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AP Chemistry Complete Master Textbook

Units 1–9 Comprehensive Theory, Essential Equations, Comparison Tables & Step-by-Step Worked Problems

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📘 Structured Theory · Comparison Tables · Step-by-Step Worked Examples · FRQ Traps

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CHAPTER 1 · CORE CURRICULUM

AP Exam Weighting: 7–9%

Unit 1: Atomic Structure and Properties

Unit 1 establishes the quantitative and quantum-mechanical foundations of chemistry. Students bridge the particulate scale of individual atoms, ions, and molecules to macroscopic laboratory measurements using the mole, Avogadro's constant, mass spectrometry, and elemental composition analysis. Furthermore, Coulomb's Law, electron configurations, and Photoelectron Spectroscopy (PES) provide the physical basis for explaining periodic trends in atomic radius, ionization energy, electronegativity, and ionic charges.

CHAPTER 1 ESSENTIAL EQUATIONS, LAWS & CONSTANTS

$n = m / M$	Moles (mol) = sample mass (g) / molar mass (g·mol^{-1})
$N = n \times N_A$	Number of particles = moles × Avogadro's constant (6.022 × 10^{23} mol^{-1})
$A = Z + N_n$	Mass number (A) = atomic number / protons (Z) + neutrons (N_n)
$Ar = \Sigma (f_i \times m_i)$	Average atomic mass (amu) = sum of (fractional abundance × isotopic mass)
$\%\ Mass = (m_{element} / m_{total}) \times 100\%$	Mass percent of an element or compound in a pure substance or mixture
$F_{elec} \propto (q_1 \times q_2) / r^2$	Coulomb's Law: Electrostatic force is proportional to charge product over distance squared

§ 1.1 The Mole, Avogadro's Constant & Molar Mass

The fundamental SI unit for measuring the amount of a chemical substance is the **mole (mol)**. Just as one dozen always denotes exactly 12 items, one mole is defined as **6.022 × 10^{23} representative particles**. This proportionality constant is known as **Avogadro's number (N_A = 6.022 × 10^{23} mol^{-1})**, and it bridges the gap between unimaginably tiny subatomic/molecular entities and the macroscopic gram-scale quantities measured on an analytical balance in the laboratory.

Because counting individual atoms directly is physically impossible, chemists count atoms by weighing them using **molar mass (M)**. On the periodic table, the numerical value listed for an element's atomic mass serves a dual role: for iron (Fe), **55.85 amu** is the average mass of a single iron atom, whereas **55.85 g·mol^{-1}** is the mass of one full mole (6.022 × 10^{23} atoms) of iron. For ionic and molecular compounds, the molar mass is calculated by summing the molar masses of every constituent atom in the chemical formula, taking care to distribute any subscript outside parentheses to every element inside the polyatomic group.

- **Pure Atomic Elements (e.g., Fe):** 1 mol Fe = 6.022 × 10^{23} individual iron atoms (M = 55.85 g·mol^{-1}).
- **Molecular Compounds (e.g., NH_3, CH_4, C_3H_8):** 1 mol = 6.022 × 10^{23} discrete, covalently bonded molecules.
- **Ionic Compounds (e.g., $MgCl_2$, KBr, $Ca(NO_3)_2$):** Exist as 3D crystal lattices; 1 mol = 6.022 × 10^{23} formula units.
- **Charged Species (e.g., Al^{3+}, Na^+):** 1 mol = 6.022 × 10^{23} individual ions.
- **Parenthetical Subscript Distribution:** In $Ca(NO_3)_2$, the outer subscript 2 multiplies everything inside: 1 Ca + 2 N + 6 O → M = 40.08 + 2(14.01) + 6(16.00) = 164.10 g·mol^{-1}.

Table 1.1 · Representative Particles and Molar Masses Across Substance Classes

Substance Class	Chemical Example	Representative Particle	Atom Inventory per Unit	Molar Mass (g·mol^{-1})
Atomic Element	Iron (Fe)	Atom	1 Fe	55.85
Molecular Compound	Propane (C_3H_8)	Molecule	3 C + 8 H	3(12.01) + 8(1.008) = 44.09
Binary Ionic Compound	Potassium Bromide (KBr)	Formula Unit	1 K^+ + 1 Br^-	39.10 + 79.90 = 119.00
Binary Ionic Oxide	Iron(III) Oxide (Fe_2O_3)	Formula Unit	2 Fe^{3+} + 3 O^{2-}	2(55.85) + 3(16.00) = 159.70
Polyatomic Ionic Salt	Calcium Nitrate, $Ca(NO_3)_2$	Formula Unit	1 Ca + 2 N + 6 O	40.08 + 28.02 + 96.00 = 164.10

EXAMPLE 1.1 **Dimensional Analysis Between Moles and Representative Particles**

Problem: (a) How many molecules of methane (CH_4) are present in 0.650 mol of CH_4? (b) A sample containing 2.10 × 10^{24} sodium ions (Na^+) is equivalent to how many moles of Na^+?

STEP-BY-STEP SOLUTION:

1. Part (a) Moles to Molecules: Multiply given moles by Avogadro's constant so mol cancels in the denominator: N = 0.650 mol CH_4 × (6.022 × 10^{23} molecules / 1 mol) = 3.91 × 10^{23} molecules of CH_4 (rounded to 3 significant figures).
2. Part (b) Particles to Moles: Place Avogadro's number in the denominator to cancel ions: n = (2.10 × 10^{24} Na^+ ions) × (1 mol / 6.022 × 10^{23} ions) = 3.49 mol Na^+.

Final Answer: (a) 3.91 × 10^{23} molecules CH_4; (b) 3.49 mol Na^+

EXAMPLE 1.2 **Multi-Step Molar Mass & Subscript Atom Counting**

Problem: (a) How many oxygen atoms are present in a 41.03 g sample of calcium nitrate, $Ca(NO_3)_2$ (M = 164.10 g·mol^{-1})? (b) How many molecules of propane (C_3H_8, M = 44.09 g·mol^{-1}) are contained in a 35.3 g sample?

STEP-BY-STEP SOLUTION:

1. Part (a) Step 1 — Grams to Moles of Compound: n($Ca(NO_3)_2$) = 41.03 g / 164.10 g·mol^{-1} = 0.2500 mol $Ca(NO_3)_2$.
2. Part (a) Step 2 — Formula Unit to Oxygen Moles: Each $Ca(NO_3)_2$ unit contains 2 × 3 = 6 oxygen atoms, so n(O) = 0.2500 mol × 6 = 1.500 mol O atoms.
3. Part (a) Step 3 — Moles to Atoms: N(O) = 1.500 mol × (6.022 × 10^{23} atoms·mol^{-1}) = 9.033 × 10^{23} oxygen atoms.
4. Part (b) Grams of Propane to Molecules: First find moles: n(C_3H_8) = 35.3 g / 44.09 g·mol^{-1} = 0.8006 mol C_3H_8. Multiply by N_A: N = 0.8006 mol × (6.022 × 10^{23} molecules·mol^{-1}) = 4.82 × 10^{23} molecules of C_3H_8.

Final Answer: (a) 9.033 × 10^{23} O atoms; (b) 4.82 × 10^{23} C_3H_8 molecules

⚠ **AP EXAM TRAP & FRQ SCORING GUIDELINE**

AP Exam Trap: When counting individual atoms inside polyatomic salts such as $Ca(NO_3)_2$, $Al_2(SO_4)_3$, or $(NH_4)_3PO_4$, students frequently forget to distribute the subscript outside the parentheses before multiplying by Avogadro's number. Always write out the explicit atom ratio (e.g., 6 mol O per 1 mol $Ca(NO_3)_2$) as a dimensional-analysis step.

§ 1.2 Isotopes, Atomic Nuclei & Mass Spectrometry (MS)

In standard nuclear notation (ᴬ_Z X), the bottom-left subscript is the **atomic number (Z)**, which equals the number of protons in the nucleus and uniquely defines the identity of the element. The top-left superscript is the **mass number (A)**, representing the total integer sum of protons and neutrons in that specific nucleus. To determine the number of neutrons (N_n), subtract the atomic number from the mass number: **N_n = A − Z**. For example, neutral **Bromine-79 ($^{79}_{35}$Br)** contains 35 protons, 35 electrons, and 79 − 35 = 44 neutrons. Because all isotopes of a given element possess the exact same number of protons and therefore the identical ground-state electron configuration, **isotopes exhibit identical chemical behavior**.

A **mass spectrometer** ionizes a sample, accelerates the ions through a magnetic or electric field to separate isotopes by their mass-to-charge ratio (m/z), and measures the relative abundance of each isotope. The **average atomic mass** reported on the periodic table is the weighted average of all naturally occurring isotopes, calculated by multiplying each isotope's exact mass by its fractional abundance and summing the contributions.

- **Atomic Number (Z):** Number of protons; equals number of electrons in a neutral atom.
- **Mass Number (A):** Protons + neutrons (always an exact integer for a single nuclide).
- **Weighted Average Atomic Mass:** Always lies closer to the mass of the most abundant isotope in the mass spectrum.
- **Mass Spectrum Bar Heights:** Each vertical bar position on the horizontal axis gives the isotopic mass number (amu), while the bar height gives relative or percent abundance.

EXAMPLE 1.3 Working Backward from Average Atomic Mass to Find an Unknown Isotopic Mass

> **Problem:** Gallium (Ga) has two naturally occurring isotopes and an average atomic mass of 69.72 amu. Gallium-69 (^{69}Ga) has an isotopic mass of 68.93 amu and a relative abundance of 60.11%. What is the exact isotopic mass of Gallium-71 (^{71}Ga)?

STEP-BY-STEP SOLUTION:

1. Step 1 — Find Fractional Abundance of ^{71}Ga: Since total abundance must equal 100%, the percent abundance of ^{71}Ga is 100.00% − 60.11% = 39.89% (f_2 = 0.3989).
2. Step 2 — Set Up the Weighted Average Equation: 69.72 amu = (0.6011)(68.93 amu) + (0.3989)(m_71).
3. Step 3 — Solve for m_71: (0.6011)(68.93) = 41.43 amu. Subtracting from the average gives 69.72 − 41.43 = 28.29 amu. Dividing by 0.3989 gives m_71 = 28.29 / 0.3989 = 70.92 amu.

