INTERMOLECULAR FORCES

FORCES BETWEEN MOLECULES

Intermolecular forces hold molecules together.
Their strength determines the state of matter of the substance at a certain temperature:

- *Intermolecular forces increase if the temperature decreases*
- *Intermolecular forces decrease if the temperature increases*

Intermolecular forces are always weaker than intramolecular forces → Coulomb's law
→ Bonding forces are the result of large charges (protons and electrons) interacting at very close distances; while intermolecular forces are the result of smaller charges interacting at greater distances.

Intermolecular forces originate from the interactions among

- Charges → **IONS**
- Partial charges → **DIPOLES**
- Temporary charges → **TEMPORARY DIPOLES**
- Induced charges → **INDUCED DIPOLES** – induced by ions, dipoles or temporary dipoles

INTERMOLECULAR FORCES ARE FORMED BY ELECTROSTATIC ATTRACTION

LONDON DISPERSION FORCE

- Intermolecular force present **between all molecules** – polar and apolar.
- RESULT OF ELECTRON MOTION: electrons in an atom or molecule may, at any instant, be unevenly distributed and develop an INSTANTANEOUS DIPOLE.
- An instantaneous dipole on one atom ***induces*** an instantaneous dipole on its neighboring atoms, causing an interaction between them.

Factors that influence the dispersion forces:

1) *SIZE OF THE ELECTRON CLOUD*: a larger electron cloud results in a greater dispersion force because the electrons are held less tightly by the nucleus and therefore polarize more easily.
2) *MOLAR MASS*: dispersion force increases with increasing molar mass because molecules or atoms of higher molar mass generally have more electrons dispersed over a greater volume.
3) *MOLECULAR SHAPE*: at constant molar mass, the strength of dispersion forces depends on the shape of the molecule.
   → Long molecules can interact with one another along their entire length.
   → Round shape molecules have a smaller area of interaction.

GREATER DISPERSION FORCES = HIGHER BOILING POINT

(a) *n*-Pentane **(b) Neopentane**

DIPOLE–DIPOLE FORCE

- Dipole–dipole forces exist between **polar molecules** → PERMANENT DIPOLE
- Polar molecules have regions with a partial negative charge and regions with a partial positive charge.
- When molecules with dipole moments are put together, they orient themselves to take advantage of their charge distribution: the positive end of one permanent dipole attracts the negative end of another.

→ Polar molecules have higher melting and boiling points than nonpolar molecules of similar molar mass because of these additional interactions.
→ Hydrogen bonds maintain the 3D structure of many biological molecules (*e.g. DNA or proteins*)

HYDROGEN BONDING

- SPECIAL DIPOLE–DIPOLE INTERACTION.
- STRONGEST INTERMOLECULAR FORCE.
- Occurs in pure substances.
- Hydrogen bond acts between **polar molecules** that contain hydrogen covalently bonded to a small, highly electronegative atom such as F, O, N.
- When hydrogen is bonded to a strong electronegative atom it has a partial positive charge that will be attracted to an oxygen atom of another molecule that is partially negatively charged.
  → The oxygen atom can form two hydrogen bonds since it has two lone pairs

Hydrogen bonds form a *three-dimensional* aggregate of water molecules.

Hydrogen bonding explains some properties of water: high melting point, boiling point, heat of fusion, and heat of vaporization.

ION–DIPOLE FORCE

- Occurs when an ionic compound is mixed with a polar compound → aqueous solutions of ionic compounds.
- IONS INTERACT WITH WATER MOLECULES

→ The positive ions interact with the negative poles of water molecules, while the negative chloride ions interact with the positive poles – **HYDRATION**.

STATES OF MATTER

SOLIDS

PROPERTIES

- Definite volume and shape (independent from the container).
- Particles pack closely to each other in fixed locations but can vibrate.
- Incompressible.
- Most solids are slightly denser than their corresponding liquids because the molecules move closer together upon freezing → *thermal contraction*

CLASSIFICATION

According to molecular arrangement:

→ to determine the arrangement of atoms: **X-RAY DIFFRACTION**

- **AMORPHOUS** – atoms or molecules with aperiodic covalent bonds and intermolecular forces arranged with no long-range order.

- **CRYSTALLINE** – atoms or molecules arranged in a well-ordered array (*CRYSTALLINE LATTICE*) to minimize their energy.

  A crystalline lattice can be seen as a

→ series of *UNIT CELLS*: simple cubic, body-centered cubic, face-centered cubic.

→ result of *CLOSEST-PACKED STRUCTURE*: hexagonal or cubic closest packing

CRYSTALLINE SOLIDS CAN BE DIVIDED INTO

MOLECULAR SOLIDS

- Unit cells made of MOLECULES
- Intermolecular forces between molecules – affect their properties
- Some molecular solids crystallize in different structures called polymorphs that have different properties.

  Polymorphism is important in pharmaceuticals because different forms of a drug can have different physiological activities.

IONIC SOLIDS

- Unit cells made of IONS
- Electrostatic forces – stronger than intermolecular forces → higher melting points than molecular solids.
- Properties: soluble in H_2O and low conductivity.

