

AP CHEMISTRY STUDY GUIDE

184 High-Yield Concepts

Advanced Placement Course | College Board CED-aligned

- All 9 CED units: Atomic Structure to Thermodynamics Applications
 - Every concept: explanation + high-yield exam tip + example
- Stoichiometry, equilibrium, kinetics, acids & bases, electrochemistry
 - Perfect for the AP Chemistry exam in May

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How to Use This Guide

This guide condenses the AP Chemistry course and exam description into high-yield concepts. It is not a textbook replacement -- it is the fastest way to review everything the exam covers and to target your weak units.

The AP Chemistry exam is 60 minutes of 60 multiple-choice questions, then 105 minutes of 7 free-response questions (3 long, 4 short). A scientific or graphing calculator is allowed for the entire exam. The nine units below map directly to the College Board Course and Exam Description.

How to use the concepts

- Each concept = term + concise explanation + high-yield exam tip (+ example where useful).
- First pass: read every concept in order. Underline anything unfamiliar.
- Second pass: focus only on the concepts you underlined.
- Two weeks before the exam: rapid-review every tip line (they are the highest-yield).
- Use the Table of Contents to jump straight to your weakest units.

Table of Contents

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Total: 184 high-yield concepts

How to use the TOC: work through the units in order on your first pass, then jump back to your weakest units for review. Each concept includes an Explanation, a high-yield exam tip, and where useful an Example. Mark the concepts you miss with a small dot in the margin and revisit them 48 hours later.

Unit 1: Atomic Structure & Properties

7-9% of the exam. Moles, mass spectrometry, Coulomb's law, and electron configuration.

1 Moles & Molar Mass

Explanation: The mole is Avogadro's number (6.022×10^{23}) of particles. Molar mass = grams per mole of a substance, numerically equal to atomic/molecular mass in amu. Conversions: mass / molar mass = moles; moles x Avogadro's number = particles.

AP Chem Tip: *Mole conversions are the foundation of every stoichiometry problem. Convert mass $\rightarrow$ moles $\rightarrow$ particles (or molecules/atoms) using molar mass and Avogadro's number. Always track units.*

Example: 18.0 g of H₂O = 1.00 mol (molar mass 18.0 g/mol) = 6.022×10^{23} molecules of water.

2 Mass Spectrometry

Explanation: Mass spectrometry measures the mass-to-charge ratio (m/z) of ions, giving the relative abundance of isotopes and molecular fragments. Atomic masses on the periodic table are weighted averages of isotopes.

AP Chem Tip: *The average atomic mass = sum of (isotope mass x fractional abundance). A mass spectrum peak height reflects abundance; peak position reflects mass.*

Example: Chlorine has two isotopes, ³⁵Cl (75.8%) and ³⁷Cl (24.2%): average = $(35 \times 0.758) + (37 \times 0.242) = 35.5$ amu.

3 Elemental Composition & Empirical Formula

Explanation: Empirical formula = simplest whole-number ratio of atoms. Molecular formula = actual number of atoms (a multiple of the empirical formula). Percent composition by mass can be converted to empirical formulas.

AP Chem Tip: *To find an empirical formula: assume 100 g, convert each % to moles, divide by the smallest, and multiply to get whole numbers. Molecular mass / empirical mass = the multiplier for the molecular formula.*

Example: A compound is 40.0% C, 6.7% H, 53.3% O: moles give C₁H₂O₁ (empirical). If molar mass is 90 g/mol, the molecular formula is C₃H₆O₃ (x3).

4 Coulomb's Law

Explanation: Electrostatic force $F = k \cdot q_1 \cdot q_2 / r^2$. Force increases with charge magnitude and decreases with distance squared. Explains periodic trends: more protons (higher Z) pull electrons in tighter; electron shielding reduces effective nuclear charge.

AP Chem Tip: *Coulomb's law drives ALL periodic trends. Higher effective nuclear charge (Z_{eff}) = smaller atomic radius, higher ionization energy, higher electronegativity. More shielding = larger radius, lower IE.*

Example: F⁻ (9 protons, 10 electrons) is smaller than O²⁻ (8 protons, 10 electrons) -- same electron count, more protons, stronger pull.

5 Atomic Radius

Explanation: Atomic radius increases DOWN a group (new shells added) and DECREASES across a period (more protons pull electrons in, Z_{eff} increases). Cations are smaller than their atoms; anions are larger.

AP Chem Tip: *Trend: radius increases down, decreases right. Ion size: cations < neutral atom < anions. Across a period the same shell fills while protons increase, shrinking the radius.*

Example: Radius order: K > Na > Mg > Al (down and right rules). Fe²⁺ > Fe³⁺ (more positive charge = smaller).

6 Ionization Energy

Explanation: First ionization energy = energy to remove the first electron. IE increases across a period (higher Z_{eff}) and decreases down a group (more shielding, larger radius). Removing subsequent electrons takes more energy (each removal is harder).

AP Chem Tip: *IE trend: increases right, decreases down. Big jumps in IE occur when removing a core (inner-shell) electron after a filled valence shell -- e.g., Na ($IE_2 \gg IE_1$).*

Example: Na $\rightarrow$ Na⁺ removes an easy 3s electron (496 kJ/mol); removing a second electron (core, 2p) costs 4,562 kJ/mol -- a huge jump.

7 Electronegativity

Explanation: Electronegativity = ability of an atom to attract shared electrons in a bond. Increases across a period (F is highest) and decreases down a group. Used to predict bond polarity (ionic vs polar covalent vs nonpolar covalent).

AP Chem Tip: *F > O > N > Cl electronegativity ladder. A difference > ~1.7-2.0 suggests ionic character; 0.4-1.7 polar covalent; < 0.4 mostly nonpolar covalent.*

Example: Na-Cl: difference 2.1 -> ionic. H-Cl: 0.9 -> polar covalent. C-H: 0.4 -> nonpolar covalent.

8 Electron Configuration

Explanation: Electrons fill orbitals by the Aufbau principle (lowest energy first), Hund's rule (one electron per orbital before pairing), and Pauli exclusion (max 2 electrons per orbital, opposite spins). Order: 1s 2s 2p 3s 3p 4s 3d 4p...

AP Chem Tip: *Know the filling order (4s fills before 3d). Hund's rule: the p3 configuration (e.g., N) has 3 unpaired electrons. Exceptions: Cr and Cu (d4 and d9 prefer d5 and d10 by promoting an s electron).*

Example: Nitrogen: 1s2 2s2 2p3 -- three unpaired 2p electrons. Chromium is [Ar]4s1 3d5 (not 4s2 3d4).

9 Orbital Diagrams & Valence Electrons

Explanation: Orbital diagrams show electrons in boxes (arrows = spins). Valence electrons = outermost shell electrons, responsible for bonding and periodic properties. Core electrons = inner shells.

AP Chem Tip: *Valence electrons determine chemistry: same group = same valence count. For transition metals, the d electrons also participate. Count valence electrons for Lewis structures.*

Example: Oxygen (2s2 2p4) has 6 valence electrons. All halogens have 7 valence electrons.

10 Photoelectron Spectroscopy (PES)

Explanation: PES measures the ionization energies of electrons, producing peaks at binding energies. Peak position = subshell (1s farthest left), peak height = number of electrons in that subshell.

AP Chem Tip: *A PES spectrum identifies an element: 2 electrons in 1s, 2 in 2s, 6 in 2p -> element with 10 electrons = neon. Peak positions reflect Zeff (core electrons have higher binding energy).*

Example: A PES with peaks at ~280, ~30, ~8 (eV) with heights 2:2:6 is carbon (1s2 2s2 2p2... check counts carefully).

11 Periodic Trends & Zeff

Explanation: Effective nuclear charge (Zeff) = nuclear charge minus shielding. Increases across a period (more protons, same shells) and stays similar down a group (more shells add shielding). Zeff explains radius, IE, and electronegativity trends.

AP Chem Tip: *Zeff is the unifying concept: higher Zeff = electrons held tighter = smaller atom, higher IE. Shielding by inner electrons reduces Zeff.*

Example: Across period 3 (Na -> Cl), Zeff rises from +1 to +7, so radius shrinks and IE rises.

12 Ionic Bonding Basics

Explanation: Ionic bonds form by electron transfer between a metal (low IE) and a nonmetal (high EA), creating ions held by electrostatic attraction. Ionic compounds are crystalline solids with high melting points, hard and brittle, conductive when molten or dissolved.

AP Chem Tip: *Ionic compounds: high melting/boiling points, hard, brittle, conduct electricity ONLY in solution or molten (ions must be mobile). No discrete molecules -- formula units.*

Example: NaCl melts at 801 C; solid NaCl does not conduct, but molten NaCl does.

13 Covalent Bonding Basics

Explanation: Covalent bonds form by electron sharing between nonmetals. Pure (nonpolar) covalent: equal sharing. Polar covalent: unequal sharing (electronegativity difference). Molecules have discrete, independent units with low melting points.

AP Chem Tip: *Covalent compounds: low melting points, often gases/liquids/solids that do NOT conduct electricity. Polarity depends on electronegativity difference and molecular shape.*

Example: H2O is polar covalent (O pulls electrons); CH4 has polar C-H bonds but is a nonpolar molecule (symmetry).

14 Lewis Structures & Octet Rule

Explanation: Lewis structures show valence electrons as dots and shared pairs as lines. Atoms tend to gain, lose, or share electrons to achieve 8 valence electrons (octet rule). Exceptions: H (2), Be (4), B (6), and expanded octets in period 3+ (P, S, Xe).

AP Chem Tip: Count valence electrons first, draw single bonds, then distribute remaining electrons to satisfy octets. Expanded octets possible for elements with d orbitals (period 3 and beyond).

Example: SF₆ has 6 bonds around S (12 electrons) -- an expanded octet. BF₃ has only 6 electrons around B.

15 Formal Charge & Resonance

Explanation: Formal charge = valence electrons - (lone pairs + 1/2 bonding electrons). Lowest formal charges (closest to zero) give the best structure; negative formal charges go on the most electronegative atoms. Resonance: multiple valid Lewis structures (delocalized electrons).

AP Chem Tip: Resonance structures differ only in electron positions, not atom positions. The real molecule is a hybrid (e.g., O₃, NO₃⁻, benzene). Minimize formal charge; put - on electronegative atoms.

Example: Ozone (O₃) has two resonance forms; the actual O-O bonds are identical (bond order 1.5).

16 VSEPR Theory

Explanation: Valence Shell Electron Pair Repulsion: electron pairs (bonding and lone) arrange to minimize repulsion. Shapes: linear (2), trigonal planar (3), tetrahedral (4), trigonal bipyramidal (5), octahedral (6). Lone pairs compress bond angles.

AP Chem Tip: Determine electron geometry from electron domains, then molecular shape from atoms only. Lone pairs reduce bond angles ~2.5 degrees each (e.g., H₂O 104.5 instead of 109.5).

Example: NH₃: 4 domains, 1 lone pair -> trigonal pyramidal (107). CO₂: 2 domains -> linear (180).

17 Molecular Polarity

Explanation: A molecule is polar if it has polar bonds AND an unsymmetrical shape (dipoles don't cancel). Symmetric molecules with identical bonds (CO₂, CCl₄, BF₃) are nonpolar even with polar bonds.

AP Chem Tip: Check two things: polar bonds (electronegativity difference) and geometry. If the dipoles cancel by symmetry, the molecule is nonpolar.

Example: CO₂ is linear with C=O dipoles canceling -> nonpolar. H₂O is bent, dipoles add -> polar.

18 Bond Order, Length & Energy

Explanation: Bond order = number of shared electron pairs (single = 1, double = 2, triple = 3). Higher bond order = shorter bond, stronger bond, higher bond energy. Bond length: triple < double < single.

AP Chem Tip: Triple bonds are shortest and strongest. In resonance, bond order is fractional (e.g., benzene C-C = 1.5). Know the order: single > double > triple in length (reverse in strength).

Example: C=C (614 kJ/mol, 134 pm) vs C-C (348 kJ/mol, 154 pm): double bond shorter and stronger.

19 Metallic Bonding

Explanation: Metals consist of cations in a 'sea' of delocalized valence electrons. This electron sea explains conductivity (both electrical and thermal), malleability (atoms slide without breaking bonds), ductility, and luster.

AP Chem Tip: The electron sea model explains metal properties: mobile electrons conduct, and layers can slide (malleable/ductile) because the electron sea re-forms bonds.

Example: Copper wire bends without breaking (malleable) and conducts electricity (delocalized electrons).

20 Isotopes & Atomic Mass

Explanation: Isotopes are atoms of the same element with different neutron numbers (same Z, different A). The periodic table atomic mass is the weighted average of naturally occurring isotopes.

AP Chem Tip: Weighted average formula: sum of (isotopic mass x abundance). Mass spec data gives the abundances.

Example: Carbon-12 (98.9%) and carbon-13 (1.1%) average to 12.01 amu on the periodic table.

Unit 2: Molecular & Ionic Compound Structure

7-9% of the exam. Bond types, Lewis structures, VSEPR, and hybridization.

21 Chemical Bonds Overview

Explanation: Ionic: transfer (metal + nonmetal). Covalent: sharing (nonmetal + nonmetal). Metallic: electron sea. Bond character depends on electronegativity difference.

AP Chem Tip: Classify by electronegativity difference: large $\rightarrow$ ionic, small $\rightarrow$ covalent. The bond type continuum: nonpolar covalent $<$ polar covalent $<$ ionic.

Example: KCl (2.2 difference) ionic; HCl (0.9) polar covalent; Cl₂ (0) nonpolar covalent.

22 Lattice Energy

Explanation: Lattice energy = energy released when gaseous ions form a solid lattice. Increases with ion charge and decreases with ion size (Coulomb's law). Higher lattice energy = higher melting point.

