is more stable than the AOs it is made of while each anti-bonding MO is less unstable than the AOs it is made of.
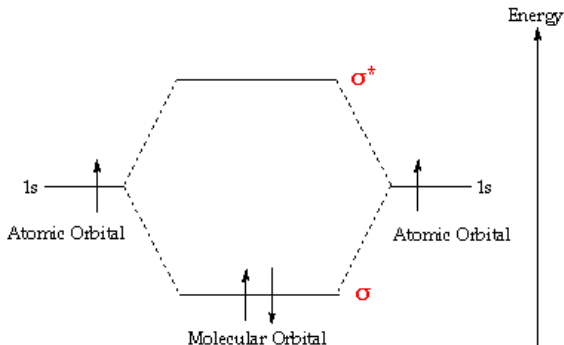
-
- Pauli exclusion principle and Hund's maximum multiplicity rule must be obeyed in filling MOs.

Molecular orbital theory

- Bond order is defined as $B.O. = \frac{NBe - NAe}{2}$.
- BO is directly proportional to bond energy and inversely proportional to bond length.
- B_2 type and F_2 type MO energy levels.

MO for B_2, C_2, N_2

MO for O_2, F_2
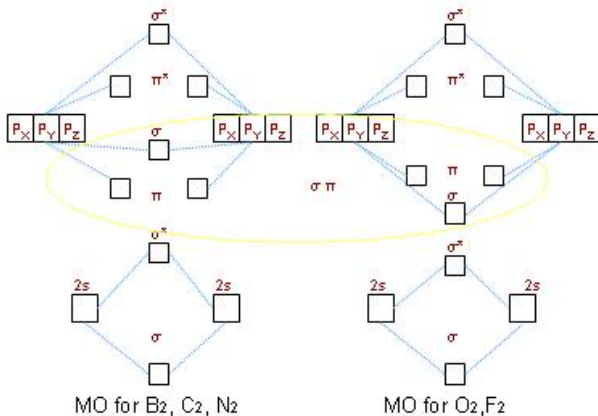
Molecular orbital theory

- Unpaired electrons and thus the materials magnetic properties can be deduced from filling MOs.
- In heteronuclear compounds bonding MO would resemble the more electronegative constituent AO while the anti-bonding MO would resemble the more electropositive constituent AO.

Molecular orbital theory
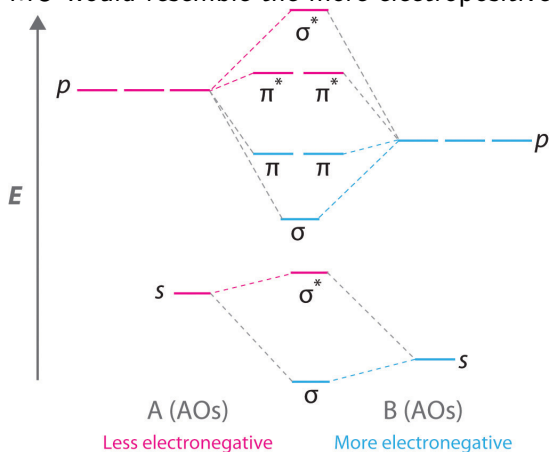
- Consider LiH as the simplest heteronuclear molecule.
- Frontier molecular orbitals:
- Highest Occupied Molecular Orbital (HOMO)
- Lowest Unoccupied Molecular Orbitals (LUMO)
- A good approximation for reactivity could be found by looking at the frontier orbitals.

Solids and Liquids

- Intermolecular forces
- Lennard-Jones potential
- Crystal structures, Bravais lattices, unit cell, and closed packed systems.
- Electron sea model from an MO view point.
- Liquid properties like viscosity, surface tension and vapor pressure.
- Phase diagram for pure material.

Physical states of matter

- Kinetic energy tends to push the molecules away from each other while attractive forces pull molecules towards each other.
- In ideal gases there is no intermolecular forces while in real gases intermolecular forces are small.
- In general $\langle K_E \rangle \propto T(K)$, for an ideal monatomic gas $K_E = \frac{3}{2} k_B T,$ $\qquad k_B = R/N_A.$
- The state of matter is determined by comparing intermolecular attractive potential energy with molecular kinetic energy.
- High portion of free space in gases causes easy diffusion of gases in one another.
- Diffusion in liquids is due to movement of layers on top of one another while in solids it is due to molecular vibrations.
- $\langle K_E \rangle = \frac{1}{2} m \langle v^2 \rangle \propto T(K)$, So the heavier a particles is the slower it is and easier to condense.

Intermolecular forces

- The weight (volume) effect is exemplified in the melting and boiling points of alkanes.

Molecular Name	Formula	Melting Point ($^{\circ}$C)	Boiling Point ($^{\circ}$C)	Density (20°C)
methane	CH_4	-182	-164	0.668 g/L
ethane	C_2H_6	-183	-89	1.265 g/L
propane	C_3H_8	-190	-42	1.867 g/L
butane	C_4H_{10}	-138	-1	2.493 g/L
pentane	C_5H_{12}	-130	36	0.626 g/mL
hexane	C_6H_{14}	-95	69	0.659 g/mL
octane	C_8H_{18}	-57	125	0.703 g/mL
decane	$C_{10}H_{22}$	-30	174	0.730 g mL

Table: Table taken from libretexts

- Melting and boiling points, solubility, surface tension and viscosity depend on intermolecular forces.

Intermolecular forces

- Coulomb interaction $\propto \frac{q_1 q_2}{r}$ is the strongest structural interaction.
- Van der waals interactions include dipole-dipole interaction $\propto \frac{\mu_1 \cdot \mu_2}{r^3}$ and London interactions.
- Polar bond as a necessary condition for molecular dipole moment.
- If a molecule is indistinguishable after rotating by $\frac{2\pi}{n}$ radians around an axes, that symmetry axes is called c_n.
- A plane of symmetry is an imaginary plane that bisects a molecule into halves that are mirror images of each other.
- An improper rotation is performed by rotating the molecule $360°/n$ followed by reflection through a plane perpendicular to the rotation axis.

Intermolecular forces

- If the resulting configuration is indistinguishable from the original, we say there exists an n-fold improper rotation axis (or S_n axis) in the molecule.
- Presence of S_{2n} in a molecule results in zero dipole moment in spite of polar bonds.
- London or dispersion forces are due to spontaneous dipoles created by quantum effects. $E_{AB}^{\mathrm{disp}} \approx -\frac{3}{2} \frac{I_A I_B}{I_A + I_B} \frac{\alpha_A \alpha_B}{r^6}$
- I represents the ionization potential while α represents polarizability.
- Increasing the size and surface area of a molecule increases its polarizability which in turn increases its London forces.
- Compare the range for these three forces.

Hydrogen bonding

- A hydrogen bond is an electrostatic attraction between two polar groups that occurs when a hydrogen atom covalently bound to a highly electronegative atom such as nitrogen, oxygen, or fluorine experiences the electrostatic field of another highly electronegative atom nearby.

- Hydrogen bonds can occur between molecules (intermolecular) or within different parts of a single molecule (intra-molecular).

- Depending on the nature of the donor and acceptor atoms which constitute the bond, their geometry, and environment, the energy of a hydrogen bond can vary between 1 and 40 kcal/mol.

- HBs are somewhat stronger than a van der Waals interaction while weaker than covalent or ionic bonds. It occurs in inorganic molecules such as water and in organic molecules like DNA and proteins.

Hydrogen bonding

- Intermolecular hydrogen bonding is responsible for the high boiling point of water (100 °C) compared to other group 16 hydrides.
- Intermolecular hydrogen bonding is partly responsible for the secondary and tertiary structures of proteins and nucleic acids. It also plays an important role in the structure of polymers.
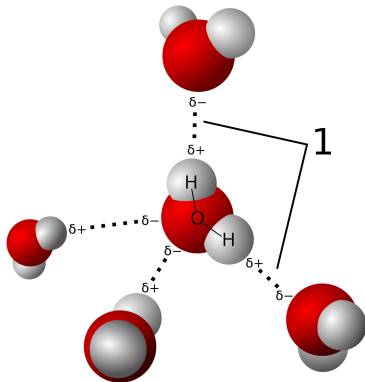
Lennard-Jones potential

- Non-bonding intermolecular interactions are qualitatively similar to bonding interactions.
- For atoms and approximately spherical molecules LJ is a good approximation to intermolecular interaction,
  $V_{LJ}(r) = 4\epsilon[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^6]$.
- r is internuclear distance while σ and ϵ are experimentally determined parameters. $\sigma/2$ can be ascribed to molecular (atomic) radius.
- LJ interaction can produce Van der waals molecules.

Solids

- There are crystalline solids with long range order where a unit cell repeats itself over and over again. E.g. ice, various salts and various metals.
- Amorphous solids lack any long range order, they are isotropic just as liquids and gases are isotropic. E.g. glasses, asphalt and polymers.
- Crystalline solids are anisotropic and have a definite melting point. While amorphous solids melt over a range of temperatures.
- Amorphous solids can be regarded as liquids with extremely high viscosity.

- Space lattice is an ordered 3-D and repeatable arrangement of points with the same environment in the crystal.
- Unit cell is the smallest building block of a lattice whose repetition in 3-D can produce the entire lattice. It determines the geometric shape of a crystal.


-
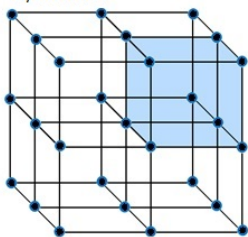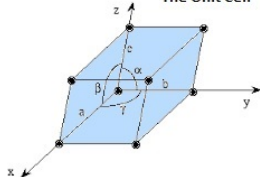
Crystal structures, space lattices and unit cells

- A crystal system is described by three basis vectors.
- The lengths of the principal axes, or edges, of the unit cell and the angles between them are the lattice constants, also called lattice parameters or cell parameters.
- The crystal structure and symmetry play a critical role in determining many physical properties, such as cleavage, electronic band structure, and optical transparency.
- The triclinic lattice is the least symmetric of the 14 three-dimensional Bravais lattices.

Bravais lattice	Parameters	Simple (P)	Volume centered (I)	Base centered (C)	Face centered (F)
Triclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} \neq \alpha_{23} \neq \alpha_{31}$				
Monoclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{23} = \alpha_{31} = 90°$ $\alpha_{12} \neq 90°$				
Orthorhombic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Tetragonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Trigonal	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} < 120°$				
Cubic	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Hexagonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = 120°$ $\alpha_{23} = \alpha_{31} = 90°$				

Table ... Bravais lattices in three dimensions

Unit cells

- In the monoclinic system, the crystal is described by vectors of unequal lengths, as in the orthorhombic system. They form a rectangular prism with a parallelogram as its side. E.g., Monoclinic sulphur, $Na_2SO_4 10H_2O$, $PbCrO_3$.

- Orthorhombic lattices result from stretching a cubic lattice along two of its orthogonal edges by two different factors, resulting in a rectangular prism with a rectangular base (a by b) and height (c), such that a, b, and c are distinct. All three bases intersect at $90°$ angles, so the three lattice vectors remain mutually orthogonal. E.g., Rhombic sulfur, KNO_3, $BaSO_4$.

