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Chapter 1

Some definitions

MATTER: is anything that has mass and volume. In chemistry the **composition** of matter is important (the types and amounts of simpler substances that make it up). **Substance:** type of matter with a defined composition.

PROPERTIES: the characteristics that give each substance its unique identity. There are **physical properties** (those that a substance shows by itself, without changing into or interacting with another substance).

physical change: a substance alters its physical form; not its composition

Example

Water (solid form) → water (liquid form), the particles are the same. **BLOW-UP CIRCLES**

chemical properties those that a substance shows as it changes into or interacts with another substance / ex. **chemical change (chemical reaction):** a substance is converted into a different one / ex.

Example

Water $\xrightarrow{\text{electric current}}$ hydrogen gas + oxygen gas **ELECTRIC CURRENT THROUGH WATER**

* A substance is identified by its own set of physical and chemical properties. (see copper p.6)

STATES OF MATTER: **solid** has a fixed shape that does not conform to the container shape; not defined by rigidity and hardness (fixed volume). **liquid** conforms to the container shape but fills the container only to the extent of liquid's volume (surface). **gas** conforms to the container shape also, but fills the entire container (not surface).

PARTICLES

- solid close together and organized.
- liquid close together but disorganized. (move around one another)
- gas far apart and disorganized. (move throughout the container)

* P. change caused by a temperature c. can generally be reversed (not g. true for ch. change) **EX. iron.**

Depending on the temperature and pressure of the surroundings, many substances can exist in each of the three physical states and undergo changes in state as well **EX. water.**

TRANSFORMATIONS:

S → L fusion
 S → G sublimation (rare)
 L → G evaporation
 L → S solidification
 G → L condensation
 G → S inverse (or reverse) sublimation → deposition

* Phase transitions are accompanied by a sharp and pronounced change of 1 or more physical properties (ex. thermal cap.) occurring for a slight change of a thermodynamic variable (ex. temperature)

CHEMISTRY: study of matter and its properties, the changes that matter undergoes and the energy associated with those changes. Observable changes to understand unobservable causes.

ENERGY: the ability to do work (the object doing the work transfers some of the energy it possesses to the object on which the work is done). The total energy an object possesses is the sum of **potential energy** (due to the position of the object) and **kinetic energy** (due to the motion of the obj.)

* Energy is conserved: it may be converted but not destroyed.

* In nature, situations of lower energy are typically favored over those of higher energy (~~less stable~~): because the weight has less potential energy (< total also) at rest on the ground than held in the air, it will fall when released. ↑ less stable, ↓ more stable.

* electrostatic forces between charged particles: opposite → ←, like ↔

* Chemical potential energy of a charge results from the relative positions and the attrac. and rep. among all its particles. Some of them are richer.

Origins — see pages 10-11

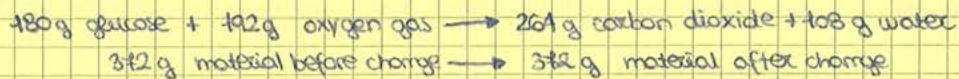
- Pre-history: the discovery of fire (combustion)
- Neolithic (12000-7000 B.C.): metallurgy, beyond the stone period.
- 6000 years ago (Mesopotamia): ceramics, tissues, glass.
- Since 3000 B.C.: wine and beer.
- Greeks and Arabs: philosophical approach to matter and energy (the four elements: water, air, fire, stone).
- From the II-III century B.C. on: Greek and oriental approaches merge, chemistry becomes magic.
- Along 15 centuries, until the end of the Middle Age: alchemia (philosopher's stone).
- Since 1500 with Paracelsus, chemistry becomes a mean to relief mankind from pains and diseases.
- Since 1600 it becomes a science: Boyle defined it as the s. that studies matter.

Chapter 2

Observations that led to an atomic view of matter

LAW OF MASS CONSERVATION (LAVOISIER) was the most fundamental chemical observation of the 18th century. «The total mass of substances does not change during a chemical reaction». The number of substances may change and also their properties, but the total amount of matter remains constant. Lavoisier first stated this law on the basis of his combustion experiments.

Example



* This law means that matter cannot be created or destroyed

THEORY OF COMBUSTION (LAVOISIER) Chemical investigation in the modern sense began in the late 17th century but was hampered by an incorrect theory of combustion. At the time, most scientists embraced the **phlogiston theory** which proposed that combustion materials contain varying amounts of an undetectable substance called phlogiston, released when a material burns (see p.11). In this context Lavoisier demonstrated the true nature of combustion: he heated mercury calx, decomposed it into mercury and a gas, whose combined masses equaled the starting mass of calx. The reverse experiment reformed the mercury calx and again the total mass remained constant. The chemist proposed that when a metal forms its calx, it does not lose phlogiston but rather combines with this gas, which must be a component of air. To test this idea, he heated mercury in a measured volume of air and noted that only 1/5 of the air volume remained. He placed a burning candle in the remaining air and it went out = gas + mercury necessary for combustion. Gas = **oxygen**. metal calxed = **metal oxides**. This theory triumphed because it relied on quantitative, reproducible measurements, so we can say that the science of chemistry began with Lavoisier.

LAW OF DEFINITE (OR CONSTANT) COMPOSITION (PROUST) «No matter what its source, a particular compound is composed of the same elements in the same parts (fractions) by mass»

Fraction by mass (mass fraction) part of the compound's mass that each element contributes and it's obtained by dividing the mass of each element by the total mass of compound.

Percent by mass (mass %) is the fraction by mass expressed as a percentage.

* We can use that mass fraction to find the actual mass of the element in any sample of the compound:

$$\left[\text{Mass of element} = \text{mass of compound} \times \frac{\text{mass of element (part by mass)}}{\text{one part by mass of compound}} \right]$$

Or, more simply, we can use that ratio directly with any mass unit and skip the need to find the mass fraction first

$$\left[\text{Mass of elem. in sample} = \text{mass of compound in sample} \times \frac{\text{mass of elem. in compound}}{\text{mass of compound}} \right]$$

LAW OF MULTIPLE PROPORTIONS (DALTON) Dalton described a phenomenon that occurs when two elements form more than one compound. «If elements A and B react to form two compounds, the different masses of B that combine with a fixed mass of A can be expressed as a ratio of small whole numbers»

Example

Carbon oxide I: 51.1 mass % oxygen and 48.9 mass % carbon

Carbon oxide II: 27.3 mass % oxygen and 72.7 mass % carbon

To see the phenomenon of multiple proportions, we use the mass percents of oxygen and carbon in each compound to find the masses of these elements in a given mass. Then we divide the mass of O by the mass of C in each compound to obtain the mass of O that combines with a fixed mass of C.

* This law tells us that in two compounds of the same elements, the mass fraction of one element relative to the other one changes in increments based on ratios of small whole numbers.

Dalton: the atomic theory

POSTULATES (DALTON) Dalton expressed his theory in a series of postulates, incorporating the ideas of others.

- All matter consists of **atoms**, tiny indivisible particles of an element that cannot be created or destroyed (remember Democrito - eternal indestructible atoms)
- Atoms of one element cannot be converted into atoms of another element. In chemical reactions, the atoms of the original substances recombine to form different substances. (ref. alchemical belief)
- Atoms of an element are identical in mass and other properties and are different from atoms of any other element (Dalton's major new idea)
- Compounds result from the chemical combination of a specific ratio of atoms of different elements.

The data showed that very few α particles were deflected at all, and that only 1/20000 was deflected by more than 90° . It seemed that this few particles (α) were ~~being~~ being repelled by something small, dense and positive within the gold atoms.
 Rutherford calculated that an atom is mostly space occupied by electrons, but in the center of that space is a tiny region (nucleus) that contains all the $(+)$ charge and essentially all the mass of the atom (protons) \rightarrow Boy within the nucleus, and then he calculated the magnitude of the nuclear charge.

- * Rutherford's model explained the charged nature of matter but it could not account for all the atom's mass. (1932) Chadwick discovered the neutron.

The Atomic theory today

STRUCTURE OF THE ATOM atom: electrically neutral, spherical entity composed of a positively charged central nucleus surrounded by one or more negatively charged electrons which move rapidly within the available atomic volume, held there by the attraction of the nucleus.

- * An atomic nucleus consists of protons and neutrons (exception - H nucleus, 1 proton) **Proton (p^+)** has a positive charge ($+1$ ch. of nucleus) **neutron (n^0)** has no charge. Magnitude of p^+ charge equal to that of an **electron (e^-)**, with opposite signs.
- * An atom is neutral because the number of protons in the nucleus equals the number of electrons surrounding the nucleus.

ATOMIC NUMBER (Z) of an element equals the number of protons in the nucleus of each of its atoms. All atoms of a particular element have the same atomic number, and each element has a different atomic number from that of any other element.

- 116 known elements: 90 in nature, 26 synthesized by nuclear scientists.

MASS NUMBER (A) total number of protons and neutrons in the nucleus of an atom. Each p^+ and each n^0 contributes 1 unit to the mass number

ATOMIC SYMBOL (or element symbol) based on English, Latin or Greek name of the element, Z is written as a left subscript, A as a left superscript to the symbol. According to the previous definition we have:

- N^0 of neutrons = mass number - atomic number, i.e. $N = A - Z$
- * Each element has its own atomic number. * $\begin{matrix} A \\ Z \end{matrix} X$

ORIGIN OF ELEMENT NAMES

Sodium - Na (Latin Natrium)
 Potassium - K (Latin Kalium)
 Iron - Fe (Latin Ferrum)
 Nitrogen - N
 Copper - Cu
 Tin - Sn (Latin Stannum)
 Lead - Pb (Latin Plumbum)
 Mercury - Hg (Latin Hydragyrium)

*False friends

Carbon - C not Ca (Calcium)
 Silicon - Si (Silicio)
 Phosphor - P

- Ångström: $1 \text{ \AA} = 1 \cdot 10^{-10} \text{ m}$... p^+ and $n^0 = 1 \cdot 10^{-15} \text{ m}$, quarks = $1 \cdot 10^{-18} \text{ m}$
 Nucleus - 5 orders of magnitude smaller than the atom.

ISOTOPES of an element are atoms that have different numbers of neutrons and therefore different mass numbers (in fact all atoms of an element are identical in atomic number but not in mass number).

- * All the isotopes of an element have nearly identical chemical behaviour because it depends on the electrons. **example** - [^1_1H protium, ^2_1H deuterium, ^3_1H tritium (changes the no. of neutrons)]
- * Most elements are characterized by isotopes with different **RELATIVE PERCENT ABUNDANCE**

ATOMIC MASS UNIT - amu (now DALTON Da) is $1/12$ the mass of a carbon-12 atom. The mass of an atom is measured relative to the mass of an atomic standard (carbon-12 atom) \rightarrow absolute mass $1,66054 \cdot 10^{-24} \text{ g}$

MASS SPECTROMETRY a method for measuring the relative masses and abundances of atomic-scale particles very precisely see tools of laboratory p.55

From this we find the **ISOTOPIC MASS** mass ratio \times mass ^{12}C

- (PA) **ATOMIC MASS or WEIGHT** average of the masses of its naturally occurring isotopes weighted according to their abundances. Each naturally occurring isotope of an element contributes a certain portion to the atomic mass. [the mass of a single atom is measured in amu and takes into account the relative amount of isotopes, when they are present]

- (PM) **MOLECULAR WEIGHT** The mass of a molecule is the sum of the masses of the present atoms.

Interconverting Moles, Mass, and Number of Chemical Entities

- The mole is a convenient unit for laboratory work cause it allows to calculate the mass or number of entities of a substance in a sample if you know the amount or number of moles of the substance and vice versa. The molar mass can be used as a conversion factor.

1 We multiply by the molar mass of an element or compound to convert a given amount (in moles) to mass (in grams):

$$\text{Mass (g)} = \text{no. of moles} \times \frac{\text{no. of grams}}{1 \text{ mol}}$$

2 Or we divide by the molar mass to convert a given mass (in grams) to amount (in moles)

$$\text{No. of moles} = \text{mass (g)} \times \frac{1 \text{ mol}}{\text{no. of grams}}$$

- In a similar way we use Avogadro's number:

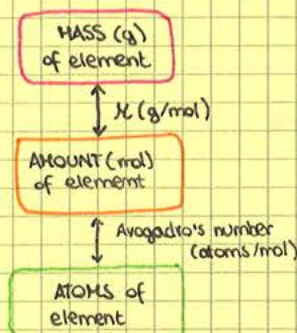
1 We multiply by Avogadro's number to convert amount of substance (in moles) to the number of entities (atoms, molecules or formula units)

$$\text{No. of entities} = \text{no. of moles} \times \frac{6.022 \cdot 10^{23} \text{ entities}}{1 \text{ mol}}$$

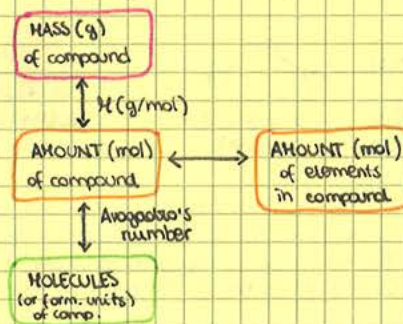
2 Or we divide by Avogadro's number to do the reverse.

$$\text{No. of moles} = \text{no. of entities} \times \frac{1 \text{ mol}}{6.022 \cdot 10^{23} \text{ entities}}$$

* Converting moles of elements



* Converting moles of compounds



Mass Percent from the Chemical Formula

Each element in a compound constitutes its own particular portion of the compound's mass. For an individual molecule (or formula unit) we use the molecular (or formula) mass and chemical formula to find the mass percent of an element X in the compound.

$$\text{Mass \% of element X} = \frac{\text{atoms of X in formula} \times \text{atomic mass of X (amu)}}{\text{molecular (or formula) mass of compound (amu)}} \times 100$$

- Since the formula also tells the number of moles of each element in the compound, we use the molar mass to find the mass percent of each element on a mole basis

$$\text{Mass \% of element X} = \frac{\text{moles of X in formula} \times \text{molar mass of X (g/mol)}}{\text{mass (g) of 1 mol of compound}} \times 100$$

As always, the individual mass percents of the elements in the compound must add up to 100% (with rounding). An important practical use of mass percent is to determine the amount of an element in any size sample of a compound.

Determining the formula of an unknown compound

In this section we will use the masses of elements in a compound to find its formula.

EMPIRICAL FORMULAS is the simplest whole-number ratio of moles of each element in the compound.

Let's see how to obtain the subscripts from the moles of each element. Suppose that a sample contains 0.21 mol of zinc, 0.14 mol of phosphorus and 0.56 mol of oxygen. First we write $\text{Zn}_{0.21}\text{P}_{0.14}\text{O}_{0.56}$, then:

- Divide each subscript by the smallest one (this step alone often gives integer subscripts)
- If any of the subscripts is still not an integer, multiply through by the smallest integer that will turn all subscripts into integers. (Here by 2)

ELECTROMAGNETIC SPECTRUM continuum of radiant energy of which ~~the~~ visible light is only a small portion. All the waves in the spectrum travel at the same speed through a vacuum but differ in frequency and wavelength. Some regions of the spectrum are utilized by particular devices and each region meets the next.

Example infrared (IR) region meets the microwave region on one end and the visible region on the other.

* We perceive different wavelengths or frequencies of visible light as different colours

monochromatic light of a single wavelength

polychromatic light of many wavelengths (white light)

ultraviolet (UV) region adjacent to visible light.

DISTINCTION : ENERGY and MATTER

Energy and matter behave very differently.

- Light of a given wavelength travels at different speeds through different transparent media. When a light wave passes from one medium into another, the speed of the wave changes. This phenomenon is known as **refraction**. If the wave strikes the boundary between air and water, at an angle other than 90°, the change in speed causes a change in direction and the wave continues at a different angle, which depends on the materials on either side of the boundary and the wavelength of the light. In the process of **dispersion**, white light separates into its component colors, as when it passes through a prism, because each incoming wave is refracted at a slightly different angle.

In contrast a particle does not undergo refraction when passing from one medium to another.

When a wave strikes the edge of an object, it bends around it in a phenomenon called **diffraction** (If the wave passes through a slit...). Once again, particles act very differently: some particles hit the edge while others go through the opening and continue linearly in a narrower group.

If waves of light pass through two adjacent slits, the emerging circular waves interact with each other through the process of **interference**. It could be **constructive** if the crests of the waves coincide and the amplitudes add together (in phase); **destructive** if the crests coincide with troughs (out of phase) and the amplitudes cancel. → diffraction pattern of brighter and darker regions. In contrast particles continue in straight paths, some colliding with each other and moving at different angles.

PARTICLE NATURE OF LIGHT

- **Blackbody radiation and quantization of Energy**

When a solid object is heated "about 1000 K, it begins to emit visible light; at about 1500 K the light is brighter and more orange; at temperatures greater than 2000 K, the light is still brighter and whiter. These changes in intensity and wavelength of emitted light as an object is heated are characteristic of **BLACKBODY RADIATION** (idealized object that absorbs all the radiation incident on it; or emits spectrum in the entire wavelength)

MAX PLANCK in 1900 developed a formula that fit the data perfectly; to find a physical explanation for his formula he was forced to make a radical assumption: he proposed that the hot, glowing object could emit (or absorb) only certain quantities of energy:

THEORY OF QUANTUM OF ENERGY

$$E = nh\nu \quad E = \text{energy of radiation} \quad \nu = \text{frequency} \quad n = \text{positive integer called quantum number}$$

$h = \text{proportionality constant now known very precisely (Planck's constant)}$

$$\rightarrow 6.626 \cdot 10^{-34} \text{ J}\cdot\text{s}$$

* Later interpretations: the hot object's radiation is emitted by the atoms contained within it. If an atom can emit only certain quantities of energy, the atom itself can have only certain quantities of energy; it is quantized (exists only in certain fixed quantities). Each change in the atom's energy results from the gain or loss of 1 or + "packets" of energy, each one called a **quantum** with energy $h\nu$.

* Thus, an atom changes its energy state by emitting (or absorbing) one or + quanta, and the E of the radiation is equal to the difference in the atom's energy states $[\Delta E_{\text{atom}} = E_{\text{emitted (or absorbed) radiation}} = \Delta nh\nu]$

* The atom can change its energy only by integer multiples of $h\nu$, so the smallest change is when $\Delta n = 1$, so $\Delta E = h\nu$. If an electron remains in a given orbit no energy is emitted or absorbed

■ See the possible electronic transition for the hydrogen atom (Lesson 4 - 20)

- **Photoelectric effect and photon theory of light**

Planck and other physicists continued to picture the emitted energy as traveling in waves. However the wave model could not explain the **PHOTOELECTRIC EFFECT**, the flow of current when monochromatic light of sufficient frequency shines on a metal plate. The existence of the current could be understood as arising when the light transfers energy to the electrons at the metal surface, which break free and are collected by the positive electrode. But it had also certain confusing features:

- Presence of a threshold frequency. Light shining on the metal must have a minimum frequency, or no current flows. The wave theory, however, associates the energy of the light with the amplitude, not frequency. Thus the wave theory predicts that an electron would break free when it absorbed enough energy from light of any color.

■ **Guitar strings**

It shows that, because the ends of the string are fixed, only certain vibrational frequencies (oral wavelengths) are possible.

* Combining the equation for mass-energy equivalence ($E=mc^2$) with that for the energy of a photon ($E=h\nu = hc/\lambda$) De Broglie derived an equation for the wavelength of any particle of mass m moving at speed u

$$\lambda = \frac{h}{mu}$$

According to this equation for the **de Broglie wavelength**, matter behaves as though it moves in a wave. An object's wavelength is inversely proportional to its mass. (p.284 table 7.1)

↳ ELECTRON MICROSCOPE

If particles travel in waves, electrons should exhibit diffraction and interference.

• In 1927, **Dawison** and **Germer** guided a beam of electrons at a nickel crystal and obtained a diffraction pattern. Even though electrons don't have orbits of fixed radius, as the Broglie thought, the energy levels of the atom are related to the wave nature of the electron. But if electrons have properties of energy, do photons have properties of matter? Talking de B. equation and substituting the speed of light (c) for speed u , solving for p gives $\left[\lambda = \frac{h}{mc} = \frac{h}{p} \rightarrow p = \frac{h}{\lambda} \right]$ → shorter wavelength photons have greater momentum.

• In 1923, **Compton** directed a beam of x-ray photons at a sample of graphite and observed that the wavelength of the reflected photons increased. This result means that the photons transferred some of their momentum to the electrons in the carbon atoms of the graphite. These studies showed that, on the atomic scale, every characteristic trait used to define the one now also defined the other.

[see p.285] - Table

* The truth is that both matter and energy show both behaviors: each possesses both faces. The distinction between a particle and a wave is meaningful only in the macroscopic world, not in the atomic one. The distinction between matter and energy is in our mind and it is known as the **wave-particle duality**.

HEISENBERG UNCERTAINTY PRINCIPLE

In 1927, Heisenberg postulated the **uncertainty principle**, which states that it is impossible to know the exact position and momentum of a particle simultaneously. For a particle with constant mass m , the principle is:

$$\left[\Delta x \cdot m \Delta u \geq \frac{h}{4\pi} \right] \quad \begin{matrix} \Delta x = \text{uncertainty in position} \\ \Delta u = \text{uncertainty in speed} \end{matrix} \quad (+ \text{position, - speed and vice versa})$$

* We cannot assign fixed paths for electrons, such as the circular orbits of Bohr's model.

The quantum-mechanical model of the atom

QUANTUM MECHANICS examines the wave nature of objects on the atomic scale (accepted the dualism energy-matter and uncertainty principle)

In 1926 **Erwin Schrödinger** derived the so-called **SCHRÖDINGER EQUATION**, which is the basis for the quantum mechanical model of the hydrogen atom (atom with a certain energy due to the allowed frequencies of an electron, behavior = wavelike, location = impossible to know). The electron's matter-wave occupies the three dimensional space near the nucleus and experiences an influence from the nuclear charge.

• $[\hat{X} \psi = E \psi]$ $E = \text{energy of the atom}$ $\psi = \text{wave function (mathem. description of the electron's matter-wave in terms of position in 3-dimensions)}$
 $\hat{X} = \text{HAMILTONIAN OPERATOR}$ (set of operations that yields on allowed energy value) → with no direct physical meaning

Each solution to the equation (energy state) is associated with a given wave function → **ATOMIC ORBITAL**, that is different from the "orbit", in the Bohr model (electron's path around the nucleus). We can only describe where an electron probably is; the square of the wave function (orbital) $\psi^2 = \text{probability density}$ (measure of the probability that the electron can be found within a particular tiny volume of the atom)

For a given energy level, we can depict this probability with an **electron density diagram** (electron probability d.d.) also called **electron cloud** representation (imaginary picture of the electron changing its position rapidly over time).

* The electron probability density decreases with distance from the nucleus along a line r .

* The probability of the electron being far from the nucleus is very small, but not zero.

TOTAL PROBABILITY to find it, we suppose to divide the volume around the nucleus into concentric, spherical layers and to ask in which one we are most likely to find the electron. Near the nucleus, the volume of each layer increases faster than its probability density decreases, so the total p . in the 2nd layer is higher than in the 1st. Electron density drops off so quickly → this effect diminishes with greater distance (volume ↑, t.p. ↓) = t.p. peaks in a layer same distance from the nucleus. **Radial prob. distribution plot.**

* At least for the ground state Sch. model predicts that the electron spends most of the time at the same distance that Bohr model predicted it spent all of its time (closest orbit)

* We cannot assign a definite volume to an atom because the probability of finding the electron far from the nucleus is not zero. However we visualize atoms with a **90% probability contour** (volume within which the e of H atom spends 90% of its time)

Chapter 8

* Like the Bohr model, Schrödinger equation does not give exact solutions for many-electron atoms, but it gives very good approximate solutions which show that the atomic orbitals of many-electron atoms resemble those of the H atom, so we can use the same quantum numbers but we have to: 1) add a 4th q.n. 2) establish a limit on the n° of e⁻ in each orbital 3) more complex set of orbital energy levels.