AP Chem Tip: Lattice energy order: MgO (2+/2-) $>$ NaCl (1+/1-); LiF $>$ KBr (smaller ions = stronger). More charge and smaller size = stronger ionic lattice.

Example: MgO melts at 2,852 C vs NaCl at 801 C -- because of the 2+ and 2- charges in MgO.

23 Lewis Structures: Expanded Octets

Explanation: Period 3+ elements (P, S, Cl, Xe) can have more than 8 valence electrons (empty d orbitals). Common: SF₄, SF₆, PCl₅, XeF₄, SO₄²⁻.

AP Chem Tip: Expanded octets only for elements in period 3 and beyond. Never give C, N, O, or F more than 8.

Example: SF₆ (12 electrons around S) and XeF₄ (12 around Xe) both violate the octet but are valid.

24 VSEPR: Electron vs Molecular Geometry

Explanation: Electron geometry counts ALL electron domains (bonds + lone pairs). Molecular geometry counts only atoms. A lone pair changes the molecular shape (e.g., tetrahedral electron $\rightarrow$ trigonal pyramidal or bent).

AP Chem Tip: Chart: 4 domains $\rightarrow$ tetrahedral electron; 0 lone = tetrahedral, 1 lone = trigonal pyramidal, 2 lone = bent. Same for 2 (linear), 3 (trigonal planar / bent).

Example: H₂O: 4 domains, 2 lone pairs $\rightarrow$ tetrahedral electron geometry, bent molecular geometry.

25 Hybridization

Explanation: Atomic orbitals mix to form hybrid orbitals: sp (2 domains, linear), sp² (3 domains, trigonal planar), sp³ (4 domains, tetrahedral), sp³d (5), sp³d² (6). Pi bonds come from unhybridized p orbitals.

AP Chem Tip: Count electron domains $\rightarrow$ hybridization: 2 = sp, 3 = sp², 4 = sp³. Double/triple bonds do NOT add domains. In ethene (C₂H₄), each C is sp² with one pi bond.

Example: CH₄: 4 domains $\rightarrow$ sp³. C₂H₄: each C has 3 domains $\rightarrow$ sp² + 1 pi bond. C₂H₂: 2 domains $\rightarrow$ sp + 2 pi bonds.

26 Sigma & Pi Bonds

Explanation: Sigma (sigma) bonds: head-on overlap, all single bonds have one. Pi (pi) bonds: side-by-side p-orbital overlap, present in double (1 pi) and triple (2 pi) bonds. Pi bonds are weaker and cannot rotate freely.

AP Chem Tip: Single = 1 sigma. Double = 1 sigma + 1 pi. Triple = 1 sigma + 2 pi. Rotation around a double bond is restricted (cis/trans isomerism).

Example: In N₂ (triple bond): 1 sigma + 2 pi. Restricted rotation around C=C explains cis-trans isomers.

27 Polarity & Dipole Moments

Explanation: Bond polarity depends on electronegativity difference; molecular polarity depends on symmetry. Dipole moment = vector sum of bond dipoles. A polar molecule has a net dipole.

AP Chem Tip: Symmetric molecules (CO₂, BF₃, CCl₄, CH₄) are nonpolar. Bent and trigonal pyramidal molecules with polar bonds (H₂O, NH₃) are polar.

Example: BF₃ is trigonal planar with dipoles canceling (nonpolar); NH₃ is trigonal pyramidal (polar).

28 Bond Enthalpy & Reaction Energy

Explanation: Bond enthalpy = energy to break 1 mole of bonds in the gas phase. $\Delta H_{\text{reaction}} = \sum(\text{bonds broken}) - \sum(\text{bonds formed})$. Breaking absorbs energy; forming releases energy.

AP Chem Tip: $\Delta H = \text{bonds broken} - \text{bonds formed}$ (using bond enthalpies). This is an estimate; formation enthalpies are more accurate.

Example: For $\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl}$: broken = H-H (436) + Cl-Cl (242) = 678; formed = $2 \times \text{H-Cl}$ (2×431) = 862; $\Delta H = 678 - 862 = -184 \text{ kJ}$ (exothermic).

29 Ionic vs Covalent Properties

Explanation: Ionic: high melting points, brittle solids, conduct when molten/dissolved, no molecules. Covalent (molecular): low melting points, soft, poor conductors, discrete molecules.

AP Chem Tip: Test question: 'which compound conducts electricity when molten?' -- the ionic one (mobile ions). Molecular compounds generally don't conduct.

Example: NaCl (ionic) melts at 801 C and conducts when molten; sugar (molecular) melts low and never conducts.

30 Polyatomic Ions & Naming

Explanation: Polyatomic ions are covalently bonded groups with a net charge: NH_4^+ , NO_3^- , SO_4^{2-} , CO_3^{2-} , PO_4^{3-} , OH^- . Naming: -ate (more O) vs -ite (fewer O); per- (most O) and hypo- (least O).

AP Chem Tip: Memorize the common polyatomic ions -- they appear constantly. Perchlorate > chlorate > chlorite > hypochlorite for the ClO_x series.

Example: ClO_4^- perchlorate, ClO_3^- chlorate, ClO_2^- chlorite, ClO^- hypochlorite. NO_3^- nitrate, NO_2^- nitrite.

31 Crystal Structures

Explanation: Ionic solids form crystal lattices (e.g., NaCl face-centered cubic, CsCl simple cubic). Lattice arrangement depends on ion sizes and charge balance.

AP Chem Tip: NaCl: each Na^+ surrounded by 6 Cl^- (octahedral). The ratio of ions maintains overall neutrality in the formula unit.

Example: In NaCl, the coordination number of each ion is 6. In CsCl (larger Cs^+), it is 8.

32 Ionic Radii & Lattice Trends

Explanation: Cation radius < parent atom (lost shell/electrons); anion radius > parent atom (gained electrons, repulsion). Smaller ions and higher charges give higher lattice energy.

AP Chem Tip: Isoelectronic series: $\text{O}^{2-} > \text{F}^- > \text{Na}^+ > \text{Mg}^{2+} > \text{Al}^{3+}$ (same electrons, more protons = smaller).

Example: In the isoelectronic series Ne: O^{2-} (8p) is largest, Al^{3+} (13p) is smallest.

33 Resonance & Delocalization

Explanation: Resonance delocalizes electrons over multiple atoms, lowering energy and stabilizing the species. Delocalized electrons explain bond-length equivalence (all bonds same length in resonance hybrids).

AP Chem Tip: More resonance structures = more stable. Delocalized charge (e.g., carboxylate anion, benzene) is very stable. The resonance hybrid is more stable than any single structure.

Example: The carbonate ion (CO_3^{2-}) has 3 equivalent resonance structures; all C-O bonds are identical (1.33 order).

34 Exceptions to the Octet

Explanation: Incomplete octets: Be (BeCl_2), B (BF_3 , often accept a lone pair to complete). Expanded octets: P, S, Xe. Odd-electron species: NO, NO_2 .

AP Chem Tip: BF_3 is an electron-pair acceptor (Lewis acid) because B has only 6 electrons. NO_2 has 17 valence electrons (odd).

Example: BF_3 reacts with NH_3 because B needs electrons (Lewis acid-base). NO (nitric oxide) is a free radical with an unpaired electron.

35 Molecular Orbital Basics

Explanation: Molecular orbitals form by combining atomic orbitals: bonding (lower energy, electrons stabilized) and antibonding (higher energy). Bond order = $(\text{bonding} - \text{antibonding})/2$. Bond order > 0 means stable.

AP Chem Tip: Bond order formula: $(B - AB)/2$. O_2 has bond order 2 with 2 unpaired electrons (paramagnetic) -- explains why O_2 is attracted to magnets.

Example: O_2 : 10 bonding, 6 antibonding $\rightarrow$ bond order 2, paramagnetic due to unpaired electrons in π^* orbitals.

36 Dipole-Dipole Forces

Explanation: Intermolecular forces (IMFs) between polar molecules: dipole-dipole attractions. Stronger with larger dipole moments. These are weaker than ionic/covalent bonds but determine boiling/melting points.

AP Chem Tip: *IMF strength order: ion-ion > hydrogen bonding > dipole-dipole > London dispersion. More polar molecules have stronger dipole-dipole forces and higher boiling points.*

Example: HCl (polar) boils at -85 C; F₂ (nonpolar, similar molar mass) boils at -188 C -- dipole-dipole makes HCl boil higher.

37 Hydrogen Bonding

Explanation: Hydrogen bonding = strong dipole-dipole attraction between H bonded to N, O, or F and a lone pair on N, O, or F in another molecule. Much stronger than ordinary dipole-dipole.

AP Chem Tip: *H-bonding requires H attached to N, O, or F (the three most electronegative). Water, DNA base pairs, and proteins depend on it.*

Example: Water's anomalously high boiling point (100 C) results from hydrogen bonding. HF and NH₃ also show elevated boiling points.

38 London Dispersion Forces

Explanation: London dispersion forces: instantaneous induced dipoles from electron fluctuations. Present in ALL molecules, stronger for larger/more polarizable molecules (more electrons, larger surface area).

AP Chem Tip: *Dispersion forces increase with molar mass and surface area. Even nonpolar molecules (I₂, CH₄) are held together by dispersion forces.*

Example: I₂ (large, polarizable) is a solid at room temperature while F₂ (small) is a gas -- dispersion forces scale with size.

39 VSEPR: 5 & 6 Domains

Explanation: Trigonal bipyramidal (5 domains): equatorial (120) vs axial (90) positions; lone pairs go equatorial. Octahedral (6 domains): all 90 degrees; lone pairs opposite each other.

AP Chem Tip: *In PCl₅ (trigonal bipyramidal), lone pairs prefer equatorial sites (SF₄ seesaw, ClF₃ T-shaped, XeF₂ linear). In octahedral, lone pairs are trans (XeF₄ square planar).*

Example: XeF₄: 6 domains, 2 lone pairs trans -> square planar. SF₄: 5 domains, 1 lone pair equatorial -> seesaw.

40 Properties from Structure

Explanation: Molecular structure determines properties: shape -> polarity -> IMFs -> boiling point, solubility, reactivity. Linear nonpolar molecules dissolve in nonpolar solvents; polar in polar (like dissolves like).

AP Chem Tip: *Structure-property reasoning: bigger IMFs = higher boiling/melting points. Nonpolar solutes dissolve in nonpolar solvents; polar/ionic dissolve in polar (water).*

Example: Oil (nonpolar) doesn't dissolve in water (polar). NaCl (ionic) dissolves in water via ion-dipole forces.

Unit 3: Intermolecular Forces & Properties

18-22% of the exam. IMFs, solids/liquids/gases, and solutions.

41 IMF Types & Strengths

Explanation: Ion-dipole (strongest, in solutions) > hydrogen bonding > dipole-dipole > London dispersion (weakest). All are much weaker than covalent/ionic bonds. IMFs determine phase and boiling point.

AP Chem Tip: *Ranking IMFs: ion-dipole > H-bond > dipole-dipole > dispersion. More/stronger IMFs = higher boiling point, higher viscosity, higher surface tension.*

Example: NaCl dissolves in water via ion-dipole forces (Na⁺ attracts water's O, Cl⁻ attracts water's H).

42 Properties & Phase Changes

Explanation: Melting point = solid → liquid; boiling point = liquid → gas; sublimation = solid → gas. Energy is absorbed on heating (endo), released on cooling (exo). Temperature stays constant during a phase change (energy goes into IMF breaking).

AP Chem Tip: *During a phase change, temperature is constant -- added heat breaks IMFs, not raising KE. Heating curves show plateaus at melting/boiling points.*

Example: Ice at 0 °C absorbs heat to melt into water at 0 °C (the heat breaks hydrogen bonds, temperature unchanged).

43 Vapor Pressure & Boiling

Explanation: Vapor pressure = pressure of vapor over a liquid. Increases with temperature. Liquids with stronger IMFs have LOWER vapor pressure and HIGHER boiling points. Boiling occurs when vapor pressure = external pressure.

AP Chem Tip: *Stronger IMFs → lower vapor pressure → higher boiling point. At high altitude (low external pressure), water boils below 100 °C.*

Example: Diethyl ether (weak IMFs) evaporates fast (high vapor pressure); water evaporates slowly.

44 Heating & Cooling Curves

Explanation: Heating curves: sloped regions (temperature change, $q = mc \Delta T$) and flat regions (phase change, $q = n \times \Delta H$). Specific heat (c), enthalpy of fusion, and enthalpy of vaporization are used.

AP Chem Tip: *Two formulas: $q = mc \Delta T$ (temperature change) and $q = n \Delta H$ (phase change). A heating curve problem usually needs both -- identify each segment.*

Example: To melt 18 g ice at 0 °C: $q = (1 \text{ mol}) \times (6.01 \text{ kJ/mol}) = 6.01 \text{ kJ}$. To then warm it to 100 °C: $q = (18 \text{ g})(4.18)(100) = 7.52 \text{ kJ}$.

45 Solids: Types & Properties

Explanation: Ionic solids: lattice, high mp, brittle, conduct molten. Molecular solids (ice, sugar): low mp, soft, poor conductors. Covalent network solids (diamond, quartz): very high mp, hard, strong. Metallic solids: conductive, malleable.

AP Chem Tip: *Identify by properties: diamond (network covalent) is the hardest, quartz (SiO₂) network, ice (molecular, H-bonded). Metals conduct as solids; ionic only when molten/dissolved.*

Example: Diamond (network covalent) and graphite (layered network) are both carbon but have very different properties.

46 Covalent Network Solids

Explanation: Atoms connected by an extended network of covalent bonds: diamond (3D), graphite (layered), quartz/SiO₂ (3D), silicon carbide. Extremely high melting points, very hard (except graphite is soft -- layers slide).