- Tetragonal crystal lattices result from stretching a cubic lattice along one of its lattice vectors, so that the cube becomes a rectangular prism with a square base (a by a) and height (c). E.g., White tin, SnO_2, TiO_2, $CaSO_4$.

- Rhombohedral: having threefold symmetry. E.g., Calcite ($CaCO_3$), cinnabar (HgS).

Closest packed structures

- Corresponding examples of triclinic are $K_2Cr_2O_7$, $CuSO_4.5H_2O$, H_3BO_3.
- Graphite, ZnO, CdS are examples of hexagonal lattice.
- NaCl, zinc blende, copper metal, KCl, Diamond, Silver are examples of crystallization in a cubic lattice.
- Most metals like Ni, Cu, Au possess FCC structures. Metals like Na, Li, Ba crystallize in BCC structures. Po crystallizes in a simple cubic structure.
- At room temperature Iron is in α phase, BCC. At temperatures greater than $910°C$ it is in γ phase, FCC.
- Closest packed structures have the least amount of free space among molecules.
- In structures made of spheres the space enclosed by 4 spheres is called a tetrahedral hole while the space enclosed by 6 spheres is called an octahedral hole.
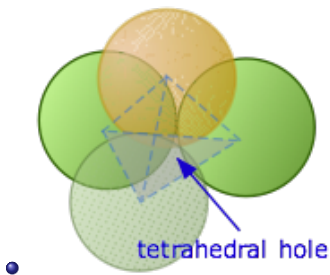
Closest packed structures
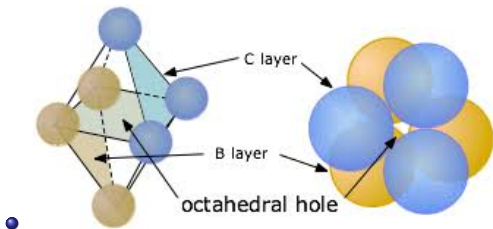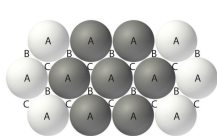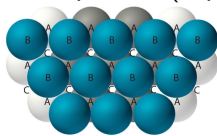

Figure: Tetrahedral hole taken from `chem.libretexts.org`

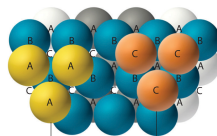Figure: Octahedral hole taken from `chem.libretexts.org`

Closest packed structures

- ababab... hexagonal closest packed (hcp)
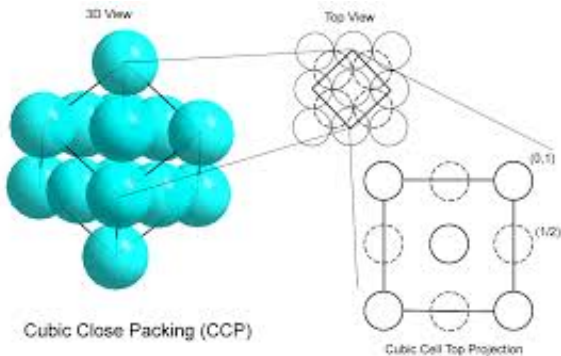- abcabcabc.... cubic closest packed (ccp)

(a) Single layer

(b) Two layers

(c) Three layers

hcp   ccp

30 View

Top View

(0,1)

(1/2)

Cubic Close Packing (CCP)

Cubic Cell Top Projection
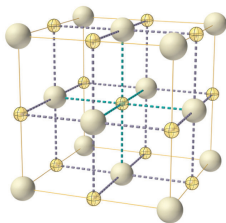
Crystal structures of ionic compounds

- Coordination number CN is the number of closest neighbors in a crystal structure. Maximum CN of 12 is observed in hcp and ccp.
- In a closest packed structure the number of tetrahedral holes are twice the number of spheres while there are as many octahedral holes as spheres.
- The octahedron is a polyhedron made from 8 regular triangles. If you connect the six centers of the surrounding spheres of a d^2sp^3 hybridized central atom you generate the octahedron.
- Packing factor is the portion of crystal volume taken up by constituting particles. It is 74% for closest packed structures while 68% for a bcc crystal (CN=8).
- In salts comonly larger ions constitute a crystal in whose holes smaller ions fit. Smaller ions should be large enough to prevent larger ions touching each other.
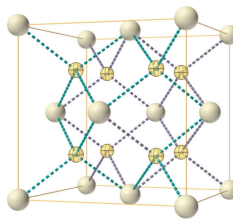
Crystal structures of ionic compounds

- When $0.73 < \frac{r_\le}{r_>} < 1$ larger ion makes a cubic structure and the smaller ion sits in cubic holes.
- When $0.414 < \frac{r_\le}{r_>} < 0.732$ larger ion makes a closest packed structure and the smaller ion sits in octahedral holes.
- E.g., in NaCl, Cl$^-$ ions constitute an fcc crystal while Na$^+$ ions sit in octahedral holes. CN=6.
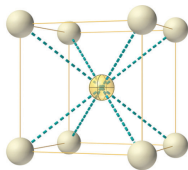
(a) Cubic hole in a single unit cell **(b) Octahedral holes in a single unit cell** **(c) Tetrahedral holes in a single unit ce**

Figure: Crystal holes taken from `saylordotorg.github.io/`

Crystal structures of ionic compounds

- When $0.225 < \frac{r_\le}{r_>} < 0.414$ larger ion makes a closest packed structure and the smaller ion sits in tetrahedral holes.
- E.g., in Zinc blende, S^{2-} constitute an fcc structure half of its tetrahedral holes occupied by Zn^{2+}.
- In Florite crystal, CaF_2, Ca^{2+} constitutes an fcc structure all of its tetrahedral holes occupied by F^- ions. CN for Ca^{2+} is 8 and for F^- ions is 4.
- In anti-Florite crystal, like Li_2O and Rb_2S anions constitute a ccp lattice while cations fill the tetrahedral holes.
- Up to now we talked about perfect crystals.

Crystal defects

- Crystal defects give rise to a variety of electrical, optical and magnetic properties.
- In point defects some of the crystal positions are empty.
- In non-stoichiometric point defects the ratio of different crystal constituents stay the same.
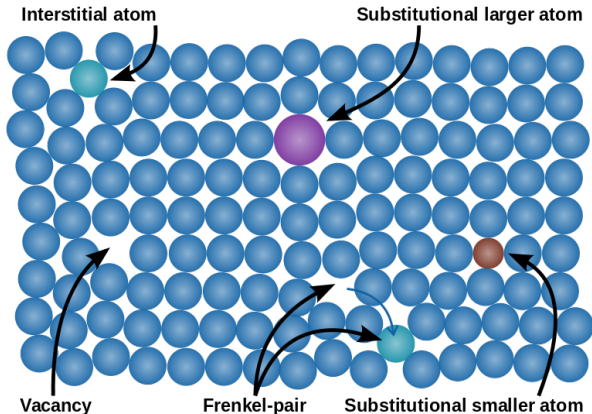
Crystal defects

- In Schottky defect cations and anions are deleted from some crystal positions (vacancies are created).
- In Frenkel defect some ions are misplaced from their ideal crystal structure positions.
- Stoichiometric defect include cationic (fewer cations than stoichiometry) and anionic (fewer anions than stoichiometry) defect.
- Cationic or anionic defects give rise to non-stoichiometric compounds. E.g., Cationic defect $Fe_{1-\delta}O$, anionic defect $NaCl_{1-\delta}$.
- Crystal electroneutrality is always maintained.

Crystal defects

- An F-center, Farbe center or color center is a type of crystallographic defect in which an anionic vacancy in a crystal is filled by one or more unpaired electrons.
- Electrons in such a vacancy tend to absorb light in the visible spectrum such that a material that is usually transparent becomes colored. This is used to identify many compounds, especially zinc oxide (yellow).

Burger's Vector

(a)

Burger's Vector

(b)

**Edge Dislocation**
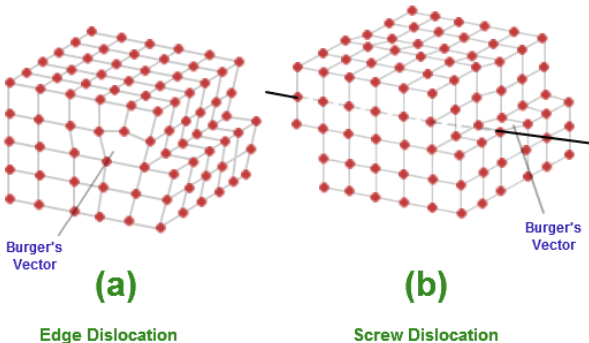
Screw Dislocation

Lattice energy and Born-Haber cycle

- The Burgers vector, is a vector, that represents the magnitude and direction of the lattice distortion resulting from a dislocation in a crystal lattice.
- Lattice energy, ΔH_L, is the energy released when gaseous ions combine forming one mole of a crystalline solid.
- One dimensional lattice.
- Born-Lande equation: $\Delta H_L = \frac{-Z_c Z_a e^2 N M}{4\pi\epsilon_0 r_0}(1 - \frac{1}{n})$
- M = Madelung constant, relating to the geometry of the crystal
- ϵ_0 = permittivity of free space $4\pi\epsilon_0 = 1.112 \times 10^{-10} C^2/(Jm)$
- r_0 = distance to closest neighbor ion.
- n = Born exponent, typically a number between 5 and 12, determined experimentally by measuring the compressibility of the solid, or derived theoretically.
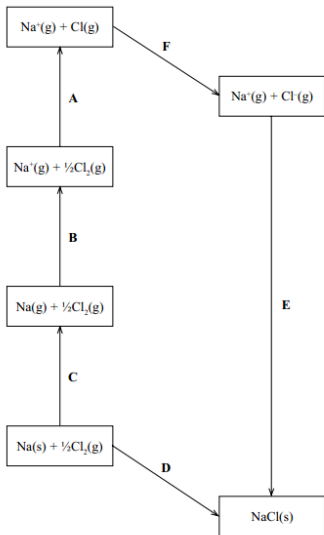
Lattice energy and Born-Haber cycle

- Hess's law states that the change in energy for a chemical reaction is independent of the path taken, it is an application of the principle of conservation of energy or first law of thermodynamics.
- Born-Haber cycle uses Hess's law to find a relation among various values of ΔH.
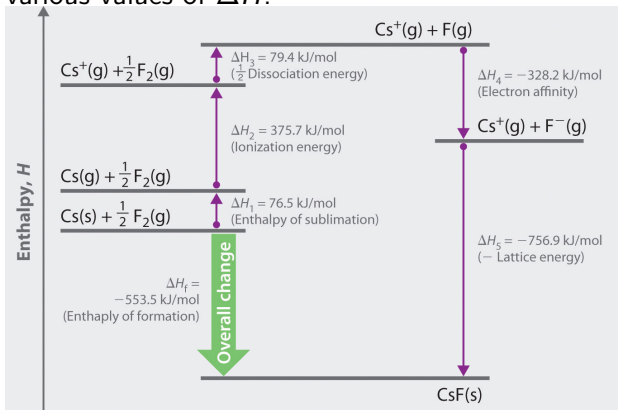
Energy change	Letter	ΔH/kJ mol^{-1}
Lattice energy for sodium chloride	E	-775
Enthalpy change of atomization of sodium	C	+109
Enthalpy change of atomization of chlorine	A	+121
First ionization energy of sodium	B	+494
First electron affinity of chlorine	F	
Enthalpy change of formation of sodium chloride	D	-411

$Na^+(g) + Cl(g)$

F

A

$Na^+(g) + Cl^-(g)$

$Na^+(g) + \frac{1}{2}Cl_2(g)$

B

E

$Na(g) + \frac{1}{2}Cl_2(g)$

C

$Na(s) + \frac{1}{2}Cl_2(g)$

D

$NaCl(s)$

X-Ray diffraction

- Bragg's law, or Wulff–Bragg's condition, a special case of Laue diffraction, gives the angles for coherent and incoherent scattering from a crystal lattice.