Final Answer: 70.92 amu

EXAMPLE 1.4 Identifying an Unknown Element from its Mass Spectrum

> **Problem:** A mass spectrum of a pure element displays five peaks at mass numbers 90 (51% abundance, tallest peak), 91 (11%), 92 (17%), 94 (17%), and 96 (4%). Which element on the periodic table does this spectrum represent?

STEP-BY-STEP SOLUTION:

1. Step 1 — Estimate the Weighted Average: The dominant peak is at 90 amu (51%), while the heavier isotopes at 91, 92, 94, and 96 pull the weighted average slightly above 90 to approximately 91.2 amu.
2. Step 2 — Compare Against Periodic Table Candidates: Strontium (Sr, 87.62 amu) is too light, and Molybdenum (Mo, 95.95 amu) is too heavy.
3. Step 3 — Identify Element: Zirconium (Zr) has an average atomic mass of 91.22 amu, matching the mass spectrum.

Final Answer: Zirconium (Zr, average atomic mass = 91.22 amu)

⚠ **AP EXAM TRAP & FRQ SCORING GUIDELINE**

AP Exam Trap: Never confuse the integer mass number (A = protons + neutrons of one specific isotope) with the decimal average atomic mass on the periodic table. Furthermore, individual atoms never have 'average' masses—no single zirconium atom has a mass of 91.22 amu.

§ 1.3 Law of Definite Proportions, Empirical Formulas & Mixture Analysis

Proust's Law of Definite Proportions states that a pure chemical compound always contains the exact same proportions of elements by mass, regardless of its natural or synthetic source. When representing compounds, chemists distinguish between two types of formulas: the **molecular formula** gives the actual number of atoms of each element in a single molecule (such as $\mathbf{C_6H_{12}O_6}$ for glucose), whereas the **empirical formula** reduces those subscripts to the simplest whole-number ratio ($\mathbf{CH_2O}$ for glucose). To scale an empirical formula up to a molecular formula, divide the compound's experimental molar mass by its empirical formula mass to find the integer multiplier *n*.

All matter is classified into **pure substances** (elements and compounds, which have fixed composition) and **mixtures** (multiple substances physically combined in variable proportions). A **homogeneous mixture** (solution) has a uniform composition throughout (e.g., air, brass, aqueous saltwater), whereas a **heterogeneous mixture** is non-uniform with distinct visible phases (e.g., sand in water, granite). Elemental mass analysis allows chemists to determine the **mass percent purity** of a specific compound inside a multi-component mixture.

- **Empirical Formula Procedure:** Assume 100 g sample (% → g) → divide each mass by atomic molar mass to get moles → divide all mole values by the smallest mole value → multiply to clear fractions if needed.
- **Molecular Formula Multiplier:** n = (Actual Molar Mass) / (Empirical Formula Mass); multiply all empirical subscripts by n.
- **Mixture Purity Strategy:** Use the unique element that comes exclusively from the target compound, convert its mass to moles, apply formula stoichiometry to find moles and grams of the compound, and divide by total mixture mass.

EXAMPLE 1.5 Determining Empirical and Molecular Formulas from Mass Percent

Problem: Determine both the empirical and molecular formulas of a nitrogen oxide compound containing 30.45% nitrogen and 69.55% oxygen by mass, given that its experimental molar mass is 92.02 $g \cdot mol^{-1}$.

STEP-BY-STEP SOLUTION:

1. Step 1 — Assume 100.0 g Sample: 30.45% N → 30.45 g N; 69.55% O → 69.55 g O.
2. Step 2 — Convert Grams to Moles: n(N) = 30.45 g / 14.01 $g \cdot mol^{-1}$ = 2.173 mol N; n(O) = 69.55 g / 16.00 $g \cdot mol^{-1}$ = 4.347 mol O.
3. Step 3 — Divide by Smallest Mole Value: N : O = (2.173 / 2.173) : (4.347 / 2.173) = 1.000 : 2.000 → Empirical formula is NO_2.
4. Step 4 — Scale to Molecular Formula: Empirical mass of NO_2 = 14.01 + 2(16.00) = 46.01 $g \cdot mol^{-1}$. Multiplier n = 92.02 / 46.01 = 2 → Molecular formula is N_2O_4.

Final Answer: Empirical formula: NO_2; Molecular formula: N_2O_4

EXAMPLE 1.6 **Elemental Analysis & Mass Percent Purity of a Mixture**

Problem: A 6.00 g solid mixture of sodium chloride (NaCl) and potassium bromide (KBr) is analyzed and found to contain 0.943 g of elemental sodium (Na). What is the mass percent of NaCl in the original mixture?

STEP-BY-STEP SOLUTION:

1. Step 1 — Moles of Unique Element (Na): Because all sodium originates exclusively from NaCl, n(Na) = 0.943 g / 22.99 $g \cdot mol^{-1}$ = 0.0410 mol Na.
2. Step 2 — Moles & Mass of NaCl: Since there is 1 Na^+ ion per formula unit of NaCl, n(NaCl) = 0.0410 mol. Multiply by M(NaCl) = 58.44 $g \cdot mol^{-1}$: m(NaCl) = 0.0410 mol × 58.44 $g \cdot mol^{-1}$ = 2.40 g NaCl.
3. Step 3 — Mass Percent in Mixture: % NaCl = (2.40 g / 6.00 g total mixture) × 100% = 40.0% NaCl.

Final Answer: 40.0% NaCl by mass

⚠ **AP EXAM TRAP & FRQ SCORING GUIDELINE**

AP Exam Trap: In mixture purity problems, never divide the mass of the single element (0.943 g Na) directly by the total mixture mass (6.00 g) when asked for the mass percent of the compound (NaCl). You must first convert moles of the tracked element into grams of the full compound.

§ 1.4 Coulomb's Law, Electron Configuration & Photoelectron Spectroscopy (PES)

To understand how electrons behave inside an atom, chemists apply **Coulomb's Law**: the electrostatic force of attraction (F_{elec}) between the positively charged nucleus and a negatively charged electron is directly proportional to the product of their charges ($q_1 \times q_2$) and inversely proportional to the square of the distance between them (r^2). In **Rutherford's gold-foil experiment**, alpha particles were deflected by a tiny, dense, positively charged nucleus at the center of the atom. By Coulomb's inverse-square law, if the distance between the nucleus and an electron doubles, the attractive force drops to **1/4 of its original strength**; conversely, if nuclear charge triples at constant distance, the attraction triples.

Electrons are organized into principal energy shells (n = 1, 2, 3, ...), subshells (s, p, d, f), and orbitals. Because each orbital holds at most **2 electrons with opposite spins** (Pauli Exclusion Principle), an **s subshell** (1 orbital) holds 2 electrons, a **p subshell** (3 orbitals) holds 6, a **d subshell** (5 orbitals) holds 10, and an **f subshell** (7 orbitals) holds 14. According to the **Aufbau Principle**, electrons fill the lowest-energy subshells first (1s → 2s → 2p → 3s → 3p → 4s → 3d → 4p). By **Hund's Rule**, degenerate orbitals in p, d, or f subshells are occupied singly with parallel spins before any pairing occurs.

Photoelectron Spectroscopy (PES) bombards a sample with high-energy X-ray or UV radiation to measure the **binding energy** required to eject electrons from each subshell. Unlike Bohr's simple planetary shell model, a PES spectrum displays distinct peaks for individual subshells (proving that the n = 2 shell splits into 2s and 2p subshells). The peak with the **highest binding energy** always corresponds to the innermost **1s core electrons** closest to the nucleus, whereas the peak with the **lowest binding energy** represents the outermost valence electrons. Furthermore, the relative height of each PES peak is directly proportional to the number of electrons in that subshell.

- **Core vs. Valence Electrons (Phosphorus, Z = 15):** Configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$ → 10 inner core electrons (n = 1, 2) and 5 valence electrons (n = 3), with 3 unpaired electrons in 3p by Hund's rule.
- **Transition Metal Cation Rule:** When a transition metal forms a cation, electrons are ALWAYS removed from the highest principal shell (4s) BEFORE the 3d subshell.
- **Isoelectronic PES Comparison (Na^+ vs. Ne):** Both have 10 electrons ($1s^2\ 2s^2\ 2p^6$), but Na^+ has 11 protons vs. Ne's 10 protons, so all of Na^+'s PES peaks appear at higher binding energies.

Table 1.2 · Subshell Capacities, Orbital Counts & PES Peak Interpretations

Subshell Type	Number of Orbitals	Max Electron Capacity	Relative PES Peak Height (Full)	Filling / Ionization Priority Note
s subshell	1	2 e^-	2 units	Spherical; 4s fills before 3d but empties first in cations
p subshell	3 (p_x, p_y, p_z)	6 e^-	6 units (3× height of full s)	Hund's rule: 3 unpaired parallel spins before pairing
d subshell	5	10 e^-	10 units (5× height of full s)	Transition metals retain 3d electrons when 4s is ionized
f subshell	7	14 e^-	14 units (7× height of full s)	Lanthanides (4f) and Actinides (5f)

EXAMPLE 1.7 **Condensed Electron Configurations of Transition Metals & Cations**

Problem: Write the noble-gas condensed ground-state electron configuration for (a) neutral nickel (Ni, Z = 28) and (b) the nickel(II) cation (Ni^{2+}).

STEP-BY-STEP SOLUTION:

1. Part (a) Neutral Nickel (28 e^-): Using Argon ([Ar] = 18 core electrons), place the next 2 electrons in 4s and the remaining 8 electrons in 3d: [Ar] $4s^2$ $3d^8$.
2. Part (b) Nickel(II) Cation (Ni^{2+}, 26 e^-): Transition metals always lose electrons from the highest principal energy level (n = 4) first, NOT from 3d. Removing the two 4s electrons yields [Ar] $3d^8$.