AP Chem Tip: *Graphite conducts electricity (delocalized π electrons between layers) and is soft (weak interlayer forces). Diamond does not conduct and is the hardest natural substance.*

Example: Graphite is used as a lubricant (layers slide) and conducts (delocalized electrons); diamond is used in cutting tools.

47 Solutions & Solubility

Explanation: Solutions are homogeneous mixtures. 'Like dissolves like': polar dissolves polar, nonpolar dissolves nonpolar. Ionic solutes dissolve in water via ion-dipole forces. Solubility depends on IMFs between solute and solvent.

AP Chem Tip: *Polarity matching determines solubility. Oil (nonpolar) and water (polar) don't mix; ethanol (has OH) and water mix fully.*

Example: I₂ (nonpolar) dissolves in CCl₄ (nonpolar) but not water. NaCl dissolves in water but not in gasoline.

48 Molarity & Dilution

Explanation: Molarity (M) = moles solute / liters solution. Dilution: $M_1V_1 = M_2V_2$ (moles of solute are conserved). Preparation involves dissolving solute then adding solvent to the final volume.

AP Chem Tip: *$M_1V_1 = M_2V_2$ only works for dilution (solute amount constant). Use $M = n/V$ for direct calculations.*

Example: To make 500 mL of 0.1 M NaCl: need 0.05 mol = 2.925 g NaCl. Dilution: 50 mL of 6 M HCl + water to 300 mL → 1 M.

49 Solution Stoichiometry

Explanation: Reactions in solution use molarity to find moles: $n = MV$. Stoichiometry proceeds as usual after converting to moles. Titrations use M_1V_1/M_2V_2 relationships at the equivalence point.

AP Chem Tip: *At the equivalence point of a titration: moles H⁺ = moles OH⁻ (for monoprotic). Use $n = MV$ to find unknown concentrations.*

Example: Titrating 25.0 mL of HCl with 0.100 M NaOH: if 20.0 mL NaOH is used, moles HCl = $(0.100)(0.020) = 0.002$ mol → [HCl] = 0.080 M.

50 Spectrophotometry & Beer's Law

Explanation: Beer-Lambert law: $A = \epsilon b c$ (absorbance = molar absorptivity x path length x concentration). Absorbance is directly proportional to concentration, enabling quantitative analysis.

AP Chem Tip: *$A = \epsilon b c$ is linear: plot A vs c gives a straight line through the origin. Higher concentration = higher absorbance. Used in kinetics and equilibrium labs.*

Example: If A = 0.400 for a 0.10 M solution, a 0.20 M solution (same cell) gives A = 0.800.

51 Separation Techniques

Explanation: Chromatography separates by differential migration (polarity). Distillation separates by boiling point. Filtration separates solids from liquids. Recrystallization purifies by solubility differences.

AP Chem Tip: *Distillation: lower boiling point component vaporizes first. Chromatography: more polar components interact more with the stationary phase and move slower.*

Example: Crude oil is separated by fractional distillation (different boiling ranges). Paper chromatography separates ink pigments by polarity.

52 Gravimetric Analysis

Explanation: Gravimetric analysis: precipitate a substance, filter, dry, weigh. The mass of precipitate gives the amount of analyte via stoichiometry. Requires complete precipitation and pure, dry product.

AP Chem Tip: *Percent composition by mass = $(\text{mass of element in precipitate} / \text{total mass of sample}) \times 100$. Work from precipitate mass back to moles to original sample.*

Example: Precipitating AgCl from a chloride sample: mass of AgCl → moles AgCl → moles Cl⁻ → mass Cl⁻ → percent Cl in original sample.

53 Titrations

Explanation: Titration: known concentration (titrant) reacts with unknown (analyte). Indicators change color at the endpoint. Equivalence point: stoichiometrically equal moles of acid and base.

AP Chem Tip: *At equivalence: $M(a)V(a) = M(b)V(b)$ (for monoprotic). The endpoint is where the indicator changes color (ideally at equivalence).*

Example: 25.0 mL of 0.20 M H₂SO₄ requires 0.010 mol H⁺; with 0.10 M NaOH, that's 100 mL to neutralize.

54 Redox Titrations

Explanation: Redox titrations use oxidation-reduction reactions: titrant oxidizes/reduces the analyte (e.g., KMnO_4 vs Fe^{2+} , iodine-thiosulfate). The equivalence point can be detected by color change (permanganate itself is purple).

AP Chem Tip: *Balance the redox equation first, then use mole ratios. KMnO_4 in acid is reduced from Mn^{7+} to Mn^{2+} (5 e⁻ per MnO_4^-).*

Example: $\text{MnO}_4^- + 8\text{H}^+ + 5\text{Fe}^{2+} \rightarrow \text{Mn}^{2+} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O}$: 1 mol MnO_4^- oxidizes 5 mol Fe^{2+} .

55 Light & Spectroscopy

Explanation: Spectroscopy measures interaction of light with matter. Absorbance spectroscopy: sample absorbs specific wavelengths (electron transitions). Emission: excited atoms emit photons of specific energies.

AP Chem Tip: *Absorbed/emitted wavelengths correspond to energy level differences ($E = h\nu = hc/\lambda$). Each element has a unique spectrum -- used for identification.*

Example: Flame tests: strontium burns red, copper green -- the emitted wavelengths identify the element.

56 Atomic Emission & Energy Levels

Explanation: Electrons absorb photons to jump to higher levels and emit photons to drop. Energy levels are quantized: only specific transitions allowed. $E = hc/\lambda$ relates photon energy to wavelength.

AP Chem Tip: *Larger energy jumps = shorter wavelength (higher energy) photons. The Balmer series (visible) is electron transitions to $n=2$ in hydrogen.*

Example: A hydrogen electron dropping from $n=3$ to $n=2$ emits red light (656 nm); $n=5$ to $n=2$ emits violet (434 nm).

57 Beer-Lambert Law Applications

Explanation: Beer's law used to: find concentration from absorbance (calibration curve), monitor reaction progress (kinetics), and verify equilibrium. Requires monochromatic light and dilute solutions.

AP Chem Tip: *Calibration curve: A vs known concentrations, then read unknown from the line. Always check that absorbance is in the linear range ($A < 1$).*

Example: An unknown with $A = 0.500$ on a curve where 0.25 M gives $A = 0.250$ has concentration 0.50 M.

58 Phase Diagrams

Explanation: Phase diagrams map pressure-temperature conditions for solid/liquid/gas. Triple point: all three phases coexist. Critical point: beyond which liquid/gas are indistinguishable. Slopes show melting/freezing behavior.

AP Chem Tip: *The solid-liquid line slope tells whether solid or liquid is denser: water's line tilts left (ice less dense, negative slope); most substances tilt right.*

Example: Water's phase diagram shows the solid-liquid line sloping left: increasing pressure lowers the melting point (ice melts under pressure).

59 Supercritical Fluids & Beyond

Explanation: Above the critical point, a supercritical fluid has liquid-like density and gas-like viscosity -- used for decaffeination (supercritical CO_2) and extraction.

AP Chem Tip: *Supercritical CO_2 is a green solvent for decaffeinating coffee and extracting flavors without toxic organic solvents.*

Example: Supercritical CO_2 extracts caffeine from coffee beans; it evaporates cleanly, leaving decaffeinated beans.

60 Mixtures vs Pure Substances

Explanation: Pure substances: elements or compounds (fixed composition, specific properties). Mixtures: homogeneous (solutions -- uniform) or heterogeneous (visible parts -- sand, oil and water). Mixtures are separated by physical means.

AP Chem Tip: *Physical changes (melting, dissolving, filtering) do not change chemical identity; chemical reactions create new substances. Distinguishing is a classic MCQ.*

Example: Salt water is a homogeneous mixture; separating by distillation gives pure water and salt (physical change).

Unit 4: Chemical Reactions

7-9% of the exam. Reaction types, stoichiometry, redox, and net ionic equations.

61 Balancing Equations

Explanation: Chemical equations balance atoms and charge. Coefficients represent mole ratios. Matter is conserved: the same number of each atom on both sides.

AP Chem Tip: Balance by adjusting *COEFFICIENTS* only (never subscripts). Balance elements one at a time, often leaving H and O for last.

Example: $C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$: 3 C, 8 H, 10 O on each side.

62 Net Ionic Equations

Explanation: Spectator ions (unchanged on both sides) are removed to write the net ionic equation. Only species that actually change are shown. Strong electrolytes fully dissociate (soluble salts, strong acids/bases).

AP Chem Tip: Solids, liquids, gases, and weak electrolytes stay as formulas (no dissociation). Strong acids (HCl, H₂SO₄, HNO₃), strong bases, and soluble salts dissociate fully.

Example: $HCl + NaOH \rightarrow NaCl + H_2O$: net ionic is $H^+ + OH^- \rightarrow H_2O$. Na⁺ and Cl⁻ are spectators.

63 Precipitation Reactions

Explanation: Two soluble salts react to form an insoluble product (precipitate). Solubility rules predict products. Double displacement: $AB + CD \rightarrow AD + CB$.

AP Chem Tip: Solubility rules: most nitrates, alkali metal salts, and ammonium salts are soluble; most carbonates, phosphates, and sulfides are insoluble (except alkali/ammonium); AgCl, PbCl₂, BaSO₄ are insoluble.

Example: $AgNO_3 + NaCl \rightarrow AgCl(s) + NaNO_3$: AgCl precipitates (white). Net ionic: $Ag^+ + Cl^- \rightarrow AgCl(s)$.

64 Acid-Base Reactions

Explanation: Neutralization: acid + base $\rightarrow$ salt + water. Strong acid + strong base: $H^+ + OH^- \rightarrow H_2O$. Weak acids/bases only partially ionize; equilibria apply.

AP Chem Tip: Complete neutralization of a strong acid with a strong base gives pH 7. Weak acid + strong base gives a basic salt (conjugate base hydrolyzes).

Example: $HCl + KOH \rightarrow KCl + H_2O$. $CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$ (solution is basic).

65 Oxidation-Reduction (Redox)

Explanation: Redox involves electron transfer. Oxidation: loss of electrons (oxidation number increases). Reduction: gain of electrons (oxidation number decreases). The oxidizing agent is reduced; the reducing agent is oxidized.

AP Chem Tip: OIL RIG (Oxidation Is Loss, Reduction Is Gain). Assign oxidation numbers to find what changes. Oxidizing agent = species being reduced (accepts electrons).

Example: $2Na + Cl_2 \rightarrow 2NaCl$: Na is oxidized (0 $\rightarrow$ +1, reducing agent); Cl₂ is reduced (0 $\rightarrow$ -1, oxidizing agent).

66 Oxidation Numbers

Explanation: Rules: elements = 0; monatomic ions = charge; F = -1; O usually -2 (except peroxides -1); H usually +1 (except metal hydrides -1); sum = charge of the species.

AP Chem Tip: Use oxidation numbers to identify redox: if any atom's number changes, it's redox. Practice assigning to compounds like H₂SO₄ and MnO₄⁻.

Example: In H₂SO₄: H = +1 (x2), O = -2 (x4), so S = +6. In MnO₄⁻: O = -2 (x4), so Mn = +7.

67 Disproportionation

Explanation: Disproportionation: a single species is both oxidized and reduced (one part gains electrons, another loses). Example: $Cl_2 + 2OH^- \rightarrow Cl^- + ClO^- + H_2O$.

AP Chem Tip: Spot disproportionation when one element appears in two different oxidation states on the product side. Cl₂ (0) becomes Cl⁻ (-1) and ClO⁻ (+1).

Example: Hydrogen peroxide disproportionates: $2H_2O_2 \rightarrow 2H_2O + O_2$ (O goes from -1 to -2 and 0).

68 Stoichiometry & Mole Ratios

Explanation: Stoichiometry converts between reactants/products using mole ratios from the balanced equation. Grams → moles → mole ratio → moles → grams (or liters, particles).

AP Chem Tip: *The balanced equation coefficients ARE the mole ratios. Always convert to moles before using ratios. Never compare grams directly.*

Example: $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$: 4 mol H_2 (8 g) reacts with 2 mol O_2 (64 g) to give 4 mol H_2O (72 g).

69 Limiting Reactant

Explanation: The limiting reactant is consumed first and determines the maximum product. The excess reactant remains after reaction. Compare the required vs available amounts via mole ratios.

AP Chem Tip: *Find limiting reactant: convert each reactant to moles of product; the one yielding less product is limiting. Product yield is based on it.*

Example: $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$ with 4 mol H_2 and 2 mol O_2 : H_2 makes 4 mol H_2O , O_2 makes 4 mol H_2O -- neither limits (both used).

70 Percent Yield

Explanation: Percent yield = (actual yield / theoretical yield) × 100%. Theoretical yield comes from stoichiometry (limiting reactant); actual yield is measured in the lab.

AP Chem Tip: *Percent yield is always ≤ 100% (usually). Sources of loss: incomplete reactions, side reactions, transfer losses.*

Example: If theory predicts 5.00 g product and the lab obtained 4.25 g, percent yield = 85%.

71 Reaction Types

Explanation: Synthesis ($\text{A} + \text{B} \rightarrow \text{AB}$), decomposition ($\text{AB} \rightarrow \text{A} + \text{B}$), single replacement ($\text{A} + \text{BC} \rightarrow \text{AC} + \text{B}$), double replacement ($\text{AB} + \text{CD} \rightarrow \text{AD} + \text{CB}$), combustion (fuel + $\text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$).

AP Chem Tip: *Classify by pattern: combination = two make one; decomposition = one makes two; single replacement = element + compound; combustion = burning in O_2 .*

Example: $2\text{Mg} + \text{O}_2 \rightarrow 2\text{MgO}$ (synthesis). $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$ (decomposition). $\text{Zn} + \text{CuSO}_4 \rightarrow \text{ZnSO}_4 + \text{Cu}$ (single replacement).