- When X-rays are incident on an atom, they make the electronic cloud move as does any electromagnetic wave. The movement of these charges re-radiates waves with the same frequency; this phenomenon is known as Rayleigh scattering (or elastic scattering).

- Constructive wave interference condition (Bragg equation) $n\lambda = 2d\sin\theta$
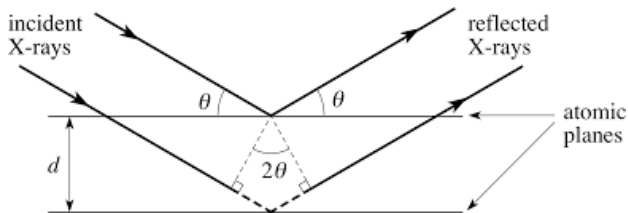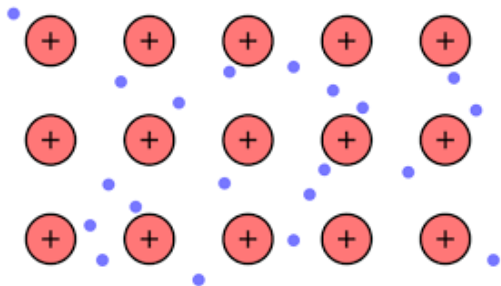
Metals

- A metal is a material that is typically hard when in solid state, shiny, and has good electrical and thermal conductivity.

- Metals are generally malleable—that is, they can be hammered or pressed permanently out of shape without breaking or cracking—as well as fusible and ductile.

- Around 90 of the 118 elements in the periodic table are metals; the others are nonmetals or metalloids, though elements near the boundaries of each category have been assigned variably to either. Some elements appear in both metallic and non-metallic forms.

- The atoms of metallic substances are typically arranged in one of three common crystal structures, namely body-centered cubic (bcc), face-centered cubic (fcc), and hexagonal close-packed (hcp). Some metals adopt different structures depending on the temperature.

Metals: Electron sea model

- Atoms of metals readily lose their outer shell electrons, resulting in a free flowing cloud of electrons within their otherwise solid arrangement.
- This provides the ability of metallic substances to easily transmit heat and electricity.
- The solid characteristic of the metal is produced by electrostatic interactions between each atom and the electron cloud. This type of bond is called a metallic bond.
- Electron sea give rise to high electrical conductivity, high thermal conductivity, and high density; being malleable and ductile (deforming under stress without cleaving).
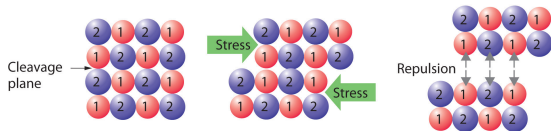
Metals: Electron sea model

-
- Metals are usually inclined to form cations through electron loss, reacting with oxygen in the air to form oxides over various time scales (iron rusts over years, potassium burns in seconds).
- The transition metals (e.g., iron, copper, zinc, and nickel) are slower to oxidize because they form a passivating layer of oxide that protects the interior.
- Other metals like palladium, platinum and gold, do not react with the atmosphere at all.

Metals and the band theory

- Some metals form a barrier layer of oxide on their surface which cannot be penetrated by further oxygen molecules thus retain their shiny appearance and good conductivity for decades.
- E.g., aluminum, magnesium, some steels, and titanium.
- To understand conduction one has to apply MO theory to solid crystals.
- Each atom contribute its 4 valence orbitals, so in a crystal of N atoms there are 4N molecular orbitals.
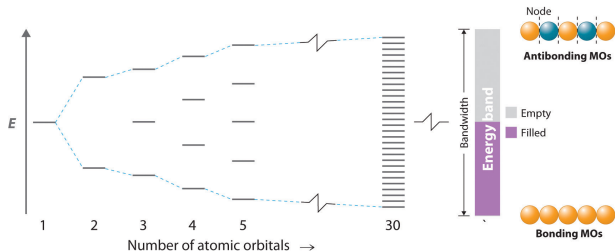
Metals and the band theory

- Large numbers of closely spaced MO's constitute an energy band.
- Fermi level is the mid-point between HOMO and LUMO.
- Portion of the energy band below the Fermi level is called valence band (VB).
- Portion of the energy band above the Fermi level is called conduction band.
- Band gap is defined as: $E_g = E_{CB} - E_{VB}$
- Electricity conduction requires some electrons in the conduction band (CB).
- Conductors: $E_g < 0.25$ eV, semi-conductors: 0.25 eV $< E_g < 2$ eV, insulators: $E_g > 2$ eV.
- Conduction-band gap relation for semi-conductors: $\ln \sigma = A - \frac{E_g}{0.00017T}$
- In a group from top to bottom electronegativity decreases and thus E_g decreases.

Network solids

- A solid crystal all of whose constituting atoms are held together by covalent bonds.
- Diamond and graphite are the most important allotropes of carbon, respectively, with sp^3 and sp^2 hybridization.
- Diamond network similar to that of Silica (SiO_2) is a 3D one while graphite network is a 2D network.


-
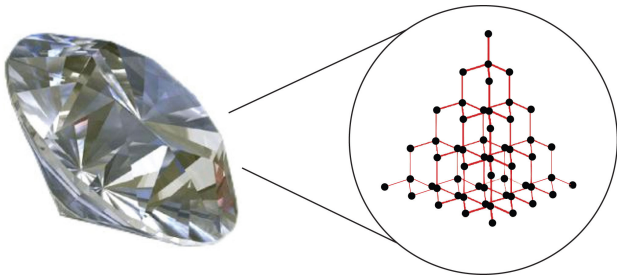
Network solids
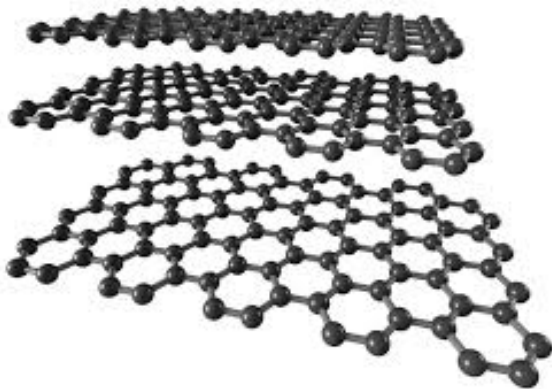
-
- Graphite is a crystalline allotrope of carbon, a semimetal, a native element mineral, and a form of coal; it is used in thermochemistry as the standard state for defining the heat of formation of carbon compounds.
- Graphite has a layered, planar structure.

Molecular solids

- The individual layers are called graphene. In each layer, the carbon atoms are arranged in a honeycomb lattice with separation of 0.142 nm, and the distance between planes is 0.335 nm.
- Glass is the amorphous form of Silica. Its properties are controlled by adding various additives.
- In molecular solids molecules take up crystalline positions. Crystal is kept together by dipole-dipole and London forces.
- Liquid crystal is an intermediate between solid and liquid in the sense that it has 2D order but not 3D order. They have anisotropy in mechanical, optical and electrical properties.
- Most substances that exhibit the properties of liquid crystals consist of long, rigid rod- or disk-shaped molecules that are easily polarizable and can orient themselves in one of three different ways.

Liquids

- Liquids are generally constituted of molecules with less than 20 atoms.
- Thermal conductivity of a fluid is the rate at which it transport energy from a surface at higher temperature to one at a lower temperature.
- Rate of energy transport per unit area $= -\kappa \frac{\Delta T}{\Delta d}$
- The viscosity of a fluid is a measure of its resistance to gradual deformation by shear stress or tensile stress.
- Couette flow occurs where a layer of fluid is trapped between two horizontal plates, one fixed and one moving horizontally at constant speed u. This fluid has to be homogeneous in the layer and at different shear stresses.

Viscosity
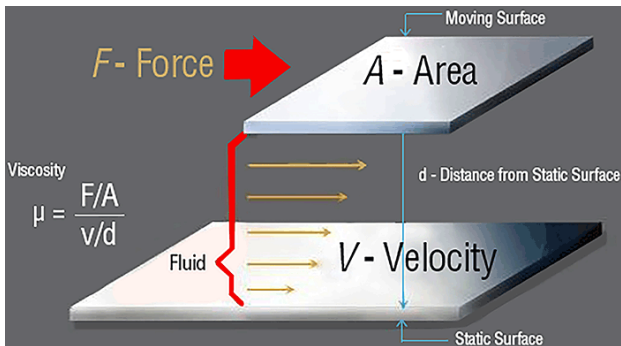
- An external force is required in order to keep the top plate moving at constant speed. $F = \mu A \frac{u}{y}$.
- Viscosity coefficient increases with the strength of inter-molecular interactions and with molecular weight.
- The more symmetric a molecule the less its viscosity and vice versa.
- Viscosity decreases with increasing temperature.

Diffusion

- Diffusion: Net rate at which one gas moves across an imaginary surface into the other gas depends on the area of the surface, the concentration change per unit length, and the nature of the gases.
- Rate of diffusion per unit area $= -D\frac{\Delta n}{\Delta d}$.
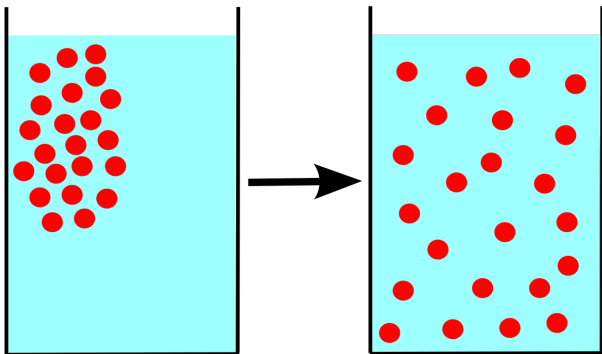
Surface tension

- The difference between the average number of interactions of a molecule in the bulk and that of the same molecule in the surface of a liquid suggest that a liquid is stabilized by minimizing its surface.
- The energy required for increasing liquid surface by unit surface area is called surface tension (in J/m^2).
- Depends on inter-molecular forces.