METALLIC ATOMIC SOLIDS

- Composite particles: ATOMS
- Metallic bond – interaction of metal cations with the **sea of electrons**
- Tend to form **closest-packed** crystal structures, since metallic bonds are not directional.
- Properties: conductivity, malleability, ductility.

NETWORK COVALENT ATOMIC SOLIDS OR RETICULAR

- Composite particles: ATOMS
- Covalent bonds – geometrical constraints due to the bond directionality
- Properties: high melting points because the crystalline solid is held together by covalent bond

E.g. diamond, graphite, fullerene → allotropes of carbon: same element, different arrangement

GRAPHITE – atoms arranged in sheets. The atoms within each sheet are tightly bound to each other, but the sheets are not tightly bound to other sheets.
Therefore, the sheets can slide past each other, which is why the graphite in a pencil leaves a trail as you write.

DIAMOND – atoms all bound together in a three-dimensional structure where layers are strongly bound to other layers, resulting in the strong, nearly unbreakable substance.

FULLERENE – atoms arranged in rings fused together to form sphere

STATES OF MATTER

LIQUIDS

PROPERTIES

- Definite volume but indefinite shape – particles assume the shape of the container.
- Particles close together but free enough to move around and slide on each other: moderate intermolecular forces
- Particles with higher kinetic energy respect to solid particles, but lower than gaseous particles.
- Slightly compressible.
- Lower density than solid
  → exception: *water* – ice is less dense than liquid water because the unique crystal structure of ice results in water molecules moving slightly farther apart upon freezing.

PROPERTIES DUE TO INTERMOLECULAR FORCES

SURFACE TENSION

TENDENCY OF LIQUIDS TO MINIMIZE THEIR SURFACE AREA

Surface tension is the result of greater cohesion forces than adhesion forces.

Molecules at the liquid surface have a higher potential energy than those in the interior.
→ A molecule at the surface has fewer neighbors to interact with, so, since attractive interactions with other molecules lower potential energy, it has higher potential energy.

→ The molecules at the surface are therefore pulled inward: this creates some internal pressure and forces liquid surfaces to contract to the minimum area.

Surface tension decreases as intermolecular forces decrease.
Surface tension decreases as the temperature increases.

VISCOSITY

RESISTANCE OF A LIQUID TO FLOW

Viscosity is measured in a unit called the poise (P).
Viscosity depends on:

1) *INTERMOLECULAR FORCES*: substances with strong intermolecular forces have molecules strongly attracted to each other, so they do not flow around each other as freely.
2) *MOLECULAR SHAPE*: longer molecules can interact over a greater area, so they have higher viscosity.
3) *MOLAR MASS*: increasing molar mass means increasing both the magnitude of dispersion forces and the length of the molecule.
4) *TEMPERATURE*: thermal energy partially overcomes the intermolecular forces, allowing molecules to flow past each other more easily

CAPILLARITY

ABILITY OF A LIQUID TO FLOW AGAINST GRAVITY UP A NARROW TUBE

Capillary action results from a combination of two forces:

- **COHESIVE FORCES**: attraction between molecules in a liquid – cause the liquid to stay together
- **ADHESIVE FORCES**: attraction between molecules and the surface of the tube – cause the liquid to spread out over the surface of the tube

The result of the differences in the relative magnitudes of cohesive and adhesive forces can be observed by comparing the meniscus.

MENISCUS: the curved shape of a liquid surface within a tube.

- *CONCAVE*: the adhesive forces are greater than the cohesive forces.
- *CONVEX*: the cohesive forces are greater than the adhesive forces.

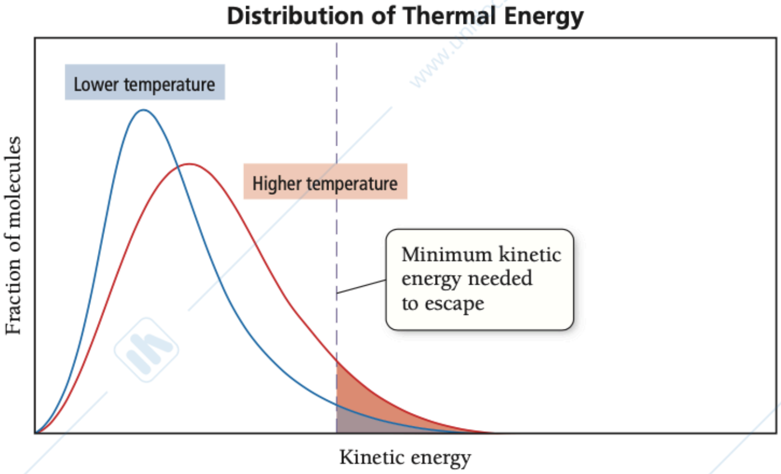
EVAPORATION AND BOILING

EVAPORATION	***BOILING***
Endothermic process	Endothermic process
Affect **surface molecules** → $\propto area$	Affect the **whole mass** of the liquid
Can happen at **any** temperature	**Fixed** temperature

Endothermic processes → thermal energy needed to overcome intermolecular forces.

MAXWELL-BOLTZMANN DISTRIBUTION TO VISUALIZE THE DISTRIBUTION OF THERMAL ENERGY

At any one time, some molecules have more thermal energy than the average and some have less.



$T_2 > T_1$ → molecules at T_2 have a higher average kinetic energy.