72 Combustion & Hydrocarbons

Explanation: Complete combustion of hydrocarbons: $\text{C}_x\text{H}_y + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$. Incomplete combustion produces CO or C (soot). Combustion is always exothermic (oxidation).

AP Chem Tip: *Complete combustion products: $\text{CO}_2 + \text{H}_2\text{O}$. Incomplete: CO (toxic) or C. Balance O_2 last in combustion equations.*

Example: $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$ (complete). $2\text{CH}_4 + 3\text{O}_2 \rightarrow 2\text{CO} + 4\text{H}_2\text{O}$ (incomplete, produces toxic CO).

73 Activity Series & Single Replacement

Explanation: The activity series ranks metals by reactivity (ability to displace others from solution/compounds). A more active metal replaces a less active one in its compound.

AP Chem Tip: *Know the order roughly: $\text{Li} > \text{K} > \text{Ca} > \text{Na} > \text{Mg} > \text{Al} > \text{Zn} > \text{Fe} > \text{Ni} > \text{Sn} > \text{Pb} > (\text{H}) > \text{Cu} > \text{Ag} > \text{Au}$. Metals above H displace H from acids.*

Example: $\text{Zn} + \text{CuSO}_4 \rightarrow \text{ZnSO}_4 + \text{Cu}$ (Zn above Cu). $\text{Cu} + \text{ZnSO}_4 \rightarrow$ no reaction (Cu below Zn). $\text{Fe} + 2\text{HCl} \rightarrow \text{FeCl}_2 + \text{H}_2$ (Fe above H).

74 Strong vs Weak Electrolytes

Explanation: Strong electrolytes (soluble salts, strong acids/bases) dissociate ~100% and conduct well. Weak electrolytes (weak acids like CH_3COOH , weak bases like NH_3) partially ionize. Nonelectrolytes (sugar, ethanol) don't ionize.

AP Chem Tip: *Strong acids: HCl , HBr , HI , HNO_3 , H_2SO_4 , HClO_4 . Strong bases: group 1 hydroxides, Ca/Sr/Ba hydroxides. Everything else is weak or non.*

Example: HCl is a strong electrolyte (full dissociation); CH_3COOH is weak (about 1% ionized); $\text{C}_6\text{H}_{12}\text{O}_6$ (glucose) is a nonelectrolyte.

75 Net Charge & Ion Spectators

Explanation: In net ionic equations, balance both mass and CHARGE. Spectator ions appear on both sides unchanged and are canceled.

AP Chem Tip: *When balancing half-reactions in acidic/basic solution, balance charge by adding electrons (or H^+/OH^-). The final net ionic must balance charge.*

Example: $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$ has zero net charge on both sides ($1+ + 1- = 0$; H_2O is neutral).

76 Solution Concentration & Dilution in Reactions

Explanation: Solution reactions: convert volume + molarity to moles ($n = MV$), use mole ratios, then convert to the desired unit. Dilution ($M_1V_1 = M_2V_2$) is used to prepare solutions of exact concentration.

AP Chem Tip: *In titration stoichiometry, moles of titrant from $M \times V$, then the mole ratio from the balanced equation gives moles of analyte.*

Example: If 30.0 mL of 0.10 M NaOH neutralizes 20.0 mL of H_2SO_4 : moles $OH^- = 0.0030$; H_2SO_4 needs 2 OH^- per $H_2SO_4 \rightarrow 0.0015$ mol $H_2SO_4 \rightarrow 0.075$ M.

77 Redox in Real Systems

Explanation: Redox reactions power batteries, fuel cells, corrosion (rusting), and biological processes (cellular respiration). Oxidation states track electron flow.

AP Chem Tip: *Rusting: Fe is oxidized ($Fe \rightarrow Fe^{2+} \rightarrow Fe^{3+}$), O_2 is reduced. Batteries: spontaneous redox separates oxidation and reduction into half-cells.*

Example: In a zinc-copper cell: Zn is oxidized at the anode, Cu^{2+} is reduced at the cathode. Electrons flow from anode to cathode.

78 The Activity of Redox Agents

Explanation: Strong reducing agents are easily oxidized (e.g., alkali metals, Zn). Strong oxidizing agents are easily reduced (F_2 , O_2 , MnO_4^- , $Cr_2O_7^{2-}$). Oxidizing power trends with electronegativity/high oxidation states.

AP Chem Tip: *The more negative the reduction potential, the stronger the reducing agent (easier to oxidize). F_2 is the strongest common oxidizing agent.*

Example: F_2 (reduction potential +2.87 V) oxidizes almost anything; Li (most negative potential, -3.05 V) is a powerful reducing agent.

79 Balancing Redox (Half-Reaction Method)

Explanation: Split into oxidation and reduction half-reactions. Balance atoms (add H_2O for O, H^+ in acid / OH^- in base), balance charge with electrons, then combine so electrons cancel.

AP Chem Tip: *In acid: add H_2O to balance O, H^+ to balance H. In base: add H_2O to balance O, OH^- to balance H. Multiply half-reactions to equalize electrons.*

Example: $MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$: oxidation half gives 5 e^- , reduction consumes 5 e^- .

80 Stoichiometry with Gases (Ideal Gas)

Explanation: Gas stoichiometry uses $PV = nRT$ to convert between moles and volume. At STP (0 C, 1 atm), 1 mol gas = 22.4 L. Coefficients still give mole ratios.

AP Chem Tip: *At STP, use 22.4 L/mol. Otherwise use $PV = nRT$ with $R = 0.0821$ L atm / (mol K). Convert everything to consistent units (atm, L, K).*

Example: $2H_2 + O_2 \rightarrow 2H_2O$: 4 L H_2 reacts with 2 L O_2 (volumes in same conditions are in mole ratio).

81 Molarity & Preparing Solutions

Explanation: To prepare a solution: dissolve the calculated mass of solute in a small volume, then dilute to the final volume in a volumetric flask. 'Water to the mark' is essential.

AP Chem Tip: *Volume is additive for dilute aqueous solutions; use a volumetric flask for accuracy. $M = \text{mol/L}$, so L is the final solution volume, not solvent added.*

Example: To make 250 mL of 0.500 M NaCl: $0.125 \text{ mol} = 7.31 \text{ g NaCl}$, dissolve, then fill to the 250 mL mark.

Unit 5: Kinetics

7-9% of the exam. Rates, rate laws, reaction orders, and the rate-determining step.

82 Reaction Rates

Explanation: Rate = change in concentration per unit time (M/s). Rates decrease over time as reactants are consumed. Average rate vs instantaneous rate (slope of the concentration-time curve).

AP Chem Tip: Rate is positive for products (appearing) and negative for reactants (disappearing) with the coefficient adjustment: rate = $-(1/a) \frac{d[A]}{dt} = (1/b) \frac{d[B]}{dt}$.

Example: For $2A \rightarrow B$: rate = $-(1/2) \frac{d[A]}{dt} = \frac{d[B]}{dt}$. If [A] drops 0.10 M in 10 s, $\frac{d[A]}{dt} = -0.010$ M/s and rate = 0.005 M/s.

83 Rate Laws

Explanation: Rate law: rate = $k[A]^m[B]^n$. k = rate constant (temperature dependent). m and n = reaction orders (determined EXPERIMENTALLY, not from coefficients). Overall order = m + n.

AP Chem Tip: Orders come from data, not the balanced equation (unless it's an elementary step). Units of k depend on overall order: $M^{(1-n)}/s$.

Example: For rate = $k[A]^2[B]$, overall order 3, k units = $M^{-2} s^{-1}$. Doubling [A] quadruples rate; doubling [B] doubles it.

84 Determining Rate Laws from Data

Explanation: Compare experiments where one concentration changes while others are held constant. If doubling [A] doubles rate, order 1 in A; if it quadruples, order 2; if no change, order 0.

AP Chem Tip: Method of initial rates: pick pairs of experiments isolating one reactant. Order = the exponent found from the ratio.

Example: Exp 1: [A]=0.1, rate=0.02; Exp 2: [A]=0.2, rate=0.08. Doubling A quadruples rate $\rightarrow$ order 2 in A.

85 Integrated Rate Laws

Explanation: Zero order: $[A] = -kt + [A]_0$ (linear [A] vs t, half-life = $[A]_0/2k$). First order: $\ln[A] = -kt + \ln[A]_0$ (linear $\ln[A]$ vs t, half-life = $0.693/k$, constant). Second order: $1/[A] = kt + 1/[A]_0$ (linear $1/[A]$ vs t).

AP Chem Tip: Which plot is linear tells the order: [A] vs t (zero), $\ln[A]$ vs t (first), $1/[A]$ vs t (second). First-order half-life is INDEPENDENT of concentration.

Example: Radioactive decay is first order: half-life constant. If a 100-g sample halves to 50 g in 5 days, it halves again in the next 5 days.

86 Half-Life

Explanation: Half-life ($t_{1/2}$) = time for concentration to halve. First order: $t_{1/2} = 0.693/k$ (independent of [A]). Zero order: $[A]_0/2k$. Second order: $1/(k[A]_0)$.

AP Chem Tip: First-order half-life is the easiest to use: after n half-lives, remaining = initial $\times (1/2)^n$. Use it for decay and many kinetics problems.

Example: If $k = 0.0693 \text{ s}^{-1}$ (first order), $t_{1/2} = 0.693/0.0693 = 10$ s. After 30 s (3 half-lives), 1/8 remains.

87 Collision Theory

Explanation: Reactions occur when particles collide with sufficient energy ($\geq E_a$) and proper orientation. Increasing concentration or temperature increases collision frequency/energy $\rightarrow$ faster rate.

AP Chem Tip: Two requirements for a productive collision: enough energy (E_a) and correct orientation. Catalysts provide an alternative pathway with lower E_a .

Example: Most molecular collisions don't react -- they lack energy or orientation. Raising temperature increases the fraction with energy $\geq E_a$.

88 Activation Energy & Arrhenius

Explanation: Arrhenius equation: $k = A e^{(-E_a/RT)}$. E_a = activation energy (minimum energy for reaction). Higher E_a = slower reaction (smaller k). Lower E_a (catalyst) = faster.

AP Chem Tip: $\ln k$ vs $1/T$ gives a line with slope = $-E_a/R$. E_a is always positive; a catalyst lowers E_a , increasing k without changing the equilibrium.

Example: Two reactions: $E_a = 50$ vs 100 kJ/mol at the same T: the 50 kJ reaction proceeds much faster (larger k).

89 Catalysts

Explanation: Catalysts speed reactions by providing an alternate pathway with lower activation energy. They are NOT consumed. Homogeneous (same phase) vs heterogeneous (different phase, e.g., solid catalyst).

AP Chem Tip: *A catalyst lowers E_a for BOTH forward and reverse directions equally -- it speeds up reaching equilibrium but does NOT shift the equilibrium position.*

Example: Catalytic converters use Pt/Pd/Rh to speed CO and NO_x conversion. Enzymes are biological catalysts.

90 Reaction Mechanisms

Explanation: Mechanisms = series of elementary steps describing how reactants become products. Elementary steps: unimolecular (A → products, first order), bimolecular (A + B →, second order), termolecular (rare, third order).

AP Chem Tip: *The molecularity of an elementary step equals its order. The slowest step (rate-determining step) determines the overall rate law.*

Example: Step 1 (slow): NO₂ + NO₂ → NO₃ + NO. Step 2 (fast): NO₃ + CO → NO₂ + CO₂. Rate = $k[\text{NO}_2]^2$ (from the slow step).

91 Rate-Determining Step

Explanation: The rate-determining step is the slowest elementary step -- it limits the overall reaction rate. The rate law for the overall reaction comes from this step (using earlier fast steps to express intermediates).

AP Chem Tip: *Intermediates (produced then consumed) must be eliminated from the rate law using prior equilibrium steps. The slow step's reactants (not intermediates) define the rate law.*

Example: If step 1 (fast, reversible) makes intermediate X, and step 2 (slow) is X + B → P, then rate = $k[\text{K}][\text{A}][\text{B}]$ after substituting X from the fast equilibrium.

92 Intermediates vs Catalysts

Explanation: Intermediates: formed in one step, consumed in a later step (not in the overall equation). Catalysts: consumed in one step and regenerated in a later step (appear in the overall equation but cancel).

AP Chem Tip: *An intermediate is a real, short-lived species that does NOT appear in the overall balanced equation. A catalyst is used and regenerated -- appears on both sides when summing steps.*

Example: In NO₂ + CO → NO + CO₂ via NO₃: NO₃ is an intermediate. A catalyst would be added, consumed, and regenerated.

93 Temperature & Rate

Explanation: Increasing temperature increases the rate constant k (Arrhenius). The rate approximately doubles per 10 °C for many reactions. More molecules exceed E_a at higher T.

AP Chem Tip: *Temperature affects k (not concentrations). Use the two-point Arrhenius form: $\ln(k_2/k_1) = (E_a/R)(1/T_1 - 1/T_2)$.*

Example: A reaction with $E_a = 50 \text{ kJ/mol}$ at 300 K vs 310 K: k increases by roughly a factor of 2.

94 Reaction Energy Diagrams

Explanation: Energy diagrams show reactants, products, E_a (forward and reverse), and the transition state (peak). $\Delta H = E_a(\text{forward}) - E_a(\text{reverse}) = \text{products} - \text{reactants}$. Endothermic: products higher; exothermic: products lower.

AP Chem Tip: *$\Delta H = E_{a,\text{fwd}} - E_{a,\text{rev}}$. A catalyst lowers both E_a peaks. The transition state is the highest-energy point (unstable, bonds partially broken).*

Example: Exothermic reaction: $E_{a,\text{fwd}} < E_{a,\text{rev}}$, products lower than reactants, ΔH negative.

95 Steady-State & Approximations

Explanation: The steady-state approximation assumes intermediate concentration stays roughly constant (formation = consumption). Used to derive rate laws for complex mechanisms.

