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Topic 3.10: Solubility

Revision Notes · AP Chemistry

UNIT 3 · PROPERTIES OF SUBSTANCES AND MIXTURES

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Dissolving Is a Contest Between Three Sets of Attractions

A solution forms when solute particles separate and disperse among solvent particles, and whether it forms depends on three sets of attractions.

Separating solute particles costs energy, and so does separating solvent particles to make room. Forming new solute-solvent attractions releases energy.

Dissolving is favoured when the released energy can pay both costs, helped by the entropy increase as ordered particles disperse.

Solubility is the amount that dissolves at equilibrium under stated conditions, not the rate of dissolving: stirring and crushing speed up dissolving without changing how much dissolves in the end.

Like Dissolves Like: Matching the Intermolecular Forces

Substances with similar intermolecular forces tend to dissolve in one another: polar solvents dissolve ionic and polar solutes because the new attractions rival the ones broken.

Hydrogen bonding makes methanol and water miscible in all proportions: the hydrogen bonds they form with each other match those they give up. Vitamin C carries several hydroxyl (-OH) groups and dissolves in water. Vitamin A is mostly hydrocarbon, so it dissolves in nonpolar fat instead.

Nonpolar solutes dissolve in nonpolar solvents, where dispersion forces match: iodine (I_2) in hexane and in carbon tetrachloride, octane in benzene.

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Chain length shifts the balance. Methanol and ethanol are miscible with water, but 1-butanol dissolves only about 7.9 g per 100 g of water and 1-hexanol only about 0.60 g: as the chain grows, the single -OH group is a smaller share of the molecule and nonpolar character wins.

The rule is a guideline, not a guarantee: the overall energy and entropy balance decides, which is why some ionic compounds refuse water entirely.

The Energy Balance for Ionic Solids: Lattice Against Hydration

For an ionic solid, the separation step is the lattice energy: the energy needed to pull the crystal apart into gaseous ions, large and positive. Surrounding dissolved particles with solvent is called solvation, or hydration when the solvent is water.

Hydration works the other way: water molecules cluster around ions, oxygen ends toward cations and hydrogen ends toward anions, and forming those ion-dipole attractions releases energy, so hydration enthalpies are negative.

Small, highly charged ions are hydrated most strongly, their charge being concentrated: the hydration enthalpy of Mg^{2+} is about -1,922 kJ/mol, roughly 4.7 times that of Na^{+} at about -406 kJ/mol. Such ions also build the strongest lattices, so both sides of the balance grow together.

Silver chloride shows the balance failing: its lattice attractions are so strong that hydration cannot pay for breaking them, so a saturated solution holds only about 0.0019 g per litre, against about 360 g per litre for sodium chloride, a factor of about 190,000.

All nitrates are soluble, so $AgNO_3$ and KNO_3 dissolve freely. Chlorides are soluble except silver chloride and a few others; sulfates are soluble except $BaSO_4$; carbonates and hydroxides are generally insoluble except Group 1 and ammonium compounds.

Entropy: Why Endothermic Dissolving Still Happens

A crystal is highly ordered; its ions dispersed through a solution are far less so, so dissolving usually increases entropy.

That increase can drive an endothermic process. Ammonium nitrate, with an enthalpy of solution of +25.7 kJ/mol, still dissolves readily, and the mixture feels cold because the process takes in heat: the instant cold pack works this way.

When enthalpy and entropy both oppose dissolving, the compound stays undissolved: the two together decide, never enthalpy alone.

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Saturated, Unsaturated and Supersaturated

An unsaturated solution holds less solute than the equilibrium amount, so more can still dissolve. A saturated solution holds the maximum amount at that temperature.

A saturated solution in contact with undissolved solid is a dynamic equilibrium. Ions leave the solid and crystallize back onto it at equal rates, so concentrations stay constant even though particles keep exchanging. For a sparingly soluble salt this is written $AgCl(s) \rightleftharpoons Ag^{+}(aq) + Cl^{-}(aq)$.

A supersaturated solution holds more than the equilibrium amount, and is metastable: undisturbed it can persist, but a seed crystal gives the excess a surface to build on and it crystallizes out rapidly, as in sodium acetate heat packs.