At T_2 the number of molecules that have enough energy to overcome the intermolecular forces and to pass to the gaseous state is **higher** than the number of molecules that can do the change of state at T_1.

Although both vaporization and condensation occur at the same time, under normal conditions evaporation takes place at a greater rate because most of the newly evaporated molecules escape into the surrounding atmosphere and never come back.

The weaker intermolecular forces allow more molecules to evaporate at a given temperature, increasing the rate of vaporization.

VOLATILE – liquids that vaporize easily

NONVOLATILE – liquids that do not vaporize easily.

Our bodies use the endothermic nature of vaporization for cooling: when we over-heat, we sweat, and our skin is covered with liquid water.

As this water evaporates, it absorbs heat from the body, cooling the skin.

VAPOR PRESSURE

PRESSURE EXERTED BY A VAPOR IN DYNAMIC EQUILIBRIUM WITH ITS CONDENSED PHASE

Dynamic equilibrium → RATE OF CONDENSATION = RATE OF EVAPORATION

As the concentration of gaseous water molecules increases, the rate of condensation also increases.

A liquid in dynamic equilibrium with its vapor is a balanced system that tends to return to equilibrium if disturbed.

Vapor pressure depends on

a) INTERMOLECULAR FORCES
  - Weak intermolecular forces → volatile substances with high vapor pressures (intermolecular forces are easily overcome by thermal energy)
  - Strong intermolecular forces → nonvolatile substances with low vapor pressures

b) TEMPERATURE: at higher temperatures, more molecules have enough thermal energy to escape into the gas state, so vapor pressure increases with increasing temperature.

The relationship between temperature and vapor pressure is **not linear**, but **exponential.**
The *Clausius-Clapeyron equation* provides a **LINEAR** relationship between the logarithm of the vapor pressure (ln P_{vap}) and the inverse of the temperature.

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

Clausius–Clapeyron equation

BOILING POINT

VAPOR PRESSURE = EXTERNAL PRESSURE

NORMAL BOILING POINT → external pressure = 1 atm

Lower external pressure → lower boiling point

Once the boiling point of a liquid is reached, additional heating only causes more rapid boiling and it **does not raise the temperature** of the liquid above its boiling point.
Therefore, at 1 atm, boiling water always has a temperature of 100°C.
As long as liquid water is present, its temperature cannot rise above its boiling point.
After all the water has been converted to steam, the temperature of the steam can continue to rise beyond 100°C.

PHASE DIAGRAM

y-axis – pressure (torr)
x-axis – temperature (°C)

Each curve represents a set of temperatures and pressures at which the substance is in equilibrium between the two states on either side of the line:

- VAPORIZATION CURVE or VAPOR PRESSURE CURVE – equilibrium between gas and liquid
- SUBLIMATION CURVE – equilibrium between solid and gas
- FUSION CURVE – equilibrium between solid and liquid

TRIPLE POINT

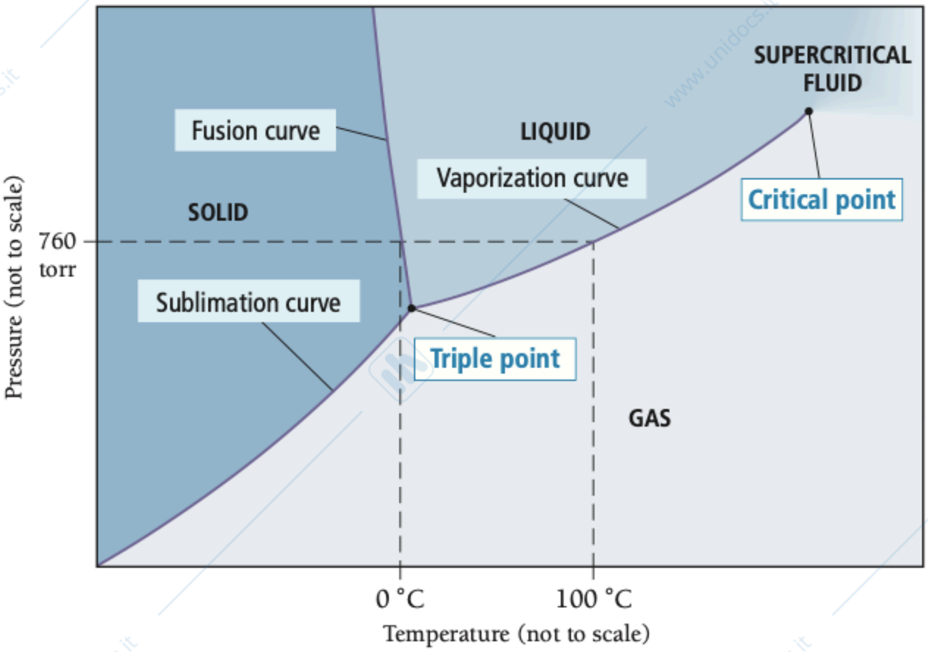
Represents the unique set of conditions at which the three states are equally stable and in equilibrium.
In the phase diagram for water, the triple point occurs at 0.0098 °C and 4.58 torr.