AP Chem Tip: *If the first step is fast and reversible (pre-equilibrium), the intermediate's concentration is set by that equilibrium, then substituted into the slow step's rate law.*

Example: For A + B ⇌ X (fast), X → P (slow): $[\text{X}] = K[\text{A}][\text{B}]$, rate = $k_2 K [\text{A}][\text{B}]$ -- overall second order.

96 Kinetics Experiments

Explanation: Common experiments: initial rates (vary one reactant), integrated rate law (plot data), half-life analysis, and absorbance monitoring (Beer's law for concentration vs time).

AP Chem Tip: Use colorimetry/spectrophotometry when a reactant or product absorbs light; absorbance is proportional to concentration, giving $[A]$ at each time.

Example: Monitoring a colored reactant: $A = \epsilon b c$, so absorbance vs time data converts to concentration vs time for rate analysis.

97 Zero-Order Reactions

Explanation: Zero order: rate = k (constant, independent of concentration). Happens when a catalyst/surface is saturated. $[A]$ decreases linearly; half-life depends on initial concentration.

AP Chem Tip: Zero-order: $[A]$ vs t is linear with slope $-k$. Occurs in enzyme-catalyzed reactions at saturation and decomposition on metal surfaces.

Example: An enzyme at full saturation (all active sites busy) has constant rate regardless of substrate: rate = $V_{\max}$.

98 First-Order Reactions

Explanation: First order: rate = $k[A]$. $\ln[A]$ vs t linear. Constant half-life ($0.693/k$). Examples: radioactive decay, most decompositions, many drug elimination processes.

AP Chem Tip: First-order half-life is constant: $t_{1/2} = 0.693/k$. Drug clearance is often first order -- each half-life removes half the remaining drug.

Example: If a drug has $t_{1/2} = 4$ h, after 8 h (2 half-lives) 25% remains; after 12 h (3 half-lives) 12.5% remains.

99 Second-Order Reactions

Explanation: Second order: rate = $k[A]^2$ (or $k[A][B]$). $1/[A]$ vs t linear. Half-life = $1/(k[A]_0)$ -- depends on initial concentration (increases as $[A]$ drops).

AP Chem Tip: Second-order half-life doubles as concentration halves (it takes longer at lower concentration). Distinguish from first order via the linear plot.

Example: If $1/[A]$ vs t is linear, it's second order in A . The slope = k , intercept = $1/[A]_0$.

100 Kinetics & Equilibrium Link

Explanation: At equilibrium, forward and reverse rates are equal (dynamic equilibrium), NOT concentrations. The equilibrium constant $K = k_f/k_r$. Catalysts speed both directions, not changing K .

AP Chem Tip: $K = k_f/k_r$ is a powerful link: measuring forward and reverse rate constants gives the equilibrium constant.

Example: If $k_f = 10 \text{ s}^{-1}$ and $k_r = 2 \text{ s}^{-1}$, $K = 5$. Adding a catalyst raises both k_f and k_r , leaving K unchanged.

101 Units of Rate Constants

Explanation: Zero order: M/s . First order: s^{-1} . Second order: $M^{-1} s^{-1}$. Third order: $M^{-2} s^{-1}$. The order determines k 's units: $M^{-(1-n)} s^{-1}$.

AP Chem Tip: Get units right: for rate = $k[A]^n$, units of $k = (M/s)/M^n = M^{-(1-n)} s^{-1}$. Quick check for $n = 0, 1, 2, 3$.

Example: For rate = $k[A]^2[B]$ (third order overall), k has units $M^{-2} s^{-1}$.

102 Rate vs Time Graphs

Explanation: Concentration-time graphs: exponential decay for first order (constant fraction per unit time). Rate vs concentration graphs: flat line for zero order, line through origin for first order, parabola for second order.

AP Chem Tip: Shape tells order: $[A]$ vs t curving down (first/second), straight down (zero). Rate vs $[A]$: flat = zero, linear = first, curving up = second.

Example: For a first-order reaction, the rate vs $[A]$ graph is a straight line through the origin (rate proportional to $[A]$).

Unit 6: Thermodynamics

7-9% of the exam. Energy changes, enthalpy, entropy, and Gibbs free energy.

103 Systems & Surroundings

Explanation: A system is what's studied; surroundings are everything else. Open (exchanges matter and energy), closed (energy only), isolated (neither).
Exothermic: heat leaves system ($\Delta H < 0$). Endothermic: heat enters ($\Delta H > 0$).

AP Chem Tip: Define the system clearly first. Heat flows INTO an endothermic reaction (feels cold), OUT of an exothermic reaction (feels hot).

Example: A coffee cup calorimeter is closed (energy exchanges, no matter). An insulated thermos is nearly isolated.

104 Energy & Heat

Explanation: Energy is conserved (first law). Internal energy $E = \text{heat} + \text{work}$ ($\Delta E = q + w$). Heat (q) flows due to temperature difference; work (w) is energy transfer by force over distance.

AP Chem Tip: Sign conventions: $q > 0 = \text{heat absorbed by system}$; $w > 0 = \text{work done ON the system (compression)}$. $\Delta E = q + w$.

Example: A gas expanding does work on the surroundings ($w < 0$). An exothermic reaction releases heat ($q < 0$).

105 Enthalpy & Enthalpy Change

Explanation: Enthalpy $H = E + PV$. At constant pressure, $\Delta H = q(p)$. ΔH is the heat of reaction at constant pressure. Exothermic: $\Delta H < 0$ (heat released). Endothermic: $\Delta H > 0$.

AP Chem Tip: AP Chem almost always uses constant-pressure conditions, so $q = \Delta H$. Sign matters: negative = heat released (products more stable, lower energy).

Example: Combustion of methane: $\Delta H = -890 \text{ kJ/mol}$ (exothermic). Melting ice: $\Delta H = +6.01 \text{ kJ/mol}$ (endothermic).

106 Calorimetry

Explanation: Calorimetry measures heat: $q = m c \Delta T$ (mass $\times$ specific heat $\times$ temperature change) or $q = C \Delta T$ (calorimeter constant).
Calorimeters: coffee cup (constant pressure) and bomb (constant volume).

AP Chem Tip: $q(\text{lost by reaction}) = q(\text{gained by water} + \text{calorimeter})$. Specific heat of water = $4.18 \text{ J/g } ^\circ\text{C}$. Bomb calorimetry measures ΔE (constant V); coffee cup measures ΔH (constant P).

Example: 50.0 g water warms 5.0°C in a coffee cup: $q = (50)(4.18)(5.0) = 1,045 \text{ J}$ absorbed by water $\rightarrow$ reaction released $1,045 \text{ J}$.

107 Specific Heat & Heat Capacity

Explanation: Specific heat (c) = energy to raise 1 g of a substance by 1°C (water: $4.18 \text{ J/g } ^\circ\text{C}$). Heat capacity (C) = energy for the whole object ($\text{J/}^\circ\text{C}$). $q = m c \Delta T = C \Delta T$.

AP Chem Tip: Water's high specific heat stabilizes temperatures. Metals have low specific heats (heat up and cool quickly).

Example: A 100-g iron pan ($c = 0.45$) vs 100-g water: the pan heats $9\times$ faster for the same energy.

108 Hess's Law

Explanation: Hess's law: enthalpy change for a reaction is the same whether it occurs in one step or many (state function). Add reactions and their ΔH values; reverse a reaction to flip ΔH ; multiply by coefficients to scale ΔH .

AP Chem Tip: Manipulate given reactions to sum to the target: reverse (flip sign), scale (multiply ΔH), add (sum ΔH). Enthalpy is a state function -- path independent.

Example: $\text{C(s)} + 1/2\text{O}_2 \rightarrow \text{CO}$ ($\Delta H = -111 \text{ kJ}$) from $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$ (-394) and $\text{CO} + 1/2\text{O}_2 \rightarrow \text{CO}_2$ (-283): $-394 - (-283) = -111$.

109 Formation Enthalpies

Explanation: Standard enthalpy of formation (ΔH_f): heat to form 1 mol of compound from its elements in their standard states. Elements in standard state have $\Delta H_f = 0$. $\Delta H(\text{rxn}) = \sum(\Delta H_f \text{ products}) - \sum(\Delta H_f \text{ reactants})$.

AP Chem Tip: $\Delta H \text{ rxn} = \sum(\Delta H_f \text{ products}) - \sum(\Delta H_f \text{ reactants})$ -- with coefficients. Elements (O_2 , C graphite, H_2) have $\Delta H_f = 0$.

Example: For $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$: $\Delta H = 2(-286) - 0 = -572 \text{ kJ}$ ($\Delta H_f \text{ H}_2\text{O(l)} = -286 \text{ kJ/mol}$).

110 Bond Enthalpies

Explanation: $\Delta H = \text{sum}(\text{bonds broken}) - \text{sum}(\text{bonds formed})$ using average bond enthalpies. Breaking bonds absorbs energy; forming bonds releases energy. Approximate (average bonds across compounds).

AP Chem Tip: *Bonds broken (reactants) minus bonds formed (products). More bonds formed (or stronger bonds) $\rightarrow$ more exothermic. Useful when formation enthalpies aren't available.*

Example: $\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl}$: broken = 436 + 242 = 678; formed = 2 x 431 = 862; $\Delta H = 678 - 862 = -184 \text{ kJ}$.

111 Entropy

Explanation: Entropy (S) = disorder/randomness. Increases with: more particles (gases), higher temperature, dissolution, phase changes to gas/liquid, mixing. Solids < liquids < gases in entropy.

AP Chem Tip: *Entropy increases when: gas is produced, molecules split into more particles, a solid dissolves, temperature rises. Gases $\gg$ liquids > solids.*

Example: $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$ increases entropy (gas produced). Freezing water decreases entropy.

112 Predicting Entropy Change

Explanation: Predict ΔS : positive if products are more disordered (more gas, more moles, dissolution), negative if more ordered. $\Delta S = S(\text{products}) - S(\text{reactants})$.

AP Chem Tip: *Quick checks: gas produced = $\Delta S > 0$; gas consumed = $\Delta S < 0$. Number of particles matters most.*

Example: $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$: gas produced, $\Delta S > 0$. $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$: 4 mol gas $\rightarrow$ 2 mol gas, $\Delta S < 0$.

113 Gibbs Free Energy

Explanation: $\Delta G = \Delta H - T \Delta S$. $\Delta G < 0$ = spontaneous. $\Delta G = 0$ = at equilibrium. $\Delta G > 0$ = nonspontaneous (needs energy input).

AP Chem Tip: *Spontaneity from signs: H- (exo), S+ (entropy up) = always spontaneous. H+, S- = never. Otherwise temperature decides ($\Delta G = \Delta H - T \Delta S$).*

Example: Melting ice at 25 C: $\Delta H > 0$, $\Delta S > 0$; spontaneous because $T \Delta S > \Delta H$ at 298 K. At -10 C, not spontaneous.

114 Temperature & Spontaneity

Explanation: $\Delta G = \Delta H - T \Delta S$. Exothermic with increasing entropy: spontaneous at all T. Endothermic with decreasing entropy: nonspontaneous at all T. The other two cases switch at $T = \Delta H / \Delta S$.

AP Chem Tip: *Find the crossover temperature: $T = \Delta H / \Delta S$ (when $\Delta G = 0$). Above/below that, spontaneity flips depending on the signs.*

Example: $\Delta H = +10 \text{ kJ}$, $\Delta S = +40 \text{ J/K}$: $T = 10,000/40 = 250 \text{ K}$. Spontaneous above 250 K ($\Delta G < 0$).

115 Free Energy & Equilibrium

Explanation: $\Delta G = \Delta G(\text{standard}) + RT \ln Q$. At equilibrium, $\Delta G = 0$ and $Q = K$, so $\Delta G(\text{standard}) = -RT \ln K$. $K > 1 \rightarrow \Delta G(\text{standard}) < 0$; $K < 1 \rightarrow \Delta G(\text{standard}) > 0$.

AP Chem Tip: *$\Delta G \text{ standard} = -RT \ln K$ connects thermodynamics to equilibrium. Large K (products favored) means negative standard free energy.*

Example: If $K = 10^5$ at 298 K, $\Delta G \text{ standard} = -(8.314)(298) \ln(10^5) = -28.5 \text{ kJ}$ (products favored).

116 Coupled Reactions

Explanation: Nonspontaneous reactions can be driven by coupling to spontaneous ones (e.g., ATP hydrolysis drives anabolic reactions). The sum of the two ΔG values determines overall spontaneity.

AP Chem Tip: *Add ΔG values: a very favorable reaction can power an unfavorable one (overall $\Delta G < 0$). This is how ATP works in biology.*

Example: ATP hydrolysis ($\Delta G = -30.5 \text{ kJ/mol}$) couples to glucose phosphorylation ($\Delta G = +13.8 \text{ kJ/mol}$): net -16.7 kJ, spontaneous.

117 Standard States & Conditions

Explanation: Standard conditions: 1 atm pressure, 1 M concentration, 25 C (298 K) temperature. Standard enthalpy/entropy/free energy use the superscript degree symbol.

AP Chem Tip: *Standard values are per mole. Be careful: standard state of carbon is graphite (not diamond); of water is liquid (not gas).*

Example: ΔH_f of $\text{O}_2(\text{g})$, $\text{C}(\text{graphite})$, and $\text{H}_2(\text{g})$ are all defined as 0 under standard conditions.

118 Free Energy & Work

Explanation: The maximum useful work a reaction can do equals ΔG (at constant T and P). Spontaneous reactions can be harnessed for work; nonspontaneous ones require work input.

AP Chem Tip: ΔG is the 'useful energy' of a reaction. Batteries convert the free energy of redox reactions into electrical work.

Example: A battery's voltage comes from $\Delta G = -nFE$. More negative ΔG = higher cell potential = more work available.