ELECTRON-SPIN QUANTUM NUMBER

We have to add a quantum number in order to describe a property of the electron itself and not of the orbital, called spin, which becomes important when more than one electron is present. When a beam of H atoms passes through a nonuniform magnetic field, it splits into two beams that bend away from each other: the explanation is that an electron generates a tiny magnetic field, as though it were a spinning charge. The single electron in each H atom can have one of two possible values of spin and each one generates a magnetic field: These two have opposite directions, so half of the e⁻ are attracted into the large external magnetic field and the other half repelled by it → result = beam of H atoms splits. The Spin quantum number (m_s) has values of either +1/2 or -1/2 $m_s = \pm 1/2$

• Each electron in an atom is described by four quantum numbers: 3 describe its orbital and 1 its spin!
STERN and GERLACH EXPERIMENT (p.305)

EXCLUSION PRINCIPLE

It was formulated by Wolfgang Pauli after observing the excited states of atoms: "no two electrons in the same atom can have the same four quantum numbers"; it means that each electron must have a unique identity expressed by its set of quantum numbers. **EXAMPLE** He, 2 e⁻ in the same orbital with opposite spin.

* Because m_s can have only two values (±1/2), the most important consequence is that "an atomic orbital can hold a maximum of two electrons and they must have opposing spins. [MAX 2 e⁻ in a orbital]

1s filled, e⁻ with paired spins

ELECTROSTATIC EFFECTS and ENERGY-LEVEL SPLITTING

Electrostatic effects play a major role in determining the energy states of many-electron atoms. Remember that in H atom all sublevels have the same energy and this because the only electrostatic interaction is the attraction between nucleus and electron. The energy states arise also from e⁻ e⁻ repulsions. Consequence: "the splitting of energy levels into sublevels of differing energies; the energy of an orbital in a many-electron atom depends mostly on its n value (size) and to a lesser extent on its l value (shape)

• By definition the electrons of an atom in its ground state occupy the orbitals of lowest energy.
EXAMPLE Li → 2e⁻ in 1s orbital (full), 3rd e⁻ must go to the n=2 level, especially 2s that has lower energy. This is based on nuclear charge, electron repulsions and orbital shape. Their interplay leads to the phenomena of shielding and penetration.

The effect of nuclear charge (Z) on Orbital Energy

Nuclear protons create an over-present pull on the electrons. Higher charges attract each other more strongly than lower charges; therefore higher nuclear charge lowers orbital energy (stabilizes the system) by increasing nucleus-electron attractions. fig. 8.3 p. 306

Shielding: the effect of Electron repulsions on orbital energy

In many-electron atoms, each electron feels not only the attraction to the nucleus but also the repulsion from other electrons. We speak of each electron "shielding", the other electrons somewhat from the nucleus. It is also called screening and reduces the full nuclear charge to an effective nuclear charge (Z_{eff}), the nuclear charge of an electron actually experiences. This lower nuclear charge makes the electron easier to remove. (fig. 8.4 A p. 307)

Much greater shielding is provided by inner electrons which spend nearly all their time between the outer electrons and the nucleus, so they shield a e⁻ much more effectively than do electrons in the same sublevel. (fig. 8.4 B)

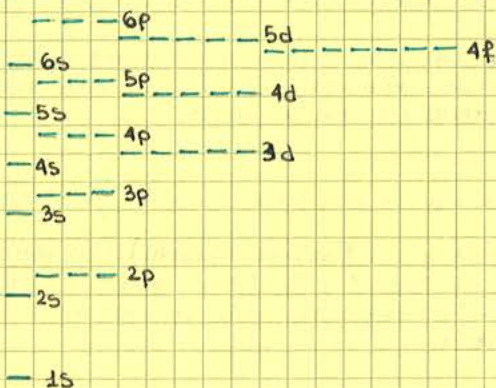
* Shielding by inner electrons greatly lowers the Z_{eff} felt by outer electrons

Penetration: the effect of orbital shape on orbital energy

Question of Li: we have to consider orbital shapes (radial probability distributions) → Book p. 307

In general, penetration and the resulting effects on shielding cause an energy level to split into sublevels of differing energy. The lower the l value of the orbital, the more its electrons penetrate and so ↑ the attraction to the nucleus. For a given n value → - l value → - sublevel energy

[s < p < d < f] → order of sublevel energies



- The clearest distinction among the elements is their classification as metals, non metals or metalloids. The staircase line that runs from the top of group 3A to the bottom of group 6A is a dividing line for this classification. **METALS** appear in the large lower-left portion of the table (3/4 elements are metals, including main-group + transition, inner transition elements). They are generally shiny solids at room temperature (mercury only liquid) that conduct heat and electricity well and can be toolled into sheets and wires. **NONMETALS** appear in the small upper-right portion of the table; they are generally gases or dull, brittle solids at room temperature (bromine only liquid) and conduct heat and electricity poorly. **METALLOIDS** along staircase line (green, also called semimetals), are elements with properties between metals and non.
- * Elements in a group have similar chemical properties and elements in a period have different chemical properties.
DÖBEREINER, NEWLANDS

PERIODIC LAW (1869, Mendeleev - Russia and Meyer - Germany) "If the elements are ordered by increasing atomic mass, some properties are changing periodically". It's curious that Mendeleev and Meyer arrived at virtually the same organization simultaneously and independently. In particular, Mendeleev was able to predict the properties of several as-yet-undiscovered elements, for which he had left blank spaces in his table. (see table 8.1 p.304)

* **Unusual configuration: transition and inner transition elements**

Periods 4-5-6-7 incorporate the d-block transition elements. The general pattern is that the (n-1)d orbitals are filled between the ns-np orbitals: period 5 = period 4; period 6 (6s) — La = 1st member of 5d transition series. At this point we find the first series of **inner transition elements**, those in which f orbitals are being filled. The period 6 inner transition series fills the 4f orbitals and consists of the lanthanides (rare earths) so called because they occur after and are similar to La. Period 7 after actinium — actinides which fill 5f orbitals. Several irregularities in filling pattern occur in both d and f blocks. However, even though minor variations from the expected configuration occur, the sum of ns electrons and (n-1)d electrons always equals the new group number.

VARIATIONS IN THREE ATOMIC PROPERTIES

All physical and chemical behavior of the elements is based ultimately on the electron configurations of their atoms. Now we focus the attention on 3 properties, all periodic: they generally increase and decrease in a recurring manner throughout the periodic table; for this reason their relative magnitudes can often be predicted and they exhibit trends within a group or period that correlate with element behavior.

• **Trends in Atomic Size**

We commonly represent atoms as spheres in which the electrons spend 90% of their time. We often define **atomic size** in terms of how closely one atom lies next to another, measuring the distance between identical, adjacent atomic nuclei in a sample of an element and dividing it in half. This size depends on the atoms near the atom considered (they do not have hard surfaces) → atomic size varies slightly from substance to substance. **Metallic radius**: 1/2 the distance between nuclei of adjacent atoms in a crystal of the element (metals); **covalent radius** (molecules - nonmetals) 1/2 distance between nuclei of identical covalently bonded atoms.

• **Trends among main-group elements**

Atomic size also influences other atomic properties: among the main-group elements it varies within both a group and a period. These variations derive from two opposing influences:

- 1- **Changes in n**. As n increases, the probability that the outer electrons will spend more time farther from the nucleus increases as well; thus, the atoms are larger.
- 2- **Changes in Z_{eff}**. As it increases, outer electrons are pulled closer to the nucleus; thus, the atoms are smaller. The effect of these influences depends on shielding of the increasing nuclear charge by inner electrons:
 - 1- **Down a group, n dominates** - each member has one + level of inner electrons that shield the outer electrons very effectively. Atomic radius generally increases in a group from top to bottom.
 - 2- **Across a period, Z_{eff} dominates** - electrons are added to the same outer level, shielding does not change. Atomic radius generally decreases in a period from left to right.

• **Trends among transition elements**

These trends do not hold as consistently for the transition elements. From left to right, size shrinks through 2-3 elements but then it remains relatively constant because shielding by the inner d electrons counteracts the usual increase in Z_{eff}. Size decrease in period 4-5-6 is greater than in period 3. fig. 8.16

TRENDS IN IONIZATION ENERGY

Ionization energy (IE) is the energy (kJ) required for the complete removal of 1 mol of electrons from 1 mol of gaseous atoms or ions. Pulling an electron away from a nucleus requires energy to overcome the attraction. Because energy flows into the system, the ionization energy is always positive.

- **The first ion. energy (IE₁)** removes an outermost electron from the gaseous atom
[Atom(g) → ion⁺(g) + e⁻ ΔE = IE₁ > 0]
- **The 2nd ion. energy (IE₂)** removes a second electron, that is pulled away from a positively charged ion so:
[Ion⁺(g) → ion²⁺(g) + e⁻ ΔE = IE₂ (always > IE₁)]

* Atoms with a low IE₁ tend to form cations during reactions, whereas those with a high IE₁ (except the noble gases) often form anions.

• Magnetic properties of transition metal ions

Only chemical species with unpaired electrons are affected by the external field. They exhibit **paramagnetism**: attraction by an external magnetic field; on the other side, a species with all electrons paired exhibits **diamagnetism**.

IONIC SIZE VS ATOMIC SIZE

Ionic radius is an estimate of the size of an ion in a crystalline ionic compound. From the relation between effective nuclear charge and atomic size, we can predict the size of an ion relative to its parent atom:

- Cations are smaller than their parent atoms. When a cation forms, electrons are removed from the outer level. The resulting decrease in electron repulsions allows the nuclear charge to pull the remaining electrons closer.
- Anions are larger than their parent atoms. When an anion forms, electrons are added to the outer level.
- Ionic size increases down a group
- Ionic size decreases across a period but increases from cations to anions
- I.S. decreases with increasing positive (or decreasing negative) charge in an isoelectronic series.
- I.S. decreases as charge increases for different cations of a given element.

Ionic charge = number of protons - number of electrons

Chapter 9

Atomic properties and chemical bonds

In general terms, bonding lowers the potential energy between positive and negative particles, whether those particles are oppositely charged ions or nuclei and the electrons between them; the type and strength of chemical bonds determine the properties of a substance.

THREE TYPES OF CHEMICAL BONDING

On the atomic level, we distinguish a metal from a nonmetal on the basis of several properties that correlate with position in the periodic table. Three types of bonding result from the three ways these two types of atoms can combine:

- 1- **Metal with nonmetal**: electron transfer and ionic bonding. **Ionic bonding**, between atoms with large differences in their tendencies to lose or gain electrons. Electron transfer from metal to nonmetal occurs, and each atom forms an ion with a noble gas electron configuration. The electrostatic attraction between these \ominus and \oplus ions draws them into the three-dimensional array of an ionic solid, whose chemical formula represents the cation-to-anion ratio (empirical formula).
- 2- **Nonmetal with nonmetal**: electron sharing and covalent bonding. When two atoms have a small difference in their tendencies to lose or gain electrons, we observe **el. shar.** and **covalent bonding**: this type of bonding most commonly occurs ~~between~~ between nonmetals; each one holds onto its electron tightly and tends to attract the other electrons. The attraction of each nucleus for the valence electrons of the other draws the atoms together \rightarrow shared e^- pair is considered to be localized between the two atoms.
- 3- **Metal with metal**: electron pooling and metallic bonding. Metal atoms are relatively large, and their few outer electrons are well shielded by filled inner levels \rightarrow they lose outer e^- easily but do not gain them as well, so we have a share of e^- diff. from covalent bonding, **metallic bonding**. Here all the metals in a sample pool their valence electrons into a source of "sea" of e^- that flows between and around the metal-ion cores, attracting and holding them together, so electrons are delocalized.

Remember that in the real world there could be exceptions!

LEWIS ELECTRON-DOT SYMBOLS

In this representation the element symbol is used to symbolize the nucleus and inner electrons, and the surrounding dots represent the valence electrons. The pattern of dots is the same of elements within a group.

It's easy to write the Lewis symbol for any main-group element:

- A-group number - n° of valence electrons
- Place 1 dot at a time on the four sides of the element symbol
- Keep adding dots, pairing them until all are used up. (valence electrons + n° of bonds = 8)
- The specific placement of dots is not important

The Lewis symbol also provides information about element's bonding behavior

- Metal - the total number of dots is the maximum n° of electrons an atom loses to form a cation.
- Nonmetal - n° of unpaired dots equals the n° of e^- an atom gains in becoming an anion or the n° it shares in forming covalent bonds

OCTET RULE: when atoms bond, they lose, gain or share electrons to obtain a filled outer level of eight (or two) electrons. This rule holds for nearly all of the compounds of period 2 elements and many others.

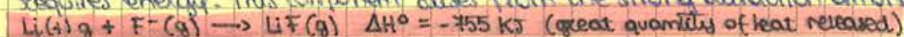
IONIC BONDING MODEL

Central idea: transfer of electrons from metal atoms to nonmetal atoms to form ions that come together in a solid ionic compound. For nearly every monatomic ion of a main-group element, the e^- config. has a filled outer level (2-8 e^-).

In ionic bonding the total number of electrons lost by the metal atoms equals the total number of e^- gained by the nonmetal atoms.

• The importance of lattice energy

The electron transfer process by itself actually absorbs energy. The reason ionic substances exist at all is because of the enormous release of energy that occurs when the ions come together as a solid (p.345 electron transfer process - lithium fluoride). The total energy needed for ion formation is even greater than this because metallic lithium and diatomic fluorine must first be converted to separate gaseous atoms, which also requires energy. This component arises from the strong attraction among many oppositely charged ions



* Metals of groups 1,2 tend to release e^- (cation), non metals (15,16,17) to acquire (anions)

The energy absorbed to break the bond is released when the bond forms. Bond formation is an exothermic process, so the sign of the enthalpy change is negative.

- Because bond energy depends on characteristics of bonded atoms, each type of bond has its own bond energy. Stronger bonds are lower in energy (deeper energy well); weaker bonds are higher in energy (shallower energy well).
- **Bond length** is the distance between the nuclei of two bonded atoms, like bond energies, these values are average bond lengths for the given bond in different substances. Bond length is related to the sum of the radii of the bonded atoms and, for a series of similar bonds it increases with atomic size.
- **Relationship**: two nuclei are more strongly attracted to two shared electron pairs than to one: the atoms are drawn close together and are more difficult to pull apart; therefore, for a given pair of atoms, a higher bond order results in a shorter bond length and a higher bond energy. \rightarrow (\uparrow bond length \rightarrow \downarrow b. energy)
- * In some cases, we can extend this relationship among atomic size, bond length and bond strength by holding one atom in the bond constant and varying the other atom within a group or period. Single bonds - longer bonds usually weaker.

How the model explains the properties of covalent substances

It proposes that electron sharing between pairs of atoms leads to strong, localized bonds, usually within individual molecules. It seems that the model is inconsistent with some physical properties of those compounds, which are mostly gases, liquids or low-melting solids. If covalent bonds are so strong, why do covalent substances melt and boil at such low temp? We have to distinguish betw. two forces: 1) strong covalent bonding forces 2) weak intermolecular forces \rightarrow between molecules, not strong covalent bonds within each molecule.

Some covalent substances, called network covalent solids, do not consist of separate molecules. Rather, they are held together by covalent bonds that extend in three dimensions throughout the sample. Properties of these substances do reflect the strength of their covalent bonds.

Unlike ionic compounds, most covalent substances are poor electrical conductors, even when melted or when dissolved in water. In cov. substances electrons are localized as either shared or unshared pairs, so are not free to move and no ions are present.

Bond energy and chemical change

The relative strengths of the bonds in reactants and products of a chemical change determine whether heat is released or absorbed.

Changes in bond strengths:

A system internal energy has kinetic and potential energy components. Of the various contributions to E_k , the most important come from the molecules moving through spaces and also from e^- moving within the atoms. Of the various contributions to E_p , most imp. electrostatic forces between the vibrating atoms, nucleus - e^- , protons - neutrons, nuclei - shared e^- . E_k doesn't change during a reaction; the only significant change in E_p is the strength of attraction of the nuclei for the shared electron pair, that is, in the bond energy. **ANSWER**: the energy released or absorbed during a chemical change is due to differences between the reactant bond energies and the product bond energies.

Bond Energies to calculate ΔH°_{rxn}

Reaction - two step process in which a quantity of heat is absorbed (ΔH° is positive) to break the reactant bonds and form separate atoms and a differ quantity is released (ΔH° negative) when atoms rearrange to form product bonds

$$\Delta H^\circ_{rxn} = \sum \Delta H^\circ_{\text{reactant bonds broken}} + \sum \Delta H^\circ_{\text{product bonds formed}}$$

- **Exothermic reaction**, ΔH for product bonds formed greater than that for reactant bonds broken (sum \ominus)
- **Endothermic reaction** vice versa (sum \oplus)
- * Recall that weaker bonds (less stable, more reactive) are easier to break than stronger bonds (more stable, less reactive) because they are higher in energy.
- We use bond energies to calculate ΔH° by assuming that all the reactant bonds break to give individual atoms, from which all the product bonds form. Hess's law allows us to imagine complete bond breakage and then sum the bond energies to arrive at the overall heat of reaction. Because bond energies are average values obtained from many different compounds, the energy of the bond in a particular substance is usually close to this average. (see p. 361-362 \rightsquigarrow Relative bond strength in fuels and foods)

Electronegativity and Bond polarity

ELECTRONEGATIVITY (EN) is the relative ability of a bonded atom to attract the shared electrons. Was the American chemist Linus Pauling that developed the most common scale of relative EN values for the elements. $[E.N \propto \frac{(I.E. + E.A.)}{2}]$

EXAMPLE

bond en. of H-F average of energies of H-H and F-F bonds. But the actual bond energy of H-F is 565 kJ/mol (289 kJ/mol higher than the average) Pauling reasoned that this difference is due to an electrostatic (charge) contribution to the H-F bond energy. If F is more EN than H, the e^- will spend more time closer to F; this inequal sharing of e^- makes the F end of the bond partially \ominus and the H end partially \oplus and the attraction between them increases the energy required to break the bond. From similar studies Pauling arrived at the scale of relative EN values.

Trends in electronegativity

Because the nucleus of a smaller atom is closer to the shared pair than that of a larger atom it attracts the bonding electrons more strongly. So electronegativity is inversely related to atomic size. It generally increases up a group and across a period. (EN \uparrow , atomic size \downarrow) Nonmetals are more electronegative than metals.

Chapter 10

Lewis Structure

The first step toward visualizing what a molecule looks like is to convert its molecular formula to its **LEWIS STRUCTURE** (or **Lewis Formula**). This two-dimensional structural formula consists of electron-dot symbols that depict each atom and its neighbors, the bonding pairs that hold them together and the lone pairs that fill each atom's outer level (valence shell).

USING THE OCTET RULE

To write a Lewis structure, we decide on the relative placement of the atoms in the molecule (or polyatomic ion) and distribute the total number of valence electrons as bonding and lone pairs. Let's start by examining Lewis structures for species that "obey" the octet rule, those in which each atom fills its outer level with eight electrons. ($H-2e^-$)

• Lewis Structures for Molecules with Single Bonds (valid unless d-type valence orbitals are present - TRANSITION METALS)

First we discuss the steps for writing Lewis structures for molecules with only 1 bond. (NF_3 - nitrogen fluoride)

- 1- Place the atoms relative to each other. For compounds of the type AB_n , place the atom with lower group number in the center because it needs more electrons to attain the octet (usually it has also the lower E.N.). If the atoms have the same group number place the atom with the higher period number in the center. (H only one bond, never central atom)
- 2- Determine the total number of valence electrons available. For molecules, add up the valence electrons of all the atoms; for polyatomic ions, add one e^- for each negative charge of the ion, or subtract one e^- for each positive charge.
- 3- Draw a single bond from each surrounding atom to the central atom, and subtract two valence electrons for each bond to find the number remaining.
- 4- Distribute the remaining electrons in pairs so that each atom ends up with eight electrons ($H-2e^-$). First, place lone pairs on the surrounding (more E.N.) atoms to give each octet. If any electrons remain, place them around central atom. Then check.

* Lewis structures do not indicate shape (so we have the same connections among the atoms)

Remember that, in nearly all their compounds:

- Hydrogen atoms form one bond.
- Carbon atoms form four bonds.
- Nitrogen atoms form three bonds.
- Oxygen atoms form two bonds.
- Halogens form one bond when they are surrounding atoms; Fluorine is always a surrounding atom.
- A slightly more complex situation occurs when molecules have two or more central atoms bonded to each other, with the other atoms around them.

• Lewis structures for Molecules with multiple Bonds

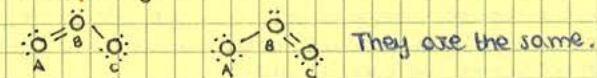
In this case the following additional step is needed:

- 5- If, after step 4, a central atom still does not have an octet, make a multiple bond by changing a lone pair from one of the surrounding atoms into a bonding pair to the central atom.

RESONANCE: Delocalized Electron-Pair Bonding

We can often write more than one Lewis structure each with the same relative placement of atoms, for a molecule or ion with double bonds next to single bonds

Example O_3



Bond length and bond energy measurements indicate that the two oxygen-oxygen bonds in O_3 are identical, with properties that lie between those of an $O-O$ and an $O=O$ bonds. The molecule is shown more correctly with two Lewis structures, called **resonance structures** (or **forms**) and two-headed resonance arrow (\leftrightarrow) between them. They have the same relative placement of atoms but different locations of bonding and lone e^- pairs. However, they're not real bonding depictions: the actual molecule is a **resonance hybrid**, an average of the resonance forms.

Our need for more than one Lewis structure to depict the same molecule is due to **electron-pair delocalization**. In a bond each electron pair is attracted by the nuclei of the two bonded atoms, and the electron density is greatest in the region between the nuclei: each electron pair is localized. In the res. hybrid of O_3 two e^- pairs are delocalized - their density is spread over the entire molecule - in O_3 2 bonds (1 bond + 1 partial bond).

* Resonance is very common, and many molecules (and ions) are best depicted as resonance hybrids.

Example - Benzene!

* Note that the Lewis structure of a polyatomic ion is shown in square brackets, with its charge as a right superscript outside the brackets.

FORMAL CHARGE: Selecting the more important resonance structure

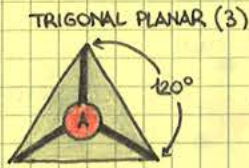
Because the resonance hybrid is an average of the resonance forms, one form may contribute more and "weight" the average in its favor. We can often select the more important resonance form by determining each atom's **formal charge** - the charge it would have if the bonding electrons were shared equally.

[Formal charge of atom = no. of valence e^- - (no. of unshared valence e^- + $1/2$ no. of shared valence e^-)

* Formal charges must sum to the actual charge on the species: 0 for a molecule and ionic charge for an ion

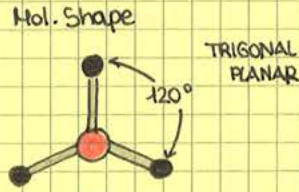
MOLECULAR SHAPES WITH THREE ELECTRON GROUPS (TRIGONAL PLANAR arrangement)

Three electron groups around the central atom repel each other to the corners of an equilateral triangle.



Class AX_3

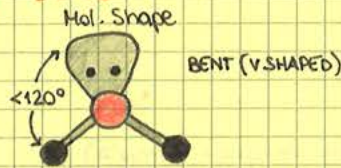
Bonding Groups 3



Examples: $SO_3, BF_3, NO_3^-, CO_3^{2-}$

Class AX_2E

Bonding Groups 3



Examples: $SO_2, O_3, PbCl_2, SnBr_2$

• Effect of Double Bonds

CH_2O - formaldehyde. The actual bond angles deviate from the ideal because the double bond, with its greater electron density, repels the two single bonds more strongly than they repel each other.

• Effect of Lone Pairs

Because a lone pair is held by only one nucleus, it's less confined and exerts stronger repulsions than a bonding pair. Thus, a lone pair repels bonding pairs more strongly than bonding pairs repel each other.