CRITICAL POINT

End point of a phase equilibrium curve when a substance is at its CRITICAL TEMPERATURE and CRITICAL PRESSURE.
In these conditions we have a transition to a **SUPERCRITICAL FLUID**:

- No interface between the gas and the liquid
- Intermediate properties of gases and liquids

Phase Diagram for Water



SOLUTIONS

HOMOGENEOUS MIXTURE OF TWO OR MORE COMPONENTS WHOSE RATIO CAN BE VARIED

SOLVENT:

- Apolar or polar
- In aqueous solutions → *WATER*

SOLUTE

- Molecular or ionic in size (less than 1 nm).
- Can be separated by physical means.
- It remains **uniformly** distributed throughout the solution.
- *ELECTROLYTES*: substances that dissolve in water to form solutions that conduct electricity
  Strong electrolytes: completely dissociate into ions – strong acids and bases.
  Weak electrolytes: not completely dissociated – weak acids and bases.
- *NONELECTROLYTES*: compounds that do not dissociate into ions when dissolved in water.

Miscibility refers to the ability of a liquid solute to dissolve in a liquid solvent.
Solubility is used to mean the ability of a solid solute to dissolve in a liquid solvent.

SOLUBILITY

PROPERTY OF A SOLUTE TO DISSOLVE IN A SOLVENT UNDER STATED CONDITIONS.

AMOUNT OF SOLUTE THAT DISSOLVES IN A GIVEN AMOUNT OF SOLVENT.

The solubility of one substance in another depends on

1) Tendency toward mixing – tend to combine into uniform mixtures.
2) Types of intermolecular forces

→ Solution from nonpolar substances: molecules with little interactions, so they easily form a homogeneous solution.

→ Solution from polar substances: more complex because of intermolecular forces that can increase or decrease the solubility (ion-dipole for ionic compounds)

A solution always forms if the solvent-solute interactions are equal or stronger than the solvent-solvent interactions and the solute-solute interactions.

SOLUBLE: it dissolves in water.
INSOLUBLE: it does not dissolve in water.
Drugs – insoluble because they have to cross the cell membrane that is made of phospholipids

LIKE DISSOLVES LIKE

SOLUTION EQUILIBRIUM

DYNAMIC EQUIBRIUM BETWEEN A SOLID SOLUTE AND THE SOLVENT

Rate of dissolution = Rate of recrystallization

SATURATED SOLUTION – contains dissolved solute in equilibrium with undissolved solute at a certain temperature.
If you add additional solute to a saturated solution, it will not dissolve.

UNSATURATED SOLUTION – contains less solute than the amount needed to saturate the solution.
If you add additional solute to an unsaturated solution, it will dissolve.

SUPERSATURATED SOLUTION – contains more solute than the amount needed to saturate the solution at a particular temperature.
A supersaturated solution is unstable, so, when it is disturbed, the **excess solute crystallizes out** rapidly, returning the solution to a saturated state by releasing heat.

FACTORS THAT AFFECT SOLUBILITY

TEMPERATURE

Solids in liquids: generally, **ENDOTHERMIC PROCESS** → increase of temperature = increase of solubility.

Gases in liquids: **EXOTHERMIC PROCESS** → increase of temperature = decrease of solubility.
Explanation: KMT – KINETIC MOLECULAR THEORY
→ In order to dissolve, the gas molecules must interact with the molecules of the liquid. An increase in temperature decreases the solubility of the gas because it increases the kinetic energy of the gas molecules and thereby decreases their ability to interact with the liquid molecules.

PRESSURE

Changes in pressure have little effect on the solubility of solids in liquids or liquids in liquids.

Changes in pressure have a marked effect on the solubility of gases in liquids.
Explanation: HENRY'S LAW: the solubility of a gas in a liquid is directly proportional to the pressure of that gas above the solution.
E.g. In a sealed can of soda, the CO_2 is maintained in solution by a ***high pressure*** *and it's dissolved. When the can is opened****, the pressure is released and the solubility of*** CO_2 ***decreases****.*

CONCENTRATION OF A SOLUTION

Quantitative expression of the amount of dissolved solute in a particular quantity of solvent.

A dilute solution contains small quantities of solute relative to the amount of solvent
A concentrated solution contains large quantities of solute relative to the amount of solvent.