119 Phase Changes & Thermodynamics

Explanation: Melting/vaporization/sublimation: $\Delta H > 0$ (endothermic, energy to break IMFs), $\Delta S > 0$ (more disorder). Freezing/condensation: reverse (exothermic, entropy down).

AP Chem Tip: At the transition temperature, $\Delta G = 0$ (phases in equilibrium): e.g., water and ice coexist at 0°C at 1 atm .

Example: Vaporization of water at 100°C : $\Delta H = +40.7\text{ kJ/mol}$, $\Delta S = +109\text{ J/mol K}$, $\Delta G = 0$ at 373 K .

120 Enthalpy of Solution & Hydration

Explanation: Dissolving: lattice energy (breaking ionic solid, endothermic) + hydration energy (ion-water IMFs, exothermic). Overall $\Delta H(\text{solution}) = \text{lattice} + \text{hydration}$; can be positive or negative.

AP Chem Tip: If hydration energy exceeds lattice energy, dissolving is exothermic (NaOH , CaCl_2 , H_2SO_4). If not, endothermic (NH_4NO_3 , KCl).

Example: NH_4NO_3 dissolving is endothermic (cold packs get cold). CaCl_2 dissolving is exothermic (heat packs).

121 Entropy of Mixing & Solutions

Explanation: Mixing increases entropy (more arrangements). Gas expansion increases entropy. Dissolving a solute increases entropy (particles spread out) -- this drives many dissolutions even when endothermic.

AP Chem Tip: The entropy increase from mixing/dissolving can overcome endothermic enthalpy -- why NH_4NO_3 dissolves despite absorbing heat.

Example: When NH_4NO_3 dissolves, the entropy gain (ions spread in water) exceeds the endothermic enthalpy, so it's spontaneous but cold.

122 Thermodynamics of Fuel & Energy

Explanation: Fuel value comes from combustion enthalpy (exothermic oxidation). Fossil fuels, hydrogen fuel cells, and batteries all convert chemical energy; efficiency depends on ΔG vs ΔH .

AP Chem Tip: Hydrogen fuel cell: $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$, $\Delta G = -474\text{ kJ/mol}$. Batteries convert ΔG directly to electricity (more efficient than heat engines).

Example: A fuel cell's maximum efficiency = $\Delta G / \Delta H$. Hydrogen fuel cells are more efficient than burning H_2 in an engine.

123 Laws of Thermodynamics

Explanation: Zeroth: thermal equilibrium. First: energy conserved ($\Delta E = q + w$). Second: entropy of the universe increases ($\Delta S_{\text{universe}} > 0$ for spontaneous). Third: perfect crystal at 0 K has $S = 0$.

AP Chem Tip: $\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$. Spontaneous = $\Delta S_{\text{universe}} > 0$. The second law explains why heat flows hot to cold.

Example: A spontaneous exothermic reaction increases surrounding entropy (heat released) enough to keep the universe's entropy rising.

124 Spontaneity & Kinetics

Explanation: Spontaneity (thermodynamics) tells whether a reaction CAN happen; kinetics tells how FAST. A reaction can be spontaneous but slow (diamond $\rightarrow$ graphite) or nonspontaneous but fast (with input).

AP Chem Tip: $\Delta G < 0$ means spontaneous but says nothing about speed. Catalysts change speed, not spontaneity. Diamond is thermodynamically unstable (spontaneous to graphite) but kinetically stable.

Example: Diamonds convert to graphite spontaneously ($\Delta G < 0$) but the activation energy is so high it essentially never happens.

Unit 7: Equilibrium

7-9% of the exam. Equilibrium constants, ICE tables, Le Chatelier's principle, and solubility equilibria.

125 Dynamic Equilibrium

Explanation: Equilibrium: forward and reverse rates are EQUAL (not stopped). Concentrations are constant. Reached from either direction. The equilibrium position is characterized by K.

AP Chem Tip: *At equilibrium, rates equal, concentrations constant -- but reactions continue. K is constant at a given temperature, regardless of starting amounts.*

Example: In a sealed flask, N₂O₄ (colorless) and NO₂ (brown) reach constant color -- dynamic equilibrium, not a stopped reaction.

126 Equilibrium Constant K

Explanation: For $aA + bB \rightleftharpoons cC + dD$: $K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$. $K > 1$: products favored. $K < 1$: reactants favored. K depends only on temperature.

AP Chem Tip: *K is products over reactants, raised to coefficients. Solids and pure liquids are excluded from K expressions. Units are usually omitted.*

Example: For $N_2 + 3H_2 \rightleftharpoons 2NH_3$: $K = \frac{[NH_3]^2}{[N_2][H_2]^3}$. Solids in heterogeneous equilibria ($CaCO_3 \rightleftharpoons CaO + CO_2$) only CO₂ appears: $K = [CO_2]$.

127 K vs Q

Explanation: Reaction quotient Q has the same form as K but with current concentrations. $Q < K$: reaction proceeds forward (toward products). $Q > K$: reverse. $Q = K$: at equilibrium.

AP Chem Tip: *Compute Q with current concentrations, compare to K: $Q < K \rightarrow$ forward; $Q > K \rightarrow$ reverse. This predicts the direction of change.*

Example: If $K = 4.0$ and $Q = 1.0$, the reaction shifts right (forward) to reach equilibrium.

128 ICE Tables

Explanation: ICE: Initial, Change, Equilibrium concentrations. Set up with the reaction stoichiometry, define x for the change, solve for x using K, then compute equilibrium concentrations.

AP Chem Tip: *ICE problems: write the balanced equation, fill I, apply -ax/+bx changes, solve K equation for x (often a perfect square to simplify). Check that x is small relative to initial if K is small.*

Example: For $A \rightleftharpoons B$, start $[A]=1.0$, $K = x^2/(1.0-x)$... solve. If K is small ($x \ll$ initial), approximate $1.0 - x \sim 1.0$.

129 Le Chatelier's Principle

Explanation: If a system at equilibrium is disturbed, it shifts to counteract the disturbance. Concentration changes: adding reactant shifts right. Pressure: higher pressure shifts toward fewer gas moles. Temperature: treat heat as a reactant/product.

AP Chem Tip: *Concentration and pressure changes do NOT change K -- only temperature does. Shifts are about Q vs K, re-establishing equilibrium at the same K.*

Example: Adding NH₃ to $N_2 + 3H_2 \rightleftharpoons 2NH_3$ shifts left ($Q > K$). Increasing pressure (fewer moles on product side) shifts right.

130 Effect of Temperature on Equilibrium

Explanation: Temperature changes K itself. Exothermic reaction: heat is a product; heating shifts LEFT (K decreases). Endothermic: heat is a reactant; heating shifts RIGHT (K increases).

AP Chem Tip: *Only temperature changes K. For exothermic reactions, K decreases with higher T; endothermic K increases. Use this with van't Hoff.*

Example: For $N_2 + 3H_2 \rightleftharpoons 2NH_3$ (exothermic), raising T decreases K -- that's why ammonia synthesis uses high pressure and moderate temperature.

131 Catalysts & Equilibrium

Explanation: Catalysts speed BOTH forward and reverse rates equally, reaching equilibrium faster. They do NOT change K or the equilibrium position.

AP Chem Tip: *A catalyst never shifts equilibrium -- it only shortens the time to get there. (Distinguish from a change that shifts position.)*

Example: Adding an enzyme to an equilibrium mixture speeds both directions; concentrations at equilibrium stay the same.

132 Heterogeneous Equilibria

- Explanation:** Solids and pure liquids have constant activity = 1 and are excluded from K expressions. Only gases and aqueous species appear. Example: $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$: $K = [\text{CO}_2]$.
- AP Chem Tip:** Exclude solids and pure liquids. If a species is a gas, include its partial pressure; if aqueous, its molarity.
- Example:** $\text{Fe}_3\text{O}_4(\text{s}) + 4\text{H}_2(\text{g}) \rightleftharpoons 3\text{Fe}(\text{s}) + 4\text{H}_2\text{O}(\text{g})$: $K = [\text{H}_2\text{O}]^4/[\text{H}_2]^4$ (only gases).
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133 Kp for Gases

- Explanation:** For gas reactions, Kp uses partial pressures (atm) instead of concentrations. $K_p = K_c(RT)^{\Delta n}$ where Δn = (gas moles products - gas moles reactants).
- AP Chem Tip:** Convert between Kc and Kp: $K_p = K_c(RT)^{\Delta n \text{ gas}}$. If $\Delta n = 0$, $K_p = K_c$.
- Example:** For $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$: $\Delta n = 2 - 4 = -2$, so $K_p = K_c(RT)^{-2}$.
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134 K for Reverse & Multiplied Reactions

- Explanation:** Reverse reaction: $K' = 1/K$. Multiplying the equation by n: $K' = K^n$. Adding reactions: multiply their K values.
- AP Chem Tip:** Manipulating reactions changes K: reverse flips it, scaling exponentiates it, adding multiplies. This is how composite K is built.
- Example:** If K for $\text{A} \rightleftharpoons \text{B}$ is 4, then $\text{B} \rightleftharpoons \text{A}$ has $K = 1/4$, and $2\text{A} \rightleftharpoons 2\text{B}$ has $K = 16$.
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135 Solubility Product Ksp

- Explanation:** For $\text{AmBn}(\text{s}) \rightleftharpoons \text{mA}(\text{n}+) + \text{nB}(\text{m}-)$: $K_{sp} = [\text{A}]^m [\text{B}]^n$ (solid excluded). Ksp measures solubility: larger Ksp = more soluble (for same stoichiometry).
- AP Chem Tip:** Ksp only includes aqueous ions. Molar solubility = moles that dissolve per liter; relate via stoichiometry. Compare Ksp only for compounds with the same ion ratio.
- Example:** AgCl : $K_{sp} = [\text{Ag}^+][\text{Cl}^-] = 1.8 \times 10^{-10}$; molar solubility $s = \sqrt{K_{sp}} = 1.3 \times 10^{-5} \text{ M}$.
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136 Common Ion Effect

- Explanation:** Adding a common ion (already present in the equilibrium) shifts the dissolution equilibrium left, DECREASING solubility. This is Le Chatelier applied to solubility.
- AP Chem Tip:** The common ion effect reduces solubility: adding Cl^- to a saturated AgCl solution precipitates more AgCl . Used in qualitative analysis.
- Example:** Adding NaCl to saturated AgCl lowers $[\text{Ag}^+]$ because $[\text{Cl}^-]$ is already high -- AgCl precipitates.
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137 Predicting Precipitation

- Explanation:** Compare Q (ion product) to Ksp: $Q > K_{sp} \rightarrow$ precipitation occurs. $Q < K_{sp} \rightarrow$ no precipitation (solution can hold more). $Q = K_{sp} \rightarrow$ saturated.
- AP Chem Tip:** Calculate Q from the mixed concentrations (after dilution), compare to Ksp. Mixing dilute solutions may not precipitate even if a solid is possible.
- Example:** Mix 10 mL of 0.01 M AgNO_3 with 10 mL of 0.01 M NaCl : $[\text{Ag}^+][\text{Cl}^-] = (0.005)(0.005) = 2.5 \times 10^{-5} > K_{sp} (1.8 \times 10^{-10}) \rightarrow$ precipitates.
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138 Selective Precipitation

- Explanation:** Ions can be separated by adding a reagent that precipitates one ion but not the other (different Ksp values). The least soluble precipitates first.
- AP Chem Tip:** Precipitate the ion with the smaller Ksp first (requires less reagent). Used to separate ions in qualitative analysis.
- Example:** Adding S^{2-} to a mixture of Cu^{2+} (Ksp tiny) and Zn^{2+} precipitates CuS first; ZnS precipitates later.
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139 Equilibrium & Free Energy

- Explanation:** $\Delta G(\text{standard}) = -RT \ln K$. $K > 1$: $\Delta G(\text{standard}) < 0$ (products favored at standard conditions). $K = 1$: $\Delta G(\text{standard}) = 0$. $K < 1$: $\Delta G(\text{standard}) > 0$.
- AP Chem Tip:** This is the thermodynamic basis of K: more negative ΔG standard = larger K. At equilibrium, $\Delta G = 0$ and $Q = K$.
- Example:** If ΔG standard = -5.7 kJ at 298 K, $K = e^{(5700/8.314 \times 298)} \sim e^{2.3} = 10$.
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140 Reaction Quotient in Action

- Explanation:** Q predicts shifts for ANY disturbance: adding/removing species, changing pressure/volume, dilution. Compare Q to K to decide direction.
- AP Chem Tip:** *Dilution: for reactions with more gas moles on one side, dilution shifts toward more gas moles (fewer particles pressure... actually toward more particles). Use Q to be precise.*
- Example:** Halving volume (doubling pressure) of $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ raises Q above K (more particles on right), so it shifts left toward N_2O_4 .
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141 Equilibrium Concentration Calculations

- Explanation:** Given K and initial concentrations, use ICE to find equilibrium concentrations. Approximate when K is small (x negligible), and check the 5% rule.
- AP Chem Tip:** *When K is very small, assume $x \ll$ initial concentration, solve without the quadratic, then verify $x < 5\%$ of initial. If not, solve the quadratic exactly.*
- Example:** For $2\text{HI} \rightleftharpoons \text{H}_2 + \text{I}_2$ with $K = 0.02$ and $[\text{HI}]_0 = 0.10 \text{ M}$: $x^2/(0.10)^2 \sim 0.02 \rightarrow x \sim 0.0045 \text{ M}$ (4.5% -- approximation valid).
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142 Van't Hoff Equation

- Explanation:** $\ln(K_2/K_1) = -(\Delta H/R)(1/T_2 - 1/T_1)$. Shows how K changes with temperature: exothermic ($\Delta H < 0$) $\rightarrow$ K decreases with T; endothermic $\rightarrow$ K increases.
- AP Chem Tip:** *Use it to find K at another temperature from ΔH . The sign of ΔH determines the temperature dependence of K.*
- Example:** For an exothermic reaction, raising T from 300 to 320 K decreases K: $\ln(K_2/K_1)$ is negative.
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143 Equilibrium & Catalysis

- Explanation:** Catalysts don't change K or equilibrium position -- only the rate of approach. Enzymes lower E_a for both directions, maintaining the same equilibrium constant.
- AP Chem Tip:** *This is why enzymes can't change the yield of a reaction at equilibrium -- only reach it faster.*
- Example:** Adding an enzyme to a reaction at equilibrium does nothing to concentrations; it only helps if the reaction hasn't equilibrated yet.
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144 Reaction Direction & Spontaneity

- Explanation:** Q vs K also connects to ΔG : $\Delta G = RT \ln(Q/K)$. $Q < K \rightarrow \Delta G < 0$ (spontaneous forward). $Q > K \rightarrow \Delta G > 0$ (nonspontaneous, proceeds reverse).
- AP Chem Tip:** *$\Delta G = RT \ln(Q/K)$ is the dynamic link between kinetics-free thermodynamics and equilibrium. At $Q = K$, $\Delta G = 0$.*
- Example:** If $Q = K/10$, $\Delta G = RT \ln(0.1) < 0$: the reaction proceeds forward spontaneously.
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Unit 8: Acids & Bases

11-15% of the exam. pH, strong/weak acids, buffers, titrations, and solubility with pH.