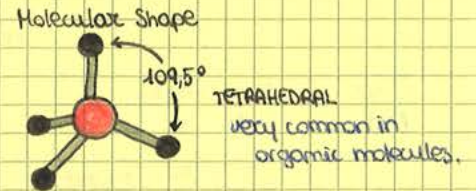
MOLECULAR SHAPES WITH FOUR ELECTRON GROUPS (Tetrahedral Arrangement)

Four electron groups must use 3D to achieve maximal separation. (PERSPECTIVE DRAWINGS)



Class AX_4

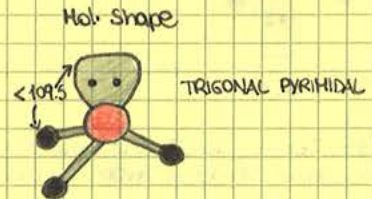
Bonding Groups 4



Examples: $CH_4, SiCl_4, SO_4^{2-}, ClO_4^-$

Class AX_3E

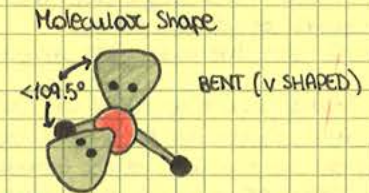
Bonding Groups 3



Examples: $NH_3, PF_3, ClO_3^-, H_3O^+$

Class AX_2E_2

Bonding Groups 2



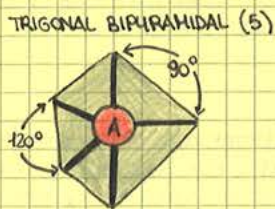
Examples: H_2O, OF_2, SCl_2

* For similar molecules with a given electron-group arrangement electron-pair repulsions cause deviations from ideal b.a.:
 [lone pair - lone pair > lone pair - bonding pair > bonding p. - bonding p.]

MOLECULAR SHAPES WITH FIVE ELECTRON GROUPS (Trigonal Bipyramidal Arrangement)

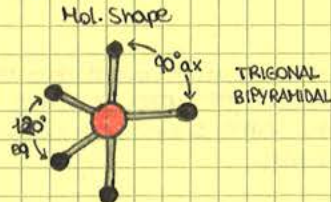
All molecules with five or six electron groups have a central atom from period 3 or higher because only these atoms have d orbitals available to expand the valence shell beyond eight electrons.

- There are two types of positions for surrounding electron groups and two ideal bond angles: 3 equatorial groups lie in a trigonal plane that includes the central atom, 3 axial groups lie above and below this plane. (e-e rep. weaker than a-e ones) Tendency to occupy eq. position!



Class AX_5

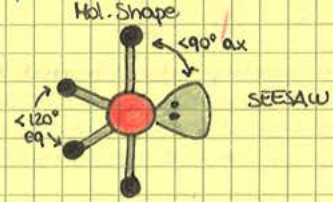
Bonding Groups 5



Examples: PF_5, AsF_5, SF_6

Class AX_4E

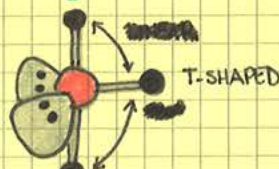
Bonding Groups 4



Examples: $SF_4, XeO_2F_2, IF_4^+, IO_2F_2^-$

Class AX_3E_2

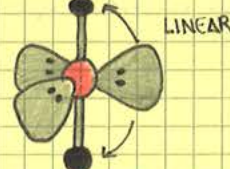
Bonding Groups 3



Examples: ClF_3, BrF_3

Class AXE_3

Bonding Groups 2



Examples: XeF_2, I_3^-, IF_2^-

Chapter 11

Valence Bond (VB) theory and orbital hybridization

CENTRAL THEMES OF VB THEORY

- * The basic principle of VB theory is that "a covalent bond forms when orbitals of two atoms overlap and the overlap region, which is between the nuclei, is occupied by a pair of electrons". (ORBITAL OVERLAP = wave f. in phase, so amplitude increases between the nuclei).
The central themes of VB theory derive from this principle:
 - 1- **Opposing spins of the electron pair.** As the exclusion principle prescribes, the space formed by the overlapping orbitals has a maximum capacity of two electrons that must have opposite spins. (H_2)
 - 2- **Maximum overlap of bonding orbitals.** The bond strength depends on the attraction of the nuclei for the shared electrons, so the greater the orbital overlap, the stronger (more stable) the bond. The extent of overlap depends on the shapes and directions of the orbital (a bond involving p or d orbitals will be oriented in the direction that maximizes ~~the~~ overlap).
 - 3- **Hybridization of atomic orbitals.** (methane) Linus Pauling proposed that "the valence atomic orbitals in the molecule are **different** from those in the isolated atoms. Mechanical calculations - mixing specific combinations of orbitals we can obtain new atomic orbitals. The spatial orientations of these new orbitals lead to more stable bonds and are consistent with observed molecular shapes. The process of orbital mixing is called **hybridization**, and the new atomic orbitals are called **hybrid orbitals**. Remember that
 - The number of hybrid orbitals obtained equals the number of atomic orbitals mixed.
 - The type of hybrid orbitals obtained varies with the types of atomic orbitals mixed.

TYPES OF HYBRID ORBITALS

- * Notice that the spatial orientation of each type of hybrid orbital corresponds with one of the five common electron-group arrangements predicted by VSEPR theory.
 - **sp Hybridization**
When two electron groups surround the central atom, we observe a linear shape, which means that the bonding orbitals must have a linear orientation. VB theory explains this by proposing that mixing two non-equivalent orbitals of a central atom, one s and one p, gives rise to two equivalent **sp hybrid orbitals** that lie 180° apart. Note the shape of the hybrid orbital (one large and one small lobe). The orientations of hybrid orbitals extend electron density in the bonding direction and minimize repulsions the electrons that occupy them. Thus, both shape and orientation maximize overlap with the orbital of the other atom in the bond. **Example - gas $BeCl_2$** (Be: sp hybridized)
 - **sp² Hybridization**
In order to rationalize the trigonal planar electron-group arrangement and the shapes of molecules based on it, we introduce the mixing of 1s and 2p orbitals of the central atom to give three hybrid orbitals that point toward the vertices of an equilateral triangle, their axes 120° apart. These are called **sp² hybrid orbitals**. **Example - BF_3**
 - **sp³ Hybridization**
VB theory proposes that the one s and all three p orbitals of the central atom mix and form four **sp³ hybrid orbitals**, which point toward the vertices of a tetrahedron. **Example - CH_4 (methane) + NH_3 and H_2O**
 - **sp³d Hybridization**
The shapes of molecules with trigonal bipyramidal or octahedral electron-group arrangements are rationalized with VB theory through similar arguments. The only new point is that such molecules have central atoms from Period 3 or higher, so atomic d orbitals, as well as s and p orbitals, are mixed to form the hybrid orbitals. **Example - PCl_5** (3s, 3p, 3d orbitals of P mix and form five **sp³d hybrid orbitals** which point to the vertices of a trigonal bipyramid)
* Sawsaw, T-shaped and linear molecules have this electron-group arrangement with lone pairs in, respectively, one, two, or three of the central atom's sp³d orbitals.
 - **sp³d² Hybridization**
The VB model proposes that the one 3s, the three 3p and two of the five 3d orbitals of the central S atom mix and form six **sp³d² hybrid orbitals**, which point to the vertices of an octahedron. (**SF_6**) Square pyramidal and square planar molecules have lone pairs in one and two of the central atom's sp³d² orbitals, respectively. (Note the similarities between the orientations of hybrid orbitals proposed by VB theory and the shapes predicted by VSEPR theory.
see p. 418 (when the concept of hybridization may not apply)

Therefore, when the antibonding orbital is occupied, the molecule is less stable than when this orbital is empty. Both the bon. and antib. MOs of H_2 are σ (σ) MOs because they are cylindrically symm. about an imaginary line that runs through the two nuclei. Bonding σ_{1s} , antibonding σ_{1s}^*
 * To interact effectively and form MOs, atomic orbitals must have similar energy and orientation.

Filling Molecular Orbitals with Electrons

Electrons fill MOs as they fill AOs:

- MOs are filled in order of increasing energy (aufbau principle)
- An MO has a maximum capacity of two electrons with opposite spins (exclusion principle)
- Orbitals of equal energy are half-filled, with spins parallel, before any of them is completely filled. (Hund's rule)

Molecular orbital (MO) diagram shows the relative energy and number of electrons in each MO, as well as the AOs from which they formed.

MO theory redefines bond order. In a Lewis structure, bond order is the number of electron pairs per linkage. The **MO bond order** is the number of electrons in bonding MOs minus the no. in antibonding MOs divided by two: **[Bond order = 1/2 [(no. of e⁻ in bonding MO) - (no. of e⁻ in antibonding MO)]**

* A bond order greater than zero indicates that the molecular species is stable relative to the separate atoms, whereas a bond order of zero implies no net stability and, thus, no likelihood that the species will form. In general, the higher the bond order, the stronger the bond.

Another similarity: we can write an e⁻ configuration for a molecule (symbol MO in parentheses; no. of e⁻ in it written as a superscript)

Existence of He₂⁺ ~ p. 424

HOMONUCLEAR DIATOMIC MOLECULES OF THE PERIOD 2 ELEMENTS

These molecules are composed of two identical atoms in addition to H₂ from Period 1, we have other diatomic molecules in period 2 (N₂, O₂, F₂ under standard conditions) and some of them (Li₂, Be₂, B₂, C₂) are observed only in high-temperature gas experiments.

Bonding in the s-Block Homonuclear diatomic molecules

Consider lithium (Li₂) and beryllium (Be).

These atoms have both inner and outer electrons (1s - 2s) but the 1s orbitals interact negligibly. We ignore the inner electrons here because, in general, only outer (valence) orbitals interact enough to form molecular orbitals. 1s AOs = 2s AOs σ orbitals cylindrically symmetrical around the nuclear axis. Li₂ = (σ_{2s})², has been observed. Be₂ = σ_{2s}^* , never been observed.

Molecular Orbitals from Atomic p-Orbital Combinations

As we move to boron in the p block, atomic 2p orbitals become involved, so let's first consider the shapes and the energies of the MOs that result from their combinations. End-to-end combinations gives a pair of σ MOs, σ_{2p} and σ_{2p}^* . Side-to-side combination gives a pair of π (π) MOs, π_{2p} and π_{2p}^* . Similar to s, bonding MOs from p-orbital combinations have their greatest electron density between the nuclei, whereas antibonding MOs from p-orbital combinations have a node between the nuclei and most of their electron density outside the internuclear region. The order of MO energy levels is based on the order of AO energy levels and on the mode of the p-orbital combination:

- MOs formed from 2s orbitals are lower in energy than MOs formed from 2p orbitals because 2s AOs are lower in en. than 2p AOs
- Bonding MOs are lower in en. than antib. MOs, so σ_{2p} is lower in en. than σ_{2p}^* and $\pi_{2p} < \pi_{2p}^*$
- Atomic p orbitals can interact more extensively end to end than they can side to side. $\sigma_{2p} < \pi_{2p}$ $\sigma_{2p}^* > \pi_{2p}^*$

Thus, we have $\sigma_{2p} < \pi_{2p} < \pi_{2p}^* < \sigma_{2p}^*$

There are three mutually perpendicular 2p orbitals in each atom. When the six orbitals in two atoms combine, the two orbitals that interact end to end form a σ and a σ^* MO, and the two pairs of orbitals that interact side to side form two π MOs of the same energy and 2 π^* . Combining these orientations with the energy order gives the expected MO diagram for the p-block period 2 homonuclear diatomic molecules.

The s and p AOs are so different in energy that they do not interact: the orbitals do not mix. This is true for O, F, Ne which are small atoms, so repulsions are strong. In contrast, B, C and N atoms are larger, so repulsions are small: some mixing occurs. The only change that affects this discussion is the reverse in energy order of the σ_{2p} and π_{2p} MOs.

Bonding in the p-Block Homonuclear diatomic molecules

- * A higher bond order correlates with a greater bond energy and shorter bond length. Orbital occupancy correlates with magnetic properties.
- * The spins of unpaired electrons in an atom cause the substance to be paramagnetic, attracted to an external magnetic field. If all electron spins are paired, the substance is diamagnetic, unaffected by the magnetic field. The same observations apply to molecules.

B₂, C₂, N₂, O₂, F₂, Ne₂

because at that point the column of mercury in the tube exerts the same pressure on the mercury surface in the dish as does the column of air that extends from the dish to the outer reaches of the atmosphere. The air pushing down keeps any more of the mercury in the tube from flowing out.

We did not specify the diameter of the barometer tube.

- * The weight of mercury is greater in the wider tube, but the area is larger also, thus the pressure, the ratio of weight to area, is the same. Since the pressure of the mercury column is directly proportional to its height, a unit commonly used for pressure is **mmHg**, the height of the mercury column in millimeters.
- * Pressure decreases with altitude: the column of air above the sea is taller and weighs more than the column of air above Mt. Everest. Laboratory barometers contain mercury because its high density allows the barometer to be a convenient size.

- * For a given pressure, the ratio of heights (h) of the liquid columns is inversely related to the ratio of the densities (d) of the liquids: $\left[\frac{h_{H_2O}}{h_{Hg}} = \frac{d_{Hg}}{d_{H_2O}} \right]$

MANOMETERS are devices used to measure the pressure of a gas in an experiment. **Closed-end manometer**: mercury filled, curved tube, closed at one end and attached to a flask at the other. When the flask is evacuated, the mercury levels in the two arms of the tube are the same because no gas exerts pressure on either mercury surface. When a gas is in the flask, it pushes down the mercury level in the near arm, so the level rises in the far arm. The difference in column heights (Δh) equals the gas pressure.

Open-end manometer consists of a curved tube filled with mercury, but one end of the tube is open to the atmosphere and the other is connected to the gas sample. The atmosphere pushes on one mercury level and the gas pushes on the other. Since Δh equals the difference between two pressures, to calculate the gas pressure with an open-end manometer, we must measure the atmospheric pressure separately with a barometer.

UNITS OF PRESSURE

Pressure results from a force exerted on an area. The SI unit of force is the newton (N): $1N = 1kg \cdot m/s^2$. The SI unit of pressure is the **pascal (Pa)** which equals a force of one newton exerted on an area of one square meter:

$[1Pa = 1N/m^2]$ **Standard atmosphere (atm)** Larger unit: average atmospheric pressure measured at sea level and 0°C. It's defined in terms of the Pascal $[1atm = 101.325 \text{ kilopascal (kPa)} = 1.01325 \cdot 10^5 Pa]$ *

Another unit **millimeter of mercury (mmHg)**, based on measurement with a barometer or manometer. In honor of Torricelli, this unit has been named the **Torr** $[1torr = 1mmHg = \frac{1}{760} atm = \frac{101.325}{760} kPa = 133.32 Pa]$

Bar used frequently in chemistry $[1bar = 1 \cdot 10^2 kPa = 1 \cdot 10^5 Pa]$ * $1atm = 1.01325 bar$

- * Despite a gradual change to SI units, many chemists still express pressure in torrs and atmospheres, so they are used.

The Gas Laws and their experimental foundations

The physical behavior of a sample of gas can be described completely by four variables: pressure (P), volume (V), temperature (T), and amount (no. of moles, n). The variables are interdependent: only one of them can be determined by measuring the other three.

Three key relationships exist among the four gas variables (Boyle's, Charles and Avogadro's Law); each one of these expresses the effect of one variable on another, with the remaining two variables held constant. Because gas volume is so easy to measure the laws are expressed as the effect on gas volume of a change in the other variables. These laws are special cases of the **ideal gas law**, which describes the state of an **IDEAL GAS**, one that exhibits simple linear relationships among vol, press, temp and amount.

- * Although no ideal gas actually exists, most simple gases (N_2, O_2, H_2) and the noble gases, show nearly ideal behavior at ordinary temperatures and pressures.

Relationship between volume and pressure: Boyle's Law

Following the invention of barometer, Robert Boyle performed a series of experiments that led him to conclude that at a given temperature, the volume occupied by a gas is inversely related to its pressure.

Boyle's experiment:

He fashioned a J-shaped glass tube, sealed the shorter end, and poured mercury into the longer end, thereby trapping some air, the gas in the experiment. From the height of the trapped air column and the diameter of the tube, he calculated the air volume.

The total pressure applied to the trapped air was the pressure of the atmosphere plus that of the mercury column. By adding mercury, he increased the total pressure exerted on the air, and the air volume decreased. With the temp. and amount of air constant, Boyle could directly measure the effect of the applied pressure on the volume of air.

- Note the following results:

- 1 The product of the corresponding P and V values is a constant
- 2 V is inversely proportional to P
- 3 V is directly proportional to 1/P and generates a linear plot of V against 1/P. This linear relationship

Solving gas problems

Gas law problems can usually be grouped into two main types:

- 1- A change in one of the four variables causes a change in another, while the two remaining variables remain constant. Here the ideal gas law reduces to one of the individual gas laws and you solve for the new value of the variable. Units must be consistent, T in kelvins, but R is not involved (a variation on the type involves the combined gas law)
 - 2- One variable is unknown, but the other three are known and no change occurs. In this type the ideal gas law is applied directly to find the unknown, and the units must conform to those in R. To solve easier these problems you've just to follow a systematic approach:
 - Summarize the information: identify the changing gas variables (known and not) and those held constant
 - Predict the direction of the change, and then check your answer against the prediction.
 - Perform only necessary unit conversions.
 - Rearrange the ideal gas law to obtain the appropriate relationship of gas variables, and solve for the unknown variable.
- * Finally, in a slightly different type of problem that depicts a simple laboratory scene, we apply the gas laws to determine the correct balanced equations for a process.

Further applications of the ideal gas law

DENSITY OF A GAS

One mole of any gas occupies nearly the same volume at a given temperature and pressure, so differences in gas density ($d = m/V$) depend on differences in molar mass.

All gases are miscible when thoroughly mixed, but in the absence of mixing, a less dense gas will lie above a more dense one (examples)

We can rearrange the ideal gas law to calculate the density of a gas from its molar mass. Recall that the no. of moles is the mass divided by the molar mass $n = m/M$. Substituting n we have:

$$PV = \frac{m}{M}RT \rightarrow \left[\frac{m}{V} = d = \frac{M \times P}{RT} \right]$$

Two important ideas are expressed

- The density of a gas is directly proportional to its molar mass because a given amount of a heavier gas occupies the same volume as that amount of a lighter gas.
- The density of a gas is inversely proportional to the temperature. As the volume of a gas increases with the temperature the same mass occupies more space \rightarrow density is lower.

MOLAR MASS OF A GAS

Through another simple rearrangement of the ideal gas law, we can determine the molar mass of an unknown gas or volatile liquid (easily vaporized)

$$\left[n = \frac{m}{M} = \frac{PV}{RT} \rightarrow M = \frac{mRT}{PV} \text{ or } M = \frac{dRT}{P} \right]$$

The French chemist Dumas pioneered a method for finding the molar mass of a volatile liquid. Fig 5.11 p. 205

- * By this procedure you have measured all the variables needed to calculate the molar mass of the gas: the mass (m) of gas occupies the flask volume (V) at a pressure (P) equal to the barometric pressure and at the temperature (T) of the water bath.

PARTIAL PRESSURE OF A GAS IN A MIXTURE OF GASES

The ideal gas law holds for virtually any gas, whether pure or a mixture, at ordinary conditions for 2 reasons:

- 1- Gases mix homogeneously (for a solution) in any proportion.
- 2- Each gas in a mixture behaves as if it were the only gas present (assuming no chemical interactions)

Dalton's Law of Partial Pressures

The second point above was discovered by John Dalton in his lifelong study of humidity. He observed that when water vapor is added to dry air, the total air pressure increases by an increment equal to the pressure of the water vapor: $P_{\text{humid air}} = P_{\text{dry air}} + P_{\text{added water vapor}}$

- * Each gas in the mixture exerts a **partial pressure** (portion of the total pressure of the mixture) that is the same as the pressure it would exert by itself. \rightarrow **DALTON'S LAW OF PARTIAL PRESSURES**: in a mixture of unreacting gases, the total pressure is the sum of the partial pressures of the individual gases

$$\left[P_{\text{total}} = P_1 + P_2 + P_3 + \dots \right] \sim \text{see example}$$

- * Each component in a mixture contributes a fraction of the total number of moles in the mixture, which is the **mole fraction** (X) of that component. Multiplying X by 100 gives the mole percent. Since the ~~total~~ total pressure is due to the total number of moles, the partial pressure of gas A is the total pressure multiplied by the mole fraction of A, X_A

$$\left[P_A = X_A \cdot P_{\text{total}} \right]$$

Collecting a Gas over Water

The law of partial pressures is frequently used to determine the yield of a water-insoluble gas formed in a reaction. The product bubbles through water is collected into an inverted container. The water vapor that mixes with the gas contributes a portion of the total pressure - water pressure, which depends on the water temperature.

4- **Charles's law** ($V \propto T$) As the temperature increases, the most probable molecular speed and the average kinetic energy increase (post. 3). Thus, the molecules hit the walls more frequently and more energetically. A higher frequency of collisions causes higher internal pressure

5- **Avogadro's law** ($V \propto n$) Adding more molecules to a container increases the total number of collisions with the walls and, therefore, the internal pressure. As a result, the volume expands until the number of collisions per unit of wall area is the same as it was before the addition.

• **Relationship between kinetic energy and temperature**

We need to explain why equal numbers of molecules of two different gases occupy the same volume. Let's first see why heavier O_2 particles do not hit the container walls with more energy than lighter H_2 particles. We know that $E_k = \frac{1}{2} \text{mass} \times \text{speed}^2$ which shows that = if a heavy object and a light object have the same kinetic energy, the heavy object must be moving more slowly, post. 3 leads to the conclusion that different gases at the same temperature have the same average kinetic energy → for this to be true, molecules with a higher mass have, on average, a lower speed. (at the same temp. O_2 moves more slowly than H_2) → H_2 collide with the walls more often, but with less force (lower mass). According to Avog. law at the same T, O_2 and H_2 have the same pressure and so the same volume (same E_k).

Now focus on the relation between kinetic energy and temperature: $\bar{E}_k = c \times T \rightarrow \bar{E}_k = \frac{3}{2} \left(\frac{R}{N_A} \right) T$
 $R =$ gas constant $N_A =$ Avogadro's number • temperature is related to the average energy of molecular motion. Remember that it's referred to the average energy.

Finally, let's derive an expression for a special type of average molecular speed → $\bar{E}_k = \frac{1}{2} m \bar{u}^2$

$m =$ molecular mass $\bar{u}^2 =$ average of square of mol. speeds.

$$\frac{1}{2} m \bar{u}^2 = \frac{3}{2} \left(\frac{R}{N_A} \right) T \rightarrow \frac{1}{2} N_A m \bar{u}^2 = \frac{3}{2} RT \rightarrow \bar{u}^2 = \frac{3RT}{M} \rightarrow \left[\bar{u} = \sqrt{\frac{3RT}{M}} \right] \text{ rms speed (4rms)} = \text{root-mean-square speed (a molecule}$$

moving at this speed has the average kinetic energy).

EFFUSION AND DIFFUSION

The movement of gases, either through one another or into regions of very low pressure, has many impo. applications.

• **Process of effusion**

One triumph of the kinetic-molecular theory was an explanation of **effusion**, the process by which a gas escapes from its container through a tiny hole into an evacuated space. In 1846, Thomas Graham studied this process and concluded that the effusion rate was inversely proportional to the square root of the gas density. The effusion rate is the number of moles (or molecules) of gas effusing per unit time. Since density is directly proportional to molar mass we state **GRAHAM'S LAW OF EFFUSION** = the rate of effusion of a gas is inversely proportional to the square root of its molar mass [Rate of effusion $\propto \frac{1}{\sqrt{M}}$]

RATIO OF THE RATES $\left[\frac{\text{Rate}_A}{\text{Rate}_B} = \frac{\sqrt{M_B}}{\sqrt{M_A}} = \sqrt{\frac{M_B}{M_A}} \right]$

Kinetic molecular theory explains that, at a given T and P, the gas with the lower molar mass effuses faster cause the most probable speed of its molecules is higher; therefore, more molecules escape per unit time.

* Graham's law is also used to determine the molar mass of an unknown gas, comparing the effusion rate of a gas X with that of a known gas.

• **Process of diffusion**

Closely related to the effusion is the **diffusion**, the movement of one gas through another. Diffusion rates are also described by Graham's law: [Rate of diffusion $\propto \frac{1}{\sqrt{M}}$]

The reason for the dependence on molar mass is the same as for effusion rates. But the presence of so many other gas particles is a major reason that diffusion rates are typically much lower than effusion rates. Although convection plays an important role, a molecule moving by diffusion does not travel very far before it collides with a molecule in the air.

Diffusion also occurs in liquids and to a small extent in solids. However, because the distances between molecules are shorter in liquids, collisions are more frequent and so diffusion is much slower.