Diagram not to scale
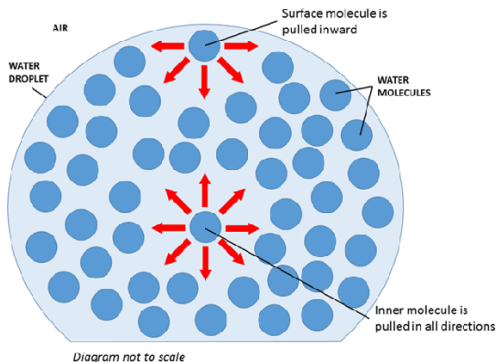
Surface tension

- Capillary effect or capillary action: is the ability of a liquid to flow in narrow spaces without the assistance of, or even in opposition to, external forces like gravity.
- The effect can be seen in the drawing up of liquids between the hairs of a paint-brush, in a thin tube, in porous materials such as paper and plaster, in some non-porous materials such as sand and liquefied carbon fiber, or in a biological cell.
- Compare a glass capillary in water with a glass capillary in Mercury.
- It occurs because of intermolecular forces between the liquid and surrounding solid surfaces.
- If the diameter of the tube is sufficiently small, then the combination of surface tension (which is caused by cohesion within the liquid) and adhesive forces between the liquid and container wall act to propel the liquid.
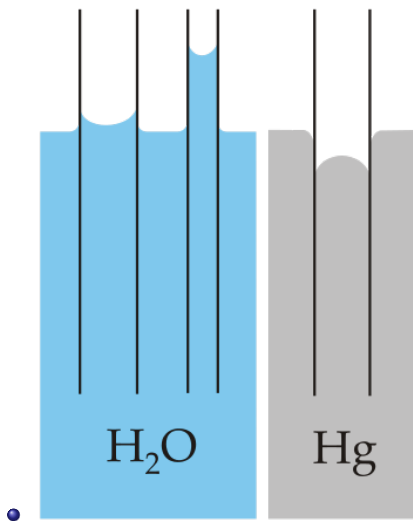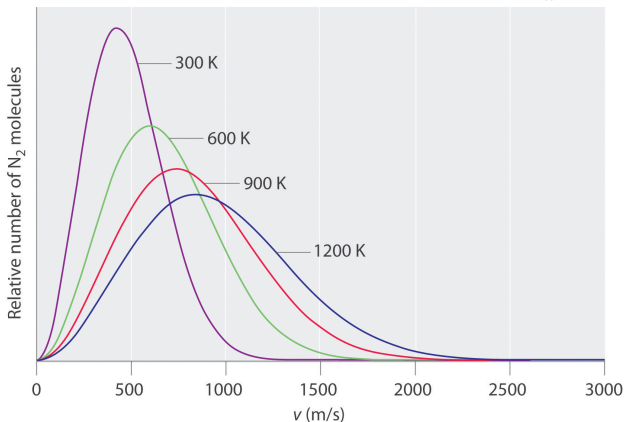
Surface tension

Figure: Capillarity in water and mercury taken from wikipedia

Vaporization and vapor pressure of liquids

- Conditions for vaporization
- Speed of vaporization.
- Temperature determines the velocity distribution of molecules.
- Maxwell-Boltzmann distribution, $\frac{dN}{N} = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{mc^2}{2kT}} c^2 dc$

Vaporization and vapor pressure of liquids

- Vapor liquid equilibrium
- Vapor pressure
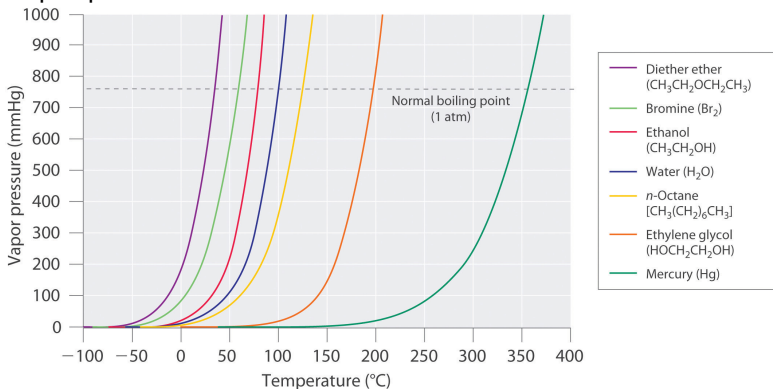
- Clapeyron equation: $\frac{dP}{dT} = \frac{\Delta H_{vap}}{T \Delta V_{vap}}$
- Clausius–Clapeyron equation: $\ln P = \frac{-\Delta H_{vap}}{RT} + C$
- Boiling point and normal boiling point.

Phase diagram

- Trouton's rule: $\frac{\Delta H_{vap}}{T_b} = 88$ J /mol K
- A phase diagram is used to show conditions at which thermodynamically distinct phases occur and coexist at equilibrium.
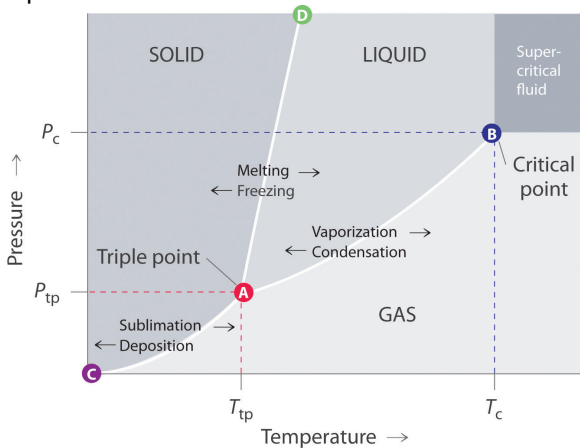
- lines of equilibrium or phase boundaries

Phase diagram

- Triple points are points on phase diagrams where three distinct phases exist in equilibrium with one another (lines of equilibrium intersect).
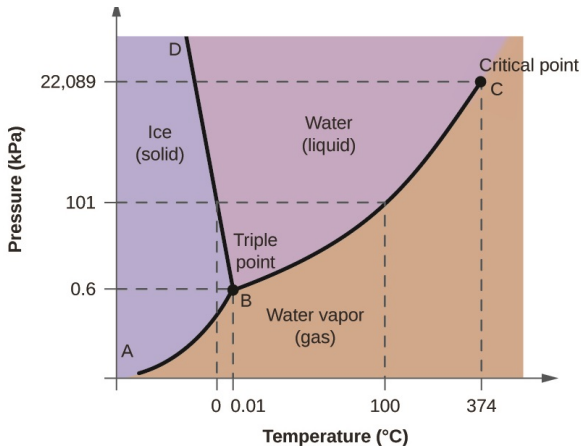
Phase diagram

- phase boundary between liquid and gas does not continue indefinitely. It terminates at a point on the phase diagram called the critical point.
- In water, the critical point occurs at around $T_c = 647.096$ K ($373.946°$C), $p_c = 22.064$ MPa (217.75 atm) and $\rho_c = 356 kg/m^3$.

-
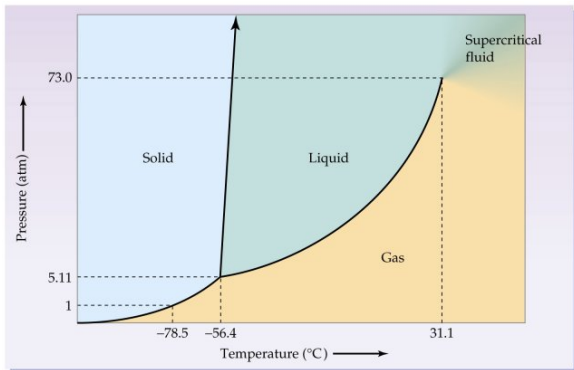
Critical point
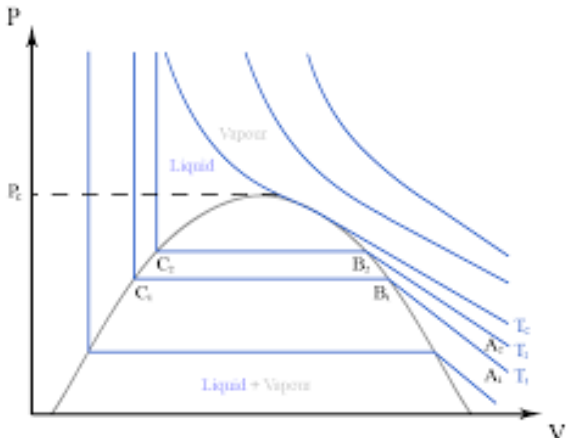
-
- Thermodynamic variables of a material at its critical point are denoted by T_c, P_c, V_{mc}. These are important properties of each material.

Gaseous state

- Reduced thermodynamic variables are defined as $T_r = T/T_c$, $P_r = P/P_c$ and $V_{mr} = V_m/V_{mc}$.

- Pressure is typically measured in units of force per unit of surface area.

- Manometer: A manometer is a scientific instrument used to measure gas pressures.

- Open manometers measures gas pressure relative to atmospheric pressure. A mercury or oil manometer measures gas pressure as the height of a fluid column of mercury or oil that the gas sample supports.

- Maxwell-Boltzmann energy distribution $dN/N = 2\pi(\frac{1}{2\pi kT})^{3/2} e^{-\epsilon/kT} \epsilon^{1/2} d\epsilon$.

Gaseous state

- Gauge vs. absolute pressure.

Figure: A fluid manometer, taken from wikipedia

Relative number of molecules vs v (m/s), at 298 K. Curves labeled Kr, Cl_2, O_2, N_2, He, H_2.
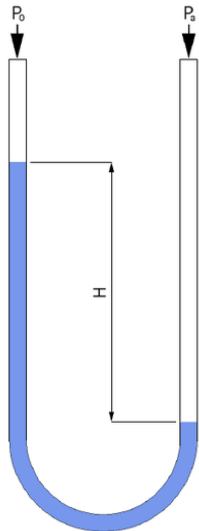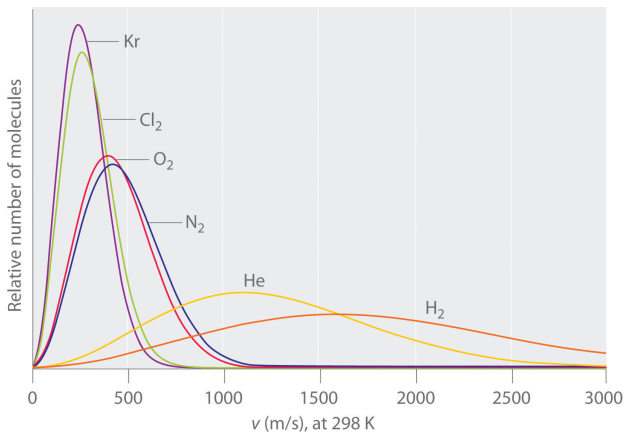
-
- Use Maxwell-Boltzmann expression to drive the most likely speed, the average speed and the average of the squared speeds.