145 Acid-Base Definitions

Explanation: Arrhenius: acid produces H^+ in water; base produces OH^- . Brønsted-Lowry: acid donates H^+ ; base accepts H^+ . Lewis: acid accepts electron pair; base donates electron pair.

AP Chem Tip: Brønsted-Lowry is about proton transfer; Lewis is about electron pairs (broader -- includes BF_3 as acid). Conjugate pairs differ by one H^+ .

Example: $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$: NH_3 is a Brønsted base (accepts H^+), H_2O is the acid; NH_4^+ is the conjugate acid.

146 Conjugate Acid-Base Pairs

Explanation: A conjugate acid-base pair differs by one proton: acid $\rightarrow$ conjugate base (minus H^+); base $\rightarrow$ conjugate acid (plus H^+). Strong acid $\rightarrow$ weak conjugate base; weak acid $\rightarrow$ strong-ish conjugate base.

AP Chem Tip: The stronger the acid, the weaker its conjugate base. Identify pairs: acid/base differ by H^+ . Example: HCl/Cl^- , NH_4^+/NH_3 , H_2O/OH^- .

Example: For H_2CO_3/HCO_3^- : H_2CO_3 is the acid, HCO_3^- its conjugate base. HCO_3^-/CO_3^{2-} is another pair (HCO_3^- as acid).

147 pH Scale

Explanation: $pH = -\log[H^+]$. $pOH = -\log[OH^-]$. $pH + pOH = 14$ at 25 C. $[H^+][OH^-] = K_w = 1.0 \times 10^{-14}$. Acidic: $pH < 7$. Basic: $pH > 7$. Neutral: 7.

AP Chem Tip: Know the conversions cold: $[H^+] = 10^{-pH}$, $[OH^-] = 10^{-pOH}$. Each pH unit = 10x change in $[H^+]$. $K_w = 1e-14$ at 25 C.

Example: pH 3 has $[H^+] = 1e-3$ M -- 100x more acidic than pH 5 ($1e-5$ M). A solution with $[OH^-] = 1e-10$ M has pH 4.

148 Strong Acids & Bases

Explanation: Strong acids ionize completely: HCl , HBr , HI , HNO_3 , H_2SO_4 (first proton), $HClO_4$. Strong bases: $LiOH$, $NaOH$, KOH , $RbOH$, $CsOH$, $Ca(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$. pH from direct concentration.

AP Chem Tip: For strong acids, $[H^+] = [acid]$ (monoprotic). For strong bases, $[OH^-] = [base] \times (OH \text{ count})$. pH of 0.01 M $HCl = 2$.

Example: 0.05 M H_2SO_4 (first dissociation complete): $[H^+] \sim 0.05$ M, $pH \sim 1.3$. 0.01 M $Ba(OH)_2$: $[OH^-] = 0.02$ M, $pOH = 1.7$, $pH = 12.3$.

149 Weak Acids & Ka

Explanation: Weak acids partially ionize: $HA \rightleftharpoons H^+ + A^-$, $K_a = [H^+][A^-]/[HA]$. Smaller K_a = weaker acid. Percent ionization = $[H^+]/[HA]_0 \times 100\%$ (increases with dilution).

AP Chem Tip: For weak acids, $[H^+] = \sqrt{K_a \times [HA]}$ (when ionization is small). Percent ionization increases as the solution is diluted.

Example: 0.10 M acetic acid ($K_a = 1.8e-5$): $[H^+] \sim \sqrt{1.8e-5 \times 0.10} = 1.3e-3$ M, $pH \sim 2.9$, ionization $\sim 1.3\%$.

150 Weak Bases & Kb

Explanation: Weak bases partially ionize: $B + H_2O \rightleftharpoons BH^+ + OH^-$, $K_b = [BH^+][OH^-]/[B]$. K_b relates to K_a of conjugate acid: $K_a \times K_b = K_w = 1e-14$.

AP Chem Tip: $K_a \times K_b = K_w$ for conjugate pairs. Stronger acid = weaker conjugate base (smaller K_b). $[OH^-] = \sqrt{K_b \times [B]}$ for weak bases.

Example: NH_3 ($K_b = 1.8e-5$): 0.10 M gives $[OH^-] \sim 1.3e-3$ M, $pOH \sim 2.9$, $pH \sim 11.1$.

151 pH of Salts

Explanation: Salt hydrolysis: cations of weak bases (NH_4^+) are acidic; anions of weak acids (CH_3COO^-) are basic. Salts of strong acid + strong base are neutral. Salts of weak+weak depend on relative K_a/K_b .

AP Chem Tip: Determine salt pH by identifying the ion: NH_4Cl acidic (NH_4^+), $NaCH_3COO$ basic (CH_3COO^-), $NaCl$ neutral. Acidic cation + basic anion: compare K_a vs K_b .

Example: $NaCH_3COO$: acetate hydrolyzes, giving $pH > 7$. NH_4NO_3 : ammonium hydrolyzes, $pH < 7$. $NaCl$: neutral pH 7.

152 Polyprotic Acids

Explanation: Polyprotic acids donate protons stepwise (H_2CO_3 , H_3PO_4 , H_2SO_4). Each step has its own K_a ; $K_{a1} \gg K_{a2} \gg K_{a3}$. The first dissociation dominates pH.

AP Chem Tip: Use K_{a1} for pH calculations (subsequent steps contribute negligibly). The conjugate species (HCO_3^- , H_2PO_4^-) act as buffers.

Example: For H_3PO_4 ($K_{a1} = 7.5 \times 10^{-3}$), the pH of 0.1 M H_3PO_4 is set mostly by the first dissociation.

153 Buffer Solutions

Explanation: Buffers resist pH change: a weak acid + its conjugate base (or weak base + conjugate acid). Henderson-Hasselbalch: $\text{pH} = \text{p}K_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right)$. Buffer capacity is best at $\text{pH} \sim \text{p}K_a$ (ratio near 1).

AP Chem Tip: Henderson-Hasselbalch: $\text{pH} = \text{p}K_a + \log\left(\frac{[A^-]}{[HA]}\right)$. Buffers work best within ± 1 pH unit of $\text{p}K_a$. Adding small amounts of acid/base shifts the ratio slightly.

Example: A buffer of 0.10 M CH_3COOH and 0.10 M NaCH_3COO has $\text{pH} = \text{p}K_a = 4.74$. Adding 0.01 mol HCl converts some acetate to acid; pH barely moves.

154 Buffer Action

Explanation: Buffers neutralize added H^+ (conjugate base absorbs it) and added OH^- (weak acid absorbs it). The pH changes only slightly as long as buffer capacity isn't exceeded.

AP Chem Tip: Added H^+ reacts with $A^- \rightarrow HA$. Added OH^- reacts with $HA \rightarrow A^- + \text{H}_2\text{O}$. The ratio $[A^-]/[HA]$ changes little.

Example: Adding HCl to the acetate buffer: $\text{H}^+ + \text{CH}_3\text{COO}^- \rightarrow \text{CH}_3\text{COOH}$. pH drops only slightly ($4.74 \rightarrow \sim 4.65$ for small additions).

155 Titration Curves: Strong-Strong

Explanation: Strong acid + strong base: pH starts low, rises steeply near equivalence, equivalence at pH 7. The steep part spans pH ~ 3 -11. Indicator: phenolphthalein or methyl red.

AP Chem Tip: Equivalence point of strong-strong = pH 7 exactly. The curve is symmetric around it. Volume of base at equivalence gives moles of acid ($n = \text{MV}$).

Example: Titrating 25 mL of 0.10 M HCl with 0.10 M NaOH: equivalence at 25 mL NaOH, pH 7.

156 Titration Curves: Weak Acid

Explanation: Weak acid + strong base: starts higher than strong acid, buffer region (flat) around half-equivalence, equivalence point $\text{pH} > 7$ (conjugate base hydrolyzes). Half-equivalence: $\text{pH} = \text{p}K_a$.

AP Chem Tip: At half-equivalence, $[\text{HA}] = [A^-]$, so $\text{pH} = \text{p}K_a$ -- read $\text{p}K_a$ directly from the curve. Equivalence $\text{pH} > 7$ for weak acid titrations. Beyond equivalence, curve follows strong base.

Example: Titrating acetic acid with NaOH: at 12.5 mL NaOH (half of 25 mL), $\text{pH} = \text{p}K_a = 4.74$; equivalence at $\sim \text{pH } 8.7$.

157 Titration Curves: Weak Base & Polyprotic

Explanation: Weak base + strong acid: starts high, equivalence $\text{pH} < 7$ (conjugate acid hydrolyzes). Polyprotic acids show multiple equivalence points and multiple buffer regions.

AP Chem Tip: Weak base equivalence $\text{pH} < 7$. Polyprotic: each proton has its own half-equivalence ($\text{pH} = \text{p}K_{a1}$, $\text{p}K_{a2}$) and equivalence point.

Example: Titrating Na_2CO_3 with HCl shows two equivalence points (carbonate $\rightarrow$ bicarbonate $\rightarrow$ carbonic acid).

158 Indicators

Explanation: Indicators are weak acids whose acid and base forms have different colors. The color change occurs around $\text{p}K_a(\text{indicator}) \pm 1$. Choose an indicator whose $\text{p}K_a$ is near the equivalence pH.

AP Chem Tip: Pick an indicator whose $\text{p}K_a$ matches the equivalence point pH: phenolphthalein ($\text{p}K_a \sim 9$) for weak acid titrations; methyl red ($\text{p}K_a \sim 5$) for weak base titrations.

Example: For a weak acid - strong base titration (equivalence $\text{pH} \sim 8.7$), phenolphthalein (colorless $\rightarrow$ pink ~ 8.2 -10) is the right choice.

159 Acid-Base Properties of Salts & Oxides

Explanation: Metal oxides are basic ($\text{Na}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{NaOH}$). Nonmetal oxides are acidic ($\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3$; $\text{SO}_2 \rightarrow \text{H}_2\text{SO}_3$). Amphoteric oxides (Al_2O_3 , ZnO) react with both acids and bases.

AP Chem Tip: *Metal oxide = basic; nonmetal oxide = acidic. Amphoteric oxides and hydroxides ($\text{Al}(\text{OH})_3$, $\text{Zn}(\text{OH})_2$) dissolve in both acid and base.*

Example: CO_2 in rainwater forms carbonic acid (acid rain component). Na_2O reacts with water to make NaOH (basic).

160 Amphoteric Species

Explanation: Amphoteric substances can act as acid OR base: water, HCO_3^- , HSO_4^- , H_2PO_4^- , $\text{Al}(\text{OH})_3$, amino acids. They react differently depending on the partner.

AP Chem Tip: *Identify amphoteric species: they have both a proton to donate and a lone pair/basic site. HCO_3^- reacts with acid (becomes H_2CO_3) or base (becomes CO_3^{2-}).*

Example: $\text{HCO}_3^- + \text{H}^+ \rightarrow \text{H}_2\text{CO}_3$ (acts as base). $\text{HCO}_3^- + \text{OH}^- \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O}$ (acts as acid).

161 pH & Solubility

Explanation: Solubility of salts with basic anions (fluorides, hydroxides, carbonates, sulfides) increases in acid: H^+ removes the anion, shifting dissolution right. Salts with neutral anions (chlorides, nitrates) are unaffected.

AP Chem Tip: *Acids dissolve insoluble hydroxides/carbonates/sulfides/fluorides by consuming the anion (Le Chatelier). This is why HCl dissolves CaCO_3 (fizzing CO_2) and rust.*

Example: $\text{CaCO}_3(\text{s}) + 2\text{H}^+ \rightarrow \text{Ca}^{2+} + \text{CO}_2 + \text{H}_2\text{O}$: acid dissolves limestone (caves, antacids). AgCl is not affected by acid (Cl^- is the conjugate of a strong acid).

162 Autoionization of Water

Explanation: Water autoionizes: $2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$, $K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1\text{e-}14$ at 25 C. K_w increases with temperature. pH 7 is neutral only at 25 C.

AP Chem Tip: *$K_w = 1\text{e-}14$ at 25 C. At higher T, K_w increases and neutral pH drops below 7 (but $[\text{H}^+] = [\text{OH}^-]$ still).*

Example: At 50 C, $K_w \sim 5.5\text{e-}14$, so neutral pH ~ 6.6 -- not 7. Neutral means $[\text{H}^+] = [\text{OH}^-]$, not pH 7.