* Diffusion of a gas through a liquid is a vital process in biological systems.

Chapter 12

An overview of physical states and phase changes

we have to distinguish two types of electrostatic forces at work among the particles.

- **Intramolecular forces** (bonding forces) exist within each molecule and influence the chemical properties of the substance.
- **Intermolecular forces** (nonbonding forces) exist between the molecules and influence the physical properties of the substance.

A Kinetic-Molecular view of the three states

Whether a substance is a gas, liquid or solid depends on the interplay of the potential energy of the intermolecular attractions, which tends to draw the molecules together, and the kinetic energy of the molecules, which tends to disperse them. Potential energy depends on the charges of the particles and the distances between them (Coulomb's law). The average kinetic energy, which is related to the particles' average speed, is proportional to the absolute temperature.

* We distinguish among the three states by focusing on three properties (shape, compressibility, ability to flow)

- In a **gas**, the energy of attraction is small relative to the energy of motion; so, on average, the particles are far apart. This large interparticle distance has several macroscopic consequences. A gas moves randomly throughout its container and fills it. Gases are highly compressible, and they flow and diffuse easily through one another.
- In a **liquid**, the attractions are stronger because the particles are in virtual contact. But their kinetic energy still allows them to tumble randomly over and around each other. → a liquid conforms to the shape of its container but has a surface. They flow and diffuse but much more slowly than gases.
- In a **solid**, the attractions dominate the motion so much that the particles remain in position relative to one another. For this reason, a solid has a specific shape and does not flow significantly. The particles are usually slightly closer together than in a liquid, so solids compress even less than liquids.

Types of Phase Changes

Phase changes are also determined by the interplay between kinetic energy and intermolecular forces. As the temperature increases, the average kinetic energy ~~increases~~ increases as well, so the faster moving particles can overcome attractions more easily; conversely, lower temperatures allow the forces to draw the slower moving particles together.

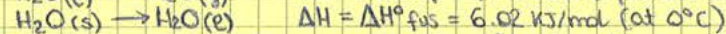
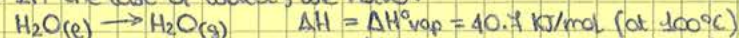
The process by which a gas changes into a liquid is called **condensation**; the opposite process, changing from a liquid into a gas, is called **vaporization**. With further cooling, the particles move even more slowly and become fixed in position as the liquid solidifies in the process of **freezing**; the opposite change is called **melting** or **fusion**.

Enthalpy changes accompany phase changes. As the molecules of a gas attract each other and come closer together in the liquid, and then become fixed in the solid, the system of particles loses energy, which is released as heat. Thus, condensing and freezing are exothermic changes. On the other hand, energy must be absorbed by the system to overcome the attractive forces that keep the particles in a liquid together and those that keep them fixed in place in a solid. Thus, melting and vaporizing are endothermic changes.

For a pure substance, each phase change has a specific enthalpy change per mole (measured at 1 atm and the temp. of the change). For vaporization, it is called the **heat of vaporization** ($\Delta H^\circ_{\text{vap}}$) and for fusion it is the **heat of fusion** ($\Delta H^\circ_{\text{fus}}$)

Example

- In the case of water, we have:

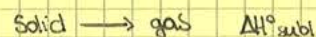
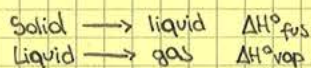


- * The reverse processes, condensing and freezing, have enthalpy changes of the same magnitude but opposite sign. Water takes much less energy to melt 1 mol of the solid than to vaporize 1 mol of the liquid. ($\Delta H^\circ_{\text{fus}} < \Delta H^\circ_{\text{vap}}$) → the reason is that a phase change is essentially a change in intermolecular distance and freedom of motion. Less energy is needed to overcome the forces holding the molecules in fixed positions than to separate them completely from each other.

The three states of water are so common because they are stable under ordinary conditions.

- Carbon dioxide is familiar as a gas and a solid (DRY ICE), but liquid CO_2 occurs only at external pressures greater than 5 atm. At ordinary conditions CO_2 becomes a gas without first becoming a liquid. This process is called **sublimation**. The opposite process, changing from a gas directly into a solid, is called **deposition**.

* The **heat of sublimation** ($\Delta H^\circ_{\text{subl}}$) is the enthalpy change when 1 mol of a substance sublimates. From Hess's law it equals the sum of the heats of fusion and vaporization.



Equilibrium nature of phase changes

In everyday experience, phase changes take place in open containers, so they are not reversible. In a closed container under controlled conditions, phase changes of any substances are reversible and reach equilibrium.

Liquid - Gas equilibria

OPEN FLASK containing pure liquid at constant temperature. If we look at the molecules at the surface, within their range of molecular speeds, some are moving fast enough and in the right direction to overcome attractions, so they vaporize. Nearby molecules immediately fill the gap, and with energy supplied by the constant temp. surroundings, the process continues until the entire liquid phase is gone.

CLOSED FLASK at constant temperature, assuming that a vacuum exists above the liquid. As before, some of the molecules at the surface have a high enough E_k to vaporize. As the no. of molecules in the vapor phase increases, the pressure of the vapor increases. At the same time, some of the molecules that collide with the surface have a low enough E_k to become attracted too strongly to leave the liquid and they

condense. For a given surface area, the number of molecules that make up the surface is constant, so the rate of vaporization is also constant. On the other hand, as the vapor becomes more populated, molecules collide with the surface more often, so the rate of condensation slowly increases. As condensation continues the increase in pressure slows. Eventually, rate of cond. equals rate of vaporization. From this time, the pressure of the vapor is constant at that temperature. Macroscopically - static, at molecular level molecules are entering and leaving the liquid surface at equal rates. The system has reached a state of dynamic equilibrium. $\text{Liquid} \rightleftharpoons \text{gas}$

* The pressure exerted by the vapor at equilibrium is called (equilibrium) **vapor pressure** of the liquid at that temperature. **LARGER FLASK** more molecules are present in the gas phase at equilibrium; as long as some liquid remains, however, the vapor pressure does not change. If we disturb this equilibrium, the rate of cond. temporarily falls below the rate of vap. (lowering pressure). Fewer molecules re-entered the liquid so the pressure rises until the cond. rate increases enough for equilibrium. If we disturb the system at constant temp. (raising pressure) the cond. rate temporarily exceeds the rate of vap. More molecules entered the liquid, but soon the condensation rate decreases, and the pressure again reaches the equilibrium value.

* This behavior is a general one for any system: when a system at equilibrium is disturbed, it counteracts the disturbance and eventually re-establishes a state of equilibrium.

The effects of Temperature and Intermolecular forces on Vapor Pressure

The vapor pressure of a substance depends on the temperature. \uparrow temp. of liquid increases the fraction of molecules moving fast enough to escape the liquid and decreases the fraction moving slowly enough to be recaptured. In general, the higher the temperature is, the higher the vapor pressure.

Vapor pressure also depends on the intermolecular forces present. The average E_k is the same for different substances at a given temperature. In general, the weaker the intermolecular forces are, the higher the vapor pressure. The nonlinear relationship between vapor pressure and temperature (fig. 12.6 p. 446) can be also expressed as a linear relationship between P and $1/T$:

$$\ln P = \frac{-\Delta H_{\text{vap}}}{R} \left(\frac{1}{T} \right) + C$$

$y = m \cdot x + b$

$\ln P$ = natural logarithm of vapor pressure
 R = universal gas constant (8.314 J/mol·K)
 C = constant
 ΔH_{vap} = heat of vaporization
 T = absolute temperature

CLAUSIUS-CLAPÉRON EQUATION way of finding ~~the~~ the heat of vaporization, the energy needed to vaporize 1 mol of molecules in the liquid state. The blue equation ($y = mx + b$) is the eq. for a straight line

$$\ln \frac{P_2}{P_1} = \frac{-\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

nongraphical det. of ΔH_{vap} If ΔH_{vap} and T_1 are known, the vapor pressure (P_2) can be calculated at any other temperature (T_2) or the temperature at any other pressure.

Vapor Pressure and boiling point

Open container: the weight of the atmosphere bears down on the liquid surface. As temp. \uparrow , molecules leave the surface more often and they also move more quickly. At some temperature, the average E_k of the molecules in the liquid is great enough for bubbles of vapor to form in the interior, and the liquid boils. At lower temp. bubbles collapse because the external pressure is greater than vapor pressure.

Boiling point: temperature at which the vapor pressure equals the external pressure. Once boiling begins, temp. remains constant until all the liquid is gone cause heat is used to overcome intermolecular attractions and allow the molecules to enter the gas phase. It varies with elevation because the atm. pressure does, in fact the boiling point depends on the applied pressure and the normal boiling point is observed at standard atmospheric pressure.

Solid - Liquid equilibria

At the molecular level, the particles in a crystal vibrate around their position; \uparrow temp. they move faster until some have enough E_k to break free of their positions. Here begins melting: as molecules enter the liquid phase, some collide with the solid and become fixed in position again, so a new equilibrium is gained. (melting rate = freezing rate); the temp. at which this occurs is called **melting point** \sim the same of freezing point, different in direction. Also here T remains fixed.

Ion - Dipole forces

When an ion and a nearby polar molecule (dipole) attract each other, an **ion-dipole force** results. The most important example takes place when an ionic compound dissolves in water. The ions become separated because the attractions between the ions and the oppositely charged poles of H_2O molecules overcome the attractions between the ions themselves.

Dipole-Dipole forces

An external electric field can orient gaseous polar molecules. When polar molecules are near one another, their partial charges act as electric fields that orient them and give rise to **dipole-dipole forces**: the positive pole of one molecule attracts the negative pole of another.

For molecular compounds of approximately the same size and molar mass, the greater the dipole moment, the greater the dipole-dipole forces between the molecules are, and so the more energy it takes to separate them.

Hydrogen Bond

A special type of dipole-dipole force between molecules with an H atom bonded to a small, highly electronegative atom with lone electron pairs. **Examples** $H-N$, $H-O$: very polar bonds, so electron density is withdrawn from H. The partially + H of one molecule is attracted to the partially - lone pair on the N, O, F of another molecule and an **hydrogen bond (H bond)** forms.

The small sizes of N, O, F are essential for H bonding for two reasons:

1. It makes these atoms so electronegative that their covalent bonded H is highly positive.
2. It allows the lone pair on the other N, O or F to come closer to the H.

Significance of H bonding

Polarizability and charge-Induced Dipole forces

Even though electrons are localized in bonding or lone pairs, they are in constant motion (cloud). A nearby electric field can distort a cloud, pulling electron density toward a positive charge or pushing it away from a negative charge; the field induces a distortion in the e^- cloud. For a non polar molecule, this distortion creates a temporary, induced dipole moment; for a polar molecule, this distortion enhances the dipole moment already present. The ease with which the electron cloud of a particle can be distorted is called its **polarizability**. Smaller atoms (ions) are less polarizable cause their e^- are closer to the nucleus. We observe several trends:

- Polarizability increases down a group cause atomic size increases (electron clouds farther from the nucleus are easier to distort).
- Polarizability decreases from left to right across a period because the increasing Z_{eff} shrinks atomic size.
- Cations are less polarizable than their parent atoms because they are smaller; anions are more polarizable because they are larger.

Two types: Ion-induced dipole, dipole-induced dipole forces. Polarizability affects all intermolecular forces.

Dispersion (London) Forces

What forces cause nonpolar substances? Some force must be acting between the particles. The intermolecular force primarily responsible for the condensed states of nonpolar substances is the **dispersion force (London force)**. This force is caused by momentary oscillations of electron's charge in atoms and, therefore, are present between all particles (atoms, ions and molecules)

EXAMPLE

Atom (nonpolar) in a sample of argon gas. At any instant, there may be more electrons on one side of the nucl. than on the other (instantaneous dipole). When far apart, a pair of argon atoms do not influence each other, but when close together, the instantaneous dipole in one atom induces a dipole in its neighbor \rightarrow synchronized motion of e^- — attraction \sim throughout the sample. At low enough temp. the attractions keep the atoms together. Thus, dispersion forces are instantaneous dipole-induced dipole forces; they are the only forces between nonpolar particles; but because they exist between all particles, contribute to the overall energy of attraction of all substances \sim it's the dominant intermolecular force.

- * The relative strength of the dispersion force depends on the polarizability of the particle. Polarizability depends on the number of electrons, which correlates closely with molar mass.

For nonpolar substances with the same molar mass, the strength of the dispersion forces is often influenced by molecular shape; shapes that allow more points of contact have more area over which e^- clouds can be distorted, so stronger attractions result.

• Packing Efficiency and the Creation of Unit Cells

Unit cells result from the various ways atoms pack together. For particles of the same size, the higher the coordination number of the crystal is, the greater the number of particles in a given volume. Let's see how to pack identical spheres to create these unit cells and the hexagonal unit cell:

1. The simple cubic unit cell. Suppose we arrange the first layer of spheres and we place the next one directly above the first, obtaining an arrangement based on the simple cubic unit cell. This is a very inefficient way, in fact calculating the **packing efficiency** (percentage of total volume occupied by the spheres) we know that it is only the 52%, so the 48% is empty space.
2. The body-centered cubic unit cell. We can use space more efficiently by placing the spheres on the diamond-shaped spaces in the first layer. This arrangement's packing efficiency is 68%, several metallic elements have a crystal structure like this one.
3. The hexagonal and face-centered cubic unit cells. We can pack spheres even shifting rows in the bottom layer so that the large diamond-shaped spaces become smaller triangular spaces and then placing the 2nd layer over these spaces. The 3rd layer can be placed into 2 different ways: • **abab layering pattern**, because they are all placed identically - **hexagonal closest packing** based on the hexagonal unit cell. • **abcabc pattern**, different from both layers a, b - **cubic closest packing** based on the face-centered cubic unit cell.

* The packing efficiency of both hexagonal and cubic closest packing is 74% and the coord number is 12. Most metallic elements crystallize in either of these arrangements.

• See Tools of Laboratory - X-Ray Diffraction p. 468-69

X-Ray Diffraction

Because x-ray wavelengths are about the same size as the spaces between layers of particles in many solids, the spaces act as slits and diffract x-rays. Let's see how this technique is used to measure a key feature of a crystal structure: the distance (d) between layers of atoms. **FIGURE** two layers in a simplified lattice.

Two waves impinge on the crystal at an angle θ and are diffracted at the same angle by adjacent layers. When the first wave strikes on the top layer and the second strikes the next layer, the waves are in phase. If they are still in phase after being diffracted, a spot appears on a nearby photographic plate.

This will occur only if the additional distance traveled by the 2nd wave is a whole no. of wave lengths

$n\lambda$, where $n = \text{integer}$; for trigonometry $\rightarrow [n\lambda = 2d \sin \theta]$ $\theta = \text{known angle of incoming light}$

$\lambda = \text{known wavelength}$ $d = \text{unknown distance between the layers in the crystal}$ **BRAGG EQUATION**
Rotating the crystal changes the angle of incoming radiation and produces a different set of spots, eventually yielding a complete diffraction pattern, analyzed mathematically to obtain the dimensions of the crystal and the distances and angles within the lattice.

Modern x-ray diffraction equipment automatically rotates the crystal and measures thousands of diffractions, and computer calculates the parameters of interest.

X-ray diffraction analysis is used to answer questions in many branches of chemistry, but its greatest impact has been in biochemistry: it has shown that DNA exists as a double helix and it's currently helping biochemists learn how a protein three-dimensional structure is related to its function.

Amorphous Solids

Amorphous solids are noncrystalline. Many have small, ordered regions connected by large disordered ones. The absence of regularity in the structure confers some properties of a liquid: in fact glasses are sometimes referred to as supercooled liquids.

EXAMPLE

SiO_2

Bonding in Solids: Molecular Orbital Band Theory

Quantum mechanics offers an extension of molecular orbital (MO) theory, called **band theory**. It is more quantitative than the electron sea model and therefore more useful.

Remember that when 2 atoms form a diatomic molecule, their atomic orbitals combine to form an equal number of molecular orbitals (MOs). **EXAMPLE - Lithium (Li) - see figure p. 474**

The band model proposes that the lower energy MOs are occupied by the valence electrons and make up the **valence band**. The empty MOs that are higher in energy make up the **conduction band**.

Li - valence band derives from the 2s AOs, conduction band derives from an intermingling of 2s and 2p AOs.

- * In metals, the valence and conduction bands are contiguous, it means that e^- can jump from the filled valence band to the unfilled conduction band if they receive even an infinitesimally small quantity of energy, i.e. the electrons are completely delocalized and free to move throughout the piece of metal. Thus, metals conduct energy so well because an applied electric field easily excites the highest energy electrons into empty orbitals and they move through the sample.
- **Metallic luster (shininess)** is another effect of the continuous band of MO energy levels; with so many closely spaced levels available, e^- can absorb and release photons of many frequencies as they move between valence and conduction bands. Malleability and thermal conductivity from completely delocalized electrons.
- Large number of nonmetal or metalloid atoms can also combine to form bands of MOs.
 1. **Conductors (metals)** The valence and conduction bands of a **conductor** have no gap between them, so electrons flow when even a tiny electrical potential difference is applied. When the T is raised, greater random motion of the atoms hinders electron movement, which decreases the conductivity of a metal.
 2. **Semiconductors (metalloids)** In a **semiconductor**, a relatively small energy gap exists between the valence and conduction bands. Thermally excited electrons can cross the gap, allowing a small current to flow. Thus, in contrast to a conductor, conductivity of a semicond. increases when it is heated.
 3. **Insulators (nonmetals)** In an **insulator** the gap between the bands is too large for electrons to jump even when the substance is heated, so no current is observed.
- * **Superconductivity** When metals conduct at ordinary temperatures, electron flow is restricted by collisions with atoms vibrating in their lattice sites. It appears as resistive heating and represents a loss of energy. To superconduct (conduct with no E. loss) requires extreme cooling to minimize atom movement. This remarkable phenomenon had been observed in metals only by cooling them to near absolute zero, which can be done only with liquid helium.
- * Like metal conductors, oxide superconductors have no band gap.

Electronic Materials

The ideal of a perfectly ordered crystal is attainable only if the crystal is grown very slowly under carefully controlled conditions. When crystals form more rapidly, **crystal defects** inevitably form. Although crystal defects usually weaken a substance, they are sometimes introduced intentionally to create materials with improved properties.

• Doped Semiconductors

Conductivity of pure silicon can be greatly enhanced by **doping**, adding small amounts of other elements to increase or decrease the number of valence electrons in the bands. **N-type**: extra negative charges are present; **P-type**: empty orbitals act as positive holes. A union forms an n-p junction.

TRANSISTORS

Chapter 13

Types of solutions: Intermolecular forces and solubility

We usually describe a solution as a **solute** which dissolves in a **solvent**. Generally, the solvent is the most abundant component of a given solution but in some cases the substances are **miscible** (soluble in each other in any proportion) so it may be not useful to distinguish between solute and solvent.

Solubility (s) - maximum amount that dissolves in a fixed quantity of a particular solvent at a specific T, given that excess solute is present. Important the qualitative concepts of **dilute** and **concentrated** that refer to the relative amounts of solute: a dilute solution contains much less dissolved solute than a concentrated one.

* We know that some solvents can dissolve a given solute, whereas other can't. The intermolecular forces' strength within and between solute and solvent is a **key-factor** to determine whether a solution forms: substances with similar types of intermolecular forces dissolve in each other. This is summarized in the rule-of-thumb **like dissolves like**.

Intermolecular forces in solutions

All the intermolecular forces occur between solute and solvent in solutions:

1 Ion-dipole forces are the principal force involved in the solubility of ionic compounds in water.

Salt dissolved: each ion attracts the oppositely charged end of water dipole.

This forces overcome those between ions and break the crystal structure; here H_2O molecules cluster around it in **hydration shells**. Normal H bonding is altered only among molecules in the closest hydration shell. — less freedom of motion.

For monoatomic ions the no. of H_2O molecules in the closest shell depends on ion's size.

2 Hydrogen bonding is especially important in aqueous solution - it is a primary factor in the solubility in water (cell fluid) of many oxygen and nitrogen containing organic and biological compounds.

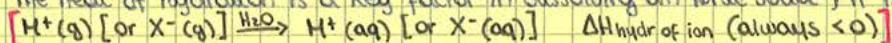
3 Dipole-dipole forces; in the absence of H bonding, account for the solubility of polar organic molecules.

4 Ion-induced dipole forces are one of 2 types of charge-induced dipole forces. They result when an ion's charge distorts the electron cloud of a nearby nonpolar molecule (**BIOLOGICAL ROLE IN BLOOD**).

5 Dipole-induced dipole forces, also based on polarizability, are weaker than the previous ones. They arise when a polar molecule distorts the e^- cloud of a nearby nonpolar molecule.

6 Dispersion forces contribute to the solubility of all solute in all solvents but they are the principal type of intermolecular force in solutions of nonpolar substances.

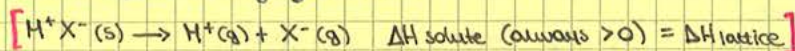
The heat of hydration is a key factor in dissolving an ionic solid, it is always exothermic for an ion.



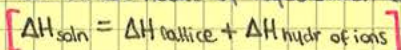
Heats of hydration ~~exhibit~~ exhibit trends based on the **charge density** of the ion, the ratio of the ion's charge to its volume. * The higher the charge density is, the more $\ominus \Delta H_{hydr}$ is. The greater the ion's charge is and the closer the ion can approach the oppositely charged end of the water molecule's dipole, the stronger the attraction, so:

- A $2+$ ion attracts H_2O molecules more strongly than a $1+$ ion of similar size.
- A small $1+$ ion attracts H_2O molecules more strongly than a large $1+$ ion.

* The energy required to separate an ionic solute (ΔH_{soln}) into gaseous ions is its lattice energy (ΔH_{latt}) and ΔH_{soln} is highly positive.



* Thus, the heat of solution for ionic compounds in water combines the lattice energy (always +) and the combined heats of hydration of cation and anion (always -)



The sizes of the individual terms determine the sign of the heat of solution **Examples!**

The Solution Process and the Change in Entropy

The heat of solution (ΔH_{soln}) is one of two factors that determine whether a solute dissolves in a solvent. The other factor concerns the natural tendency of a system to spread out, distribute, or disperse, its ways in as many ways as possible. **Entropy (S)** is a thermodynamic variable related to the number of ways a system can distribute its energy, linked to the freedom of motion of the particles and the no. of ways can be arranged. **DISPERSE ITS ENERGY** - solid p. fixed positions, liquids p. more free, so can distribute E_k in more ways $\rightarrow S_{liquid} > S_{solid} \rightarrow S_{gas} > S_{liquid}$

* Similarly, a solution usually has higher entropy than the pure solute and the pure solvent. Here, the number of ways to distribute the energy and the freedom of motion of the particles is related to the different molecules becoming interspersed and to the number of different interactions between the molecules. There are for more interactions possible when solute and solvent are mixed than when they are pure. $\rightarrow S_{soln} > (S_{solute} + S_{solvent})$ or $S_{soln} > 0$

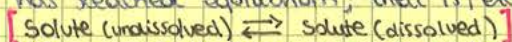
* The solution process involves the interplay of two factors: change in enthalpy and in entropy. Systems tend toward a state of lower enthalpy and higher entropy. In many cases, the relative magnitudes of ΔH_{soln} and ΔS_{soln} determine whether a solution forms.

Examples

- 1 The sum of the endothermic terms is much larger than the exothermic term, so ΔH_{soln} highly positive. In this case, a solution does not form because the entropy increase that would accompany the mixing of solute and solvent is much smaller than the enthalpy increase required to separate the ions.
- 2 With no enthalpy change driving the process, acetone dissolves in hexane because the entropy increases greatly when the pure substances mix \rightarrow the large increase in entropy drives formation of this solution.
- 3 The increase in entropy that occurs when the crystal breaks down and the ions mix with water molecules more than compensates for the increase in enthalpy.