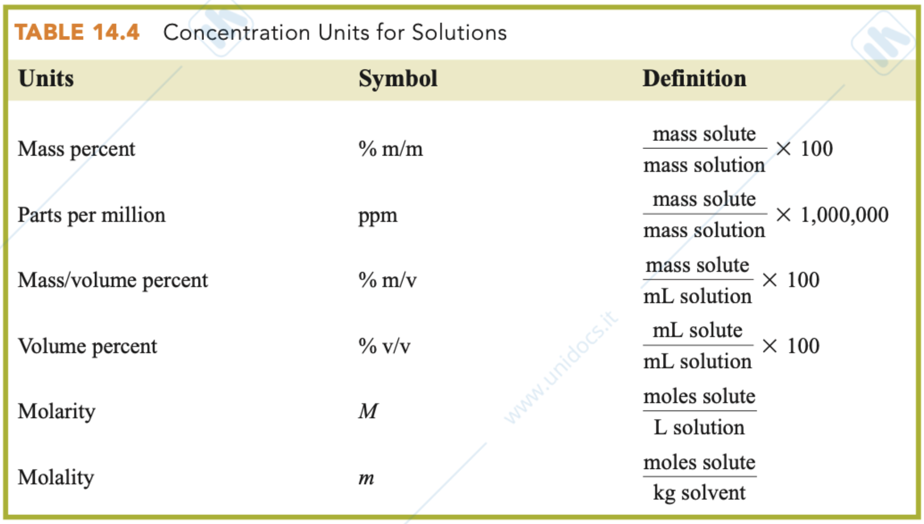
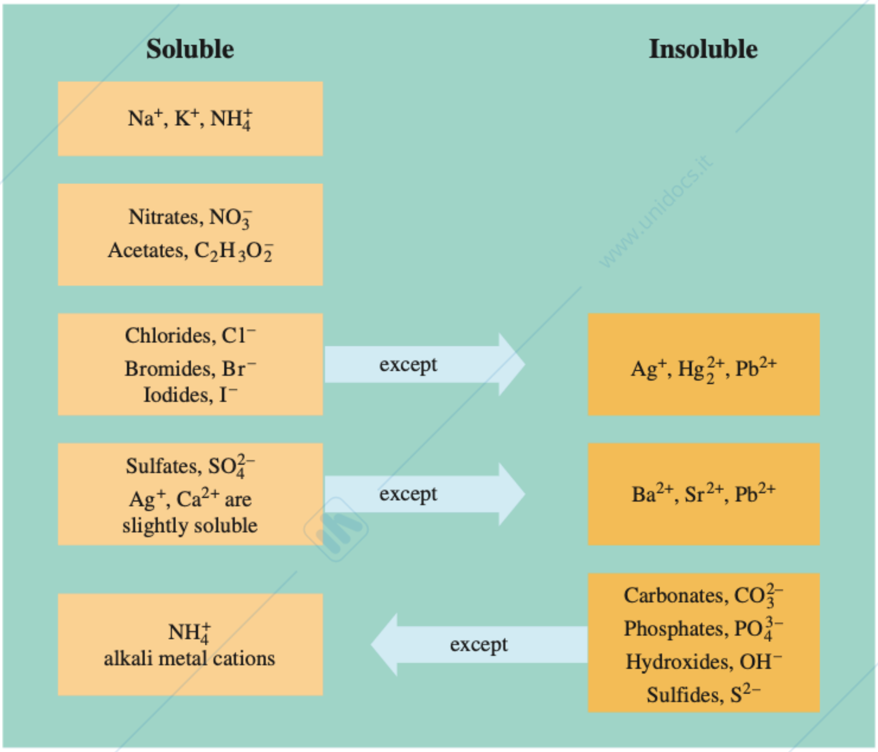


TABLE 14.4 Concentration Units for Solutions

Units	Symbol	Definition
Mass percent	% m/m	$\frac{\text{mass solute}}{\text{mass solution}} \times 100$
Parts per million	ppm	$\frac{\text{mass solute}}{\text{mass solution}} \times 1{,}000{,}000$
Mass/volume percent	% m/v	$\frac{\text{mass solute}}{\text{mL solution}} \times 100$
Volume percent	% v/v	$\frac{\text{mL solute}}{\text{mL solution}} \times 100$
Molarity	M	$\frac{\text{moles solute}}{\text{L solution}}$
Molality	m	$\frac{\text{moles solute}}{\text{kg solvent}}$

SOLUBILITY RULES



RATE OF DISSOLVING SOLIDS

The rate at which a solid dissolves is governed by

1) SIZE OF THE SOLUTE PARTICLES: the rate of dissolving increases as the size of particles decreases, due to the fact that a solid can dissolve only at the surface in contact with the solvent and surface-to-volume ratio increases as size decreases.
2) TEMPERATURE: the rate of dissolving of a solid increases as temperature increases due to kinetic effect: the solvent molecules move more rapidly at higher temperatures and strike the solid surfaces more often.
3) CONCENTRATION OF THE SOLUTION: the rate of dissolving decreases as the concentration of the solution increases.
4) AGITATION OR STIRRING: the rate of dissolving increases if the solution is stirred.
   If the mixture is not stirred the solution becomes more concentrated and the rate of dissolving slows down.
   Stirring brings more solvent into contact with the solid, causing it to dissolve more rapidly.

SOLUBILITY PRODUCT CONSTANT – K_{sp}

EQUILIBRIUM CONSTANT REPRESENTING THE DISSOLUTION OF AN IONIC COMPOUND.

The value of K_{sp} is a measure of the solubility of a compound.

Once we have K_{sp} we can calculate the solubility.

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

	$[Ag^+]$	$[Cl^-]$
Initial	0.00	0.00
Change	$+S$	$+S$
Equil	S	S

$$\begin{aligned} K_{sp} &= [Ag^+][Cl^-] \\ &= S \times S \\ &= S^2 \end{aligned}$$

$$\begin{aligned} S &= \sqrt{K_{sp}} \\ &= \sqrt{1.77 \times 10^{-10}} \\ &= 1.33 \times 10^{-5}\,M \end{aligned}$$

COMMON ION EFFECT

Shift of the equilibrium due to the addition of an ion already contained in the solution.

As Le Chatelier's principle states, the increasing in concentration of one of the species in solution causes the reaction to shift in the opposite direction.