Final Answer: (a) Ni: [Ar] $4s^2$ $3d^8$; (b) Ni^{2+}: [Ar] $3d^8$

EXAMPLE 1.8 **Analyzing a PES Spectrum & Converting Binding Energy to Joules per Electron**

Problem: Moving from highest to lowest binding energy, a PES spectrum displays four peaks with relative heights of 2, 2, 6, and 2. (a) Write the electron configuration and identify the element. (b) Given that the outermost $3s^2$ peak has a binding energy of 0.74 MJ·mol^{-1}, calculate the first ionization energy in joules per electron (J/electron).

STEP-BY-STEP SOLUTION:

1. Part (a) Peak Assignment: From highest to lowest binding energy (closest to nucleus outward), the peaks follow Aufbau order: $1s^2$ (height 2), $2s^2$ (height 2), $2p^6$ (height 6), and $3s^2$ (height 2). Total electrons = 12 → Magnesium (Mg).
2. Part (b) Step 1 — Megajoules to Joules per Mole: 0.74 MJ·mol^{-1} × (10^6 J / 1 MJ) = 7.4 × 10^5 J·mol^{-1}.
3. Part (b) Step 2 — Divide by Avogadro's Constant: E = (7.4 × 10^5 J·mol^{-1}) / (6.022 × 10^{23} electrons·mol^{-1}) = 1.2 × 10^{-18} J per electron.

Final Answer: (a) $1s^2$ $2s^2$ $2p^6$ $3s^2$ (Magnesium, Mg); (b) 1.2 × 10^{-18} J/electron

⚠ AP EXAM TRAP & FRQ SCORING GUIDELINE

AP Exam Trap: PES x-axes on the AP exam often plot high binding energy on the LEFT and low binding energy on the RIGHT (or vice versa). Never read left-to-right blindly! Always locate the highest binding energy value on the axis first—that peak is ALWAYS the 1s subshell.

§ 1.5 Periodic Trends, Successive Ionization Energies & Ionic Radii

All major periodic trends are governed by two competing Coulombic factors: **effective nuclear charge (Z_eff)** across a period and **principal shell distance (n) / core electron shielding** down a group. Moving **left to right across a period**, electrons are added to the same principal energy shell while the number of protons in the nucleus increases; this raises Z_eff, pulling the electron cloud closer to the nucleus, which **decreases atomic radius**, **increases first ionization energy (IE_1)**, and **increases electronegativity**. Moving **top to bottom down a group**, valence electrons occupy higher energy shells (larger n) farther from the nucleus with increased inner-shell shielding; Coulombic attraction weakens, causing **atomic radius to increase** while **IE_1 and electronegativity decrease**.

Across Period 2 and Period 3, two classic subshell exceptions occur in first ionization energy: (1) **Group 13 vs. Group 2 (Al vs. Mg, or B vs. Be)**: Aluminum has a slightly lower IE_1 than magnesium because Al's outermost electron sits in a higher-energy **3p subshell** farther from the nucleus than Mg's **3s** electrons. (2) **Group 16 vs. Group 15 (S vs. P, or O vs. N)**: Sulfur has a slightly lower IE_1 than phosphorus because pairing two electrons in one of sulfur's $3p^4$ orbitals creates extra **electron–electron repulsion**, making that paired electron easier to remove.

When neutral atoms form ions, their radii change dramatically. **Cations are much smaller** than their parent atoms because losing valence electrons often vacates the outermost shell and reduces electron–electron repulsion. **Anions are much larger** than their parent atoms because adding electrons increases electron–electron repulsion while nuclear charge remains unchanged. In an **isoelectronic series** (species sharing the exact same electron configuration, such as O^{2-}, F^-, Ne, Na^+, Mg^{2+}, all with 10 electrons), the species with the **most protons** pulls the 10-electron cloud in the tightest: radius decreases in the order **$O^{2-} > F^- > Ne > Na^+ > Mg^{2+}$**.

- **Electronegativity:** The ability of an atom in a covalent bond to attract shared electrons. Fluorine (F) is the most electronegative element (small radius, only 2 shells, high Z_eff); noble gases are excluded.
- **FRQ Justification Rule (Same Group, e.g., Se vs. S):** State explicitly that Se's valence electrons occupy a higher principal energy shell (n = 4 vs. n = 3), placing them farther from the nucleus with weaker Coulombic attraction.
- **Successive Ionization Energy Jump:** A massive (4-fold to 10-fold) jump between IE_k and IE_(k+1) indicates that the (k+1)th electron is being removed from an inner core shell, proving the element has exactly k valence electrons.
- **Periodic Group Charges:** Group 1 → +1; Group 2 → +2; Group 13 → +3; Group 15 → −3; Group 16 → −2; Group 17 → −1. Elements in the same group form analogous compounds (e.g., MgO, CaO, SrO).

Table 1.3 · Summary of Periodic Trends and Underlying Coulombic Explanations

Periodic Property	Trend Across a Period (Left → Right)	Trend Down a Group (Top → Bottom)	Coulombic Justification (FRQ Language)
Atomic Radius	Decreases	Increases	Across: Higher proton count (Z_eff) pulls same shell closer. Down: More occupied shells (n) increase distance.
First Ionization Energy (IE_1)	Increases (except Grp 2→13 & 15→16)	Decreases	Across: Stronger Z_eff holds valence e^- tighter. Down: Greater distance & core shielding weaken attraction.
Electronegativity	Increases (F is maximum)	Decreases	Across: Higher Z_eff & smaller radius attract shared bonding e^- more strongly.
Ionic Radius (Isoelectronic)	Decreases as Z increases	Increases with shell n	For 10 e^- series (O^{2-} to Mg^{2+}), more protons pull identical e^- cloud tighter.

EXAMPLE 1.9 Identifying an Unknown Period 3 Element from Successive Ionization Energies

Problem: An unknown Period 3 element exhibits the following successive ionization energies (in kJ·mol^{-1}): IE_1 = 578, IE_2 = 1,817, IE_3 = 2,745, IE_4 = 11,577, and IE_5 = 14,842. Identify the element and write the formula of its oxide.

STEP-BY-STEP SOLUTION:

1. Step 1 — Locate the Core-Shell Jump: IE_1 (578) → IE_2 (1,817) → IE_3 (2,745) increase gradually, but between IE_3 and IE_4 the energy skyrockets from 2,745 to 11,577 kJ·mol^{-1} (more than a 4-fold jump).
2. Step 2 — Count Valence Electrons: The first three electrons were removed from the outer valence shell (n = 3), whereas the fourth electron was pulled from an inner core shell (n = 2) much closer to the nucleus. Thus, the element has 3 valence electrons.
3. Step 3 — Identify Element & Oxide: A Period 3 element with 3 valence electrons is in Group 13 → Aluminum (Al), which forms Al^{3+} ions and reacts with O^{2-} to form Al_2O_3.

Final Answer: Aluminum (Al); oxide formula: Al_2O_3

⚠ **AP EXAM TRAP & FRQ SCORING GUIDELINE**

AP Exam Trap: Stating 'atomic radius decreases across a period because it moves to the right on the periodic table' earns ZERO points on an AP FRQ! A trend is an observation, not a physical cause. You MUST cite either 'increased effective nuclear charge (more protons pulling electrons in the same shell)' for across-period comparisons, or 'valence electrons occupying a higher principal energy level (greater distance and shielding from the nucleus)' for down-group comparisons.

✅ **CHAPTER 1 MASTERY CHECKLIST (AP EXAM READINESS)**

☑ Convert fluently among sample mass (g), moles (mol), formula units/molecules, and individual constituent atoms using M and N_A = 6.022 × 10^{23} mol^{-1}.

☑ Calculate average atomic mass or unknown isotopic mass from mass spectrometry data and determine empirical/molecular formulas and mixture mass percent purity.

☑ Write full and noble-gas condensed electron configurations for neutral atoms and ions (remembering to remove 4s electrons before 3d in transition metal cations).

☑ Interpret Photoelectron Spectroscopy (PES) spectra by matching peak binding energies to subshell distance/nuclear charge and peak heights to electron counts.

☑ Justify periodic trends (atomic/ionic radius, IE_1 including 2→13 and 15→16 exceptions, successive IE jumps, and electronegativity) using Coulomb's Law.

CHAPTER 2 · CORE CURRICULUM

AP Exam Weighting: 7–9%

Unit 2: Molecular and Ionic Compound Structure and Properties

Unit 2 explores how atoms bond to lower their electrostatic potential energy and how bonding dictates macroscopic physical properties. Students classify nonpolar covalent, polar covalent, ionic, and metallic bonds, interpret internuclear potential energy curves, apply Coulomb's Law to lattice energies, and contrast substitutional and interstitial alloys. Finally, Lewis structures, resonance, formal charge, orbital hybridization, and VSEPR theory enable rigorous predictions of 3D molecular geometry and molecular polarity.

CHAPTER 2 ESSENTIAL EQUATIONS, LAWS & CONSTANTS

$E_lattice \propto (q_1 \times q_2) / r$	Coulomb's Law for Lattice Energy: proportional to ion charge product over internuclear distance
$FC = V - N_dots - B_lines$	Formal Charge = valence e^- of neutral atom − unshared lone-pair dots − number of bonds (lines)
$\text{Bond Order} = (\text{Total Bonding Pairs}) / (\text{Positions})$	Average bond order in a resonance hybrid (e.g., 4 / 3 = 1.33 in CO_3^{2-})
$\text{Single} = 1\sigma;\ \text{Double} = 1\sigma + 1\pi;\ \text{Triple} = 1\sigma + 2\pi$	Sigma (head-on) and Pi (side-by-side) bond composition of covalent bonds

§ 2.1 Types of Chemical Bonds, Bond Polarity & Potential Energy Curves

Atoms form chemical bonds because doing so lowers their electrostatic potential energy and creates a more stable electronic arrangement. Chemists classify bonds along a continuum based on the **electronegativity difference (ΔEN)** between the bonding atoms. When two nonmetals have ΔEN < 0.4 (such as in Cl_2 or a C–H bond), electrons are shared essentially equally, forming a **nonpolar covalent bond**. When ΔEN lies between 0.4 and 1.7 (as in HBr or C–F), electrons are shared unequally, creating a **polar covalent bond** with partial positive (δ+) and partial negative (δ−) ends (a bond dipole). When a metal reacts with a nonmetal and ΔEN > 1.7, valence electrons are transferred completely from the metal to the nonmetal, forming an **ionic bond**. On the AP exam, no electronegativity table is provided—you rank bond polarity by periodic position: the farther apart two nonmetals are, or the closer one atom is to fluorine (F), the more polar the bond.