Solubility as an Equilibrium Process

When an ionic solid dissolves, ions leave the solid and become dispersed in the solvent. Some dissolved ions collide occasionally with the undissolved solute and recrystallize. As long as the rate of dissolving is greater than the rate of recrystallizing, the concentration of ions rises. Eventually, given enough solid, ions are dissolving at the same rate as ions in the solution are recrystallizing. Now, even though dissolving and recrystallizing continue, there is no further change in the concentration with time. The system has reached equilibrium; that is, excess undissolved solute is in equilibrium with the dissolved solute:



This solution is called **saturated**: it contains the maximum amount of dissolved solute at a given T in the presence of undissolved solute. A solution that contains less than this concentration of dissolved solute is called **unsaturated**. In some cases, we can prepare a solution that contains more than the equilibrium concentration of dissolved solute. Such a solution is called **supersaturated**. It is unstable relative to the saturated solution

- You can often prepare a supersaturated solution of a solute if it has greater solubility at a higher T.

Effect of Temperature on Solubility

Temperature affects the solubility of most substances.

Temperature and the solubility of solids

Like sugar, most solids are more soluble at higher temperatures. We might think that the sign of ΔH_{soln} would indicate the effect of temperature. Most solids have + cause their lattice energies are greater than their heats of hydration. Thus, heat is absorbed to form the solution from solute and solvent and if heat = reactant \rightarrow a rise in T should increase the rate of the forward process



A common symbol for volume percent is % (v/v). It is most often used for liquids and gases. A measure of concentration frequently used for aqueous solutions is % (w/v), a ratio of solute weight (usually mass) to solution volume.

Mole Fraction

Mole fraction (x) of a solute ~ ratio of no. of solute moles to the total number of moles (solute + solvent) (parts by mole). It is the mole fraction expressed by percentage.

$$\text{Mole fraction (X)} = \frac{\text{amount (mol) of solute}}{\text{am. solute (mol) + am. solvent (mol)}} \quad \text{Mole percent (mol \%)} = \text{mole fraction} \times 100$$

Interconverting Concentration Terms

- To convert a term based on amount (mol) to one based on mass, u need the molar mass.
- To convert a term based on mass to one based on volume, u need the solution density. Given the mass of a solution, the density (mass/volume) gives you the volume, or vice versa.
- Molarity involves quantity of solute whereas the other concentration terms involve quantity of solution.

Colligative Properties of Solutions

In the case of four important solution properties, known as **colligative properties**, the number of solute particles makes the difference, not their chemical identity. Even though most of these effects are small, they have many practical applications.

- An aqueous solution of an **electrolyte** conducts an electric current because the solute separates into ions as it dissolves. An electrolyte is classified as strong or weak depending on whether its solution is a good or poor conductor at moderate solute concentrations. Soluble salts, strong acids and strong bases are strong electrolytes because they dissociate completely and, thus, their solutions conduct well. Weak a. and b. are weak electrolytes - dissociate very little and conduct poorly. Many compounds do not dissociate into ions at all - **nonelectrolytes** cause their solutions do not conduct a current (figure p. 52f)
- To predict the magnitude of colligative properties, we refer to the solute formula to find the no. of particles in a solution. Each mole of nonelectrolyte yields 1 mol of particles in the solution. Each mole of strong electrolyte dissociates into the no. of moles of ions in the formula unit.

Colligative Properties of Nonvolatile Nonelectrolyte Solutions

nonvolatile nonelectrolytes - solutes that do not dissociate into ions and have negligible vapor pressure even at the boiling point of the solvent.

Vapor Pressure Lowering

The vapor pressure of a solution of a nonvolatile nonelectrolyte is always lower than the vapor pressure of the pure solvent. We can understand this **vapor pressure lowering (ΔP)** in terms of opposing rates and change in entropy. Consider a pure solvent and opposing rates of vaporization and condensation, which are equal at equilibrium. Adding some nonv. solute, the no. of solvent molecules on the surface ↓, so vaporize per unit time. To maintain eq., fewer gas molecules need to enter the liquid (↓ vapor pressure). In terms of entropy change, we know that a pure solvent vaporizes because the vapor has a greater entropy than the liquid, but the solvent already has a greater entropy than as pure, so it has less tendency to vaporize. Thus equilibrium = lower vap. pressure.

In quantitative terms, vapor pressure is expressed by **Raoult's Law**.

$$P_{\text{solvent}} = X_{\text{solvent}} \cdot P^{\circ}_{\text{solvent}} \quad (\text{always } X < 1, P < P^{\circ}) \quad (P^{\circ} - P) / P^{\circ} = n / n + N$$

vap. pressure ↓ mol fraction ↓ vap. pressure pure s.

N = solvent moles
P = total vap. pressure
P° = solvent vap. pressure
n = solute moles

Ideal solution one that follows Raoult's Law at any concentration. However most soln deviate from ideality.

- How does the amount of solute affect the magnitude of the vapor pressure lowering, ΔP?

$$X_{\text{solvent}} + X_{\text{solute}} = 1 \rightarrow X_{\text{solvent}} = 1 - X_{\text{solute}}$$

$$P_{\text{solvent}} = X_{\text{solvent}} \cdot P^{\circ}_{\text{solvent}} = (1 - X_{\text{solute}}) \cdot P^{\circ}_{\text{solvent}} \quad (\text{RAOULT'S LAW}) \rightarrow$$

$$\rightarrow P_{\text{solvent}} = P^{\circ}_{\text{solvent}} - X_{\text{solute}} \cdot P^{\circ}_{\text{solvent}} \rightarrow (\text{rearranging and introducing } \Delta P) \rightarrow$$

$$[P^{\circ}_{\text{solvent}} - P_{\text{solvent}} = \Delta P = X_{\text{solute}} \cdot P^{\circ}_{\text{solvent}}] \rightarrow \Delta P = \text{mole fraction of solute} \times \text{vapor pressure of pure solvent.}$$

Boiling Point elevation

A solution boils at a higher T than the pure solvent: boiling point (T at which vapor pressure = external pressure). P is lower than ext. pressure at solvent's b.p. cause P is lower than that of pure solvent at any T → solution does not yet boil. **Boiling point elevation (ΔT_b)** can be seen superimposing a phase diagram for the solution on a phase diagram for the pure solvent.

- Gas-liquid line for the solution lies below that for the pure solvent at any T and to the right of any P.
- $$[\Delta T_b \propto m \text{ or } \Delta T_b = K_b m] \quad m = \text{molality} - \text{used cause it's related to mole fraction} \rightarrow \text{particles.}$$
- $$K_b = \text{molal b.p. elevation constant} \quad \Delta T_b = \text{b.p. elevation (+ ~ subtract lower to high T)}$$
- prop. to concentration of solute particles $\Delta T_b = T_{b(\text{soln})} - T_{b(\text{solvent})}$

Freezing Point Depression

In many cases, only solvent molecules can solidify, leaving solute molecules behind to form a slightly ↑ conc. solution. Freezing point - temperature at which P_{solvent} = that of pure solvent (EQUILIBRIUM of 2 phases). Because P_{soln} is lower than that of the solvent at any T, the soln freezes at a lower T than the solvent. **Freezing point depression (ΔT_f)**! Solid-liquid line for soln lies to the left of that of pure solvent at any P.

Finally, for both real gases and real solutions, we use empirically determined numbers to transform theories into more useful relations.

Structure and Properties of Colloids

Suspension - heterogeneous mixture containing particles large enough to be seen by the naked eye and clearly distinct from the surrounding fluid. **Solution** - a homogeneous mixture in which the particles are individual molecules distributed evenly throughout the surrounding fluid. Between these two extremes there are the **colloids** (colloidal dispersions) - here a dispersed substance is distributed throughout a dispersing substance. Colloidal particles are larger than simple molecules and they may consist of a single macromolecule or an aggregate of many atoms, ions or molecules; they have an enormous total surface area as a result of their small size. (see Table p. 539)

↳

Chapter 16

Factors that influence reaction rate

Under any given set of conditions, each reaction has its own characteristic rate, which is determined by the chemical nature of the reactants. We can control four factors that affect the rate of a given reaction: the concentrations of the reactants, the T at which the reaction occurs, and the use of a catalyst.

- 1 - Concentration: molecules must collide to react.** Reactant concentration influences the rate of a given reaction. The more molecules present in the container, the more frequently they collide, and the more often a reaction occurs → reaction rate is proportional to the concentration of reactants
[Rate of collision frequency of concentration] **Example** $\text{NO}(g) + \text{O}_3(g) \rightarrow \text{NO}_2(g) + \text{O}_2(g)$
- 2 - Physical state: molecules must mix to collide.** The frequency of collisions between molecules also depends on the physical state of reactants. When they are in the same phase (ex: aqueous solution) random thermal motion brings them into contact. When they are in different phases, contact occurs only at the interface. In these cases, the more finely divided a solid or liquid reactant, the greater its surface area per unit volume, the more contact it makes with the other reactant, and the faster the reaction occurs.
- 3 - Temperature: molecules must collide with enough energy to react.** It has a major effect on the speed of a reaction. At a higher T, more collisions occur in a given time. Even more important is the fact that T affects the Ek of molecules and so, the energy of the collisions. Some collisions occur with sufficient energy for the molecules to react (more at higher T) → Raising the T increases the reaction rate by increasing the number and, especially, the energy of the collisions: [Rate of collision energy of temperature]

Expressing the reaction rate

Mathematically, a **rate** is a change in some variable per unit of time.

EXAMPLE - Spin of an object (change in position / change in time)

$$\text{Rate of motion (speed)} = \frac{\text{change in position}}{\text{change in time}} = \frac{x_2 - x_1}{t_2 - t_1} = \frac{\Delta x}{\Delta t}$$

In chemistry - **reaction rate** → changes in concentrations of reactants or products per unit time; reactant concentrations decrease while product concentrations increase. Consider a general reaction $A \rightarrow B$. The change in concentration / change in time gives the average rate

$$\text{Rate of reaction} = \frac{\text{change in conc. of A}}{\text{change in time}} = \frac{\text{conc } A_2 - \text{conc } A_1}{t_2 - t_1} = -\frac{\Delta(\text{conc } A)}{\Delta t}$$

Minus sign (by convention, reaction rate is +, but $\text{conc } A_2 < \text{conc } A_1$, so the change in concentration of reactant A is always negative, (minus to convert neg. into pos.))

Rate = $k[A]^0 = k(1) = k$

Examples → demonstrate that = Reaction orders cannot be deduced from the balanced equation, they must be determined from rate data.

- Reaction orders are usually positive integers or zero, but they can also be fractional or negative
- A negative exponent means that the rate decreases when the concentration of that component increases. Negative orders are often seen for reactions whose rate laws include products.

Determining Reaction Orders Experimentally.

- * Consider the reaction $O_2 + 2NO \rightarrow 2NO_2$ whose rate (general form) is $Rate = k[O_2]^m[NO]^n$
- To find the reaction orders, we run a series of experiments, starting each one with a different set of reactant concentrations and obtaining an initial rate in each case.
- We compare the experiments (see p. 696-697) and obtain that the rate law is $Rate = k[O_2][NO]^2$

Determining the Rate Constant.

The sole remaining unknown now is the rate constant, k . It is specific for a particular reaction at a particular temperature. For example, the experiments with the reaction of O_2 and NO were run at the same T , so we can use data from any to solve for k .

- * Always check that the values of k for a series are constant within experimental error.

Note the units for the rate constant **Example** $\frac{mol}{L \cdot s} = \frac{L^2}{mol \cdot s} \cdot \frac{mol}{L} \cdot \left(\frac{mol}{L}\right)^2$

The rate constant will always have these units for an overall 3rd order reaction with the time unit in seconds.

Integrated Rate Laws: Concentration Changes over Time

Notice that the rate law we've developed do not include time as a variable; they tell us the rate or conc. at a given instant. However, by employing different forms of the rate laws, called **integrated rate laws**, we can consider the time factor.

Integrated Rate Laws for First, second, and zero - Order Reactions.

- Consider a simple first order reaction $A \rightarrow B$. As we discussed previously, the rate can be expressed as the change in the concentration of A divided by the change in time $Rate = -\Delta[A]/\Delta t$; it can also be expr. in terms of the rate law $Rate = k[A]$, setting them equal to each other → $-\frac{\Delta[A]}{\Delta t} = k[A]$ we obtain:

$\left[\ln \frac{[A]_0}{[A]_t} = kt \right]$ (first order reaction; rate = $k[A]$) ↳ $\ln =$ natural logarithm ↳ $[A]_0 =$ conc A at $t=0$ ↳ $[A]_t =$ conc of A at any time during the experiment.

↳ OBTAINED INTEGRATING

We can also write $\ln[A]_0 - \ln[A]_t = kt$

- Consider a general 2nd order reaction, with only one reactant → $Rate = -\Delta[A]/\Delta t = k[A]^2$ INTEGRATING →

$\left[\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt \right]$ (second order reaction; rate = $k[A]^2$)

- For a zero-order reaction, we have $Rate = -\Delta[A]/\Delta t = k[A]^0$ INTEGRATING →

$\left[[A]_t - [A]_0 = -kt \right]$ (zero-order reaction; rate = $k[A]^0 = k$)

Determining the Reaction Order from the Integrated Rate Law

Another method for finding reaction orders is a graphical technique that uses concentration and time data directly. An integrated rate law can be arranged into an equation for a straight line, $y = mx + b$, with $m =$ slope and $b =$ y-axis intercept.

1 First order reaction → $\ln[A]_0 - \ln[A]_t = kt \rightarrow \ln[A]_t = -kt + \ln[A]_0$ ($y = mx + b$)

2 Simple 2nd order reaction → $\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt \rightarrow \frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$ ($y = mx + b$)

3 Zero-order reaction → $[A]_t - [A]_0 = -kt \rightarrow [A]_t = -kt + [A]_0$ ($y = mx + b$)

- * Therefore, some trial-and-error graphical plotting is required to find the reaction order from the conc. and time data:

- If you obtain a straight line when you plot $\ln[\text{reactant}]$ vs. time, the reaction is 1st order wrt that reactant.
- If you obtain a straight line when you plot $1/[\text{reactant}]$ vs. time, the reaction is 2nd order wrt that reactant.
- If you obtain a straight line when you plot $[\text{reactant}]$ vs. time, the reaction is 0-order wrt that reactant.

• Why Concentrations are Multiplied in the Rate Law

If particles must collide to react, the laws of probability tell us why the rate depends on the product of the reactant concentrations, not their sum. Consider four particles A and B (2A + 2B) confined in a reaction vessel. If you add another A there can be six A-B collisions (3x2) not 5 (3+2), add another B → 9 collisions (3x3) → collision theory is consistent with the observation that conc. are multiplied in the rate law.

• How T affects Rate: the importance of Activation Energy

Increasing the temperature of a reaction increases the average speed of particles and so collision frequen. But it can't be the only factor affecting rate, or every gaseous reaction would be almost instantaneous. Instead, in the vast majority of collisions, the molecules rebound without reacting.

Arrhenius proposed that every reaction has an energy threshold that the colliding molecules must exceed in order to react. The minimum is the **activation energy (E_a)**, the energy required to activate the molecules into a state from which reactant bonds can change into product bonds.

* Only those collisions with enough energy to exceed E_a can lead to reaction.

* The temp. rise enlarges the fraction of collisions with enough energy to exceed the activation energy.

At a given temperature, the fraction f of molecular collisions with energy greater than or equal to the activation energy E_a , is given by $f = e^{-E_a/RT}$ where $e =$ base of \ln , $R =$ universal gas constant, $T =$ absolute temperature.

* The magnitudes of both E_a and T affect the fraction of sufficiently energetic collisions.

A reversible reaction has two activation energies: the activation energy for the forward reaction $E_{a(\text{fwd})}$ is the energy difference between the activated state and the reactants; the activation energy for the reverse reaction, $E_{a(\text{rev})}$, is the energy difference between the activated state and the products.

These figures illustrate several ideas:

- In both reaction directions, a larger fraction of collisions exceeds the activation energy at the higher temp. T_2 : higher T increases reaction rate.
- For an exothermic process (forward reaction) at any temp., the fraction of reactant collisions with energy exceeding $E_{a(\text{fwd})}$ is larger than the fraction of product collisions with energy exceeding $E_{a(\text{rev})}$. (forward faster). In an endothermic process (reverse reaction) $E_{a(\text{rev})}$ is greater than $E_{a(\text{fwd})}$, so the fraction of product collisions with energy exceeding $E_{a(\text{rev})}$ is larger, and the reverse reaction is faster.

* These conclusions are consistent with the Arrhenius equation, that is, the smaller the E_a (or the higher the T), the larger the value of k and the faster the reaction:

Smaller E_a (or higher T) \implies larger $k \implies$ increased rate

Conversely, the larger the E_a (or the lower T), the smaller the value of k , and the slower the reaction:
Larger E_a (or lower T) \implies smaller $k \implies$ decreased rate

• How molecular structure affects Rate

Even this tiny fraction of the total collisions (those with enough energy to react) does not reveal the true number of **effective collisions** - which actually lead to product. In addition to colliding with enough energy, the molecules must collide so that the reacting atoms make contact → to be effective, a collision must have enough energy and a particular molecular orientation. **STERIC EFFECTS**

In the Arrhenius equation, the effect of molecular orientation is contained in the term A . $k = A e^{-E_a/RT}$

$A =$ frequency factor, the product of the collision frequency Z and an orientation probability factor p , specific for each reaction → $A = pZ$, p is related to the structural complexity of the colliding particles

- Collisions between individual atoms have p values near 1: almost no matter how they hit, as long as the collision has enough energy, the particles react. In such cases, the rate constant depends only on the frequency and energy of the collisions. At the other extreme are biochemical reactions, in which the reactants are often two small molecules that can react only when they collide with a specific tiny region of a giant molecule.

Transition State Theory: Molecular nature of the Activated Complex

Transition state theory - focuses on the high-energy species that forms through an effective collision.

• Visualizing the Transition State

When two molecules approach each other, some kinetic energy is converted to potential energy as the e^- clouds repel each other. At the moment of a head-on collision, the molecules stop, and their kinetic energy is converted to the potential energy of the collision. If this potential energy is less than the activation energy, the molecules recoil.

The tiny fraction of molecules that are oriented effectively and moving at the highest speed behave differently. Their kinetic energy pushes them together with enough force to overcome repulsions and react → transformation (electrons attraction, some bonds, some start to form) → at some point what exists is neither reactant nor product but a transitional species with partial bonds, which is called **transition state** (or **activated complex**). It exists only at the instant when the reacting system is highest in E_p . Thus, the activation energy is the quantity needed to stretch and deform bonds in order to reach the transition state. Because transition states cannot be isolated, our knowledge of them, until recently, came from reasoning and studies of analogous, more stable species.

Thus, the overall rate law includes only species active in the reaction up to and including those in the rate determining step.

• Mechanisms with a Fast Initial Step

If the rate limiting step in a mechanism is not the initial step, it acts as a bottleneck later in the reaction sequence. As a result, the product of a fast initial step builds up and starts reacting to reactant, while waiting for the slow step to remove it → the product of the initial step is changing back to reactant as fast as it is forming. (the fast initial step reaches equilibrium.)

Example: $2\text{NO}(g) + \text{O}_2(g) \rightarrow 2\text{NO}_2(g)$ (p. 719)

To test a mechanism with a fast initial, reversible step:

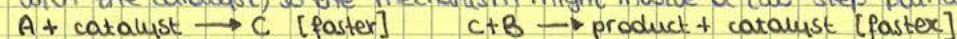
- 1 Write rate laws for both directions of the fast step and for the slow step.
- 2 Show that the slow step's rate law is equivalent to the overall rate law, by expressing [intermediate] in terms of [reactant]: set the forward rate law of the fast, reversible step equal to the reverse rate law, and solve for [intermediate]
- 3 Substitute the expression for [intermediate] into the rate law for the slow step to obtain the overall rate law

Catalysis: speeding up a chemical reaction

There are many situations in which the rate of a reaction must be increased for it to be useful. In an industrial process a higher rate often determines whether a new product can be made economically. Sometimes, we can speed up a reaction sufficiently with a higher temperature, but energy is costly and many substances are heat sensitive and easily decomposed. Alternatively, we can employ a **catalyst** - substance that increases the rate without being consumed in the reaction. Because catalysts are not consumed, only very small nonstoichiometric quantities are generally required. (**EXAMPLE - ENZYMES**) Each catalyst has its own specific way of functioning, but in general, a catalyst causes a lower activation energy, which in turn makes the rate constant larger and the rate higher.

- A catalyst speeds up the forward and reverse reactions. A reaction with a catalyst does not yield more product than one without a catalyst, but it yields the product more quickly.
- A catalyst causes a lower activation energy by providing a different mechanism for the reaction and thus a new lower energy pathway

* Consider a general uncatalyzed reaction that proceeds by a one-step mechanism involving a bimolecular collision: $\text{A} + \text{B} \rightarrow \text{product}$ [slower]. In the catalyzed reaction, a reactant molecule interacts with the catalyst, so the mechanism might involve a two-step pathway:



Note that the catalyst is not consumed; rather it is used and then generated, and the activation energies of both steps are lower than the activation energy of the uncatalyzed pathway.

Catalysts: homogeneous and heterogeneous.

Homogeneous Catalysis

Homogeneous catalyst exists in solution with the reaction mixture → they are gases, liquids or soluble solids.

Example: Hydrolysis of an organic ester (RCOOR') (p. 721)

Heterogeneous Catalysis

Heterogeneous catalyst speeds up in a reaction that occurs in a separate phase → it is most often a solid interacting with gaseous or liquid reactants. Because reaction occurs on the solid's surface, het. catalysts usually have enormous surface areas for contact (many on metal surface)

Example: Petroleum, plastics and food industries frequently use catalytic **HYDROGENATION**

ENZYMES → biochemical catalyst containing an **active site** holding a geometry interacting selectively with some molecules. It boosts reaction rate and the selectivity towards desired products. It's very active and promotes reactions at room temperature.

The work done here is not very useful because it simply pushes back the piston and outside air.
2. work done on a system. If we increase the external pressure on the piston, the system gains energy, cause work is done on the system by the surroundings: w is positive, so ΔE is positive.

The law of Energy Conservation

The **law of conservation of energy** restates the previous observations saying that: the total energy of the universe is constant. This law is also known as **first law of thermodynamics**. Conservation of energy applies everywhere. We've seen that energy transfer between system and surround can be in the form of heat and/or various types of work, but the energy of the system plus the en. of the surroundings remains constant: energy is conserved. Mathematically, this law is expressed by:
 $[\Delta E_{\text{universe}} = \Delta E_{\text{system}} + \Delta E_{\text{surroundings}} = 0]$ This idea pertains to all systems.

Units of Energy

The SI unit of energy is the **joule (J)**, a derived unit composed of three base units: $1 \text{ J} = 1 \text{ kg} \cdot \text{m}^2/\text{s}^2$. Both heat and work are expressed in joules \rightarrow The work (w) done on a mass is the force (F) times the distance (d) that the mass moved ($w = F \cdot d$). A force changes the velocity of a mass (acceleration). Velocity units = m/s \rightarrow acceleration units = m/s^2 \rightarrow Force units $F = m \cdot a$ ($\text{kg} \cdot \text{m/s}^2$)
 Therefore $w = F \cdot d$ ($\text{kg} \cdot \text{m/s}^2$) \cdot $\text{m} = \text{kg} \cdot \text{m}^2/\text{s}^2 = \text{J}$
 Potential energy, kinetic energy and PV work are combinations of the same physical quantities and are also expressed in joules.

Calorie (cal) - older unit, defined originally as the quantity of E needed to raise the temp of 1 g of water by 1°C \rightarrow now are defined in terms of Joule $1 \text{ cal} = 4,184 \text{ J}$ \rightarrow $1 \text{ J} = \frac{1}{4,184} = 0,2390 \text{ cal}$

The quantities of energy involved in chemical reactions are usually quite large, so kilojoule or kilocalorie are used $1 \text{ kJ} = 1000 \text{ J} = 0,2390 \text{ kcal} = 239 \text{ kcal}$

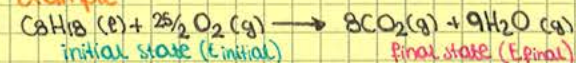
British thermal unit (Btu) - quantity of energy required to raise the T of 1 lb of water by 1°F (1055 J)

State functions and the Path Independence of the Energy Change

An important point is that there is no particular sequence by which the internal energy (E) of a system must change, because $E =$ **state function**, a property dependent only on the current state of the system, not on the path the system took to reach that state; the current state depends only on the difference between the final and initial states.

In fact, the energy change of a system can occur by countless combinations of heat and work. No matter what the combinations, however, the same overall energy change occurs, because ΔE does not depend on how the change takes place.