- $c_{mp} = \sqrt{\frac{2RT}{M}}$ $\qquad$ $\bar{c} = \sqrt{\frac{8RT}{\pi M}}$

- Boyle's law is an experimental gas law that describes how the pressure of a gas tends to increase as the volume of the container decreases, $PV = k(n, T)$.
- The absolute pressure exerted by a given mass of an ideal gas is inversely proportional to the volume it occupies if the temperature and amount of gas remain unchanged within a closed system.

(a)
$V_{gas} = V$
$P_{gas} = 760$ mmHg

(b)
$V_{gas} = V/2$
$P_{gas} = 1520$ mmHg

(c)
$V_{gas} = V/3$
$P_{gas} = 2280$ mmHg
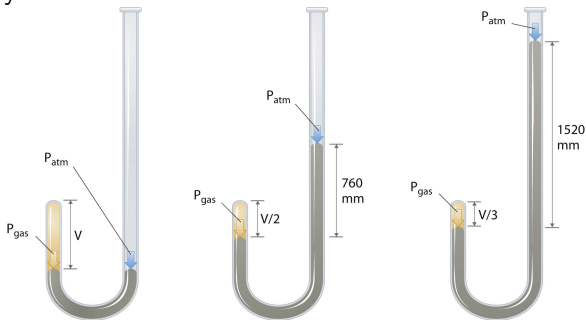
Ideal gas equation of state

- Charles law or law of volumes, When the pressure on a sample of a dry gas is held constant, the Kelvin temperature and the volume will be in direct proportion: $\frac{V}{T} = k'(n, P)$.
- Gay-Lussac's law, $\frac{P}{T} = k''(n, V)$.
- What about a process which changes, P, V and T?
- $P_1, V_1, T_1 \rightarrow P_2, V_2, T_2$, divide this process into one at constant $T = T_1$, $P_1, V_1 \rightarrow P_2, V_3$ and a second at constant $P = P_2$, $V_3, T_1 \rightarrow V_2, T_2$ thus showing that $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$.
- Volume is an extensive quantity: At constant T and P, V is proportional to n (Avogadro's law). Thus $\frac{PV}{T} = nR$.

- Ideal gas thermometer: $T = \lim_{P \to 0} \frac{PV}{nR}$.
- Definition: $X_i = \frac{n_i}{n_{total}}$, $P_i = X_i P_{total}$.
- Dalton's law states that the presence of other molecules has no effect on the pressure exerted by molecules of species i. I.e., $P_i = n_i \frac{RT}{V}$
- $P_{total} = \sum_i P_i = \frac{RT}{V} \sum_i n_i = \frac{RT}{V} n_{total}$
- $\frac{P_i}{P_{total}} = \frac{n_i}{n_{total}}$
- Ideal gas law can be deduced from classical mechanics

Kinetic theory of gases.

- 1- A gas is composed of many small particles which are widely separated from each other.
- 2- Gas particles are moving in random directions and frequently make elastic collisions.
- 3- There are no intermolecular forces.
- 4- Energy is widely and unevenly distributed among molecules but its average is proportional to the temperature.
- Assume that $N/3$ of molecules are moving along each coordinate axis. In each molecule-wall collision momentum exchanged is $2mc_i$ and the collision frequency for each molecule is $\frac{c_i}{2l}$.
- Thus each molecule transfers momentum of mc_i^2/l per unit time. Total transferred momentum to the wall perpendicular to the x axis per unit time $= \sum_{i=1}^{N/3} mc_i^2/l = \frac{Nm}{3l}\bar{c^2}$

Kinetic theory of gases.

- $P = \frac{F}{A} = \frac{1}{A}\frac{d(mc)}{dt} = \frac{Nm}{3l^3}\bar{c}^2$

- $\bar{c}^2 = \int_0^\infty c^2 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{mc^2}{2kT}} c^2 dc =$
  $4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} \int_0^\infty c^4 e^{-\frac{mc^2}{2kT}} dc =$
  $4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} 3\frac{kT}{m} \int_0^\infty c^2 e^{-\frac{mc^2}{2kT}} dc =$
  $4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} 3\frac{kT}{m}\frac{kT}{m}\frac{1}{2}\sqrt{\frac{2\pi kT}{m}} = 3\frac{kT}{m}$

- Thus average root mean squared velocity, $c_{rms} = \sqrt{\frac{3kT}{m}}$

- $PV = NkT$

- Collision cross section, $\sigma_{AB} = \pi(r_A + r_B)^2$

Collision

Free path

■ Figure 10.21
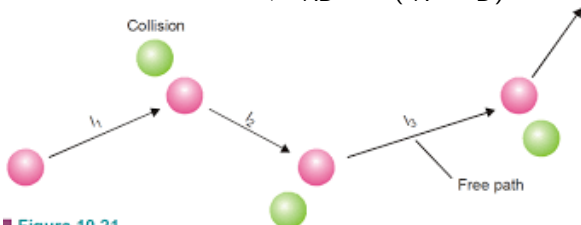
Molecular diffusion

- Average number of collisions per unit time = volume of collision cylinder$\times$ molecules/unit volume = $\pi d^2 \bar{c} n$.
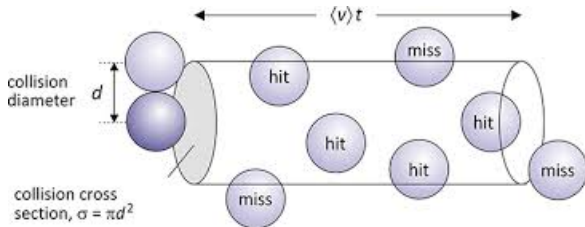
- Mean free path of a molecule? $\lambda = \frac{\bar{c}}{\pi d^2 \bar{c} n} = \frac{1}{\pi \rho^2 n}$. Assuming $d \approx 3 \times 10^{-8}$ cm, $\lambda \approx 10^{-5}$ cm explains poor diffusion and thermal conduction in gases.

- Diffusion is the movement of a substance from a region of high concentration to a region of low concentration without bulk motion.

Molecular diffusion

- Fick's first law: the diffusion flux is proportional to the negative of the concentration gradient: $\mathbf{J} = -D \nabla n$, $J_i = -D \frac{\partial n}{\partial x_i}$.
- Transfer of a physical quantity N through a small area ΔS with normal ν per time Δt, $\quad \Delta N = (\mathbf{J} \cdot \nu) \, \Delta S \, \Delta t$.
- Dimensional analysis: $D(\frac{cm^2}{s}) \propto \lambda \bar{c}(\frac{cm^2}{s})$
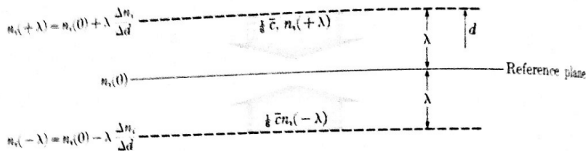
The transport of molecules across a reference plane. The quantities $n_i(+\lambda)$ and $n_i(-\lambda)$ are the concentrations of molecules at a distance of λ above and below the reference plane, respectively.

Figure: Molecular diffusion taken from University Chemistry by Mahan

Viscosity coefficient

- The rate at which molecules cross a unit area in one direction is $n\bar{c}/6$.
- Number of molecules crossing from above $\frac{\bar{c}}{6}[n_i(0) + \lambda\frac{\Delta n_i}{\Delta d}]$.
  Number of molecules crossing from below $\frac{\bar{c}}{6}[n_i(0) - \lambda\frac{\Delta n_i}{\Delta d}]$.
- Net flux $= -\frac{1}{3}\lambda\bar{c}\frac{\Delta n_i}{\Delta d} = -D\frac{\Delta n_i}{\Delta d}$. Thus $D = \frac{1}{3}\lambda\bar{c}$.
- Dimensional analysis for viscosity coefficient: force/area $= -\eta\frac{\Delta u}{\Delta d}$. Thus η (gr/s cm). Achieved by writing $\eta \propto nm\bar{c}\lambda$
- Average values of transported momentum one mean free path above and below the reference plane is, respectively, $m(u + \lambda\frac{\Delta u}{\Delta d})$ and $m(u - \lambda\frac{\Delta u}{\Delta d})$.
- Multiplying by $n\bar{c}/6$ one finds momentum transport in each direction.
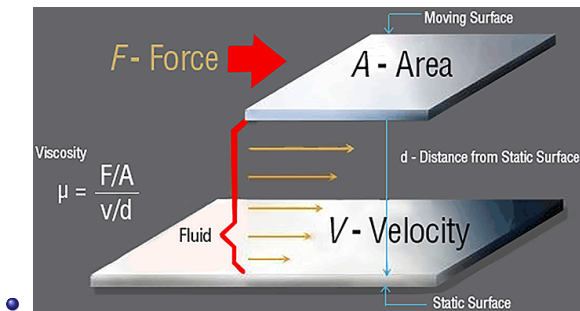
Figure: Schematic for measuring viscosity courtesy of Hydraulic Institute http://pumps.org

- momentum transport rate per unit area $= -\frac{1}{3} nm\bar{c}\lambda \frac{\Delta u}{\Delta d}$
- $\eta = \frac{1}{3} nm\bar{c}\lambda$
- To determine thermal conductivity we consider a reference plane perpendicular to the temperature gradient. At this plane average molecular energy is $c_v T$.

- Average energies λ above and below the the reference plane is respectively $c_v(T + \lambda\frac{\Delta T}{\Delta d})$ and $c_v(T - \lambda\frac{\Delta T}{\Delta d})$
- rate of energy transport per unit area $= -\frac{1}{3}n\bar{c}c_v\lambda\frac{\Delta T}{\Delta d} = -\kappa\frac{\Delta T}{\Delta d}$
- $\kappa = \frac{1}{3}n\bar{c}c_v\lambda$
- Effusion is the process in which a gas escapes from a container through a hole of diameter considerably smaller than the mean free path of the molecules

Molecular effusion

- Such a hole is often described as a pinhole and the escape of the gas is due to the pressure difference between the container and the exterior.
- Graham's law: $\frac{\text{Molecular effusion speed for A}}{\text{Molecular effusion speed for B}} = \frac{\bar{c}_A}{\bar{c}_B} = \sqrt{\frac{M_B}{M_A}}$.
- Can be used to separate gases based on their molecular masses.
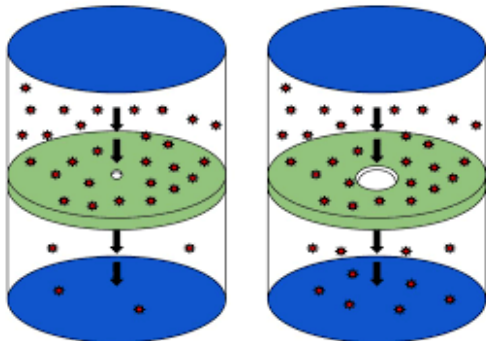
Figure: Flux vs. effusion taken from https://en.wikipedia.org