Temperature and Pressure Pull Differently on Solids and Gases

Most solid solutes dissolve better as temperature rises: for endothermic dissolving, heat acts like a reactant, so warming shifts the balance toward dissolving. The effect tracks the enthalpy of solution: the KNO_3 curve climbs steeply, while sodium chloride, its enthalpy of solution close to zero, barely changes.

Gases behave the opposite way: raising the temperature lowers gas solubility, because faster-moving dissolved particles escape more easily, so a warm bottle of soda goes flat faster than a cold one.

Pressure matters almost only for gases: by Henry's law, the concentration of a dissolved gas is proportional to its partial pressure above the liquid, while pressure changes barely affect solids and liquids.

Worked Examples

> **Example 1: The energy cycle for sodium chloride. Separating the lattice takes +787 kJ/mol; hydration releases 406 kJ/mol for Na^{+} and 378 kJ/mol for Cl^{-}, totalling -784 kJ/mol. The enthalpy of solution is 787 - 784 = +3 kJ/mol, matching the measured value of about +3.9 kJ/mol. The near tie explains the almost unchanged temperature on dissolving, and a solubility rising only slightly, from about 36 g per 100 g of water at 25 °C to about 40 g at 100 °C.**

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Example 2: Reading the KNO_3 solubility curve. KNO_3 dissolves 110 g per 100 g of water at 60 °C and 31.6 g per 100 g at 20 °C. A saturated solution at 60 °C holds 110 g; cooled to 20 °C it can hold only 31.6 g, so 110 - 31.6 = 78.4 g crystallizes out. Warmed again to 40 °C, where the solubility is 63.9 g per 100 g, some solid redissolves: 63.9 - 31.6 = 32.3 g redissolves and 78.4 - 32.3 = 46.1 g stays solid.

Example 3: Henry's law and a bottle of soda. The Henry's law constant for CO_2 in water at 25 °C is 3.4×10^{-2} mol per litre per atm. Sealed under a CO_2 partial pressure of 3.0 atm, the concentration is $3.4 \times 10^{-2} \times 3.0 = 0.102$ mol/L, which is $0.102 \times 44.01 = 4.49$ g of CO_2 per litre. Opened to air, where the CO_2 partial pressure is only 4.0×10^{-4} atm, the equilibrium concentration falls to $3.4 \times 10^{-2} \times 4.0 \times 10^{-4} = 1.36 \times 10^{-5}$ mol/L. About 99.99 percent of the dissolved gas must escape, so the drink goes flat.

Traps That Cost Marks in Topic 3.10

Like dissolves like guarantees dissolving. It is a guideline about matching forces; the energy and entropy balance decides, which is why ionic AgCl stays undissolved in polar water.

In a saturated solution, dissolving has stopped. Dissolving and crystallizing continue at equal rates; concentrations are constant because the rates match, not because nothing happens.

Pressure raises the solubility of every solute. Pressure barely affects solids and liquids; gas solubility is what follows the partial pressure above the liquid.

Heating a solvent always increases solubility. For gases the opposite holds: a warmer liquid holds less dissolved gas.

An endothermic process cannot dissolve anything. Ammonium nitrate absorbs 25.7 kJ/mol and still dissolves, driven by entropy. The cold you feel is the absorbed heat.

Stirring and grinding increase solubility. They increase the rate of dissolving only. The equilibrium amount dissolved is unchanged.

Hydration energy is positive because it is large. Forming attractions always releases energy, so hydration enthalpy is negative. Separating the lattice is the step that costs energy, with the positive sign.

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Key Relationships to Remember

- Dissolving: separating solute particles and solvent particles (both cost energy) plus forming solute-solvent attractions (releases energy); the balance, with entropy, decides solubility
- Like dissolves like: solute and solvent with similar intermolecular forces tend to mix; polar and ionic in polar solvents, nonpolar in nonpolar solvents
- Ionic solids: soluble when hydration energy can pay the lattice energy; small, highly charged ions have the largest hydration enthalpies and the strongest lattices
- Entropy: dispersing ordered particles increases disorder and can drive endothermic dissolving, as in cold packs
- Saturated solution in contact with solid: dissolving and crystallizing at equal rates, concentrations constant; supersaturated solutions are metastable and crystallize when seeded
- Temperature: raises the solubility of most solids, lowers the solubility of gases; pressure changes gas solubility in proportion to partial pressure (Henry's law) and barely affects solids or liquids

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