A **potential energy vs. internuclear distance graph** (Lennard-Jones curve) illustrates the balance between attractive and repulsive forces as two atoms approach each other. At the far right, the atoms are too far apart to interact, so potential energy is zero. As the atoms approach, each nucleus attracts the other atom's valence electrons, lowering the potential energy into negative values. At the bottom of the energy well, attractions and repulsions are balanced: the **horizontal position (x-coordinate) of the minimum** defines the **equilibrium bond length**, and the **depth of the well (y-coordinate)** represents the **bond dissociation energy** (the energy required to break the bond). If pushed even closer together at the far left, strong proton–proton and core–core repulsions cause the potential energy to shoot sharply upward into positive values.

- **Ranking Carbon Bond Polarity:** C–C (ΔEN = 0, nonpolar) < C–N < C–O < C–F (most polar; F is closest to upper right corner).
- **Effect of Bond Order on PE Curve:** Increasing bond order (single → double → triple) pulls nuclei closer together and deepens the energy well.

- **Carbon–Carbon Bond Progression:** C–C single (154 pm, 348 kJ·mol^{-1}) → C=C double (134 pm, 614 kJ·mol^{-1}) → C≡C triple (120 pm, 839 kJ·mol^{-1}).
- **Comparing Two Curves on One Graph:** A curve whose minimum well is shifted further to the LEFT and DEEPER DOWN corresponds to a shorter, stronger bond (e.g., N≡N triple bond vs. Br–Br single bond).

EXAMPLE 2.1 **Ranking Bond Polarity & Interpreting Potential Energy Wells**

Problem: (a) Without consulting numerical tables, rank the following bonds in order of increasing bond polarity: C–O, C–C, C–F, C–N. (b) On a potential energy vs. internuclear distance graph comparing N_2 and Br_2, which substance has its energy minimum further to the left and deeper down?

STEP-BY-STEP SOLUTION:

1. Part (a) Bond Polarity Ranking: A C–C bond is between identical atoms (ΔEN = 0, completely nonpolar). Moving across Period 2 from N to O to F, electronegativity increases steadily toward fluorine. Therefore, ΔEN increases in the order C–C < C–N < C–O < C–F.
2. Part (b) PE Curve Comparison: Nitrogen gas (N_2) contains a strong N≡N triple bond between small Period 2 atoms, whereas Br_2 contains a single bond between large Period 4 atoms. Thus, N_2 has a much shorter bond length (minimum further to the left) and a much higher bond dissociation energy (deeper potential well).

Final Answer: (a) C–C < C–N < C–O < C–F; (b) N_2 has the minimum further to the left and deeper down.

⚠ **AP EXAM TRAP & FRQ SCORING GUIDELINE**

AP Exam Trap: Remember that a C–H bond is treated as NONPOLAR covalent on the AP Chemistry exam, so hydrocarbons (like CH_4, C_3H_8, C_6H_{14}) are always completely nonpolar molecules.

§ 2.2 Ionic Lattice Energy, Crystal Lattices & Metallic Alloys

For ionic compounds, bond strength is measured by **lattice energy** and governed directly by **Coulomb's Law**: E_lattice ∝ (q_1 × q_2) / r, where q_1 and q_2 are the ionic charges and r is the distance between ion centers (sum of ionic radii). When comparing lattice energies and melting points of ionic solids, **always check ion charges first** because charge differences dramatically outweigh radius differences. When two ionic compounds have the exact same ion charges, compare **ionic radii**: smaller ions pack closer together (smaller r), producing stronger Coulombic attraction and a higher melting point.

In a solid ionic compound, cations and anions are locked into a rigid, alternating 3D **crystal lattice** that maximizes attractions and minimizes repulsions. Because Coulombic attractions are strong, ionic solids have high melting points and very low vapor pressures. However, they are **brittle**: if mechanical stress shifts one crystal plane by even a single ion width, like-charged ions align and repel violently, cleaving the crystal. Furthermore, ionic solids **do not conduct electricity as solids** because the ions are fixed in place, but they become excellent electrical conductors when **melted (molten) or dissolved in water (aqueous)** because the ions become mobile.

Metallic solids consist of a regular array of positive metal cations surrounded by a mobile 'sea' of delocalized valence electrons. Because the electron sea adapts seamlessly when cation layers slide past one another, metals are **malleable and ductile** and conduct heat and electricity in both solid and liquid states. Mixing metals with other elements forms two distinct types of **alloys**: a **substitutional alloy** (e.g., brass, where similar-sized Zn atoms replace Cu atoms directly in the lattice) and an **interstitial alloy** (e.g., steel, where tiny C atoms fit into the interstitial spaces between large Fe atoms, making the lattice much harder, stronger, and less malleable).

- **Charge Comparison (MgS vs. NaCl):** MgS has +2/−2 ions ($|q_1q_2|$ = 4) whereas NaCl has +1/−1 ions ($|q_1q_2|$ = 1) → MgS has a much higher lattice energy and melting point.
- **Radius Comparison (LiF vs. KBr):** Both are +1/−1 salts, but Li^+ and F^- have much smaller ionic radii than K^+ and Br^- → LiF has a shorter internuclear distance r and higher melting point.

- **Particulate Diagram Rule for Ionic Solids:** Always draw cations smaller than anions (losing valence electrons shrinks the electron cloud) in an alternating +/- lattice.

Table 2.1 · Comparison of Ionic Crystals, Pure Metals, Substitutional Alloys & Interstitial Alloys

Material Class	Example	Particulate Structure	Mechanical & Electrical Properties
Ionic Solid	NaCl, MgS, LiF	Alternating 3D lattice of fixed cations (smaller) and anions (larger)	Hard, brittle (cleaves when layers shift); conducts ONLY when molten or (aq)
Pure Metallic Solid	Cu, Fe, Al	Uniform array of metal cations in a mobile sea of delocalized valence e^-	Malleable, ductile; conducts electricity as both (s) and (l)
Substitutional Alloy	Brass (Cu + Zn)	Solute metal atoms of SIMILAR radius replace host metal atoms at lattice sites	Retains malleability and conductivity; density lies between components
Interstitial Alloy	Steel (Fe + C)	Tiny nonmetal atoms (C) fit into interstitial spaces between large host atoms (Fe)	Much harder, stronger, and less malleable (C atoms block layer sliding)

EXAMPLE 2.2 Ranking Melting Points of Ionic Solids Using Coulomb's Law

> **Problem:** Rank the following ionic compounds in order of increasing melting point and justify your ranking using Coulomb's Law: KBr, MgS, LiF.

STEP-BY-STEP SOLUTION:

1. Step 1 — Evaluate Ionic Charges ($|q_1q_2|$): KBr (K^+, Br^-) and LiF (Li^+, F^-) both have $|q_1q_2| = (+1)(-1) = 1$, whereas MgS (Mg^{2+}, S^{2-}) has $|q_1q_2| = (+2)(-2) = 4$. Because charge product is 4× larger in MgS, MgS has the strongest Coulombic attraction and highest melting point.
2. Step 2 — Compare Ionic Radii for Tied Charges (KBr vs. LiF): Li^+ (Period 2) and F^- (Period 2) have much smaller ionic radii than K^+ (Period 4) and Br^- (Period 4). Shorter internuclear distance r in LiF produces a stronger lattice energy than in KBr.
3. Step 3 — Final Order: KBr < LiF < MgS.

Final Answer: KBr < LiF < MgS

⚠ AP EXAM TRAP & FRQ SCORING GUIDELINE

AP Exam Trap: Never say ionic solutions conduct electricity because of 'free electrons.' Metals conduct via mobile delocalized electrons; molten and aqueous ionic compounds conduct electricity exclusively via MOBILE IONS.

§ 2.3 Lewis Electron-Dot Diagrams, Octet Exceptions, Resonance & Formal Charge

Lewis electron-dot diagrams show how valence electrons are distributed as bonding pairs (lines) and nonbonding lone pairs (dots). To construct a Lewis structure: (1) sum the valence electrons of all atoms (adding electrons for negative ionic charges or subtracting for positive charges); (2) place the least electronegative atom in the center (hydrogen is always terminal) and connect each outer atom with a single bond; (3) add lone pairs to complete the octets of all outer atoms (duet for H) and place any leftover electrons on the central atom; (4) if the central atom lacks an octet, convert one or more lone pairs from an outer atom into double or triple bonds.

While Period 2 elements C, N, O, and F strictly obey the octet rule, three classes of exceptions occur: (1) **Incomplete octets** in small, electron-deficient atoms like beryllium (**$BeCl_2$**, 4 valence e^- around Be) and boron (**BF_3**, 6 valence e^- around B—never draw a double bond to F!); (2) **Odd-electron molecules (free radicals)** such as nitrogen monoxide (**NO**, 11 valence e^-, leaving one unpaired electron on N); and (3) **Expanded octets** (10 or 12 valence electrons around the central atom), which can ONLY occur when the central atom is in **Period 3 or lower** (e.g., **SF_4** with 34 valence e^- and 10 e^- around S, or **XeF_4** with 36 valence e^- and 12 e^- around Xe).

When more than one valid Lewis structure can be drawn simply by shifting π electrons and lone pairs without moving atoms, the species exhibits **resonance**. In the carbonate ion ($\mathbf{CO_3^{2-}}$, 24 valence e^-), three equivalent resonance structures exist with one C=O double bond and two C–O single bonds. In reality, the π electrons are delocalized equally over all three C–O regions, giving every C–O bond an identical **bond order of 4/3 = 1.33** and intermediate length/strength. When evaluating non-equivalent resonance structures, chemists calculate **Formal Charge (FC = Valence e^- − Dots − Lines)**: the most stable structure has formal charges closest to zero on all atoms, and any unavoidable negative formal charge must reside on the **most electronegative atom**.