Real gases

- Intermolecular forces and or molecular volume becomes important.
- Compressibility factor $Z \equiv \frac{PV}{nRT} = \frac{PV_m}{RT}$ is used to quantify deviations of a gas from ideal behavior.
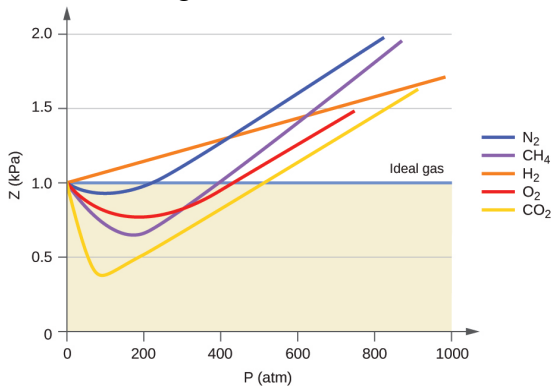
Real gases

- The law of corresponding states
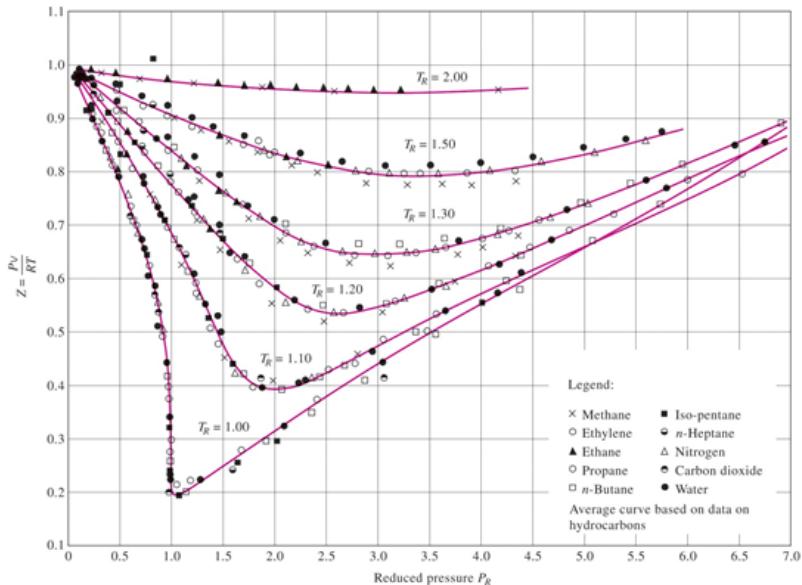
- There are many equations of state for real gases. The most conceptually appealing is the Van der Waals equation of state.
- Each molecule makes $4/3\pi d^3$ inaccessible to other molecules. Define forbidden volume (inaccessible space) per mole $b = N_A 4/3\pi d^3$
- Attractive forces between molecule A and every other molecule reduces the impact of A on the walls. Since every other molecule is affected similarly, effect of attractive forces on pressure is proportional to N^2.

Van der Waals gases

- To account for the dependence of attractive forces on distance their affect on pressure is assumed to be proportional to $1/V^2$, i.e., intermolecular forces are implicitly assumed to be proportional to $1/r^6$.
- Thus start with the ideal gas equation of state and substitute V by $V - nb$. Further substitute P by $P + a\frac{n^2}{V^2}$.
- Van der Waals equation of state: $(P + a\frac{n^2}{V^2})(V - nb) = nRT$. Van der Waals constants a and b are treated as phenomenological constants to be determined experimentally for each material.
- $\bar{V}^3 - (b + \frac{RT}{P})\bar{V}^2 + \frac{a}{P}\bar{V} - \frac{ab}{P} = 0$

Thermodynamics: Equilibrium

- Universe:
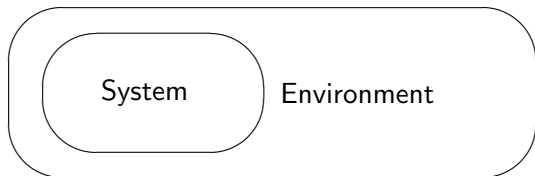
- Equilibrium vs. non-equilibrium thermodynamics.
- Thermal equilibrium, Mechanical equilibrium, Chemical equilibrium.
- Static vs. dynamic equilibrium
- Chemical equilibrium, use of isotopes.
- Le Chatelier's principle, examples. Effect of changes in pressure, number of moles, volume and temperature.

Thermodynamics: zeroth law

- Intensive vs. extensive properties.
- Reversible vs. irreversible process.
- 0'th law of thermodynamics: If system A is in thermal equilibrium with system B and system B is in thermal equilibrium with system C, then system A is in thermal equilibrium with system C.
- Energy is the ability of doing work, it can be exchanged in an orderly manner as work or in a disorderly manner as heat.
- Work is energy transferred by virtue of a mechanical link between systems.
- Heat is energy transferred due to a temperature difference.

Thermodynamics: work and heat

- $\delta w = F dz = P_{ext} A dz = P_{ext} dV$

- By thermodynamic convention:
  $\delta w = -P_{ext} dV, \quad w = -\int_{V_1}^{V_2} P_{ext} dV$.

- Free expansion.

- Maximum work in expansion of an ideal gas:
  $w_{max} = -\int_{V_1}^{V_2} P dV = -nRT \ln(V_2/V_1)$

- Heat in absence of a phase transition:
  $m_h c_h(T_h - T_f) = m_c c_c(T_f - T_c) = q$ where c is specific heat.

- $\delta q_p = m c_p dT \quad q_p = m \int_{T_1}^{T_2} c_p(T) dT \quad c_p = \frac{\delta q_p}{m dT}$

- $C_p = \frac{\delta q_p}{n dT} \quad C_p = M c_p$

- $q_v = m \int_{T_1}^{T_2} c_v(T) dT \quad q_v = n \int_{T_1}^{T_2} C_v(T) dT$

- $C_v = \frac{\delta q_v}{n dT}$

- State function vs. path function.

Thermodynamics: First law

- Internal energy is the sum of all energies that can be ascribed to the system.
- $E = E_{inter-molec} + E_{trans} + E_{rot} + E_{vib} + E_{elec} + E_{nucl}$
- First law implies that internal energy is a state function.

-

- Conservation of energy = first law, $dE = dw + dq$.
- $\Delta E = q + w$, positive sign would denote an increase in the internal energy of the system while negative sign would denote a decrease in the systems internal energy.
- In a typical system only pressure-volume work occurs, $q_V = \Delta E$.
- Enthalpy is defined as $H = E + PV$. We have $dH = dE + d(PV) = dq - pdV + pdV + Vdp$ thus at constant pressure $\Delta H = q_p$.

- Exothermic reaction (releasing energy, a) graph vs. Endothermic reaction (absorbing energy, b).
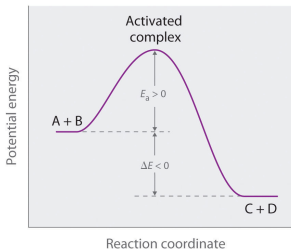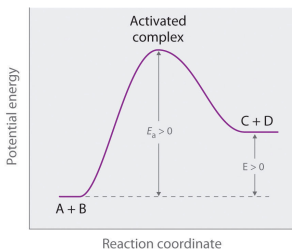
(a) (b)

- Hess's law states that enthalpy is a state function. One should combine enthalpies of reactions the same way he combines reactions themselves.

Thermodynamics: Thermochemistry

- E.g., Hydrogenation of propene: $CH_2CHCH_3(g) + H_2(g) \rightarrow CH_3CH_2CH_3(g)$ $\Delta H = -124 kJmol^{-1}$
  Combustion of propane $CH_3CH_2CH_3(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$ $\Delta H = -2220 kJmol^{-1}$
  Combustion of Hydrogen
  $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ $\Delta H = -286 kJmol^{-1}$
- Calculate enthalpy change of propene combustion?
- Enthalpy of formation, e.g.,
  $C(graphite) + O_2(g) \rightarrow CO_2(g)$ $\Delta H = \Delta H_f^0(CO_2)$
- Reaction enthalpy in terms of the standard enthalpy of formation ΔH_f^0.

- Using the fact that enthalpy is a state function:
  $\Delta H^0 = \Delta H^0_f(Products) - \Delta H^0_f(Reactants)$
- Enthalpy of reactions only involving gaseous species can be approximated using bond energies.
- Judge whether $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ is exo or endo thermic?

Thermodynamics: Second law

- Ω denotes the number of micro states available to a system (solutions to the Schrodinger equation).
- Entropy is defined as $S = k \ln \Omega$ or $S = -k \sum_{i=1}^{\infty} p_i \ln p_i$
- Second law of thermodynamics states that for every spontaneous process $\Delta S_{uni} \geq 0$
- Heat flows from bodies of higher temperature to bodies of lower temperature spontaneously.
- It is impossible to convert all heat extracted from a body to work.
- $\Delta S_{uni} = \Delta S_{sys} + \Delta S_{env}$
- Clausius inequality $dS \geq \frac{dQ}{T}$ (1855) specifically $dS = \frac{dQ_{rev}}{T}$ thus at constant pressure $\Delta S_{env} = \frac{Q_{env}}{T} = \frac{-\Delta H}{T}$.
- $\Delta S_{uni} = \Delta S_{sys} - \frac{\Delta H}{T}$.
- Define Gibbs free energy as: $G = H - TS$.
- At constant temperature $\Delta G = \Delta H - T\Delta S = -T\Delta S_{uni}$.

Thermodynamics: Second law

- Alternative expression for the second law: $\Delta G \leq 0$, useful at constant temperature and pressure conditions.
- Consider the relative importance of ΔH and ΔS in reaction spontaneity.
- $dE_{closed} = dq + dw \quad dE = TdS - PdV + \mu dn$ thus $dH = TdS + VdP + \mu dn$ and $dG = VdP - SdT + \mu dn$
- Chemical potential is defined as $\mu = (\frac{\partial E}{\partial n})_{s,v} = (\frac{\partial H}{\partial n})_{s,p} = (\frac{\partial G}{\partial n})_{p,T}$
- Chemical potential also equals molar Gibbs free energy.
- $(\frac{\partial \mu}{\partial P}) = V_m$ for an ideal gas $\frac{\partial \mu}{\partial P} = \frac{RT}{P}$ thus $\mu - \mu^0 = RT \ln\{P\}$
- Equilibrium condition for $aA(g) + bB(g) \leftrightharpoons cC(g) + dD(g)$; $dG = 0$.
- $c\mu_C + d\mu_D - a\mu_A - b\mu_B = 0$.