163 pH of Strong Acid + Strong Base Mixtures

Explanation: For leftover strong acid/base after mixing: compute excess moles, divide by total volume to get $[\text{H}^+]$ or $[\text{OH}^-]$, then pH/pOH.

AP Chem Tip: *Find which reactant is in excess, calculate the excess moles, divide by the total volume. Then pH from $[\text{H}^+]$.*

Example: Mix 30 mL 0.1 M HCl with 20 mL 0.1 M NaOH : excess $\text{H}^+ = 0.001$ mol in 50 mL = 0.02 M, pH = 1.7.

164 Equivalence Point & Stoichiometry

Explanation: At equivalence, moles acid = moles base (accounting for stoichiometry, e.g., H_2SO_4 has 2 H^+). $n = M \times V$ for each, use the mole ratio.

AP Chem Tip: *For diprotic acids, 1 mol H_2SO_4 neutralizes 2 mol NaOH . Equivalence volume: $V(\text{base}) = (M(\text{acid}) \times V(\text{acid}) \times n_{\text{H}})/M(\text{base})$.*

Example: 25.0 mL of 0.10 M H_2SO_4 (0.0025 mol acid, 0.0050 mol H^+) needs 50.0 mL of 0.10 M NaOH .

165 Percent Ionization & Dilution

Explanation: Percent ionization of a weak acid = $([\text{H}^+]/[\text{HA}]_0) \times 100\%$. It INCREASES with dilution (the equilibrium shifts right as concentration drops), even though $[\text{H}^+]$ decreases.

AP Chem Tip: *Diluting a weak acid increases percent ionization but decreases $[\text{H}^+]$. This is Le Chatelier: fewer particles favor more dissociation.*

Example: Acetic acid at 0.1 M is $\sim 1.3\%$ ionized; at 0.01 M it is $\sim 4.2\%$ ionized (but $[\text{H}^+]$ is lower).

Unit 9: Applications of Thermodynamics

7-9% of the exam. Electrochemistry, free energy, and coupled processes.

166 Galvanic (Voltaic) Cells

Explanation: Galvanic cells convert spontaneous redox into electrical energy. Anode (oxidation, negative) and cathode (reduction, positive) connected by a salt bridge. Electrons flow anode → cathode externally.

AP Chem Tip: *Anode = oxidation = negative = anions flow toward it in the salt bridge (A O N: Anode Oxidation Negative). Cathode = reduction = positive.*

Example: In a Zn/Cu cell: Zn anode (oxidized, mass decreases), Cu cathode (Cu²⁺ reduced, mass increases). Electrons flow Zn → Cu.

167 Cell Potential E

Explanation: Cell potential $E(\text{cell}) = E(\text{cathode}) - E(\text{anode}) = E(\text{red, cathode}) - E(\text{red, anode})$. Positive $E(\text{cell})$ = spontaneous ($\Delta G < 0$). Standard reduction potentials are tabulated.

AP Chem Tip: *$E(\text{cell}) = E(\text{red cathode}) - E(\text{red anode})$ using standard reduction potentials. A positive $E(\text{cell})$ means spontaneous. Larger difference = more voltage.*

Example: Zn/Cu: $E(\text{cell}) = +0.34 - (-0.76) = +1.10 \text{ V}$ -- positive, so spontaneous.

168 Standard Reduction Potentials

Explanation: Standard reduction potentials ($E(\text{red})$) measure tendency to gain electrons vs SHE (0 V). More positive = better oxidizing agent (easier to reduce). More negative = better reducing agent.

AP Chem Tip: *The more positive $E(\text{red})$, the stronger the oxidizing agent (it wants electrons). F₂ (+2.87) is the strongest oxidizer; Li (-3.05) the strongest reducer.*

Example: Cu²⁺ (+0.34) will oxidize Zn (-0.76) because Cu²⁺ is the better oxidizer; the reaction is spontaneous.

169 Delta G, E, and K Relationship

Explanation: $\Delta G = -nFE$. At standard conditions: $\Delta G^\circ = -nFE^\circ$. Also $\Delta G^\circ = -RT \ln K$. So $E^\circ = (RT/nF) \ln K$.

AP Chem Tip: *All three connect: $\Delta G = -nFE = -RT \ln K$. Positive $E \leftrightarrow$ negative $\Delta G \leftrightarrow K > 1$ (all mean spontaneous).*

Example: For $E = 0.0592 \text{ V}$ and $n = 1$ (at 25 °C): $K = 10^{(nE/0.0592)} = 10^1 = 10$.

170 Nernst Equation

Explanation: Nernst: $E = E^\circ - (0.0592/n) \log Q$ (at 25 °C). Accounts for nonstandard concentrations. As Q increases (reactants consumed), E decreases toward zero at equilibrium.

AP Chem Tip: *$E = E^\circ - (0.0592/n) \log Q$. At equilibrium ($Q = K$), $E = 0$. $Q < K$ (early reaction) gives $E > E^\circ$... actually $\log(Q/K)$ negative.*

Example: A Zn/Cu cell with [Cu²⁺] lowered from 1 M to 0.01 M: E drops by $(0.0592/2) \log(0.01) = 0.059 \text{ V}$.

171 Electrolytic Cells

Explanation: Electrolytic cells use external voltage to drive nonspontaneous reactions. Anode is positive (oxidation), cathode negative (reduction). Used for electroplating, electrolysis of water, aluminum production.

AP Chem Tip: *In electrolytic cells the signs flip: anode = + (external power forces oxidation). Electrolysis of water: $2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2$ needs voltage $> 1.23 \text{ V}$.*

Example: Electroplating silver: Ag⁺ is reduced at the cathode (object being plated). Electrolysis of NaCl produces Cl₂ at the anode, H₂ and OH⁻ at the cathode.

172 Electrolysis & Faraday's Law

Explanation: Faraday: moles of electrons = $Q/F = (I \times t)/F$ where Q = charge (C), I = current (A), t = time (s), $F = 96,485 \text{ C/mol e}^-$. Mass = moles e⁻ × (moles substance/moles e⁻) × molar mass.

AP Chem Tip: *$Q = I \times t$, then $n(\text{e}^-) = Q/F$, then stoichiometry to the substance. Track electrons per ion (Ag⁺ needs 1 e⁻, Cu²⁺ needs 2 e⁻, Al³⁺ needs 3 e⁻).*

Example: 1.00 A for 1,930 s = 1,930 C = 0.0200 mol e⁻. That deposits 0.0200 mol Ag (2.16 g) or 0.0100 mol Cu (0.635 g).

173 Electrolysis of Water & Aqueous Solutions

Explanation: Electrolysis of water: $2\text{H}_2\text{O} \rightarrow 2\text{H}_2(\text{g}) + \text{O}_2(\text{g})$ (2:1 volume ratio). In aqueous electrolysis, water's redox can compete: H_2O reduces before Na^+ , H_2O oxidizes before SO_4^{2-} .

AP Chem Tip: *Volume ratio of $\text{H}_2:\text{O}_2 = 2:1$ from $2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2$. In NaCl electrolysis, Cl^- is oxidized (not water) due to overpotential; Na^+ is NOT reduced (water is).*

Example: Electrolysis of water at 2.00 A for 965 s gives 0.0200 mol $\text{e}^- \rightarrow 0.0100$ mol H_2 (0.224 L at STP) and 0.00500 mol O_2 .

174 Batteries & Fuel Cells

Explanation: Primary batteries (non-rechargeable: alkaline, zinc-carbon). Secondary (rechargeable: lead-acid, Li-ion). Fuel cells: continuous fuel supply ($\text{H}_2/\text{O}_2 \rightarrow \text{H}_2\text{O}$, 1.23 V).

AP Chem Tip: *Lead-acid: $\text{Pb} + \text{PbO}_2 + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{PbSO}_4 + 2\text{H}_2\text{O}$ (discharge). Li-ion batteries shuttle Li^+ between electrodes. Fuel cells keep supplying H_2 and O_2 .*

Example: A hydrogen fuel cell produces water and electricity: $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$, $E = 1.23$ V. Used in spacecraft and emerging vehicles.

175 Corrosion

Explanation: Corrosion: metal oxidation (rusting = $\text{Fe} \rightarrow \text{Fe}^{2+} \rightarrow \text{rust}$). Requires O_2 and water. Prevented by: coatings, galvanizing (Zn sacrificial), cathodic protection (sacrificial anode), alloying (stainless steel).

AP Chem Tip: *Sacrificial anodes (Zn, Mg) are more active (more negative E) and corrode instead of the protected metal. Galvanized steel = zinc coating.*

Example: A magnesium anode attached to a ship's hull corrodes instead of the steel (Mg is more negative than Fe). Zinc protects iron the same way.

176 Thermodynamics of Electrochemistry

Explanation: The maximum electrical work = $\Delta G = -nFE$. Efficiency: fuel cells convert chemical energy to electricity directly (not via heat), giving higher efficiency than combustion engines.

AP Chem Tip: *Electrical work = nFE . Fuel cells bypass heat engines, avoiding Carnot limits -- much higher efficiency for H_2 .*

Example: A H_2 fuel cell at $E = 1.23$ V, $n = 2$: max work = $2 \times 96,485 \times 1.23 = 237$ kJ per mol H_2 .

177 Nonstandard Cells & Concentration Cells

Explanation: Concentration cells: same redox couple, different concentrations; $E = (0.0592/n) \log([\text{higher}]/[\text{lower}])$. Current flows until concentrations equalize.

AP Chem Tip: *Concentration cells produce voltage purely from concentration differences. At equal concentrations, $E = 0$.*

Example: Two Cu^{2+}/Cu half-cells at 1.0 M and 0.01 M: $E = (0.0592/2) \log(1/0.01) = 0.0592$ V.

178 Free Energy & Work in Cells

Explanation: $\Delta G = -nFE$ tells the maximum useful work. A battery's voltage is fixed by the reaction, but total energy depends on the amount of material (n).

AP Chem Tip: *Voltage (E) is intensive (per mole of reaction); energy ($\Delta G \times \text{moles}$) depends on how much reactant is stored.*

Example: A D-cell and AAA both give ~ 1.5 V, but the D-cell stores more reactants $\rightarrow$ more total energy.

179 Redox in Biological Systems

Explanation: Biological redox couples (NAD^+/NADH , FAD/FADH_2 , $\text{O}_2/\text{H}_2\text{O}$) drive metabolism. The electron transport chain uses a series of redox potentials to release energy stepwise.

AP Chem Tip: *Electrons flow from more negative to more positive reduction potentials: $\text{NADH} (-0.32) \rightarrow \dots \rightarrow \text{O}_2 (+0.82)$. Each step releases usable energy.*

Example: In respiration, NADH donates electrons (oxidized) that ultimately reduce O_2 to water, releasing ~ 220 kJ/mol.

180 Thermodynamic Favorability Summary

- Explanation:** $\Delta G < 0$, $E > 0$, $K > 1$ all indicate spontaneity at the given conditions. They are linked: $\Delta G = -nFE = -RT \ln K = RT \ln(Q/K)$.
- AP Chem Tip:** *One framework: compare Q to K . $Q < K \rightarrow$ forward spontaneous ($\Delta G < 0$, $E > 0$). At $Q = K \rightarrow$ equilibrium. $Q > K \rightarrow$ reverse.*
- Example:** A reaction with $K = 100$ at current $Q = 10$ proceeds forward: $\Delta G < 0$ and $E > 0$ until Q reaches 100.
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181 Thermodynamics of Real Processes

- Explanation:** Real processes have inefficiencies: heat loss, overpotentials, side reactions. Cell voltage under load drops below E standard (polarization). Entropy increases in the surroundings.
- AP Chem Tip:** *Overpotential: extra voltage needed to overcome activation barriers in electrolysis. Real fuel cells operate below the theoretical 1.23 V.*
- Example:** Water electrolysis in practice needs $\sim 1.5\text{--}2.0$ V (overpotential), not exactly 1.23 V.
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182 Energy Storage & Thermodynamics

- Explanation:** Energy storage compares: batteries (chemical, high efficiency), capacitors (electric field), pumped hydro (gravitational), hydrogen (chemical). Thermodynamics sets the limits; kinetics and materials set the practical performance.
- AP Chem Tip:** *Batteries store energy as chemical potential; supercapacitors store charge physically. Round-trip efficiency differs by technology.*
- Example:** Pumped hydro storage: energy = mgh ; round-trip efficiency $\sim 75\text{--}80\%$. Li-ion batteries: $\sim 90\%+$ round-trip.
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183 Spontaneity with Nonstandard Conditions

- Explanation:** Use $\Delta G = \Delta G^\circ + RT \ln Q$ (or the Nernst equation in electrochemistry) to evaluate spontaneity under actual (nonstandard) concentrations.
- AP Chem Tip:** *Even a 'nonspontaneous' standard reaction can run if conditions shift Q (e.g., removing product keeps Q low). Industrial processes use this.*
- Example:** Producing metals via electrolysis uses external energy because the standard reaction is nonspontaneous ($\Delta G^\circ > 0$).
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184 Thermodynamics & Life

- Explanation:** Living systems are open systems: they take in energy (food, light) and export entropy (heat, waste). $\Delta S_{\text{universe}} > 0$ overall, even as organisms maintain local order.
- AP Chem Tip:** *Organisms maintain order locally by increasing entropy elsewhere (releasing heat). This satisfies the second law.*
- Example:** A plant builds ordered sugar from CO_2 and H_2O using light energy; it releases entropy as heat and O_2 .
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What's Next?

You have now reviewed every unit of the AP Chemistry course. The concepts that matter most are the ones you almost knew -- go back to the Table of Contents, find the units you marked, and reread just those tip lines. Two weeks out, do a rapid pass over the entire guide; the day before, review only the tip lines. On exam day, show your work on free-response questions -- partial credit is real -- and watch significant figures.

Pair it with the Study Mastery Cheat Sheet (\$19) -- how to actually retain all of it

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