- **Phosphorus Trichloride (PCl_3):** 5 + 3(7) = 26 valence e^- → three P–Cl single bonds (6 e^-), 3 lone pairs on each Cl (18 e^-), and 1 lone pair on central P (2 e^-).
- **Formaldehyde (CH_2O) & Cyanide (CN^-):** CH_2O (12 e^-) has a C=O double bond and two C–H single bonds. $[CN]^-$ (4 + 5 + 1 = 10 e^-) has a C≡N triple bond and one lone pair on each atom inside brackets.
- **Formal Charge Sum Check:** The sum of all formal charges must equal 0 for a neutral molecule and equal the ion charge for a polyatomic ion.

EXAMPLE 2.3 **Using Formal Charge to Select the Most Stable Lewis Structure of Thiocyanate (SCN^-)**

> **Problem:** The thiocyanate ion (SCN^-, 16 valence electrons) has three candidate resonance structures with carbon in the center: Structure A: $[:S{=}C{=}N:]^-$ (two double bonds); Structure B: $[:S{-}C{\equiv}N:]^-$ (single bond to S with 3 lone pairs, triple bond to N with 1 lone pair); Structure C: $[:S{\equiv}C{-}N:]^-$ (triple bond to S with 1 lone pair, single bond to N with 3 lone pairs). Calculate the formal charges in each structure and identify the most stable contributor.

STEP-BY-STEP SOLUTION:

1. Step 1 — Formal Charges in Structure A ($[S{=}C{=}N]^-$): FC(S) = 6 − 4 dots − 2 lines = 0; FC(C) = 4 − 0 − 4 = 0; FC(N) = 5 − 4 dots − 2 lines = −1. (Formal charges: 0, 0, −1 on N).
2. Step 2 — Formal Charges in Structure B ($[S{-}C{\equiv}N]^-$): FC(S) = 6 − 6 dots − 1 line = −1; FC(C) = 4 − 0 − 4 = 0; FC(N) = 5 − 2 dots − 3 lines = 0. (Formal charges: −1 on S, 0, 0).
3. Step 3 — Formal Charges in Structure C ($[S{\equiv}C{-}N]^-$): FC(S) = 6 − 2 dots − 3 lines = +1; FC(C) = 4 − 0 − 4 = 0; FC(N) = 5 − 6 dots − 1 line = −2. Eliminate Structure C immediately because of the large −2 and +1 formal charges.
4. Step 4 — Compare A vs. B by Electronegativity: Both A and B have two zeros and one −1 formal charge. Because nitrogen (N) is more electronegative than sulfur (S), placing the −1 formal charge on N (Structure A, $[S{=}C{=}N]^-$) makes it the most stable resonance contributor.

Final Answer: Structure A ($[:S{=}C{=}N:]^-$, with FC = −1 on the more electronegative N atom and 0 on S and C)

⚠ **AP EXAM TRAP & FRQ SCORING GUIDELINE**

AP Exam Trap: Never say a resonance molecule like CO_3^{2-}, O_3, or NO_3^- 'flips back and forth' or 'oscillates' between single and double bonds! A resonance hybrid is a single, static electronic structure with delocalized π electrons and equal, fractional bond orders.

§ 2.4 Sigma (σ) and Pi (π) Bonds, Orbital Hybridization & VSEPR Theory

Covalent bonds are classified as **sigma (σ) bonds** or **pi (π) bonds** based on how atomic orbitals overlap. A **σ bond** forms from head-on overlap of orbitals along the internuclear axis, whereas a **π bond** forms from side-by-side overlap of unhybridized parallel p orbitals above and below the axis. Every **single bond is 1 σ bond**; a **double bond is 1 σ + 1 π bond**; and a **triple bond is 1 σ + 2 π bonds**. While atoms can rotate freely around a single σ bond, π bonds lock the atoms in a fixed plane and prevent rotation.

Orbital hybridization explains how an atom mixes its valence s and p orbitals to form degenerate hybrid orbitals for σ bonding and lone pairs. You can determine the hybridization of any atom instantly by counting its **electron domains**

(steric number), where one domain is any single bond, double bond, triple bond, or lone pair attached to that atom: **2 domains = sp (180°)**, **3 domains = sp^2 (120°)**, and **4 domains = sp^3 (109.5°)**.

VSEPR Theory (Valence Shell Electron Pair Repulsion) states that negatively charged electron domains around a central atom repel one another and arrange themselves in 3D space to be as far apart as possible. Because a **lone pair** is held by only one nucleus, it occupies more angular space than a bonding pair, compressing the bond angles between adjacent bonding pairs (Lone Pair–Lone Pair > Lone Pair–Bonding Pair > Bonding Pair–Bonding Pair repulsion). In 5-domain **trigonal bipyramidal** systems, lone pairs ALWAYS occupy **equatorial positions first** (120° apart) to minimize 90° repulsions. In 6-domain **octahedral** systems with two lone pairs (such as XeF_4), the two lone pairs position themselves trans (180° apart), leaving the four bonds in a flat **square planar** geometry.

- **Acrylonitrile (CH_2=CH–C≡N) σ and π Count:** Contains four single bonds + one C=C double bond + one C≡N triple bond → Total = 6 σ bonds and 3 π bonds.
- **Acetic Acid (CH_3COOH) Hybridization:** Methyl carbon (–CH_3, 4 single bonds) = sp^3; carbonyl carbon (C=O, 3 domains) = sp^2; hydroxyl oxygen (–OH, 2 bonds + 2 lone pairs = 4 domains) = sp^3.
- **Molecular Polarity Rule:** A molecule is NONPOLAR if all its bonds are nonpolar OR if polar bond dipoles are arranged in a completely symmetrical VSEPR geometry with identical outer atoms (linear, trigonal planar, tetrahedral, trigonal bipyramidal, octahedral, square planar) so all dipole vectors cancel to zero.

Table 2.2 · Complete AP Chemistry VSEPR Geometry, Hybridization, Bond Angle & Polarity Master Table

Total Domains	Bonding / Lone Pairs	Electron-Domain Geometry	Molecular Geometry	Ideal Bond Angle(s)	Hybridization	Example & Polarity (Identical Outer Atoms)
2	2 / 0	Linear	Linear	180°	sp	CO_2, $BeCl_2$ (Nonpolar)
3	3 / 0	Trigonal Planar	Trigonal Planar	120°	sp^2	BF_3, SO_3, CO_3^{2-} (Nonpolar)
3	2 / 1	Trigonal Planar	Bent	< 120° (~118°)	sp^2	SO_2, O_3, NO_2^- (Polar)
4	4 / 0	Tetrahedral	Tetrahedral	109.5°	sp^3	CH_4, CF_4, CCl_4 (Nonpolar; CH_2Cl_2 is Polar)
4	3 / 1	Tetrahedral	Trigonal Pyramidal	< 109.5° (~107°)	sp^3	NH_3, PF_3, PCl_3 (Polar)
4	2 / 2	Tetrahedral	Bent	<< 109.5° (~104.5°)	sp^3	H_2O, H_2S, OF_2 (Polar)
5	5 / 0	Trigonal Bipyramidal	Trigonal Bipyramidal	90° (axial), 120° (eq)	—	PCl_5, PF_5 (Nonpolar)
5	4 / 1	Trigonal Bipyramidal	Seesaw	< 90°, < 120°	—	SF_4 (Polar — 1 equatorial LP)
5	3 / 2	Trigonal Bipyramidal	T-Shaped	< 90°	—	ClF_3, BrF_3 (Polar — 2 equatorial LPs)
5	2 / 3	Trigonal Bipyramidal	Linear	180°	—	I_3^-, XeF_2 (Nonpolar — 3 equatorial LPsCancel)
6	6 / 0	Octahedral	Octahedral	90°, 180°	—	SF_6 (Nonpolar)
6	5 / 1	Octahedral	Square Pyramidal	< 90°	—	BrF_5, IF_5 (Polar)
6	4 / 2	Octahedral	Square Planar	90°, 180°	—	XeF_4 (Nonpolar — 2 trans LPs cancel)

EXAMPLE 2.4 Predicting VSEPR Geometry, Bond Angles & Overall Molecular Polarity

Problem: For each of the following species, determine the number of bonding pairs and lone pairs on the central atom, the molecular geometry, the bond angle(s), and whether the molecule is polar or nonpolar: (a) PF_3, (b) H_2O, (c) SF_4, (d) XeF_4.

STEP-BY-STEP SOLUTION:

1. Part (a) PF_3 (26 valence e^-): Central P has 3 bonding pairs and 1 lone pair (4 domains, sp^3). Molecular geometry is trigonal pyramidal with bond angles compressed to ~107°. Asymmetric lone pair → Polar.
2. Part (b) H_2O (8 valence e^-): Central O has 2 bonding pairs and 2 lone pairs (4 domains, sp^3). Molecular geometry is bent with bond angle compressed further to ~104.5°. Asymmetric → Polar.
3. Part (c) SF_4 (34 valence e^-): Central S has 4 bonding pairs and 1 equatorial lone pair (5 domains). Molecular geometry is seesaw with bond angles < 90° and < 120°. Asymmetric → Polar.
4. Part (d) XeF_4 (36 valence e^-): Central Xe has 4 bonding pairs and 2 lone pairs positioned 180° opposite each other (6 domains). Molecular geometry is flat square planar (90° bond angles). Because the four Xe–F dipoles cancel symmetrically, XeF_4 is Nonpolar.

Final Answer: (a) PF_3: Trigonal pyramidal, ~107°, Polar; (b) H_2O: Bent, ~104.5°, Polar; (c) SF_4: Seesaw, Polar; (d) XeF_4: Square planar, 90°, Nonpolar

⚠ AP EXAM TRAP & FRQ SCORING GUIDELINE

AP Exam Trap: Notice that the College Board AP Chemistry curriculum does NOT use 'sp^3d' or 'sp^3d^2' hybridization labels for 5- and 6-domain molecules! Only assign sp, sp^2, and sp^3 hybridization (for 2, 3, and 4 electron domains). Also remember that CF_4 and XeF_4 have very polar individual C–F and Xe–F bonds, yet both molecules are NONPOLAR overall because their symmetrical geometries (tetrahedral and square planar) cause all bond dipoles to cancel.