Thermodynamics: Equilibrium constant

- $c(\mu_C^0 + RT \ln\{P_C\}) + d(\mu_D^0 + RT \ln\{P_D\}) - a(\mu_A^0 + RT \ln\{P_A\}) - b(\mu_B^0 + RT \ln\{P_B\}) = 0$

- $a\mu_A^0 + b\mu_B^0 - c\mu_C^0 - d\mu_D^0 = RT \ln \frac{\{P_C\}^c \{P_D\}^d}{\{P_A\}^a \{P_B\}^b}$

- $RT \ln K_P^0 = -\Delta G^0$

- $\ln K_P^0 = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$

- If the change in entropy and enthalpy are assumed independent of temperature

- $\frac{d \ln K_P^\circ}{dT} = \frac{\Delta H^\circ}{RT^2}$

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

Thermodynamics: Chemical equilibrium

- The law of mass action or chemical equilibrium law determines the relation between concentration of species in equilibrium.
- For the reaction $aA(g) + bB(g) \leftrightarrow cC(g) + dD(g)$, reaction concentration quotient is defined as $Q_c = \frac{\{C\}^c\{D\}^d}{\{A\}^a\{B\}^b}$ where $\{A\} \equiv \frac{[A]}{c_0}$ $c_0 = 1$ mol L^{-1}
- The value of reaction quotient at equilibrium is called equilibrium constant.
- Eg., for $H_2(g) + \frac{1}{2}O_2(g) \leftrightarrow H_2O(g)$ $K_c = \frac{\{H_2O\}_{eq}}{\{H_2\}_{eq}\{O_2\}_{eq}^{1/2}}$
- If $Q_c = K_c$ we have equilibrium.
- If $Q_c < K_c$ reaction will proceed to right.
- If $Q_c > K_c$ reaction returns to the left.

Thermodynamics: Chemical equilibrium

- For the reaction $aA(g) + bB(g) \leftrightarrow cC(g) + dD(g)$ reaction pressure quotient is defined as $Q_p = \frac{\{P_C\}^c\{P_D\}^d}{\{P_A\}^a\{P_B\}^b}$ where $\{P_I\} \equiv \frac{P_I}{P_0}$ $P_0 = 1$ bar

- $K_p = \frac{P_C^c P_D^d}{P_A^a P_B^b} P_0^{(a+b-c-d)} = \frac{[C]^c[D]^d}{[A]^a[B]^b}(\frac{RT}{P_0})^{\Delta\nu} = \frac{\{C\}^c\{D\}^d}{\{A\}^a\{B\}^b}(\frac{c_0 RT}{P_0})^{\Delta\nu} = K_c(\frac{c_0 RT}{P_0})^{\Delta\nu}$ $\Delta\nu = c + d - a - b$

- Molar fraction reaction quotient is defined as $Q_x = \frac{x_C^c x_D^d}{x_A^a x_B^b}$

- Equilibrium condition: $Q_x = K_x$

- $K_P = \frac{(x_C P)^c(x_D P)^d}{(x_A P)^a(x_B P)^b} P_0^{a+b-c-d} = \frac{x_C^c x_D^d}{x_A^a x_B^b}(\frac{P}{P_0})^{\Delta\nu} = K_x(\frac{P}{P_0})^{\Delta\nu}$

- Le Chatelier's principle.

Solutions

- A phase is a region of space (a thermodynamic system), throughout which all physical properties of a material are essentially uniform.

- Physical properties include density, index of refraction, magnetization and chemical composition. A simple description is that a phase is a region of material that is chemically uniform, physically distinct, and (often) mechanically separable.

- In a system consisting of ice and water in a glass jar, the ice cubes are one phase, the water is a second phase, and the humid air is a third phase over the ice and water. The glass of the jar is another separate phase.

- Mixing material $\rightarrow \begin{cases} \text{Mixture (Any ratio)} \\ \text{Solution (A range of ratios)} \\ \text{Compound (Specific ratio)} \end{cases}$

- A solution is a homogeneous substance that has, over certain limits, a continuously variable composition.

- Comparison of physical (e.g., color, molecular weight and volume) and chemical (e.g., reactivity, flammability and oxidation states) properties.
- Tell-tale signs of a chemical change include bubbling, color change, temperature change, and precipitation formation.
- In a binary solution there is a solvent and a solute. solvating ions.
- Classifying solutions either based on the solvent or solute.

Solutions

- Air and natural gas are examples of gas mixtures.
- Tap water is an example of liquid solutions. Liquid solutions provide a medium for many chemical reactions.
- Solid solution is called an alloy and is kinetically difficult to make.
- Thermodynamic functions of solution depend on amount of each constituent in addition to their natural variables.
- I.e., $dE = TdS - PdV + \sum_i \mu_i dn_i$ thus
  $dH = TdS + VdP + \sum_i \mu_i dn_i$ and
  $dG = VdP - SdT + \sum_i \mu_i dn_i$
- $\Delta H_{Solution} = E_{AA} + E_{BB} - E_{AB}$
- Simplifying assumption of similar sized A and B allow for a more explicit relation.
- In an ideal solution $r_A \approx r_B$ and $E_{AB} \approx \frac{E_{AA} + E_{BB}}{2}$

Concentration units

- Units of concentration:
- mole fraction $x_i = \frac{n_i}{\sum_j n_j} = \frac{n_i}{n_{tot}}$ $\sum_i x_i = 1$,
- mole percentage $p_i = 100\% x_i$,
- molarity $C_i = \frac{n_i}{V(Lit)}$ has temperature dependence, formality used for compounds lacking independent molecules,
- mass percentage
  $(w_i/w)100\% = \frac{m_i}{\sum_j m_j}100\% = \frac{m_i}{m_{tot}}100\%$; $\sum_i (w_i/w)100\% = 1$.
- Molality $m_i = \frac{n_i}{\text{Solvent mass (kg)}}$, normality $N_i = \frac{\#\text{ equivalents of i}}{V(lit)}$.
- The number of equivalents engaging in a chemical reaction are always equal. Thus $N_1 V_1 = N_2 V_2$.
- Parts per million, $ppm = \frac{\#\text{ gr solute}}{10^3 \text{ kg solution}}$. Parts per billion, $ppb = \frac{\#\text{ gr solute}}{10^6 \text{ kg solution}}$.

Ideal solution

- Solution $\begin{cases} \text{Ideal} \\ \text{Real} \end{cases}$
- Examples of Ideal solutions are Benzene-Toluene, Octane-Heptane, Chloroethane-Bromoethane and Tetraethylsilane-Pentane.
- For ideal solutions Raoult law: $P_i \propto x_i \qquad p_i = x_i p_i^*$.
- $P_t = P_A + P_B = x_A P_A^* + x_B P_B^*$
- Ideal solutions: $P_i = x_i P_i^*, \quad P_t = P_B^* + (P_A^* - P_B^*) x_A$

ideal solution
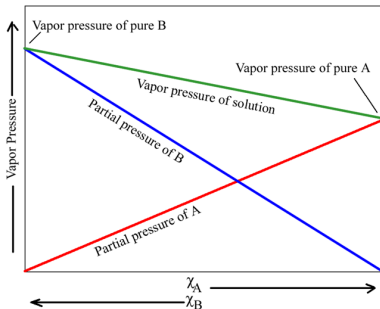
Liquids - Vapor Pressure

Table: Approximate vapor pressure in the range $20°C–25°C$ ($68°F–77°F$).
From www.engineeringtoolbox.com/vapor-pressure-d_312.html

| Fluid Name	Vapor Pressure (kPa)	Fluid Name	Vapor Pressure (kPa)
Acetaldehyde	120	Benzyl alcohol	0.013
Acetic acid	2.1	Bromine	28
Acetic acid anhydride	0.68	Butyl acetate	1.5
Acetone	30	Butyl alcohol, 1-butanol	0.93
Allyl alcohol	2.3	Butyric acid n	48
Allyl chloride	40	Calcium chloride, 25% solution in water	2.4
Aluminum nitrate, 10% solution in water	2.4	Calcium chloride, 5% solution in water	2.4
Aluminum sulphate, 10% solution in water	2.4	Benzene	14
Amyl acetate	0.47	Carbon disulphide	48
Aniline	0.09	Carbon tetrachloride	15.3
Beer	2.4		

Ideal solution

- Dalton's law yield mole fractions in the gaseous phase:
$$P_i = y_i P_t \rightarrow y_i = \frac{X_i P_i^*}{\sum_j X_j P_j^*}$$
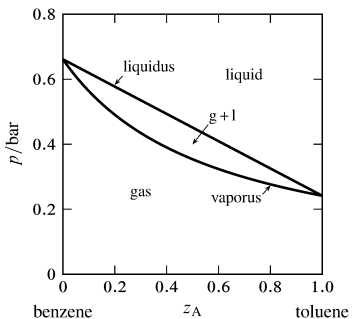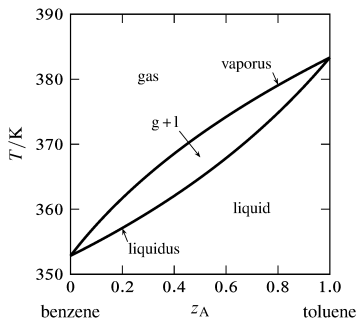

(a)   (b)

-
- b is called a "boiling diagram." Notice that at the edges we have points representing the boiling points of the pure components. The lower curve gives the boiling point of the liquid mixture as a function of composition.

Ideal solution

- A point inside the two phase region does not give us the composition of either the liquid or the vapor phase, it give the overall composition of the whole system.
- The tie line is a horizontal line through system point which intersects the two boundary lines of the two phase region.
- The intersection of the tie line with the boundary line on the liquid side of the region tells us the composition of the liquid and the intersection of the tie line with the boundary curve on the vapor side tells us the composition of the vapor phase.

Ideal solution

- In an ideal solution inter-molecular interactions and fluid structure are similar thus $\Delta E_{mix} = 0$ for an ideal solution. Also $\Delta V_{mix} = 0$ and $\Delta H_{mix} = \Delta E_{mix} + P\Delta V_{mix} = 0$
- $\Delta S_{mix} > 0$, $\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} < 0$
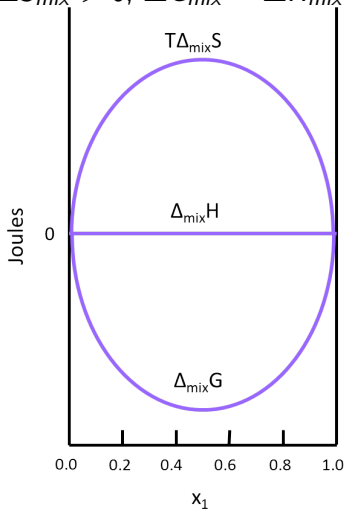
Real solution

- Ideal solutions form a first approximation to solution behavior as does ideal gas to real gas behavior.

- Real solutions: $\begin{cases} \text{Positive deviation solution} \\ \text{Negative deviation solution} \end{cases}$

- In a positive deviation solution, vapor pressure is greater than that of ideal solution, e.g., carbondisulfide-Acetone.

- In a negative deviation solution, vapor pressure is smaller than that of ideal solution, e.g., Acetone-Chloroform.

- In negative deviation solutions $f_{AB} > \frac{1}{2}(f_{AA} + f_{BB})$, Also $\Delta V_{mix} < 0$ and $\Delta H_{mix} = \Delta E_{mix} + P\Delta V_{mix} < 0$. E.g., aqueous electrolyte solutions.

- In positive deviation solutions $f_{AB} < \frac{1}{2}(f_{AA} + f_{BB})$, Also $\Delta V_{mix} > 0$ and $\Delta H_{mix} > 0$. E.g., Water and oil mixture.