COLLIGATIVE PROPERTIES

PHYSICAL PROPERTIES THAT DEPEND ON THE NUMBER OF PARTICLES DISSOLVED IN SOLUTION AND NOT ON THE TYPE

When you add a **nonvolatile solute** to a solvent, the physical properties of the solution are different from the ones of the pure solvent.

VAPOR PRESSURE LOWERING

Solute-solvent interactions lower the vapor pressure of the solution.
The nonvolatile solute particles interfere with the vaporization of the solvent particles.
RATE OF VAPORIZATION < RATE OF CONDENSATION → need to reach a new equilibrium

Demonstration:
Concentrated solution and a beaker of the pure solvent placed in a sealed container.
→ A concentrated solution has the ability to draw solvent to itself.
→ Over time the pure solvent molecules will vaporize, and they will condense into the solution.
→ The net transfer of solvent from the beaker containing pure solvent to the one containing the solution shows that the vapor pressure of the solution is lower than that of the pure solvent.

Raoult's law quantifies the *VAPOR PRESSURE OF A SOLUTION*:

$$P_{\text{solution}} = \chi_{\text{solvent}} P^{\circ}_{\text{solvent}}$$

x = 1 → pure solvent

Modification of Raoult's law: *VAPOR PRESSURE LOWERING (ΔP)*:

$$\Delta P = P^{\circ}_{\text{solvent}} - P_{\text{solution}}$$

$$\Delta P = P_{solvent} - x_{solvent}\, P^{\circ}{}_{solvent}$$

$x_{solvent} = 1 - x_{solute}$

$$\Delta P = P_{solvent}\,(1 - x_{solvent})$$

$$\Delta P = P_{solvent}\,(1 - 1 - x_{solute})$$

$$\Delta P = i\, P_{solvent}\,(-x_{solute})$$

This last equation indicates that the lowering of the vapor pressure is directly proportional to the mole fraction of the solute.

If the solute is also volatile, both the solvent and the solute contribute to the overall vapor pressure of the solution.
The vapor pressure of each solution component is described by Raoult's law.

$$P_{\text{A}} = \chi_{\text{A}} P^{\circ}_{\text{A}}$$
$$P_{\text{B}} = \chi_{\text{B}} P^{\circ}_{\text{B}}$$

The total pressure above such a solution is the sum of the partial pressures of the components:

$$P_{\text{tot}} = P_{\text{A}} + P_{\text{B}}$$

Raoult's law describes an *IDEAL SOLUTION* – all the intermolecular forces have the same strength.

In a *NONIDEAL SOLUTION*, the solute-solvent interactions are either stronger or weaker than the solvent-solvent interactions, so we can observe some deviations from ideality.

POSITIVE DEVIATIONS:

Solute-solvent interactions are weaker than interactions within pure components.

Solute-solvent particles interact less, so the two components tend to have a higher vapor pressure and to vaporize more easily.

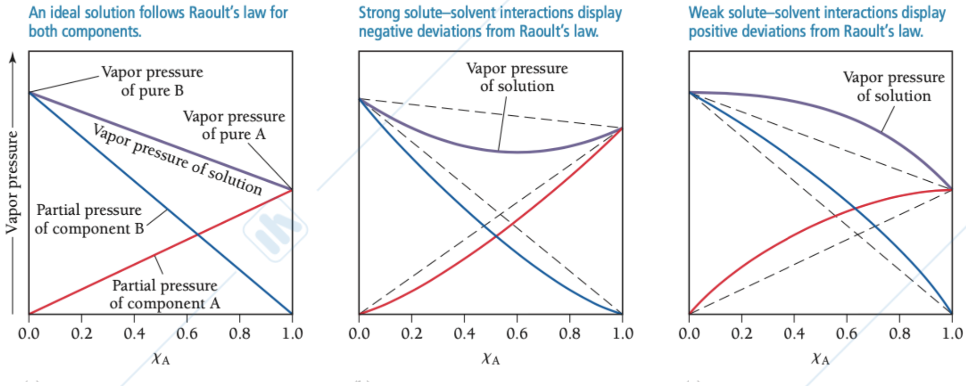
The vapor pressure of the solution will be greater than predicted by Raoult's law.

NEGATIVE DEVIATIONS:

Solute-solvent interactions are stronger than interactions within pure components.

More solute-solvent interactions solute tends to prevent the solvent from vaporizing as readily as it would otherwise.

The vapor pressure of the solution will be less than that predicted by Raoult's law.



FREEZING POINT DEPRESSION

RATE OF DISSOLUTION > RATE OF SOLIDIFICATION → the equilibrium will be reached at a lower temperature.

The tendency of mixing acts in opposite to freezing.

$$\Delta T_f = \boldsymbol{i}\, K_f \times m$$

BOILING POINT ELEVATION

RATE OF CONDENSATION > RATE OF VAPORIZATION → the equilibrium will be reached at a higher temperature.

These variations can be observed by comparing the phase diagrams for a pure solvent and for a solution containing a nonvolatile solute.