✅ CHAPTER 2 MASTERY CHECKLIST (AP EXAM READINESS)

☑ Rank covalent bond polarities using periodic position and interpret internuclear potential energy curves (bond length vs. bond dissociation energy).

☑ Use Coulomb's Law (charge product first, ionic radius second) to rank lattice energies and melting points of ionic solids.

☑ Contrast ionic solids, pure metals, substitutional alloys (brass), and interstitial alloys (steel) in terms of particulate structure, malleability, and conductivity.

☑ Draw Lewis structures including incomplete octets ($BeCl_2$, BF_3), expanded octets (SF_4, XeF_4), resonance hybrids, and formal charge evaluations.

☑ Determine σ/π bond counts, sp/sp^2/sp^3 hybridization, VSEPR 3D molecular geometry, compressed bond angles, and overall molecular dipole polarity.

CHAPTER 3 · CORE CURRICULUM

AP Exam Weighting: 18–22%

Unit 3: Intermolecular Forces and Properties

Unit 3 is the most heavily weighted unit on the AP Chemistry exam (18–22%). It connects particulate structure and intermolecular forces (London dispersion, dipole–dipole, hydrogen bonding, and ion–dipole) to macroscopic physical properties of liquids, solids, gases, and solutions. Students master crystalline and amorphous solids, the Ideal Gas Law, Dalton's Law, Kinetic Molecular Theory, Maxwell–Boltzmann distributions, solution molarity/dilution, chromatography, distillation, electromagnetic spectroscopy, and the Beer–Lambert Law.

CHAPTER 3 ESSENTIAL EQUATIONS, LAWS & CONSTANTS

$P_1V_1 / T_1 = P_2V_2 / T_2$	Combined Gas Law (T must be in Kelvin: T(K) = T(°C) + 273.15)
$PV = nRT$	Ideal Gas Law (R = 0.08206 L·atm·mol^{-1}·K^{-1}; 1 mol ideal gas = 22.4 L at STP: 273.15 K, 1.00 atm)
$M = dRT / P$	Molar Mass of a Gas from gas density d (g·L^{-1}), temperature T (K), and pressure P (atm)
$P_total = \Sigma P_i$ and $P_A = X_A \times P_total$	Dalton's Law of Partial Pressures, where mole fraction X_A = n_A / n_total
$KE_avg = (3/2)RT$ and $r_1/r_2 = \sqrt{(M_2/M_1)}$	Average Kinetic Energy (depends on T alone) & Graham's Law of Effusion
$M = n / V_L$ and $M_1V_1 = M_2V_2$	Solution Molarity (mol·L^{-1}) and Dilution Equation
$c = \lambda\nu$ and $E = h\nu = hc / \lambda$	Electromagnetic Wave Speed (c = 2.998 × 10^8 m·s^{-1}) & Planck Photon Energy (h = 6.626 × 10^{-34} J·s)
$A = \varepsilon bc$	Beer–Lambert Law: Absorbance = molar absorptivity (ε) × path length (b, cm) × concentration (c, M)

§ 3.1 Intermolecular Forces (IMFs) & Physical Properties of Liquids

To explain physical properties such as boiling point, vapor pressure, surface tension, and viscosity, we must strictly distinguish between **intramolecular bonds** (the strong covalent or ionic bonds holding atoms together within a compound) and **intermolecular forces (IMFs)** (the weaker noncovalent electrostatic attractions between separate molecules). **When a molecular liquid boils or evaporates, covalent bonds do NOT break—only intermolecular forces are overcome.**

The most universal intermolecular force is the **London Dispersion Force (LDF)**, which exists between ALL atoms and molecules (both polar and nonpolar). Random motion of electrons creates a momentary uneven charge distribution called an **instantaneous dipole**, which induces a temporary dipole in a neighboring molecule. The strength of LDFs depends on **polarizability**—the ease with which an electron cloud is distorted: (1) molecules with a **greater total number of electrons** have larger, more diffuse, more polarizable electron clouds and stronger LDFs (explaining why at room temperature F_2 and Cl_2 are gases, Br_2 is a liquid, and I_2 with 106 electrons is a solid); (2) for isomers with the exact same number of electrons, **linear molecules (e.g., n-pentane)** have a larger surface area for intermolecular contact than compact spherical molecules (e.g., neopentane), giving n-pentane stronger LDFs and a higher boiling point.

Polar molecules experience **dipole–dipole forces** (attractions between permanent δ+ and δ− ends) in addition to LDFs. An especially strong dipole–dipole interaction is **hydrogen bonding**, which occurs ONLY when a hydrogen atom is **covalently bonded directly to a small, highly electronegative N, O, or F atom** and interacts with a lone pair on a

neighboring N, O, or F atom (drawn as a dashed line between molecules). Finally, when an ionic salt dissolves in water, **ion–dipole forces** form as cations attract the δ− oxygen of H_2O and anions attract the δ+ hydrogens.

- **Hierarchy of Attractive Forces (Comparable Size):** London Dispersion Only (Nonpolar) < Dipole–Dipole + LDF (Polar) < Hydrogen Bonding + LDF (N–H, O–H, F–H) << Ion–Dipole << Full Ionic / Covalent Network Bonds.
- **Vapor Pressure vs. IMF Strength:** Stronger IMFs hold molecules in the liquid phase more tightly, resulting in a LOWER equilibrium vapor pressure and a HIGHER normal boiling point.
- **Surface Tension & Viscosity:** Stronger IMFs (especially extensive hydrogen bonding, as in water or glycerol) increase both surface tension and resistance to flow (viscosity).

EXAMPLE 3.1 **Ranking Boiling Points Across Four Substance Classes by Dominant Attractive Forces**

> **Problem:** Rank the following four substances in order of increasing normal boiling point and identify the dominant attractive force overcome when each boils: Ethanol (CH_3CH_2OH), Propane (C_3H_8), Lithium Chloride (LiCl), and Acetaldehyde (CH_3CHO).

STEP-BY-STEP SOLUTION:

1. Step 1 — Propane (C_3H_8): Completely nonpolar hydrocarbon; experiences only weak London dispersion forces → Lowest boiling point (−42 °C).
2. Step 2 — Acetaldehyde (CH_3CHO): Polar molecule due to the C=O carbonyl group (no O–H bond); experiences dipole–dipole forces in addition to LDFs → Boils at 20 °C.
3. Step 3 — Ethanol (CH_3CH_2OH): Contains a direct O–H covalent bond capable of strong intermolecular hydrogen bonding (plus dipole–dipole and LDFs) → Boils at 78 °C.
4. Step 4 — Lithium Chloride (LiCl): Ionic crystalline solid held together by full Coulombic ionic bonds throughout a 3D lattice → Highest boiling point (1,382 °C).

Final Answer: Propane (−42 °C, LDF) < Acetaldehyde (20 °C, Dipole–Dipole) < Ethanol (78 °C, H-Bonding) < LiCl (1,382 °C, Ionic Bonds)

⚠ **AP EXAM TRAP & FRQ SCORING GUIDELINE**

AP Exam Trap: Never say 'molar mass causes stronger London dispersion forces' on an AP FRQ! Molar mass is related to nucleus mass (protons + neutrons), whereas LDFs are purely electrostatic. Always state: 'Molecule X has a greater number of electrons, giving it a larger, more polarizable electron cloud and stronger London dispersion forces.'

§ 3.2 Classification of Crystalline Solids, Amorphous Solids & States of Matter

At the particulate level, the three states of matter differ in particle spacing and motion. In a **solid**, particles are packed tightly together and only vibrate in fixed positions, giving a solid both a definite volume and a definite shape. While **crystalline solids** possess a highly ordered, repeating 3D geometric lattice and melt sharply at a specific temperature, **amorphous solids** (such as glass, rubber, and plastics) have disordered particle arrangements and soften gradually over a wide temperature range. In a **liquid**, particles remain close together (nearly incompressible, definite volume) but slide past one another freely. In a **gas**, particles are separated by vast empty distances and move independently at high speeds, expanding to fill any container.

Crystalline solids are classified into **four fundamental categories** based on the particles occupying their lattice points and the bonds/forces holding them together: (1) **Ionic solids** (e.g., KCl, MgO), (2) **Molecular solids** (e.g., dry ice CO_2(s), solid I_2, sucrose $C_{12}H_{22}O_{11}$), (3) **Covalent network solids** (e.g., diamond, graphite, silicon Si, and quartz SiO_2), and (4) **Metallic solids** (e.g., Cu, Fe, Au).

- **Diamond vs. Graphite (Both Pure Carbon Covalent Networks):** In diamond, every C is sp^3 hybridized in a rigid 3D tetrahedral network (electrical insulator, hardest natural solid). In graphite, C forms flat sp^2-hybridized 2D sheets with delocalized π electrons between layers (conducts electricity and acts as a soft lubricant as layers slide over weak LDFs).

- **Molecular vs. Covalent Network Contrast:** Dry ice (CO_2) is a molecular solid held by weak LDFs (sublimes at −78 °C), whereas quartz (SiO_2) is a 3D covalent network solid requiring the breaking of strong Si–O covalent bonds to melt (~1,710 °C).