Henry's law

- As $X_i \rightarrow 1$ for each component in a binary mixture the vapor pressure of that component obeys Raoult's law.
- for small mole fractions, P_i becomes proportional to X_i, but the proportionality constant is not P_i^*. $P_i = K_i X_i$
- In a concentration region where one component obeys Raoult's law the other will necessarily obey Henry's law.
- Henry's law is most often used to describe the solubility of gases in liquids.
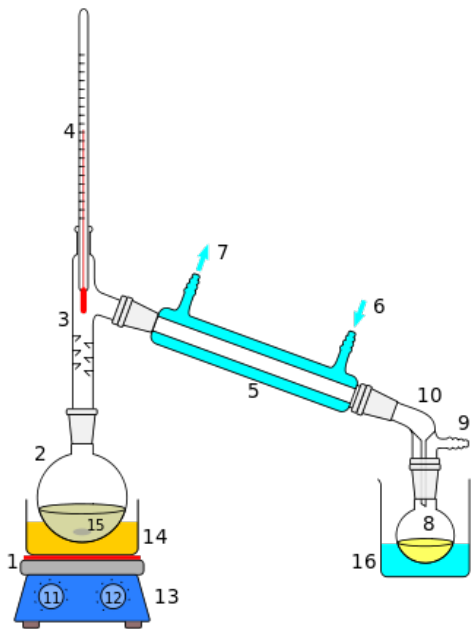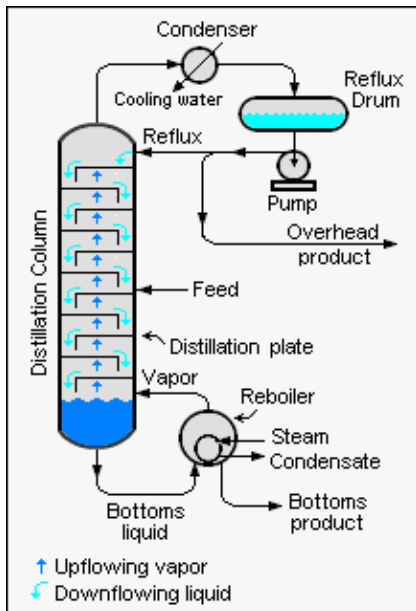
Distillation

- Simple distillation can be used in cases with large difference in boiling point.
- for separating compounds with smaller boiling point difference fractional distillation is used.
- Use an example where $P_A^* = 800 torr$ $P_B^* = 600 torr$ $x_A = 0.8$ to analyze fractional distillation.
- As evaporation continues the solution becomes richer in B and thus its boiling point increases.
- Strong deviations from ideal solution can give rise to an azeotrope or constant boiling point solution.
- Azeotropic vapor and liquid phases have the same composition, thus an azeotropic solution's composition cannot be altered by distillation.
- Positive deviations from Raoult's law result in a minimum boiling point azeotrope.

Distillation

205/1

Distillation
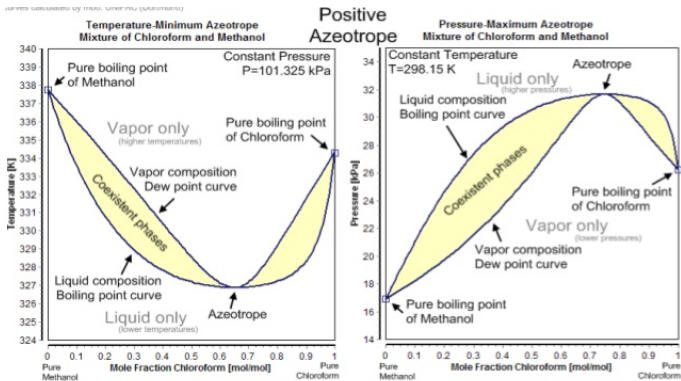
- E.g., 95.6% by volume ethanol+4.4% water mixture boils at 78.2°C. Ethanol boils at 78.4°C.
- Negative deviations from Raoult's law result in a maximum boiling point azeotrope.
- E.g., 68% nitric acid (boiling at 356 K) and 32% water by mass boils at 393.5 K.

- Colligative properties arise from solutes present in the liquid phase but absent from gas and solid phases.
- E.g., vapor pressure reduction, boiling point elevation, freezing point reduction and the osmosis phenomena.
- Consider non-electrolyte solutions.
- $P_t = P_A = X_A P_A^* = (1 - x_B)P_A^*$, change in vapor pressure is a colligative property because it does not depend on the nature of solute.
- Reduction in vapor pressure give rise to an increase in boiling point.

Colligative properties

- Liquid (concentration x1) = vapor (1 atm)
- $K = \frac{[Vapor]}{[liquid]} = \frac{1}{x_1}$
- $\ln \frac{K_2}{K_1} = -\frac{\Delta H^0}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$
- $\ln x_1 = \frac{\Delta H_{vap}}{R}\left(\frac{T_b - T}{T T_b}\right)$
- $\ln x_1 = -\frac{\Delta H_{vap}}{R T_b^2}\Delta T$
- $\Delta T_b = \frac{R T_b^2}{\Delta H_{vap}}x_2 \quad x_2 \approx \frac{M_1}{1000}m$
- $\Delta T_b = \left(\frac{R T_b^2 M_1}{1000 \Delta H_{vap}}\right)m = K_b m$
- To understand the most stable phase of a substance, consider
  $d\mu = V_m dP - S_m dT \quad \left(\frac{\partial \mu}{\partial T}\right)_{P,n} = -S_m \quad \left(\frac{\partial \mu}{\partial P}\right)_{T,n} = V_m$
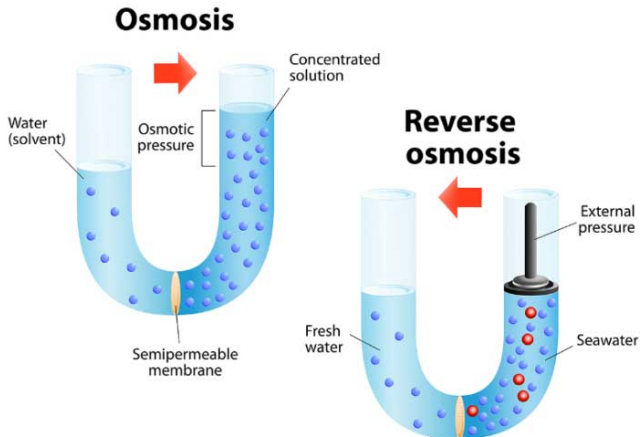
Colligative properties
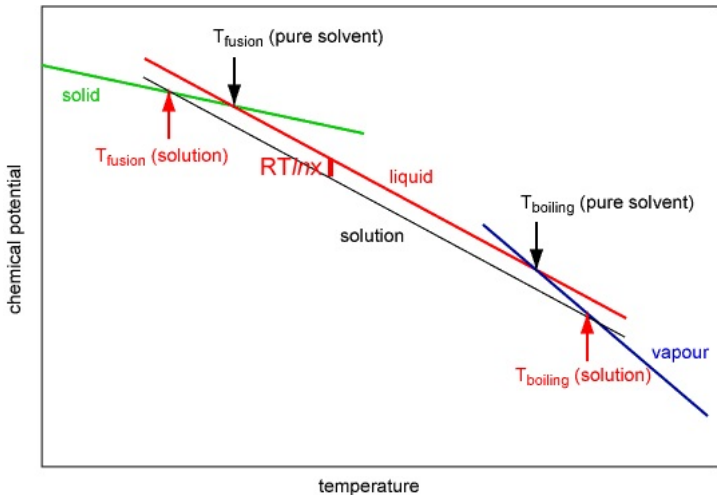
-
- $\Delta T_f = -K_f m_B$

Colligative properties: Osmosis

- A semipermeable membrane, permeable to some molecules (e.g., solvent) but impermeable to other molecules (e.g., solute), gives rise to the osmosis phenomena.

-

Colligative properties: Osmosis

- Cell membrane is an example of a semipermeable membranes.
- Osmotic pressure $\pi = C_B RT$
- Reverse osmosis is used to extract drinking water from sea water.
- Colligative properties for electrolyte solutions are $\Delta P = -i X_B P_A^*$, $\quad \Delta T_b = i K_b m \quad \Delta T_f = -i K_f m \quad \pi = i C_B RT$, i is the Van Hoff coefficient.
- Strong electrolytes dissociate completely in solution.
- $\lim_{m_B \to 0} i = \nu$ where ν is the number of particles resulting from dissociation.
- At higher concentration electrostatic interaction prevent independent effect of ions.

Colligative properties: Electrolytes

- For a weak electrolyte i depends on the dissociation multiple, α.
- $A_aB_b \rightleftarrows aA^{b+}(aq) + bB^{a-}(aq)$
- \# of particles $=$
  $m - m\alpha + am\alpha + bm\alpha = m[(1 - \alpha) + (a + b)\alpha]$. Thus
  $i = 1 - \alpha + \alpha\nu$.

Environmental chemistry

- Hydrosphere: Include all bodies of water on earth.
- Lithosphere: include all the outer solids of planet earth, most importantly soil.
- Atmosphere: Gases that surround the earth.
- Biosphere: Living organisms and their very immediate surrounding.
- Freshwater limitation is the greatest challenge facing human society (except for Canada and Brazil)

-
- Construction of the Gotvand dam is called a crime.
- High heat capacity of water temper's temperature changes
- In static waters higher layers are aerobic while lower levels are anaerobic.
- Aerobic cellular respiration: $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$ slowly produces 36 ATP/glucose

Water chemistry

- Anaerobic respiration: Glucose $\rightarrow$ Pyruvic acid ($CH_3COCOOH$), 2 ATP/Glucose.
- Dissolved oxygen is necessary for fish while dissolved CO_2 is necessary for algae. Dissolved N_2 is toxic for fishes.
- $A(g) \rightleftarrows A(aq)$. Henry's law $P_A = X_A K'$. Alternatively, $[A] = K P_A$
- $CO_2 + H_2O \rightleftarrows HCO_3^- + H_3O^+$
- $SO_2 + H_2O \rightleftarrows HSO_3^- + H_3O^+$
- Acidic water can dissolve Calcium and Magnesium salts abundant on the earth's crust. Water containing Ca^{2+} and Mg^{2+} is called hard water.
- Hard water can be softened by boiling.

Climate change

- Atmospheric models predict that the earth temperature will increase from 1 to 3.5°C by the year 2100, which is more than temperature changes during the past 10,000 years.
- Emission of greenhouse gases, production of aerosols in the atmosphere, changes in the earths reflection index and thermal pollution are the factors affecting climate change.
- The earth absorbs most of solar radiations that reach the earth through its atmosphere and, after getting warm, reflects the thermal waves back to space.
- Portion of this infrared radiation passes through the atmosphere and a fraction of it is absorbed by greenhouse gases and reflected back to the earth surface which results in an energy balance between the earth and space.
- The earths average temperature would have been about 15.5 degrees lower than the temperature that it has now without greenhouse effect and another ice age would occur.

- Increased exposure to droughts, floods and storms is already destroying opportunity and reinforcing inequality. Meanwhile, there is now overwhelming scientific evidence that we are getting closer to an irreversible ecological catastrophe.
- Today we are living with what we did yesterday; tomorrow we will all live with what we do today. We need to take action now.