Example



Energy is released to warm the surroundings and/or do work on them, so ΔE is negative.

Even though the separate quantities of work and heat available from the change do depend on how the change occurs, the change in internal energy ($q+w$) does not. \rightarrow i.e. for a given change, ΔE ($q+w$) is constant, even though q and w can vary. Thus, heat and work are not state functions because their values do depend on the path the system takes in undergoing the energy change.

The pressure (P) of an ideal gas or the volume (V) of water in a beaker are **examples** of state functions. This path independence means that changes in state functions - $\Delta E, P, \Delta V$ - depend only on their initial and final states.

Enthalpy: Heats of reaction and chemical change

The Meaning of Enthalpy

To determine ΔE , we must measure both heat and work. The two most important types of chemical work are electrical work (done by moving charged particles) and PV work (done by an expanding gas). PV can be found by multiplying the external pressure (P) by the change in volume of the gas ($\Delta V = V_{\text{final}} - V_{\text{initial}}$)

Example open flask, here a gas works by pushing back the atmosphere. If the work is done on the surroundings $\rightarrow W = -P\Delta V$

* For a reaction at constant pressure, a thermodynamic variable called **enthalpy (H)** eliminates the need to consider PV work separately. The enthalpy of a system is defined as the internal energy + the product of pressure and volume $H = E + PV$.

* The **change in enthalpy (ΔH)** is the change in internal energy plus the product of the constant pressure and the change in volume: $[\Delta H = \Delta E + P\Delta V]$ but we know that $\Delta E = q + w$ so $\rightarrow \Delta E = q + w = q + (-P\Delta V) = q - P\Delta V$, at constant pressure $q = q_p \rightarrow q_p = \Delta E + P\Delta V \rightarrow [q_p = \Delta E + P\Delta V = \Delta H]$

Thus, the change in enthalpy equals the heat gained or lost at constant pressure. With most changes occurring at constant pressure, ΔH is more relevant than ΔE and easier to find: to find ΔH , measure q_p .

Comparing ΔE and ΔH

Knowing the enthalpy change of a system tells us a lot about its energy change as well. Because many reactions involve little PV work, most of the energy changes occurs as a transfer of heat. Here are 3 cases:

1. **Reactions that do not involve gases.** Gases do not appear in many reactions.

Example - $2\text{KOH} (\text{aq}) + \text{H}_2\text{SO}_4 (\text{aq}) \rightarrow \text{K}_2\text{SO}_4 (\text{aq}) + \text{H}_2\text{O} (\ell)$ cause ℓ and solids undergo very small V changes.

2. **Reactions in which the amount (mol) of gas does not change.** When the total amount of gas reactants equals the total amount of gaseous products, $\Delta V = 0$, $P\Delta V = 0 \rightarrow \Delta H = \Delta E$

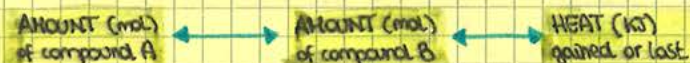
Example - $\text{N}_2 (\text{g}) + \text{O}_2 (\text{g}) \rightarrow 2\text{NO} (\text{g})$

Stoichiometry of Thermochemical Equations

Thermochemical equation - balanced equation that includes the heat of reaction (ΔH_{rxn}). ΔH_{rxn} value refers to the amounts (moles) of substances and their states of matter in that specific equation. The enthalpy change of any process has two aspects:

- 1 Sign:** The sign of ΔH depends on whether the reaction is exothermic (-) or endothermic (+). A forward reaction has the opposite sign of the reverse reaction.
- 2 Magnitude:** The magnitude of ΔH is proportional to the amount of substance reacting.

* Note that, in thermochemical equations, we often use fractional coefficients to specify the magnitude of ΔH_{rxn} for a particular amount of substance. Moreover, in a particular reaction, a certain amount of substance is thermochemically equivalent to a certain quantity of energy.



Hess's Law of heat summation

Many reactions are difficult or impossible to carry out separately. A reaction may be part of a complex biochemical process; or it may take place only under extreme environmental conditions, for example. One of the most powerful applications of the state-function property of enthalpy (H) allows us to find the ΔH of any reaction for which we can write an equation.

This application is based on **Hess's Law of heat summation** - the enthalpy change of an overall process is the sum of the enthalpy changes of its individual steps.

To use this law, we imagine a reaction as the sum of a series of reaction steps, whether or not it really occurs in that way. Each step is chosen cause its ΔH is known. Cause the overall ΔH depends only on the initial and final states, Hess's law says that we add together the known ΔH values for the steps to get the unknown ΔH of the overall reaction. Similarly, if we know the ΔH values for the overall reaction and all but one of the steps, we can find the unknown ΔH of that step. see **EXHRE** p. 251 - 252.

* To summarize, calculating an unknown ΔH involves three steps:

- 1 Identify the target equation, the step whose ΔH is unknown, and note the number of moles of each reactant and product.
- 2 Manipulate the equations with known ΔH values so that the target numbers of moles ^{of} reactants and products are on the correct sides. Remember to:
 - Change the sign of ΔH when u reverse an equation.
 - Multiply numbers of moles and ΔH by the same factor.
- 3 Add the manipulated equations to obtain the target equation. All substances except those in the target equation must cancel. Add their ΔH values to obtain the unknown ΔH .

Standard Heats of Reaction

To use heats of reaction, chemists have established **standard states**, a set of specified conditions and concentrations:

- For a gas, the standard state is 1 atm* with the gas behaving ideally.
- For a substance in aqueous solution, the standard state is 1 M concentration.
- For a pure substance (element / compound) the standard state is usually the most stable form of the substance at 1 atm and the temp. of interest (usually 25°C - 298K)

* We use the standard-state symbol to indicate these standard states. In other words, when the heat of reaction, ΔH_{rxn} has been measured with all the reactants and products in their standard states, it is referred to as the **standard heat of reaction**, ΔH°_{rxn} .

Formation Equations and their Standard Enthalpy Changes.

In a **formation equation**, 1 mole of a compound forms from its elements. The **standard heat of formation** (ΔH°_f) is the enthalpy change for the formation equation when all the substances are in their standard states. **Example** - methane (CH_4)

* Standard heats of formation have been tabulated for many substances. (see Table 6.3 p.253)

The values in the table were selected to make two points:

- 1 An element in its standard state is assigned a ΔH°_f value of zero.
- 2 Most compounds have a negative ΔH°_f , i.e., most compounds have exothermic formation reactions under standard conditions: heat is given off when the compound forms.

Determining ΔH°_{rxn} from ΔH°_f Values of Reactants and Products.

By applying Hess's law, we can use ΔH°_f values to determine ΔH°_{rxn} for any reaction. We have to view the reaction as an imaginary two-step process.

Step 1 Each reactant decomposes to its elements. This is the reverse of the formation reaction for each reactant, so each standard enthalpy change is $-\Delta H^\circ_f$.

Step 2 Each product forms from its elements - formation reaction for each product, so each standard enthalpy change is ΔH°_f .

According to Hess's law, we add the enthalpy changes for these steps to obtain the overall enthalpy change for the reaction (ΔH°_{rxn}). **Example** - $TiCl_4(l) + 2H_2O(g) \rightarrow TiO_2(s) + 4HCl(g)$.

A word about units for Q and K

The values of Q and K are shown as unitless numbers. This is because each term in the reaction quotient represents the ratio of the measured quantity of the substance to the thermodynamic standard-state quantity of the substance.

Form of Q for an overall reaction

If an overall reaction is the sum of two or more reactions, the overall reaction quotient (or eq. constant) is the product of the reaction quotients (or equilibrium constants) for the steps:

$$Q_{\text{overall}} = Q_1 \times Q_2 \times Q_3 \times \dots \quad \text{and} \quad [K_{\text{overall}} = K_1 \times K_2 \times K_3]$$

Form of Q for a Forward and a Reverse Reaction

The form of the reaction quotient depends on the direction in which the balanced equation is written. A reaction quotient (or equilibrium constant) for a forward reaction is the **reciprocal** of the reaction quotient (or equilibrium constant) for the reverse reaction:

$$[Q_{\text{c(forw)}} = \frac{1}{Q_{\text{c(rew)}}} \quad \text{and} \quad K_{\text{c(forw)}} = \frac{1}{K_{\text{c(rew)}}}]$$

Form of Q for a Reaction with coefficients multiplied by a common factor

Multiplying all the coefficients of the equation by some factor also changes the form of Q. The same property holds for equilibrium constants.

A particular K has meaning only in relation to a particular balanced equation.

* In general, if all the coefficients of the balanced equation are multiplied by some factor, that factor becomes the exponent for relating the reaction quotients and the equilibrium constants. For a multiplying factor n, we have $n(aA + bB \rightleftharpoons cC + dD)$ the reaction quotient and equilibrium constant are

$$[Q' = Q^n = \left(\frac{[C]^c [D]^d}{[A]^a [B]^b}\right)^n \quad \text{and} \quad K' = K^n]$$

Form of Q for a Reaction Involving Pure Liquids and Solids

Until now, we've looked at **homogeneous** equilibria, systems in which all the components of the reaction are in the same phase, such as a system of reacting gases. When the components are in different phases, the system reaches **heterogeneous** equilibrium.

Example $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$

The concentration of a pure solid is constant, as is the concentration of a pure liquid (not that of a dissolved solute). Because we are concerned only with concentrations that change as they approach equilibrium, we eliminate the terms for pure liquids and solids from the reaction quotient.

In this case, the only whose concentration can change is the gas CO_2 .

No matter how much CaO and CaCO_3 are in the reaction vessel, as long as some of each is present, the reaction quotient for the reaction equals the CO_2 concentration.

Expressing equilibria with Pressure terms: relation between K_c and K_p .

It's easier to measure the pressure of a gas than its concentration and the ideal gas law allows us to relate these variables to each other:

$$PV = nRT \rightarrow P = \frac{n}{V} RT \quad \text{or} \quad \frac{P}{RT} = \frac{n}{V} \quad \text{where } P = \text{pressure of a gas} \quad \frac{n}{V} = \text{molar conc. (M)}$$

Thus, with R constant and T kept constant, pressure is directly proportional to molar concentration. When the substances in the reaction are gases, we can express and calculate Q in terms of partial pressure. The equilibrium constant obtained when all components are present at their equilibrium partial pressures is designated K_p , the equilibrium constant based on pressures.

In many cases $K_c \neq K_p$, but knowing one, we can calculate the other by noting the change in amount (mol) of gas, Δn_{gas} , from the balanced equation.

EXAMPLE - $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g}) \rightarrow \Delta n_{\text{gas}} = \text{moles of gaseous product} - \text{moles of gaseous reactant}$

$$Q_c = \frac{[\text{NO}_2]^2}{[\text{NO}]^2 [\text{O}_2]} \rightarrow Q_c = Q_p (RT)$$

Also $K_c = K_p (RT) \rightarrow K_p = \frac{K_c}{(RT)^{\Delta n_{\text{gas}}}}$. Notice that the exponent of the RT term equals the change in the amount (mol) of gas (Δn_{gas}) from the balanced equation, -1 . Thus, in general $[K_p = K_c (RT)^{-\Delta n_{\text{gas}}}]$

Reaction Direction: comparing Q and K

With product terms in the numerator of Q and reactant terms in the denominator, more product makes Q larger, and more reactant makes Q smaller.

The 3 possible relative sizes of Q and K are:

- $Q < K$ In this case, the denominator (reactants) is large relative to the numerator (products). For Q to become equal to K, the reactants must decrease and the products increase.
If $Q < K$, reactants \rightarrow products
- $Q > K$ In this case the numerator (products) will decrease and the denominator (reactants) increase until eq. is reached. If $Q > K$, reactants \leftarrow products
- $Q = K$ Only if react. and prod. concentrations (or pressures) have attained their equilibrium values
If $Q = K$, reactants \rightleftharpoons products

Of course the component must be one that appears in Q . The system will always act to reduce the disturbance, so it will reduce the increase in reactant by proceeding toward the product side, consuming some of the additional compound. We have $\uparrow []$ and Q_c falls. With the reaction and formation of product, again $Q_c \uparrow$ until $Q_c = K_c$. (however different conc.)

We describe this change by saying that the equilibrium position shifts to the right when a component on the left is added.

If we remove some component, the system reduces the disturbance (the decrease in reactant) by proceeding toward the reactant side (consuming some react). Here too conc. are different from those of the original equilibrium, but K_c is not. We say that the equilibrium position shifts to the left when a component on the left is removed.

* No matter how the disturbance in conc. comes about, the system responds to make Q_c and K_c equal again. To summarize:

- The eq. position shifts to the right if a reactant is added or a product is removed: [reactant] increases or [product] decreases.
- The eq. position shifts to the left if a reactant is removed or a product is added: [reactant] decreases or [product] increases.

* In general, whenever the concentration of a component changes, the equilibrium system reacts to consume some of the added substance or produce some of the removed substance.

* The value of K_c at a given temperature does not change with a change in concentration.

The effect of a change in pressure (volume)

Changes in pressure have significant effects only on equilibrium systems with gaseous components. Aside from phase changes, a change in pressure has a negligible effect on liquids and solids because they are nearly incompressible. Pressure changes can occur in three ways:

- Changing the conc. of a gaseous component
- Adding an inert gas (one that does not take part in the reaction)
- Changing the volume of the reaction vessel.

We just considered the effect of changing the conc. of a component, and that reasoning holds here. Next, let's see why adding an inert gas has no effect on the equilibrium position - it does not change the volume, so all reactant and product concentrations remain the same. (partial pressure also not change) - the eq. position cannot change. Moreover, the inert gas does not appear in Q . On the other hand, changing the pressure by changing the volume often causes a large shift in the eq. position.

Example - PISTON (pressing down we halve the volume) - gas pressure doubles

A change in pressure due to a change in volume does not alter K_c , because it's just another way to change concentration.

Thus, for a system that contains gases at equilibrium, in which the amount (mol) of gas, n_{gas} , changes during the reaction:

- If the volume becomes smaller (pressure \uparrow) the reaction shifts so that the total number of gas molecules decreases.
- If the volume becomes larger (pressure \downarrow) the reaction shifts so that the total number of gas molecules increases.

* In many cases n_{gas} does not change, $\Delta n_{\text{gas}} = 0$, there's no effect on the eq. position.

Effect of a Change in Temperature

Of the 3 types of disturbances, only temperature changes alter K .

If we consider heat as a component of the equilibrium system, a rise in temp. occurs when heat is added to the system and a drop in temp. occurs when heat is removed from the system.

- A temperature increase (+ heat) favors the endothermic (heat-absorbing) direction, and a temp. decrease (- heat) favors the exothermic (heat-releasing) direction.

At equilibrium, $Q = K$

- A temp. rise will increase K for a system with a positive $\Delta H_{\text{rxn}}^\circ$
- A temp. rise will decrease K for a system with a negative $\Delta H_{\text{rxn}}^\circ$

* The van't Hoff equation: The Effect of T on K

van't Hoff equation shows how the equilibrium constant is affected by changes in temperature:

$$\ln \frac{K_2}{K_1} = - \frac{\Delta H_{\text{rxn}}^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad \begin{matrix} K_1 = \text{equilibrium constant at } T_1 \\ K_2 = \text{equilibrium constant at } T_2 \end{matrix} \quad R = \text{universal gas constant}$$

If we know $\Delta H_{\text{rxn}}^\circ$ and K at one temp., we can find K at the other temp.

- For an endothermic ~~reaction~~ reaction ($\Delta H_{\text{rxn}}^\circ > 0$), the $-(\Delta H_{\text{rxn}}^\circ/R)$ term is < 0 . With $1/T_2 - 1/T_1 < 0$ the right side of the equation is > 0 . Thus, $\ln(K_2/K_1) > 0 \rightarrow K_2 > K_1$
- For an exothermic reaction ($\Delta H_{\text{rxn}}^\circ < 0$), the $-(\Delta H_{\text{rxn}}^\circ/R)$ term is > 0 . With $1/T_2 - 1/T_1 < 0$, the right side of the eq. is < 0 . Thus $\ln(K_2/K_1) < 0 \rightarrow K_2 < K_1$.

The Lack of Effect of a Catalyst

A catalyst shortens the time it takes to reach equilibrium but has no effect on the equilibrium but has no effect on the equilibrium position.

- **Weak acids**. There are many more weak
 - 1 The hydrohalic acid HF
 - 2 Acids in which H is not bonded to O or to a halogen (HCN, H₂S)
 - 3 Oxoacids with no. of O atoms = or exceeds by one the no. of ionizable protons (HClO, HNO₂, H₃PO₄)
 - 4 Carboxylic acids
- **Strong bases** Water soluble compounds containing O²⁻ or OH⁻ ions are strong bases. The cations are usually those of the most active metals
 - 1 H₂O, MOH with M = Group 1(A) metal
 - 2 MO, M(OH)₂ with M = Group 2A metal
- **Weak bases**. Many compounds with an electron-rich nitrogen atom are weak bases (none Arr. bases) The common structural feature is an N atom with a lone electron pair.
 - 1 Ammonia (NH₃)
 - 2 Amines (gen. formulas RNH₂, R₂NH, R₃N)

Autoionization of water and the pH scale

Now let's examine an important property of water: it is extremely weak electrolyte. The electrical conductivity of tap water is due almost entirely to dissolved ions, but even distilled and deionized, it exhibits a tiny conductance → This because water itself dissociates into ions very slightly in an equilibrium process known as **autoionization** (or self-ionization)

The Equilibrium nature of Autoionization: the Ion-Product constant for water (K_w)

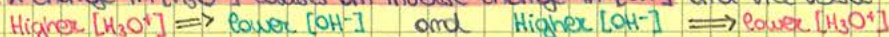
Like any eq. process, the autoionization of water is described quantitatively by an equilibrium constant: $K_c = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$ Because [H₂O] is essentially constant here, we simplify this expression to obtain a new equilibrium constant, the **ion-product constant for water, K_w**

$$[K_c [H_2O]^2 = K_w = [H_3O^+][OH^-] = 1.0 \cdot 10^{-14} \text{ (at } 25^\circ\text{C)}]$$

* Notice that one H₃O⁺ ion and one OH⁻ ion appear for each H₂O molecule that dissociates. Therefore, in pure water $[H_3O^+] = [OH^-] = \sqrt{1.0 \cdot 10^{-14}} = 1.0 \cdot 10^{-7} \text{ M (at } 25^\circ\text{C)}$

* Autoionization of water has two main consequences for aqueous acid-base chemistry:

1 A change in [H₃O⁺] causes an inverse change in [OH⁻] and vice versa.



Recall that a change in conc. of either ion shifts the equilibrium position, but it does not change the eq. constant, so if an acid is added [H₃O⁺] ↑, [OH⁻] ↓ and vice versa adding base. (from H₂O → K_w maintained)

2 Both ions are present in all aqueous systems. Thus, all acidic solutions contain a low conc. of OH⁻ ions and all basic solutions contain low [H₃O⁺]. we can so define acidic and basic solutions:

Acidic solution [H₃O⁺] > [OH⁻]

Neutral solution [H₃O⁺] = [OH⁻]

Basic solution [H₃O⁺] < [OH⁻]

Moreover → $[H_3O^+] = \frac{K_w}{[OH^-]}$ or $[OH^-] = \frac{K_w}{[H_3O^+]}$

Expressing the Hydronium Ion Concentration: the pH scale

Aqueous solutions [H₃O⁺] from 10⁻¹ M to 10⁻¹⁵ M. To handle numbers with negative exponents more conveniently in calculations, we use the p-scale, the negative of the log of the number (we obtain positive numbers).

Applying this numerical system to [H₃O⁺] gives pH → $[pH = -\log [H_3O^+]]$

* A pH value is a log, so the no. of significant figures in a pH value reflects the precision the conc. equals the number of digits to the right of the decimal point in the pH value.

* Note that the higher the pH, the lower the [H₃O⁺]. Therefore an acidic solution has a lower pH (↑[H₃O⁺]) than a basic solution.

pH of a neutral solution = 7.00

pH of an acidic solution < 7.00

pH of a basic solution > 7.00

* A p-scale is used to express other quantities as well:

• Hydroxide ion concentration can be expressed as pOH → $[pOH = -\log [OH^-]]$

Acidic solutions have a higher pOH (↑[OH⁻]) than basic solutions

• Equilibrium constants can be expressed as pK → $[pK = -\log K]$

A low pK corresponds to a high K. A reaction that reaches equilibrium with mostly products present has a low pK (↑K), while one that has mostly reactants present at equilibrium has a high pK (↓K)

• Relations Among pH, pOH and pK_w

$$K_w = [H_3O^+][OH^-] = 1.0 \cdot 10^{-14} \text{ (at } 25^\circ\text{C)} ; -\log K_w = (-\log [H_3O^+]) + (-\log [OH^-]) = -\log (1.0 \cdot 10^{-14})$$

$$\rightarrow [pK_w = pH + pOH = 14.00 \text{ (at } 25^\circ\text{C)}]$$

The sum of pH and pOH is pK_w for any aqueous solution at any temperature, with pK_w = 14 at 25°C.

• Measuring pH

In laboratory, pH values are usually obtained with an acid-base indicator or with an instrument called pH meter. Acid-base indicators are organic molecules whose colors depend on the acidity or basicity of the solution in which are dissolved. The pH of a solution is valued with pH paper (impregnated with 1 or + indicators). pH meter measures [H₃O⁺] by means of two electrodes immersed in the test solution. One - stable reference voltage, the other - glass membrane separating internal and external [H₃O⁺] - difference = voltage difference across the membrane, measured in pH units.

The Behaviour of Polyprotic Acids

Acids with more than one ionizable proton are **polyprotic acids**. In a soln of a polyprotic acid, one proton at a time dissociates from the acid molecule, and each dissociation step has a different K_a .

Example - phosphoric acid.

- * In every case the first proton comes off to a much greater extent than the 2nd and, where applicable, the 3rd does to a much greater extent than the 2nd ($K_{a1} \gg K_{a2} \gg K_{a3}$)
- This is because it is more difficult for an H^+ ion to leave a singly charged anion than to leave a neutral molecule, and more difficult leaving a doubly charged anion. Successive acid-dissociation constants differ by several orders of magnitude \rightarrow simplifies pH calculations for those acids cause we can usually neglect the H^+ coming from the subsequent dissociations.

Weak Bases and their Relation to Weak Acids

By focusing on where the proton comes from and goes to, the B-L concept expands the definition of a base to encompass a host of species that the Arr. def. excludes: to accept a proton, a base must have a lone electron pair.

Let's examine the eq. system of a weak base (B) dissolving in water. When B dissolves, it accepts a proton from H_2O (acid) leaving an OH^- ion: $B(aq) + H_2O(l) \rightleftharpoons BH^+ + OH^- \rightarrow K_c = \frac{[BH^+][OH^-]}{[B][H_2O]}$

H_2O - treated as a constant, we find the **base dissociation constant (or base ionization constant) K_b** :

$K_b = \frac{[BH^+][OH^-]}{[B]}$ despite the name, no base dissociate in the process. As in the relation $pK_a - K_a$, we know that pK_b decreases when $K_b \uparrow$

Molecules as Weak Bases: Ammonia and the Amines

Ammonia - simplest nitrogen containing compound that acts as a weak base in water (solution of unprotonated NH_3 molecules - K_b small). If 1 or + of the H atoms in ammonia are replaced by an organic group, an amine result - key feature = lone pair of e^- that can bind the proton donated by the acid. To find the pH of a solution of molecular weak base, we use an approach similar to that used for acids: write eq. expression; set up a table to find [base] react.; make assumptions; solve for $[OH^-]$ (we must convert $[OH^-]$ to $[H_3O^+]$ to find pH).

Anions of weak Acids as weak Bases

The other large group of B-L bases consists of anions of weak acids

$A^- + H_2O \rightleftharpoons AH + OH^-$ **Example** HF (anion F^-)

Why is a sol. of HA acidic and one of A^- basic?