Table 3.1 · The Four Categories of Crystalline Solids on the AP Chemistry Exam

Solid Category	Lattice Point Particles	Attractive Forces Broken Upon Melting	Melting Point & Hardness	Electrical Conductivity	Classic AP Examples
Ionic Solid	Positive cations & negative anions	Strong Coulombic ionic bonds	High MP; hard & brittle	Insulator as (s); conducts as (l) or (aq)	NaCl, KCl, MgO, CaF_2
Molecular Solid	Discrete neutral molecules	Weak IMFs (LDF, dipole–dipole, H-bonds)	Low MP; relatively soft	Never conducts in any phase	CO_2(s), I_2(s), H_2O(s), $C_{12}H_{22}O_{11}$
Covalent Network	Nonmetal/metalloid atoms	Continuous 3D network of covalent bonds	Extremely high MP; very hard (except graphite)	Insulator (except graphite's sp^2 π sheets)	C (diamond/graphite), Si, SiO_2 (quartz), SiC
Metallic Solid	Metal cations	Metallic bonds (mobile sea of valence e^-)	Variable MP; malleable & ductile	Conducts strongly as both (s) and (l)	Fe, Cu, Ag, Al, Brass

EXAMPLE 3.1B **Classifying Unknown Crystalline Solids from Melting Point & Conductivity Data**

Problem: Identify the solid class (ionic, molecular, covalent network, or metallic) for each substance and explain why: (a) Solid X melts at 1,713 °C and does not conduct electricity as either a solid or a liquid (SiO_2). (b) Solid Y sublimes at 114 °C and does not conduct electricity in any phase or in solution (I_2). (c) Solid Z melts at 801 °C, does not conduct as a solid, but conducts strongly when melted or dissolved in water (NaCl).

STEP-BY-STEP SOLUTION:

1. Part (a) Quartz (SiO_2): Extremely high melting point and zero electrical conductivity in any state indicate a 3D covalent network solid in which strong Si–O covalent bonds must be broken to melt.
2. Part (b) Solid Iodine (I_2): Low sublimation/melting point and nonconductivity in all states indicate a molecular solid held together only by London dispersion forces between neutral I_2 molecules.
3. Part (c) Sodium Chloride (NaCl): High melting point and conductivity only when molten or aqueous (where Na^+ and Cl^- ions become mobile) identify an ionic crystalline solid.

Final Answer: (a) Covalent network solid; (b) Molecular solid; (c) Ionic solid

⚠ **AP EXAM TRAP & FRQ SCORING GUIDELINE**

AP Exam Trap: Students frequently misclassify silicon dioxide (SiO_2, quartz) as a molecular solid by analogy to CO_2, or misclassify sucrose/glucose as ionic solids. Memorize that C(diamond), C(graphite), Si, SiO_2, and SiC are covalent network solids, while all organic sugars/alcohols and I_2(s) are molecular solids.

§ 3.3 Gas Laws, Dalton's Law, Kinetic Molecular Theory & Real Gases

Four empirical gas laws relate pressure (P), volume (V), absolute temperature (T in Kelvin), and moles (n): **Boyle's Law** ($P_1V_1 = P_2V_2$ at constant T, n; inverse relationship), **Charles's Law** ($V_1/T_1 = V_2/T_2$ at constant P, n), **Gay-Lussac's Law** ($P_1/T_1 = P_2/T_2$ at constant V, n), and **Avogadro's Law** ($V_1/n_1 = V_2/n_2$ at constant T, P). Combining these gives the **Combined Gas Law ($P_1V_1/T_1 = P_2V_2/T_2$)** and the **Ideal Gas Law (PV = nRT)**, where R = 0.08206 L·atm·mol^{-1}·K^{-1}. At **Standard**

Temperature and Pressure (STP: 0 °C = 273.15 K and 1.00 atm), 1 mole of any ideal gas occupies **22.4 L**. Substituting n = m/M into PV = nRT yields the gas density and molar mass formula: **M = dRT / P**.

In a mixture of non-reacting gases, **Dalton's Law of Partial Pressures** states that the total pressure equals the sum of the individual partial pressures ($P_{total} = P_1 + P_2 + \ldots$), and each gas's partial pressure equals its mole fraction times total pressure (**$P_A = X_A \times P_{total}$**). When a gas is collected over water by water displacement, the total measured pressure is the sum of the dry gas pressure and the vapor pressure of water at that temperature: **$P_{total} = P_{dry\ gas} + P_{H_2O}$**.

The **Kinetic Molecular Theory (KMT)** explains ideal gas behavior via five postulates: (1) gases consist of particles in constant, random, straight-line motion; (2) the volume of the gas particles themselves is negligible compared to the container volume; (3) gas particles exert zero attractive or repulsive forces on one another; (4) collisions are completely elastic; and (5) **the average kinetic energy of any gas sample depends solely on its Kelvin temperature**. Thus, at the same temperature, light He(g) and heavy Xe(g) have the **exact same average kinetic energy**, but because $KE = \frac{1}{2}mv^2$, lighter gas molecules move at a much higher root-mean-square speed and effuse faster according to **Graham's Law: $r_1/r_2 = \sqrt{(M_2/M_1)}$**. Finally, **real gases** behave most ideally at **high temperature and low pressure**, and deviate from ideal behavior at **low temperature** (where intermolecular attractions pull molecules together, making observed $P_{real} < P_{ideal}$) and **high pressure** (where finite particle volume becomes a significant fraction of container volume).

- **Maxwell–Boltzmann Speed Distribution:** Heating a gas shifts the distribution peak to the RIGHT (higher average speed) and FLATTENS/BROADENS the curve (area under curve remains constant).
- **Graham's Law Comparison (He vs. SO_2):** $M(He) = 4\ g{\cdot}mol^{-1}$, $M(SO_2) = 64\ g{\cdot}mol^{-1} \rightarrow r(He)/r(SO_2) = \sqrt{(64 / 4)} = \sqrt{16} = 4$. Helium effuses 4 times faster than SO_2.
- **Which Gas Deviates Most from Ideality?:** Gases with strong IMFs (like polar NH_3 or H_2O) or large, highly polarizable electron clouds (like Xe or Cl_2) deviate the most from PV = nRT.

EXAMPLE 3.2 **Combined Gas Law, Ideal Gas Law & Molar Mass from Gas Density**

Problem: (a) A 4.50 L sample of neon gas at 1.20 atm and 27 °C is heated to 127 °C while the pressure rises to 2.00 atm. What is the final volume? (b) Calculate the pressure of 0.450 mol of $N_2(g)$ in a 6.00 L rigid container at 298 K. (c) An unknown fluorocarbon gas has a density of $3.75\ g{\cdot}L^{-1}$ at 1.10 atm and 305 K. Calculate its molar mass.

STEP-BY-STEP SOLUTION:

1. Part (a) Combined Gas Law: Convert Celsius to Kelvin first: $T_1 = 27 + 273 = 300$ K; $T_2 = 127 + 273 = 400$ K. Rearranging $P_1V_1/T_1 = P_2V_2/T_2$ gives $V_2 = (P_1V_1T_2) / (T_1P_2) = (1.20\ atm \times 4.50\ L \times 400\ K) / (300\ K \times 2.00\ atm) = 3.60\ L$.
2. Part (b) Ideal Gas Law: $P = nRT / V = (0.450\ mol \times 0.08206\ L{\cdot}atm{\cdot}mol^{-1}{\cdot}K^{-1} \times 298\ K) / 6.00\ L = 1.83\ atm$.
3. Part (c) Molar Mass from Density: $M = dRT / P = (3.75\ g{\cdot}L^{-1} \times 0.08206\ L{\cdot}atm{\cdot}mol^{-1}{\cdot}K^{-1} \times 305\ K) / 1.10\ atm = 85.3\ g{\cdot}mol^{-1}$.

Final Answer: (a) 3.60 L; (b) 1.83 atm; (c) $85.3\ g{\cdot}mol^{-1}$

EXAMPLE 3.3 **Dalton's Law of Partial Pressures & Collecting a Gas Over Water**

Problem: (a) A rigid tank contains 2.0 mol of He and 6.0 mol of Ar at a total pressure of 4.0 atm. What is the partial pressure of He? (b) Oxygen gas (O_2) is collected over water at 25 °C where the total barometric pressure is 758.0 torr and the vapor pressure of water is 23.8 torr. What is the partial pressure of dry O_2 in torr and in atm?

STEP-BY-STEP SOLUTION:

1. Part (a) Mole Fraction & Partial Pressure: Total moles $n_{total} = 2.0 + 6.0 = 8.0$ mol. Mole fraction $X_{He} = 2.0 / 8.0 = 0.25$. Partial pressure $P_{He} = X_{He} \times P_{total} = 0.25 \times 4.0\ atm = 1.0\ atm$.
2. Part (b) Subtract Water Vapor Pressure: $P(dry\ O_2) = P_{total} - P(H_2O) = 758.0\ torr - 23.8\ torr = 734.2\ torr$. Converting to atmospheres: $734.2\ torr / (760\ torr{\cdot}atm^{-1}) = 0.966\ atm$.

Final Answer: (a) $P_{He} = 1.0$ atm; (b) $P(dry\ O_2) = 734.2$ torr = 0.966 atm

⚠ AP EXAM TRAP & FRQ SCORING GUIDELINE

AP Exam Trap: When comparing two gases at the same temperature (e.g., He and Xe at 300 K), students often claim the lighter gas has a higher average kinetic energy. FALSE! At the same temperature, ALL gases have the exact same average kinetic energy; the lighter gas simply has a higher average molecular SPEED.

§ 3.4 Solutions, Molarity, Particulate Hydration Diagrams & Separation Techniques

A **solution** is a homogeneous mixture composed of a solute dissolved in a solvent. The primary concentration unit in chemistry is **molarity (M)**, defined as **moles of solute divided by liters of total solution** (never liters of solvent!). When diluting a concentrated stock solution by adding pure solvent, the moles of solute remain unchanged ($n_1 = n_2$), giving the dilution equation $\mathbf{M_1V_1 = M_2V_2}$. In the laboratory, a precise volume of stock solution is measured with a **graduated or volumetric pipet** (never a beaker!), transferred into a **volumetric flask** partially filled with distilled water, swirled, and filled to the calibration mark.

Solutes in aqueous solution are classified into three groups: **strong electrolytes** (soluble ionic salts like NaCl, $Ba(NO_3)_2$ and strong acids like HCl, HNO_3) dissociate 100% into free mobile ions and conduct electricity strongly; **weak electrolytes** (weak acids/bases like HF and CH_3COOH) ionize only slightly (< 5%), existing mostly as intact molecules; and **nonelectrolytes** (soluble covalent molecules like methanol CH_3OH, ethanol, and glucose) dissolve as intact neutral molecules without producing any ions.