They are both consequences of vapor pressure lowering and solute-solvent interactions.

$$\Delta T_b = \boldsymbol{i}\, K_b \times m$$

m – molality → depends on ***mass***, an intrinsic property not influenced by temperature

OSMOTIC PRESSURE

PRESSURE TO APPLY TO THE HYPOTONIC SOLUTION IN ORDER TO STOP THE OSMOTIC FLOW.

OSMOSIS: flow of solvent from a hypotonic solution to a hypertonic one (against concentration gradient) through a semipermeable membrane in order to reach an equilibrium.

SEMIPERMEABLE MEMBRANE: a membrane that selectively allows some substances to pass through but not others.

The solute molecules on one side of the membrane want to spread homogeneously and they impact with the membrane, exerting a pressure.

$$\pi = \boldsymbol{i}\, C\, R\, T$$

C = molarity of the solution

Intravenous solutions (IV) must have osmotic pressures equal to those of body fluids.
These solutions are called isosmotic or isotonic.
Isosmotic saline solution contains 0.9 g NaCl per 100 mL of solution → 0.9% mass/volume

i = van't Hoff coefficient

Need to be taken into account if strong electrolyte solutions are involved because they dissolve.

$$i = \frac{\text{moles of particles in solution}}{\text{moles of formula units dissolved}}$$

$$i = 1 + \alpha\,(\nu - 1)$$

α = dissociation degree → $\frac{dissociated\ moles}{total\ moles}$

ν = number of particles formed
E.g. $NaCl \rightarrow Na^+ + Cl^- \rightarrow \nu = 2$

Van't Hoff factors do not exactly equal expected values because some cations pair with anions, slightly reducing the number of dissociated particles in solution.

WATER

PROPERTIES

- Polar molecule with bent geometry
- Main solvent → aqueous solutions
- Density $_{liquid}$ > Density $_{solid}$

  Unlike other substances, which contract upon freezing, water expands upon freezing. Consequently, ice is less dense than liquid water, which is why ice floats.

K$_w$ → ION PRODUCT CONSTANT

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

Same concentration of H$^+$ and OH$^-$

$$K_w = [H^+][OH^-]$$

The numerical value of K_w is 1.00×10^{-14} for pure water at 25°C,

$$K_w = [H^+][OH^-] = (1.00 \times 10^{-7})(1.00 \times 10^{-7}) = 1.00 \times 10^{-14}$$

$$K_w = [H^+][OH^-] \qquad [H^+] = \frac{K_w}{[OH^-]} \qquad [OH^-] = \frac{K_w}{[H^+]}$$

ACIDS AND BASES

Three definitions – we decide which definition to use according to the reaction under consideration.

ARRHENIUS

Acid: substance that produces H$^+$ ions in aqueous solution

Base: substance that produces OH$^-$ ions in aqueous solution

BRØNSTED–LOWRY

Acid: proton (H$^+$) donor

Base: proton (H$^+$) acceptor

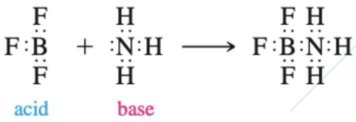
→ Concept of conjugate base/acid

→ H$^+$ is a bare proton and does not exist by itself in an aqueous solution but it combines with a polar water molecule to form **H$_3$O$^+$ - HYDRONIUM ION**.

LEWIS

Base: electron pair donor – it has an unshared pair of electrons

Acid: electron pair acceptor – any substance that will attach itself to or accept a pair of electrons.



POLYPROTIC ACIDS

More than one ionizable proton → more than one equilibrium.

E.g. H_2SO_4 *sulfuric acid* → strong in its first ionizable proton, but weak in its second.

$$H_2SO_4(aq) \longrightarrow H^+(aq) + HSO_4^-(aq)$$

$$HSO_4^-(aq) \rightleftharpoons H^+(aq) + SO_4^{2-}(aq)$$

STRONG ACIDS AND STRONG BASES

Complete ionization

The initial concentration of the acid/base (C_a/C_b) equals the H^+ concetration or OH^-

0.1 HCl *(aq).* → 0.1 H^+ → pH = - log (0.1) = 1.0

0.1 NaOH *(aq)* → 0.1 OH^- → pOH= - log (0.1) = 1.0 → pH= 14 – 1= 13

WEAK ACIDS AND WEAK BASES

IONIZATION CONSTANTS – indicate the relative strength of a weak electrolyte

The higher the ionization constant, the stronger the electrolyte.

K_a – acid ionization constant

K_b – base ionization constant

$$K_a \times K_b = K_w$$

ICE Table for Acetic Acid

Ionization:	$CH_3CO_2H + H_2O \rightleftharpoons$	H_3O^+ +	$CH_3CO_2^-$
Initial [M]	0.100	0.00	0.00
Change [M]	$-x$	$+x$	$+x$
Equilm. [M]	$(0.100 - x)$	x	x

$$K_a = \frac{[H_3O^+][CH_3CO_2^-]}{[CH_3COOH]} = \frac{x^2}{(0.100 - x)} = 1.8 \times 10^{-5}$$

$$K_a = \frac{[H^+]^2}{C_a}$$

$$If \ \frac{K_a}{C_a} < 5\% \rightarrow 0.100 - x = 0.100$$

PERCENT IONIZATION

The more dilute the concentration, the higher the ionization.