- 1 The acidity of $HA(aq)$.** Because HF is a weak acid, most of it is undissociated. Small fraction of HF that dissociates \rightarrow small conc. of $[H_3O^+]$ and $[F^-]$. Eq. position lies far to the left. The only two species that can influence the acidity of soln are H_3O^+ from HF and OH^- from water. The sol. is acidic cause $[H_3O^+]_{from HF} \gg [OH^-]_{from H_2O}$ (small conc.)
- 2 The basicity of $A^-(aq)$** Now consider 1M NaF. It dissociates completely \rightarrow stoich. conc. of F^- , Na^+ behaves like a spectator and some F^- reacts \rightarrow HF, OH^- (as weak base) Acidity/basicity influenced by OH^- from F^- , H_3O^+ from water (small conc.). $[OH^-]_{from F^-} \gg [H_3O^+]_{from water}$ the solution is basic.

- * HA and A^- conc. determine the acidity/basicity of the solution.

The Relationship between K_a and K_b of a conjugate acid-base pair

There's an imp. relationship between K_a of HA and K_b of A^- , that we can see treating the 2 dissociation reactions as a reaction sequence and adding them together.

- * The sum of the two dissociation reactions is the autoionization of water. The overall eq. constant is the product of the individual ones $[K_a \cdot K_b = K_w]$ (K_a, K_b for molecular species only)

Molecular properties and acid strength

The strength of an acid depends on its ability to donate a proton, which depends in turn on the strength of the bond to the acidic proton.

Trends in Acid Strength of Nonmetal Hydrides

Two factors determine how easily a proton is released from a nonmetal hydride: the electronegativity of the central nonmetal (E) and the strength of the E-H bond.

- 1 Across a period, nonmetal hydride acid strength increases.** Across a period, the electronegativity of the nonmetal E determines the trend. As E becomes more electronegative, e^- density around H is withdrawn and E-H bond becomes more polar \rightarrow H^+ is released more easily to an O atom of a water molecule. In aq. solutions, hydrides of Group 3A to 5A do not behave as acids, but an increase in acid strength is seen in Groups 6A-7A
- 2 Down a group, nonmetal hydride acid strength increases.** Down a group, E-H bond strength determines the trend. E larger \rightarrow E-H bond longer and weaker, H^+ comes off more easily. A similar trend in increasing acid strength is seen down group 6A

Trends in Acid Strength of Oxoacids

All oxoacids have the acidic H atom bonded to an O atom, so bond strength (length) is not a factor in their acidity. Two factors determine the acid strength of oxoacids: the electronegativity of the central nonmetal (E) and the number of O atoms.

- 1 For oxoacids with the same no. of oxygens around E, acid strength increases with the electronegativity of E.** **Example** - hypochalous acids (HOE , E = halogen atom)

proton; because acetic acid is a weaker base than water, the three acids protonate it to different extents $\rightarrow K_{HI} > K_{HBr} > K_{HCl}$

Electron-pair donation and the Lewis acid-base definition

Now we consider the acid-base concept developed by Lewis, that highlights the role of the electron pair. The **Lewis acid-base definition** holds that

- A base is any species that donates an electron pair
- An acid is any species that accepts an electron pair

The Lewis definition requires that a base have an electron pair to donate, so it does not expand the classes of bases. However, it greatly expands the classes of acids. Many species that do not contain H in their formula function as L-acids by accepting an electron pair in their reactions. - proton is not the def. feature of an acid. Moreover, in the Lewis sense, the proton itself functions as an acid because it accepts the e⁻ pair donated by a base \rightarrow *all B-L acids donate H⁺, a Lewis acid.

* The product of any L-acid-base reaction is called **adduct** - single species that contains a **new** covalent bond.

Thus, the Lewis concept radically broadens the idea of acid-base reactions. Arrhenius: formation of H₂O from H⁺ + OH⁻ \rightarrow B. and L. transfer of a proton from a stronger acid to a stronger base to form a weaker base and a weaker acid. \rightarrow Lewis: donation and acceptance of an electron pair to form a covalent bond in an adduct.

* Main feature of a Lewis base = lone pair of electrons to donate; of a L. acid = vacant orbital to accept that lone pair and form a new bond.

Molecules as Lewis acids

Many neutral molecules function as Lewis acids. In every case, the atom that accepts the e⁻ pair is low in e⁻ density because of either an electron deficiency or a polar multiple bond.

Lewis Acids with Electron-Deficient atoms

Some molecular Lewis acids contain a central atom that is electron deficient, one surrounded by fewer than eight valence electrons. The most important of these acids are covalent compounds of the Group 3A elements boron and aluminum, which react to complete their octet. **Example** - boron trifluoride.

• Unexpected solubility behavior is sometimes due to adduct formation. **Example** - aluminum chloride.

* This acidic behavior of boron and aluminum halides is put to use in many organic syntheses.

Lewis acids with polar multiple bonds

Molecules that contain a polar double bond also function as Lewis acids. As the e⁻ pair on the Lewis base approaches the partially positive end of the double bond, one of the bond breaks to form the new bond in the adduct. **Example** - SO₂ in water.

Metal cations as Lewis Acids

We saw that certain hydrated metal ions act as B-L acids. In the Lewis sense, the hydr. process itself is an acid-base reaction. The hydrated cation is the adduct, as lone electron pairs on the O atoms of water form covalent bonds to the positively charged ion \rightarrow any metal ion acts as a Lewis acid when it dissolves in water.

* Ammonia is a stronger Lewis base than water because it displaces H₂O from a hydrated ion when aqueous NH₃ is added.

An overview of Acid-Base definitions

Let's stand back and survey the scope of the three acid-base definitions and see how they fit together.

- 1 The **Arrhenius definition** is the most limited and narrow of the three definitions; it applies only to species whose structures include H atom or OH group.
- 2 The **B-L definition** is more general, seeing acid-base reactions as a proton-transfer process and eliminating the requirement that they occur in water. B-L acids must have H, but B-L base is defined as any species with an e⁻ pair available to accept a transferred proton.
- 3 The **Lewis definition** has the widest scope of the 3. - don. and acceptance of an electron pair to form a new covalent bond. L-base electron pair to donate, L-acids include many species not encompassed by the other definitions.

Preparing a Buffer

In many cases, a common buffer is not available with the desired conc. and you have to make it yourself. Several steps are required to prepare a buffer of a desired pH:

1. Choose the conjugate acid-base pair. Choice determined by the desired pH. Remember that a buffer is most effective when the ratio of its components conc. is close to 1 (pH ≈ pK_a of the acid)
 2. Calculate the ratio of buffer component concentrations ($[A^-]/[HA]$) → Henderson-Hasselbalch eq.
 3. Determine the buffer concentration. Remember that the higher the conc. of components, the greater buffer capacity. (conc. 0.5 M suitable)
 4. Mix the solution and adjust the pH. Because of the behavior of nonideal solutions, a buffer prepared in this way may vary from the desired pH by a few tenths of a pH unit → adjust the buffer pH by adding strong acid or strong base.
- * Another way to prepare a buffer is to form one of the components during the final mixing step by partial neutralization of the other component

Acid-Base titration curves

Acid-base titration curve, a plot of pH vs. volume of titrant added. The behavior of an acid-base indicator and its role in the titration are described first

Monitoring pH with Acid-Base Indicators

The two common devices for measuring pH in the lab. are pH meters and acid-base indicators. An **acid-base indicator** is a weak organic acid that has a different color than its conjugate base, with the color change occurring over a specific and relatively narrow pH range. Only a tiny amount of the indicator is needed, cause they are intensely colored.

- * Indicators are used for estimating the pH of a solution and for monitoring the pH in acid-base titrations and in reactions. To select an indicator you've to know the pH of titr. end point (ionic species present) Ratio governed by $[H_3O^+]$ (weak acid!)
- How we perceive colors has a major influence in the use of indicators → indicator changes color over a range about 2 pH units (10^{-2} in the ratio)

Strong Acid - Strong Base titration curves (see figure p. 843)

Features of the curve

There are three distinct regions of the curve, which correspond to three major changes in slope:

1. The pH starts out low, reflecting the high $[H_3O^+]$ of the strong acid, and increases slowly as acid is gradually neutralized by the added base
2. Suddenly, the pH rises steeply → it begins when the moles of OH^- that have been added equal the moles of H_3O^+ originally present. Additional drop (excess of base and not of acid)
3. Beyond this steep portion, the pH increases slowly as more base is added.

Equivalence point is the point at which the no. of moles of added OH^- equals the no. of moles of H_3O^+ originally present. At the equivalence point of a strong acid-strong base titration the solution consists of the anion of the strong acid and the cation of the strong base (pH ≈ 7, they don't react)

Before titration begins, we add a few drops of an indicator to acid solution to signal when we reach eq. point. The **end point** of the titration occurs when the indicator changes color. We choose an indicator with an end point close to the eq. point, one that changes color in the pH range on the vertical portion of the curve.

- * The visible change in color of the indicator signals the invisible point at which moles of added base equal the original moles of acid.

Calculating the pH

By knowing the chemical species present during the titration, we can calculate the pH at various points

1. **Original solution of strong HA**. Because a strong acid is completely dissociated, $[HA] = [H_3O^+] = 0.1 M$. Initial pH = 1
2. **Before the equivalence point**. When we start adding base: 1) some acid is neutralized 2) the volume increases we calculate the initial amount of $H_3O^+ =$ amount of OH^- added → $[H_3O^+]$ through ΔV and convert to pH. (we use the total volume.)
3. **At the equivalence point**. All the H_3O^+ from the acid has been neutralized, $B^+ A^-$ do not react with water
4. **After the equivalence point**. From this point the pH calculation is based on the moles of excess OH^- present

Weak Acid - Strong Base titration curves (see figure p. 845)

Features of the curve

Comparing this graph with the previous curve we observe four imp. features:

1. The initial pH is higher (the weak acid dissociates slightly)
2. A gradually rising portion of the curve (**BUFFER REGION**) appears before the steep rise to the eq. point. At the midpoint (half HA has reacted) pH equals the pK_a (equal conc.)
3. The pH at the eq. point is greater than 7 (weak acid anion acts as a weak base)
4. Beyond the equivalence point, the pH increases slowly as excess OH^- is added.

Here our choice of indicator is not limited.

Calculating the pH

Here the procedure is different, cause we have to consider the partial dissociation of the weak acid and the reaction of the conj. base with water. Each key region requires a different method (Tot. 4)

1. **Solution of HA** - we find $[H_3O^+]$ (that of a weak-acid solution)
2. **Solution of HA and added base** - mixture of acid and conj. base (from this relation we find $[H_3O^+]$)
Here we have not to consider the total volume cause cancel in the ratio of concentrations.

Effect of pH on Solubility

the H_3O^+ concentration can have a profound effect on the solubility of an ionic compound. If the compound contains the anion of a weak acid, addition of H_3O^+ (from a strong acid) increases its solubility. Once again, Le Chatelier's principle explains why. **Example** - sat. solution of calcium carbonate

Predicting the Formation of a Precipitate: Q_{sp} vs K_{sp}

Now we compare Q_{sp} and K_{sp} to see if a precipitate will form and, if not, what changes in ion conc. will cause it to do so. **1** if $K_{sp} = Q_{sp}$ when the solution is saturated; **2** if $Q_{sp} > K_{sp}$ the solution is momentarily supersaturated and some solid precipitates until the remaining solution becomes saturated; **3** if $Q_{sp} < K_{sp}$, the solution is unsaturated and no precipitate forms at that temperature (more solid can dissolve)

Selective Precipitation of Ions

We can often separate one ion in a solution from another by exploiting differences in the solubility of their compounds with a given precipitating ion. In the process of **selective precipitation**, we add a solution of precipitating ion until the Q_{sp} value of the soluble (more sol.) compound is almost equal to its K_{sp} value. This method ensures that the K_{sp} value of the less soluble compound is exceeded as much as possible → max amount of the less soluble compound precipitates.

Sometimes 2 or 3 types of ionic equilibria are controlled simultaneously to precipitate ions selectively. (approach commonly used to sep. ions as their sulfides)

- * Principles of ionic equilibria often help to understand (or to solve) the chemical bases of complex environmental problems.

Equilibria involving complex ions

The final type of aqueous ionic equilibrium we consider involves a different kind of ion than we've examined up to now. A simple ion consists of one or a few bound atoms, with an excess or deficit of e^- . A **complex ion** consists of a central metal ion covalently bonded to two or more anions or molecules called **ligands**. All complex ions are Lewis adducts. The metal ion acts as a Lewis acid.

Formation of Complex ions

Whenever a metal ion enters water, a complex ion forms, with water as the ligand. In many cases, we treat this hydrated cation with a solution of another ligand, the bound water molecules exchange for the other ligand.

Once again, because the conc. of water is essentially constant in aqueous reactions, we incorporate it into K_c and obtain the expression for a new equilibrium constant, the **formation constant, K_f**

Example - $M(H_2O)_6^{n+}$ in aqueous NH_3 - the actual process is stepwise. The sum of the equations gives the overall equation, so the product of the individual formation constants gives the overall formation constant ($K_f = K_{f1} \times K_{f2} \times K_{f3} \times K_{f4}$)

- * K_f values are all 10^6 or greater, which means that these ions form readily.

Complex Ions and the Solubility of Precipitates

A ligand increases the solubility of a slightly soluble ionic compound if it forms a complex ion with the cation. **Example** - zinc sulfide is very slightly soluble.

Complex Ions of Amphoteric Hydroxides

Many of the same metals that form amphoteric oxides also form slightly soluble amphoteric hydroxides. These compounds dissolve very little in water, but they dissolve to a much greater extent in both acidic and basic solutions

Example - Aluminum hydroxide, it's insoluble in water but: **1** it dissolves in acid because H_3O^+ reacts with OH^- anion **2** it dissolves in base through the formation of a complex ion

When we dissolve a soluble aluminum salt in water and then slowly add a strong base, a white precipitate first forms and then dissolves as more base is added. What reactions are occurring? It acts as a weak polyprotic acid and reacts with added OH^- ions in a stepwise manner: in each step, one of the bound H_2O molecules loses a proton and becomes a bound OH^- ion, so the no. of bound H_2O molecule is reduced by 1. This complex ion is not created by ligands substituting for bound water molecules but through an acid-base reaction in which added OH^- ions titrate bound water molecules.

- * Several other slightly soluble hydroxides are amphoteric and exhibit similar reactions.
- * In contrast to the preceding hydroxides, the slightly soluble hydroxides of iron (II), iron (III) and calcium dissolve in acid, but do not dissolve in base because the three remaining water molecules are not acidic enough to lose any of their protons.

• Changes in Entropy

If a physical or chemical change results in a greater number of microstates, there are more ways to disperse the energy of the system. Thus, the entropy increases. $S_{\text{more microst.}} > S_{\text{fewer microst.}}$

If the change results in a lower number of microstates, the entropy decreases.

* Like internal energy (E) and enthalpy (H), entropy is a state function and so it depends only on the difference between its final and initial values $\Delta S_{\text{sys}} = S_{\text{fin}} - S_{\text{init}}$

Like any state function, $\Delta S_{\text{sys}} > 0$ when its value increases during a change.

• Quantitative Meaning of an Entropy Change

Two approaches for quantifying an entropy change are different but give the same result. The first is a statistical approach based on the number of microstates possible for a system at any given instant; the second is based on the heat absorbed (or released) by the system.

We'll explore both for a system of 1 mol of gas expanding from 1L to 2L and behaving ideally.

1 Approach based on the number of microstates. We have a container consisting of two identical flasks connected by a stopcock, with 1 mol of neon in the left flask and an evacuated right flask. When we open the stopcock, the gas will expand to fill both to 0.5 mol each, but why? \uparrow volume, \uparrow translational energy levels available as increases the no. of particle locations; particles occupy more en. levels so no. of possible microstates and entropy \uparrow . (fig. p. 885) Other figure - idea in a box of changeable volume, here when stopcock opens there are more energy levels, close together, so more distrib. of particles are possible. Seeing the other figure (p. 886) we can observe this relationship:

$$\frac{W_{\text{fin}}}{W_{\text{init}}} = 2^{N_A} \quad \text{With 1 mol } (N_A) \text{ of Ne, there are } 2^{N_A} \text{ times as many microstates possible for the atoms in the larger volume } (W_{\text{final}}) \text{ as in the smaller } (W_{\text{initial}})$$

Now let's find ΔS_{sys} through Boltzmann equation $|\Delta S_{\text{sys}} = S_{\text{fin}} - S_{\text{init}} = k_B \ln W_{\text{fin}} - k_B \ln W_{\text{init}} = k_B \ln \frac{W_{\text{fin}}}{W_{\text{init}}}|$

2 Approach based on heat changes. You know that when a sample of a gas is heated, it expands.

Let's compare the entropy change we found from the statistical approach to the entropy change that occurs when a gas is heated and does work on the surroundings. This approach uses the relationship $[\Delta S_{\text{sys}} = q_{\text{rev}}/T]$

T = temperature at which the heat change occurs. q = heat absorbed. rev = reversible process, one that occurs slowly enough for the eq. to be maintained, so that the direction of the change can be reversed by an infinitesimal reversal of conditions.

We can approximate the reversible expansion of the same sample of neon gas by placing it in a piston-cylinder assembly surrounded by a heat reservoir to maintain constant T , and confining the gas by the pressure of a beaker of sand resting on the piston (see fig. 887). If we calculate the entropy change, we obtain the same value. The first approach allow us to visualize the changes in terms of energy dispersal; the 2nd one, which involves incremental heat changes is applicable to more complex systems.

Entropy and the second law of Thermodynamics

The change in entropy is the key to det. the direction of a spontaneous process, but we've to consider more than just the system. Some processes occur spontaneously and the system ends up with higher entropy; other ones occur spontaneously and the system ends up with lower entropy.

* If we consider changes in both the system and its surroundings, we find that all real processes occur spontaneously in the direction that increases the entropy of the universe (syst. + surroundings). That's one way to state the **second law of thermodynamics**. This law places no limitations in the entropy change of syst. or surr., either may be negative (lower entropy after the process). However, it states that the sum of entropy changes must be positive. $S_{\text{syst}} \uparrow - S_{\text{surr}} \downarrow$ more than surroundings decrease, so that the Δ of universe increases.

$$[\Delta S_{\text{univ}} = \Delta S_{\text{syst}} + \Delta S_{\text{surr}} > 0]$$

Standard molar entropies and the third law

Both entropy and enthalpy are state functions, but the nature of their values is very different. Recall that we can measure only enthalpy changes. In contrast, we can determine the absolute entropy of a substance by applying the **third law of thermodynamics**: a perfect crystal has zero entropy at a temperature of absolute zero ($S_{\text{sys}} = 0$ at 0K; perfect = particles aligned flawlessly). At absolute 0 have the min. energy \rightarrow there's only one microstate. When we warm crystal, its tot. energy increases, so \neq microstates.

* To obtain the value of S at a given T , we first cool a crystalline sample of the substance as close to 0K as possible. Then we heat it in small increments, dividing q by T to get the increase in S for each increment, and add up all the entropy increases to the temp. of interest (298K). The entropy of a substance at a given T is an absolute value equal to the entropy increase obtained when the substance is heated from 0K to that T .

* We compare entropy, as usual, for substances in their standard states at the T of interest: 1 atm for gases, 1 M for solutions, and the pure substance in its most stable form for solids or liquids. Because entropy is an **extensive property** (depends on the amount of substance) we are interested in the **standard molar entropy** (S°)

• Predicting Relative S° values of a System

We can see now how the entropy is affected by conditions. We start considering the effects of temperature, the most fundamental condition, and also physical state, dissolution, and atomic or molecular complexity.

1 Temperature changes. For a given substance, S° increases as the temperature rises (as heat is absorbed \rightarrow increase in average E_k of the particles). With \uparrow microstates in which energy can be dispersed at any instant, the entropy of the substance goes up \rightarrow raising the temperature allows more possible microstates.

2 Physical states and phase changes. For a phase change as melting or vaporizing, heat is absorbed ($q > 0$). The particles have more freedom of motion and their energy is more dispersed, so ΔS is positive. Thus, S° increases for a substance as it changes from a solid to a liquid to a gas. **Example** - molecular oxygen

* The increase in entropy from liquid to gas is much larger than that from solid to liquid $\Delta S_{\text{vap}} \gg \Delta S_{\text{fus}}$

3 Dissolving a solid or liquid. The entropy of a dissolved molecular solid or liquid is greater than the entropy of the pure solute. For ionic solutes, the nature of solute and solvent affects the overall change. When a ionic solid dissolves in water, the crystal breaks down, ions are more free to move

Spontaneous Exothermic and Endothermic Reactions : Summary

Now we can see why an Exo and Endo spontaneous reaction occurs, no matter what is ΔS , a reaction occurs cause the Tot. entropy of the reacting syst. and its surr. increases. Two possibilities:

1. For an exothermic reaction ($\Delta H_{sys} < 0$) heat released by the system \rightarrow freedom in motion, en. dispersed and entropy of surroundings \uparrow ($\Delta S_{surr} > 0$)
 - If reac. syst yields product with entropy greater than that of reactants ($\Delta S_{sys} > 0$), tot ΔS_{univ} positive.
 - If entropy of system decreases with reaction ($\Delta S_{sys} < 0$), ΔS_{surr} must increase \gg to make ΔS_{univ} positive.
2. For an endothermic reaction ($\Delta H_{sys} > 0$) heat lost by the surroundings \rightarrow less freedom in motion and en. dispersed, entropy \downarrow ($\Delta S_{surr} < 0$). The only way an endothermic reaction can occur spontaneously is if ΔS_{sys} is positive and large enough to outweigh $-\Delta S_{surr}$.
 - In the sol. process for many ionic compounds, heat is absorbed to form the solution, so the entropy of the surr. decreases ($\Delta S_{surr} < 0$); when ions form, the ΔS_{sys} increase is so large ($\Delta S_{sys} \gg 0$) that outweighs the $-\Delta S_{surr} \rightarrow \Delta S_{univ} > 0$.
 - Spontaneous endothermic reactions have similar features

Entropy, free energy and work

By making two separate measurements, ΔS_{sys} and ΔS_{surr} , we can predict whether a reaction will be spontaneous at a particular T. However it could be useful to have one criterion for spontaneity that we can find by examining the system only. The Gibbs free energy, or free energy (G) is a function that combines the system's enthalpy and entropy [$G = H - TS$] and provides the spontaneity we've been seeking.

Free Energy Change and Reaction Spontaneity

The free energy change ΔG is a measure of the spontaneity of a process and of the useful energy available from it. Let's see how it's derived from 2nd law of thermodynamics; the entropy change of the universe is the sum of ΔS of the system and the surroundings $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$

At constant pressure $\Delta S_{surr} = -\frac{\Delta H_{sys}}{T} \rightarrow \Delta S_{univ} = \Delta S_{sys} - \frac{\Delta H_{sys}}{T} \rightarrow [\Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys}]$ Gibbs equation

Combining this equation with the T previous one shows that

$$-T\Delta S_{univ} = \Delta H_{sys} - T\Delta S_{sys} = \Delta G_{sys}$$

- * The sign of ΔG tells if a reaction is spontaneous. The 2nd law dictates
 - $\Delta S_{univ} > 0$ for a spontaneous process
 - $\Delta S_{univ} < 0$ for a nonspontaneous process
 - $\Delta S_{univ} = 0$ for a process at equilibrium
- * Absolute T is always positive, so $T\Delta S_{univ} > 0$ or $-T\Delta S_{univ} < 0$ for a spont. process
- * Because $\Delta G = -T\Delta S_{univ}$, we know that
 - $\Delta G < 0$ for a spontaneous process
 - $\Delta G > 0$ for a non spontaneous process
 - $\Delta G = 0$ for a process at equilibrium

If a process is nonspontaneous in one direction, it is spontaneous in the opposite direction. By using ΔG we can predict reaction spontaneity from only one variable. The degree of spontaneity of a reaction (sign and magnitude of ΔG) tells us nothing about the reaction.

Calculating Standard free energy changes

Because G combines three ~~energy~~ state functions (H, S, T), it's also a state function.

The Standard Free Energy Change

As we already did, to compare the free energy changes of different reactions we calculate the **standard free energy change** (ΔG°) which occurs when all components of the system are in their standard states

Adopting Gibbs equation, we have [$\Delta G^\circ_{sys} = \Delta H^\circ_{sys} - T\Delta S^\circ_{sys}$]

This relationship is freq. used to find any one of these thermodynamic variables.

The Standard Free Energy of Formation

ΔG° can also be calculated with values for the **standard free energy of formation** (ΔG°_f) of the comp. - which is the free en. change that occurs when 1 mol of compound is made from its elements, with all components in their standard states. Because G is a state function, we can combine ΔG°_f values of reactants and products to calculate ΔG°_{rxn} : [$\Delta G^\circ_{rxn} = \sum m\Delta G^\circ_f(\text{prod}) - \sum n\Delta G^\circ_f(\text{react})$]

- * ΔG°_f values have properties similar to ΔH°_f values:
 - ΔG°_f of an element in its standard state is zero
 - An eq. coefficient (m, n) multiplies ΔG°_f by that number.
 - Reversing an equation changes the sign of ΔG°_f

ΔG and the work a system can do

One of the most practical relationships in thermodynamics is that between the ΔG and the work a system can do

- For a spontaneous process ($\Delta G < 0$) at constant T and P, ΔG is the maximum useful work ~~that can be obtained~~ to make the process take place, obtainable from the system [$\Delta G = w_{max}$]
 - For a nonspontaneous process ($\Delta G > 0$) at constant T and P, ΔG is the minimum work that must be done to the system to make the process take place.
- i.e. ΔG max work the system can possibly do; but the work the system actually does depends on how that change in free energy is released

Example - gas confined in a cylinder \rightarrow as the number of steps increases, the quantity of work done by the gas increases.

Only in a hypothetical process in which the work is done in an infinite number of steps, and an infinitesimal increase in the ~~weight~~ reverses the expansion, can the maximum work be done: the max work

Another look at the meaning of spontaneity

- consider the general reaction $A \rightleftharpoons B$ ($K > 1$) which proceeds largely to right. From pure A to eq. point $Q < K$ and the reaction is spontaneous ($\Delta G < 0$). From there on, the reaction is nonspontaneous ($\Delta G > 0$). From pure B to equilibrium point $Q > K$ and the reaction is nonspontaneous ($\Delta G < 0$) but not thereafter. In either case, the free en. decreases as the reaction proceeds, until it reaches a minimum at the eq. mixture ($Q = K, \Delta G = 0$). For the overall reaction $\Delta G_R^\circ = \Delta G_P^\circ \rightarrow \Delta G^\circ$ negative. ($K > 1$) - product favoured reaction because the final state of the system contains mostly product.
- Now consider the reaction $C \rightleftharpoons D$ ($K < 1$) which proceeds to right only slightly. Here we start with pure C and D, the reaction is spontaneous ($\Delta G < 0$) until equilibrium point. But there, eq. mixture contains mostly C (reactant) so the reaction is **reactant favoured**. $G^\circ_D > G^\circ_C \rightarrow \Delta G^\circ$ positive ($K < 1$). Spontaneous refers to that portion of the reaction in which the free en. is decreasing, that is, from some starting mixture to the equilibrium mixture, whereas product favoured refers to a reaction that goes predominantly, not necessarily completely, to product.

Chapter 21

Redox reactions and electrochemical cells

Whether an electrochemical process releases or absorbs free energy, it always involves the movement of electrons from one chemical species to another in an oxidation-reduction (redox) reaction. Here we review the redox reactions and see how such reactions are used in the two types of electrochemical cells.

* About **redox**, keep in mind these three points:

- Oxidation (electron loss) always accompanies reduction (electron gain)
- The oxidizing agent is reduced, and the reducing agent is oxidized.
- The total number of electrons gained by the atoms/ions of the oxidizing agent always equals the total number lost by the atoms/ions of the reducing agent.

Half-Reaction Method for balancing redox reactions (see from p. 924)

The major points are:

- Any redox reaction can be treated as the sum of a reduction and an oxidation half-reaction.
- Atoms and charge are conserved in each half-reaction.
- Electrons lost in one half-reaction are gained in the other.
- Although the half-reactions are treated separately, electron loss and electron gain occur simultaneously.

An overview of electrochemical cells

We distinguish two types of electrochemical cells based on the general thermodynamic nature of the reaction:

- A **voltaic cell (galvanic cell)** uses a spontaneous reaction ($\Delta G < 0$) to generate electrical energy. In the cell reaction, the difference in chemical potential energy between higher en. reactants and lower en. products is converted into electrical energy. This energy is used to operate the load. *The system does work on the surroundings. **Example** - all batteries contain voltaic cell.
- An **electrolytic cell** uses electrical energy to drive a nonspontaneous reaction ($\Delta G > 0$). In the cell reaction, electrical energy from an external power supply converts lower energy reactants into higher en. products. *The surroundings do work on the system. Electroplating and recovering metals from ores involve elec. cells **Exp.**

The two types of cell have certain design features in common. Two **electrodes** which conduct the electricity between cell and surroundings, are dipped into an **electrolyte**, a mixture of ions (usually in aqueous solution) that are involved in the reaction or that carry the charge. An electrode is identified as either **anode** or **cathode** depending on the half-reaction that takes place there:

- The oxidation half-reaction occurs at the anode. Electrons are lost by the substance being oxidized and leave the cell at the anode.
 - The reduction half-reaction occurs at the cathode. Electrons are gained by the substance being reduced and enter the cell at the cathode.
- * The relative charges of the electrodes are opposite in the two types of cell (it results from the different phenomena that causes the electrons to flow).

Voltaic cells: using spontaneous reactions to generate electrical energy

- * If you put a strip of zinc metal in a solution of Cu^{2+} ion, the blue color of the solution fades as a brown-black crust of Cu metal forms on the Zn strip. This reaction involves the reduction of Cu^{2+} ion to Cu metal and the oxidation of Zn metal to Zn^{2+} ion.

Construction and Operation of a Voltaic Cell

Electrons are being transferred in the Zn/ Cu^{2+} reaction but the system does not generate electrical energy because the oxidizing agent (Cu^{2+}) and the reducing agent (Zn) are in the same beaker. If the two reactions are physically separated and connected by an external circuit, the e^- are transferred by traveling through the circuit and an electric current is produced. This is the essential idea behind a voltaic cell. The components of each half-reaction are placed in a separate container (**half cell**) - one electrode dipping into an electrolyte ~~solution~~ solution. The 2 half-cells are joined by the circuit (wire + salt bridge). In order to measure the voltage generated by the cell, a voltmeter is inserted in the path of the wire connecting the electrodes. A switch closes and opens the circuit. By convention, the oxidation half-cell (anode compartment) is shown on the left and the red. half-cell (cathode compartment) on the right.

Standard cell potentials

The potential of a voltaic cell is affected by changes in concentration as the reaction proceeds and by energy losses due to heating of the cell and the external circuit - to compare the output of diff. cells, we obtain a **standard cell potential** (E°_{cell}) (E_{cell} measured at usually 298K, with no current flowing and all components in their standard states: 1 atm of P, 1M solutions, pure solid for electrodes).

Standard electrode (half-cell) potentials

As each half-reaction is part of the overall reaction, the potential of each cell is part of the overall pot. The **standard electrode potential** ($E^\circ_{\text{half-cell}}$) is the potential associated with a given half-reaction (electrode compartment) when all the components are in their standard states.

* A standard electrode potential always refers to the half reaction written as a **reduction**.

Example - zinc-copper reaction ($E^\circ_{\text{cell}} = E^\circ_{\text{copper}} - E^\circ_{\text{zinc}}$)

* In general, the standard cell potential is the difference between the standard electrode potential of the cathode (reduction) half-cell and the standard electrode potential of the anode (oxidation) half-cell.

[$E^\circ_{\text{cell}} = E^\circ_{\text{cathode (red)}} - E^\circ_{\text{anode (oxid)}}$] For a spont. reaction at standard conditions $\rightarrow E^\circ_{\text{cell}} > 0$.

Determining $E^\circ_{\text{half-cell}}$: the standard hydrogen electrode

How we can know half-cell potentials? They are not absolute quantities, but rather are values relative to that of a standard. This standard reference half-cell has its standard electrode potential defined as zero.

The **standard reference half-cell** is a **standard hydrogen electrode** (platinum electrode in a 1M solution of water and strong acid). Now we can construct a voltaic cell = reference cell + another half cell whose half pot. we want to determine. $E^\circ_{\text{ref}} = 0$; all the other E°_{cell} to find standard elect. potential.

H_2 oxidized - ref. cell anode ($E^\circ_{\text{cell}} = E^\circ_{\text{unknown}}$), H^+ reduced - ref. cell anode ($E^\circ_{\text{cell}} = -E^\circ_{\text{unknown}}$)

Through this process we can find many standard potentials

Relative strengths of oxidizing and reducing agents

From measuring potentials of voltaic cells we can learn the relative strengths of the oxidizing and reducing agents involved - this by writing each half reac. as a gain of electrons, with its corresponding $E^\circ_{\text{half-cell}}$. **The more positive the E° value, the more readily the reaction occurs**

List in decreasing half-cell pot order \rightarrow from top to bottom, oxidizing agents decreasing in strength and reducing agents increasing in strength.

* By combining many pairs of half-cells into voltaic cells, we can create a list of red. half-reactions; these lists are called **emp. series** or **table of standard electrode potentials**

Several key points:

• Values relative to the standard (H) reference electrode

• half reactions written as reductions \rightarrow reactants = oxidizing agents, products = reducing agents.

• + $E^\circ_{\text{half-cell}}$ - + readily reaction occurs.

• React. shown with an eq. arrow cause each can occur as a reduction or an oxidation.

• Strength of ox. agent \uparrow going up (bottom to top), strength of red. agent \uparrow going down (top to bottom)

(see table p. 938)

* A strong ox. agent forms a weak red. agent and vice versa.

Writing spontaneous redox reactions

• Every redox reaction is the sum of two half reactions, so there's a reducing agent and an oxidizing agent on each side.

Example - zinc-copper reaction. The members of a cong. acid-base pair differ by a proton (acid prot., base not); member of a redox pair (or redox couple) differ by one or more electrons (red form e^- , ox. form not)

* The stronger oxidizing agent (on the left) has a half reaction with a larger (more + or less -) E° value, and the stronger reducing agent (on the right) has a half-reaction with a smaller (less + or more -) E° value. Spont. reaction between an ox. agent and an reducing agent below the list. \rightarrow For a spont. reaction to occur, the half reaction higher in the list proceeds at the cathode as written, and the half reaction lower in the list proceeds at the anode in reverse.

We can write a spont. redox reaction also knowing the electrode potentials.

There are two steps involved

1 Reverse one of the half-reactions into an oxidation step s.t. the diff. of electrode potentials gives $E^\circ_{\text{cell}} > 0$. (we need not reverse the sign of $E^\circ_{\text{half-cell}}$)

2. Add the rearranged half reactions to obtain a balanced overall equation.

With the half-reactions written in the correct direction, we must next make sure that the number of electrons lost in the oxidation equals the number gained in the reduction

Changing the balancing coefficients of a half-reaction does not change its E° value, this because a standard electrode potential is an intensive property, one that does not depend on the amount of substance present. The pot. is the ratio of energy to charge. When we change the coefficients, the energy and the charge change proportionally, so their ratio stays the same.

Relative reactivities of Metals

1 **Metals that can displace H_2 from acid.** Combine H half-reaction with the half react of the metal chosen (written as oxidation) and see if E°_{cell} is positive. Those metals below the reference half-reac. give a + E°_{cell} . If E°_{cell} for the reduction of H^+ is more positive for metal A than for metal B, A is a stronger reducing agent than metal B and a more **active** metal.

2 **Metals that cannot displace H_2 from acid.** Metals above the reference half-reac. cannot reduce H^+ from acids, when we reverse the metal half reac. $E^\circ_{\text{cell}} < 0$, so the reaction cannot occur.

Stage 1 $E_{cell} > E^{\circ}_{cell}$ when $Q < 1$ (when the cell begins operation $[Cu^{2+}] > [Zn^{2+}]$) As cell operation continues $[Zn^{2+}]$ increases and $[Cu^{2+}]$ decreases - E_{cell} decreases.

Stage 2 $E_{cell} = E^{\circ}_{cell}$ when $Q = 1$, this happens when $[Cu^{2+}] = [Zn^{2+}]$

Stage 3 $E_{cell} < E^{\circ}_{cell}$ when $Q > 1$, that happens when the $[Zn^{2+}]/[Cu^{2+}]$ ratio continues to increase.

Stage 4 $E_{cell} = 0$ when $Q = K$. This occurs when the system reaches **equilibrium**: no more free energy is released, so the cell can do no more work.

see fig. p. 948

To conclude, let's examine cell potential in terms of the starting Q/K ratio

- $Q/K < 1$, E_{cell} is positive for the reaction as written. The smaller the Q/K ratio, the greater the value of E_{cell} , and the more electrical work the cell can do.
- $Q/K = 1$, $E_{cell} = 0$. The cell is at equilibrium and it can no longer do work.
- $Q/K > 1$, $E_{cell} < 0$ for the reaction as written. The reverse reaction will take place and the cell will do work until $Q/K = 1$ at equilibrium.

Concentration Cells

If you mix a concentrated solution of a salt with a dilute solution of the salt, the final concentration equals some intermediate value. A **concentration cell** employs this phenomenon to generate electrical energy. The two solutions are in separate half-cells, so they do not mix; rather, their concentrations become equal as the cell operates.

How a concentration cell works

Suppose both compartments of a voltaic cell have the Cu^+/Cu^2+ half-reaction. The cell reaction is the sum of identical half-reactions, written in opposite directions, so the standard half-cell potentials cancel and E°_{cell} is zero. This occurs because standard electrode potentials are based on concentrations of 1 M. In a conc. cell, however, the half-reactions are the same but concentrations are different. As a result, even though $E^{\circ}_{cell} = 0$, the non standard pot. E_{cell} does not equal zero because it depends on the ratio of concentrations.

(see fig. p. 949) → what is actually going on as this cell operates?

Applications of concentration cells

The most important application is the measurement of unknown ion concentrations, particularly $[H^+]$. Construction of a concentration cell based on the H_2/H^+ half-reaction (see p. 950 half-reactions and overall reaction); by measuring E_{cell} , we can find the pH. In the routine measurement of pH, a conc. cell incorporating two H electrodes is too bulky and difficult to maintain. Instead, a pH meter is used. Two separate electrodes dip into the solution being tested. One of them is a glass electrode (an Ag/AgCl half-reaction immersed in an HCl solution of fixed conc. and enclosed by a thin membrane made of a special glass that is highly sensitive in the presence of H^+ ions). The other electrode is a reference electrode, typically a saturated calomel electrode.

The pH electrode is one example of an ion-selective (or ion-specific) electrode. Electrodes have been designed with highly specialized membranes in order to selectively measure the conc. of many different ions in industrial, environmental and biological samples.

Electrochemical processes in batteries

Battery - self-contained group of voltaic cells arranged in series, so that their individual voltages are added together, even if the term may be applied to a single voltaic cell. Batteries are ingeniously engineered devices that house rather unusual half-reactions, and half-cells, but they operate through the same electrochemical principles we've been discussing.

Primary (nonrechargeable) Batteries

A primary battery cannot be recharged, so it is discarded when the components have reached their equilibrium concentrations (when the cell is dead).

Alkaline Battery

Its precursor was the Leclanché cell, invented in the 1860s, used during the 20th century. The anode of the dry cell was a zinc can that housed a mixture of MnO_2 and a weakly acidic electrolyte paste and starch. Powdered graphite was used to improve conductivity and the cathode was an inactive graphite rod. Although more expensive than the dry cell, the alkaline battery avoids these drawbacks. The same electrode materials, zinc and manganese dioxide, are used, but the electrolyte is a paste of KOH and water. The half reactions are essentially the same, but use of the KOH paste eliminates the NH_3 gas buildup and maintains the Zn electrode.

Like the dry cell, the alkaline battery powers portable radios, etc... It has no voltage drop, longer shelf life and better performance in terms of power capability and stored energy.

Mercury and silver (button) batteries

Mercury and silver batteries are quite similar. Both use a zinc container as the anode (reducing agent) in a basic medium. The mercury battery employs HgO as the oxidizing agent, the silver uses Ag_2O , and both use a steel can around the cathode. The solid reactants are compacted with KOH and separated with moist paper (see half-reactions). Both cells are manufactured as small button-sized batteries. The mercury cell is used in calculators.

Primary lithium batteries

It is used in watches. It offers an extremely high energy/mass ratio, producing 1 mol of e^- from less than 1/4 g of metal. The anode is lithium metal foil, which requires a nonaqueous electrolyte. The cathode is one of several metals oxides in which lithium ions enter between oxide layers.

METALS WITH FIXED OXIDATION STATES

aluminium	Al ³⁺	Al
cadmium	Cd ²⁺	Cd
calcium	Ca ²⁺	Ca
lithium	Li ⁺	Li
magnesium	Mg ²⁺	Mg
potassium	K ⁺	K
silver	Ag ⁺	Ag
sodium	Na ⁺	Na
zinc	Zn ²⁺	Zn

METALS WITH VARIABLE OXIDATION STATES

chromium	Cr ²⁺ , Cr ³⁺ , Cr ⁶⁺	Cr(II)	Cr(III)	Cr(IV)
cobalt	Co ²⁺ , Co ³⁺	Co(II)	Co(III)	
copper	Cu ⁺ , Cu ²⁺	Cu(I)	Cu(II)	
gold	Au ⁺ , Au ³⁺	Au(I)	Au(III)	
iron	Fe ²⁺ , Fe ³⁺	Fe(II)	Fe(III)	
lead	Pb ²⁺ , Pb ⁴⁺	Pb(II)	Pb(IV)	
manganese	Mn ²⁺ , Mn ³⁺ , Mn ⁴⁺ , Mn ⁷⁺	Mn(II)	Mn(III)	Mn(IV) Mn(VII)
mercury	Hg ₂ ²⁺ , Hg ²⁺	Hg(I)	Hg(II)	
nickel	Ni ²⁺ , Ni ³⁺	Ni(II)	Ni(III)	
tin	Sn ²⁺ , Sn ⁴⁺	Sn(II)	Sn(IV)	
uranium	U ³⁺ , U ⁴⁺ , U ⁵⁺ , U ⁶⁺	U(III)	U(IV)	U(V) U(VI)

MONOATOMIC ANIONS

hydride	H ⁻	oxide	O ²⁻
fluoride	F ⁻	sulfide	S ²⁻
chloride	Cl ⁻	nitride	N ³⁻
bromide	Br ⁻	phosphide	P ³⁻
iodide	I ⁻	carbide	C ⁴⁻

POLYATOMIC ANIONS

ammonium	NH ₄ ⁺	periodate	IO ₄ ⁻	sulfite	SO ₃ ²⁻
acetate	C ₂ H ₃ O ₂ ⁻	iodate	IO ₃ ⁻	hydrogen sulfite	HSO ₃ ⁻
carbonate	CO ₃ ²⁻	iodite	IO ₂ ⁻	hydroxide	OH ⁻
hydrogen carbonate	HCO ₃ ⁻	hypoiodite	IO ⁻	phosphate	PO ₄ ³⁻
perchlorate	ClO ₄ ⁻	permanganate	MnO ₄ ⁻	hydrogen phosphate	HPO ₄ ²⁻
chlorate	ClO ₃ ⁻	nitrate	NO ₃ ⁻	dihydrogen phosphate	H ₂ PO ₄ ⁻
chlorite	ClO ₂ ⁻	nitrite	NO ₂ ⁻	phosphite	PO ₃ ³⁻
hypochlorite	ClO ⁻	chromate	CrO ₄ ²⁻	hydrogen phosphite	HPO ₃ ²⁻
perbromate	BrO ₄ ⁻	dichromate	Cr ₂ O ₇ ²⁻	dihydrogen phosphite	H ₂ PO ₃ ⁻
bromate	BrO ₃ ⁻	cyanide	CN ⁻		
bromite	BrO ₂ ⁻	hydrogen sulfate	HSO ₄ ⁻		
hypobromite	BrO ⁻	sulfate	SO ₄ ²⁻		

↓

Cu ²⁺	cupric ion	Cu ⁺	cuprous ion
Fe ³⁺	ferric ion	Fe ²⁺	ferrous ion
Pb ⁴⁺	plumbic ion	Pb ²⁺	plumbous ion
Sn ⁴⁺	stannic ion	Sn ²⁺	stannous ion
Hg ₂ ²⁺	mercuric ion	Hg ₂ ²⁺	mercurous ion
Cr ³⁺	chromic ion	Cr ²⁺	chromous ion
Co ³⁺	cobaltic ion	Co ²⁺	cobaltous ion
Mn ³⁺	manganic ion	Mn ²⁺	manganous ion

Practice lesson 1

Uncertainty in measurement: significant figures

We can never measure a quantity exactly, because measuring devices are made to limited specifications and we use our imperfect senses and skills to read them. So every measurement includes some uncertainty. The measuring device we choose depends on how much uncertainty we are willing to accept.

Example

Mass 2.0 ± 0.1 kg \rightarrow 0.1 is the uncertainty

The greater number of digits in the mass of the chemical indicates that we know its mass with more certainty. We always estimate the rightmost digit when reading a measuring device. Uncertainty can be expressed by \pm sign, but generally we drop the sign and assume an uncertainty of one unit in the rightmost digit. The digits we record in a measurement, both the certain and uncertain ones, are called significant figures.

- * The greater the number of significant figures in a measurement, the greater is the certainty.

HOW TO DETERMINE WHICH DIGITS ARE SIGNIFICANT

In general, all digits are significant, except zeros that are not measured but are used only to position the decimal point. Here the procedure:

- Make sure that the measured quantity has a decimal point.
- Start at the left, move right until you reach the first nonzero digit.
- Count that digit and every digit to its right as significant.

- * We've a different situation with zeroes that end a number and lie either after or before the decimal point, in fact they are significant.
- * If there's no decimal point we assume that the zeroes are not significant; exponential notation is needed to show which of the zeroes were measured and therefore are significant.

SIGNIFICANT FIGURES IN CALCULATION

- * The least certain measurement sets the limit on certainty for the entire calculation and determines the number of significant figures in the final answer.

Significant figures and arithmetic operations 2 rules:

- For multiplication and division. The answer contains the same number of significant figures as in the measurement with the fewest significant figures.
- For addition and subtraction. The answer has the same number of decimal places as there are in the measurement with the fewest decimal places.

Rules of rounding off

- If the digit removed is more than 5, the preceding number is increased by 1.
- If the digit removed is less than 5, the preceding number is unchanged.
- If the digit removed is 5, the preceding number is increased by 1 if it is odd and remains unchanged if it is even. If the 5 is followed only by zeroes rule 3 is followed; if it is followed by nonzeros rule 1 is followed.
- Always carry one or two additional significant figures through a multistep calculation and round off the final answer only.

(see significant figures in electronic calculators)

- * The measuring device you choose determines the number of significant figures you can obtain.

EXACT NUMBERS are so called because they have no uncertainty associated with them. Some of them are part of a unit definition; others result from actually counting individual items. Because they have no uncertainty exact numbers do not limit the number of significant figures in the answer.

Names of compounds

Names and formulae of ionic compounds All ionic compounds give the positive ion (cation) first and the negative ion (anion) second.

Compounds formed from monatomic ions Binary ionic compounds (composed of ions of two elements)

- The name of the cation is the same as the name of the metal. Many metal names end in **-ium**.
- The name of the anion takes the root of the non metal name and adds the suffix **-ide**.

Example

Bromine \rightarrow Bromide (x as calcium bromide)

- * Ionic compounds are arrays of oppositely charged ions rather than separate molecular units.

FORMULA UNIT gives the relative numbers of cations and anions in the compound. Ionic compounds generally have only empirical formulas and they have zero net charge.

Some rules

- The subscript refers to the element preceding it
- The subscript 1 is understood from the presence of the element symbol alone
- The charge of one ion becomes the subscript

Rules for assigning oxidation numbers

There are several rules for assigning the oxidation number to an element. Learning these rules will simplify the task of determining the oxidation state of an element, and thus, whether it has undergone oxidation or reduction.

- 1 The oxidation number of an atom in the elemental state is zero.
- 2 The oxidation number of a monatomic ion is equal to its charge.
- 3 The algebraic sum of the oxidation numbers in the formula of a compound is zero.
- 4 The oxidation number of hydrogen in a compound is $+1$, except when hydrogen forms compounds called hydrides with active metals, and then it is -1 .
- 5 The oxidation number of oxygen in a compound is -2 , except in peroxides when it is -1 , and when combined with fluorine then it is $+2$.
- 6 The algebraic sum of the oxidation numbers in the formula for a polyatomic ion is equal to the charge on that ion.