Explanation: Le Chatelier → even if the concentration of the acid is small, the system tends to reach the equilibrium expressed by the K_a dissociating it more.

$$\text{Percent ionization} = \frac{\text{concentration of ionized acid}}{\text{initial concentration of acid}} \times 100\% = \frac{[H_3O^+]_{equil}}{[HA]_{init}} \times 100\%$$

$$\%\ ionization \propto \frac{1}{initial\ concentration\ of\ acid}$$

α – **DEGREE OF DISSOCIATION** *or* **DISSOCIATION COEFFICIENT**

$$\mathbf{0 < \alpha < 1}$$

α = 1 → strong electrolyte

$$\alpha = \frac{amount\ of\ solute\ dissociate}{mole}$$

OSTWALD'S LAW – LAW OF DILUTION

Relationship between the K and the degree of dissociation α of a weak electrolyte.

The law explains why increasing the dilution, the dissociation degree increases.

As c (initial concentration) decreases, α increases and K stays constant

$$AB \leftrightarrow A + B$$

$$AB = c\,(1 - \alpha)$$

$$A = c\,\alpha$$

$$B = c\,\alpha$$

$$K = \frac{c^2\alpha^2}{c\,(1-\alpha)}$$

$$K = \frac{c\,\alpha^2}{(1-\alpha)}$$

STRONG ACID – STRONG BASE

NEUTRALIZATION

$HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$

The only reaction that occurs is between H^+ and OH^-.

Na^+ and Cl^- ions are *spectator ions* because they do not take part in the neutralization reaction.

NaCl → neutral salt (doesn't alter the pH of the solution)

STRONG ACID – WEAK BASE

ACIDIC SALT → ACIDIC IDROLYSIS

$NH_3 + HCl \rightarrow NH_4Cl$

$NH_4Cl \rightarrow NH_4^+ + Cl^-$

$NH_4^+ + H_2O \leftrightarrow NH_3 + H_3O^+$

STRONG BASE – WEAK ACID

BASIC SALT → BASIC IDROLYSIS

$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$

$CH_3COONa \rightarrow CH_3COO^- + Na^+$

$CH_3COO^- + H_2O \leftrightarrow CH_3COOH + OH^-$

WEAK BASE – WEAK ACID

Salt either acidic or basic, depending on the relative strength of the acid and the base.

$K_a > K_b$ → acidic

$K_a < K_b$ → basic

The conjugate species of a strong electrolyte is so weak that cannot react with water.

BUFFER SOLUTIONS

SOLUTION THAT RESISTS pH CHANGE

COUNTERACTS THE ADDING OF SMALL QUANTITIES OF ACIDS OR BASES.

Components:

a) Weak acid and its own salt
b) Weak base and its own salt

HENDERSON-HASSELBACH EQUATION

To calculate the pH of the buffer

$$pH = pK_a + \log \frac{C_s}{C_a}$$

BUFFER RANGE OF VALIDITY

$$10^{-1} < \frac{C_s}{C_a} < 10 \qquad pK_a^{-1} < pH_{buffer} < pK_a$$

Max power of buffer: pH = pK$_a$

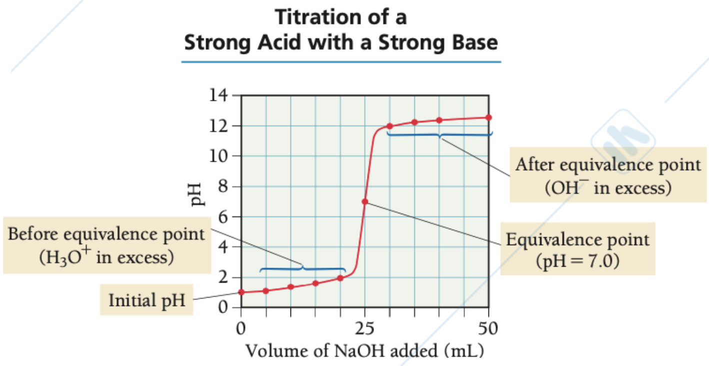
Buffer capacity increases with increasing the concentrations of the buffer components.

As the ratio of the buffer components gets closer to 1, the overall capacity of the buffer becomes greater.

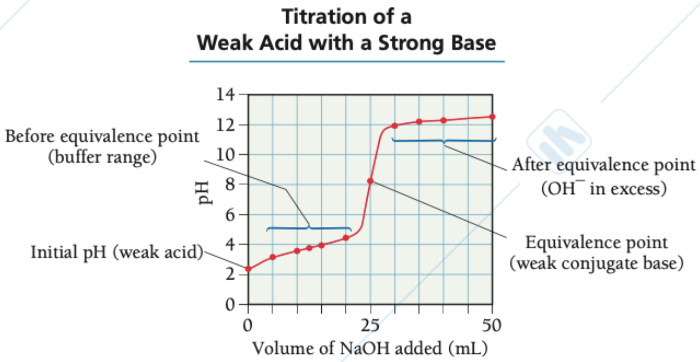
EQUIVALENT POINT: same number of moles of acid and base

Strong acid – strong base → pH 7

HALF-EQUIVALENT POINT: same number of moles of the buffer components → pH = pKa.



Sigmoid curve



TITRATION: technique of analytical chemistry used to determine the concentration of an unknown species and describes any possible condition of solution.