Solubility follows the principle **'like dissolves like'**: polar and ionic solutes dissolve in polar water via strong ion–dipole or hydrogen-bonding interactions, whereas nonpolar solutes (I_2, hexane) dissolve in nonpolar solvents (CCl_4) via London dispersion forces. Mixtures can be separated by exploiting differences in IMFs: in **chromatography**, components with stronger intermolecular attractions to the **mobile phase** travel faster and farther (larger retention factor R_f), whereas components that bind more strongly to the **stationary phase** move more slowly. In **distillation**, the liquid component with weaker IMFs (higher vapor pressure, lower boiling point) vaporizes first, condenses in the cooled condenser tube, and is collected as the distillate.

- **3 Rules for Particulate Ion Hydration Diagrams (e.g., $MgCl_2$(aq)):** (1) Preserve the stoichiometric ratio (two Cl^- anions for every one Mg^{2+} cation); (2) draw the Mg^{2+} cation smaller than the Cl^- anion; (3) orient surrounding H_2O dipoles with δ− oxygen pointing toward Mg^{2+} and δ+ hydrogens pointing toward Cl^-.
- **Alcohol Chain-Length Solubility Trend:** As the nonpolar hydrocarbon tail grows longer from methanol (CH_3OH, infinitely miscible) to octanol ($C_8H_{17}OH$, nearly insoluble), London dispersion character dominates and water solubility plummets.

EXAMPLE 3.4 Solution Molarity, Ion Concentration & Volumetric Dilution

Problem: (a) Calculate the molarity of Na_2SO_4 (M = 142.04 g·mol^{-1}) and the concentration of [Na^+] in a solution prepared by dissolving 14.2 g of Na_2SO_4 in enough water to make 250.0 mL of solution. (b) How many milliliters of a 6.00 M HCl stock solution are required to prepare 500.0 mL of 0.150 M HCl?

STEP-BY-STEP SOLUTION:

1. Part (a) Step 1 — Moles & Molarity of Na_2SO_4: n = 14.2 g / 142.04 g·mol^{-1} = 0.100 mol Na_2SO_4. Dividing by V = 0.2500 L gives M = 0.100 mol / 0.2500 L = 0.400 M Na_2SO_4.
2. Part (a) Step 2 — Sodium Ion Concentration: Because each Na_2SO_4 formula unit dissociates into 2 Na^+(aq) + SO_4^{2-}(aq), [Na^+] = 2 × 0.400 M = 0.800 M.
3. Part (b) Dilution Calculation: Using $M_1V_1 = M_2V_2$, solve for V_1 = (0.150 M × 500.0 mL) / 6.00 M = 12.5 mL of 6.00 M HCl stock solution (measured with a pipet and diluted to 500.0 mL in a volumetric flask).

Final Answer: (a) 0.400 M Na_2SO_4 and [Na^+] = 0.800 M; (b) 12.5 mL of 6.00 M HCl stock

> ⚠ **AP EXAM TRAP & FRQ SCORING GUIDELINE**
>
> AP Exam Trap: When describing how to prepare a solution of known molarity on an FRQ, never say 'add 250 mL of water to the solid.' Because the solid solute occupies volume, you must state: 'Dissolve the solid in a partial volume of distilled water inside a 250.0 mL volumetric flask, then add distilled water until the bottom of the meniscus reaches the 250.0 mL calibration line.'

§ 3.5 Spectroscopy, Electromagnetic Radiation & the Beer–Lambert Law

Spectroscopy probes matter by measuring how atoms and molecules interact with specific regions of the electromagnetic spectrum. On the AP Chemistry exam, you must match three regions of radiation to the molecular transitions they induce: (1) low-energy **microwave radiation** causes molecules to rotate faster (**rotational transitions**); (2) moderate-energy **infrared (IR) radiation** causes covalent bonds to stretch and bend (**vibrational transitions**); and (3) higher-energy **ultraviolet and visible (UV–Vis) radiation** promotes electrons from lower to higher energy levels (**electronic transitions**).

Electromagnetic radiation exhibits wave–particle duality: its wavelength (λ, in m) and frequency (ν, in s^{-1} or Hz) are inversely related by the speed of light (**$c = \lambda\nu$**, where $c = 2.998 \times 10^{8}$ m·s^{-1}), and the energy of a single photon is given by Planck's equation (**$E = h\nu = hc/\lambda$**, where $h = 6.626 \times 10^{-34}$ J·s).

Spectrophotometry measures how much visible light a colored solution absorbs to determine its molar concentration via the **Beer–Lambert Law: $A = \varepsilon bc$**, where A is absorbance (unitless), ε is the molar absorptivity constant (M^{-1}·cm^{-1}), b is the cuvette path length (typically 1.00 cm), and c is molarity (M). Because ε and b are constant for a given substance and cuvette, **absorbance is directly proportional to concentration**. Before measuring samples, the spectrophotometer is zeroed with a **blank** of pure solvent (or colorless matrix) and set to the optimal wavelength **λ_{max}** where the colored species absorbs most strongly (e.g., a blue Cu^{2+}(aq) solution absorbs orange-red light around 630 nm).

- **Calibration Curve Slope:** A plot of Absorbance (y-axis) vs. Concentration (x-axis) for standard solutions produces a straight line through the origin with slope = εb.
- **Lab Error 1 — Fingerprints, Water Droplets, or Scratches on Outside of Cuvette:** Scatters/blocks light from reaching the detector → causes an artificially HIGH absorbance and an overestimated concentration.
- **Lab Error 2 — Rinsing Cuvette with Distilled Water Right Before Filling with Sample:** Leftover water droplets inside the cuvette dilute the sample → causes an artificially LOW absorbance and an underestimated concentration.

Table 3.2 · Electromagnetic Radiation Regions and Molecular Transitions on the AP Exam

Radiation Region	Relative Photon Energy & Frequency	Molecular / Atomic Transition Induced	Analytical Application
Microwave	Lowest energy, longest λ	Molecular rotational transitions	Rotational spectroscopy of polar molecules
Infrared (IR)	Moderate energy & λ	Covalent bond stretching & bending vibrations	Identifying functional groups (O–H, C=O, etc.)
UV–Visible (UV–Vis)	High energy, shorter λ (400–700 nm Vis)	Valence electronic transitions (ground → excited)	Beer–Lambert Law (A = εbc) concentration analysis
X-Ray / Vacuum UV	Very high energy, very short λ	Complete ejection of core & valence electrons	Photoelectron Spectroscopy (PES, Unit 1)

EXAMPLE 3.5 Photon Energy Calculation & Beer–Lambert Calibration Curve Analysis

Problem: (a) Calculate the frequency (ν) and single-photon energy (E) of blue light with a wavelength of 450 nm. (b) A Beer–Lambert calibration plot of absorbance vs. concentration for standard $CuSO_4(aq)$ solutions yields a linear regression line with slope = 1.50 M^{-1}. If an unknown $CuSO_4$ solution has a measured absorbance of A = 0.450, what is its molar concentration?

STEP-BY-STEP SOLUTION:

1. Part (a) Step 1 — Wavelength to Frequency: Convert 450 nm to meters: $\lambda = 450 \times 10^{-9}$ m = 4.50×10^{-7} m. Then $\nu = c / \lambda = (2.998 \times 10^{8}\ m \cdot s^{-1}) / (4.50 \times 10^{-7}\ m) = 6.66 \times 10^{14}\ s^{-1}$.
2. Part (a) Step 2 — Photon Energy: $E = h\nu = (6.626 \times 10^{-34}\ J \cdot s)(6.66 \times 10^{14}\ s^{-1}) = 4.41 \times 10^{-19}$ J per photon.
3. Part (b) Beer–Lambert Concentration: Since A = (slope) × c, solve for c = A / slope = 0.450 / 1.50 M^{-1} = 0.300 M $CuSO_4$.

Final Answer: (a) $\nu = 6.66 \times 10^{14}\ s^{-1}$, $E = 4.41 \times 10^{-19}$ J; (b) c = 0.300 M

⚠ AP EXAM TRAP & FRQ SCORING GUIDELINE

AP Exam Trap: When choosing the optimal wavelength (λ_{max}) for a Beer–Lambert experiment, never pick the color that the solution appears to your eye! A blue Cu^{2+} solution TRANSMITS blue light (~450 nm) and ABSORBS its complementary color (orange-red light, ~630 nm). Always select the peak of the absorption spectrum.

✅ CHAPTER 3 MASTERY CHECKLIST (AP EXAM READINESS)

☑ Identify all intermolecular forces (LDF, dipole–dipole, H-bonding, ion–dipole) and justify boiling point/vapor pressure differences using polarizability and electron count.

☑ Classify any solid as ionic, molecular, covalent network (diamond vs. graphite, SiO_2), or metallic based on melting point and electrical conductivity.

☑ Solve quantitative problems using the Combined Gas Law, Ideal Gas Law (PV = nRT), gas density (M = dRT/P), Dalton's Law (including gas over water), and Graham's Law.

☑ Explain Kinetic Molecular Theory, Maxwell–Boltzmann curves, and real-gas deviations at low T (IMFs) and high P (particle volume).

☑ Perform molarity/dilution calculations, draw ion-hydration particulate diagrams, analyze chromatography/distillation, and apply Planck's equations and the Beer–Lambert Law (A = εbc).

CHAPTER 4 · CORE CURRICULUM

AP Exam Weighting: 7–9%

Unit 4: Chemical Reactions

Unit 4 focuses on how chemical changes are represented, classified, and quantified. Students distinguish physical changes from chemical reactions, apply the SNAP solubility rule to write complete and net ionic equations, master reaction stoichiometry, limiting reactants, theoretical and percent yields, and solution titrations, and analyze the three major AP reaction classes: precipitation, Brønsted–Lowry acid–base proton transfer, and oxidation–reduction (redox) electron transfer.

📐 CHAPTER 4 ESSENTIAL EQUATIONS, LAWS & CONSTANTS

$n = m / M$ and $n = M \times V_L$	Converting solid mass or solution volume into moles for stoichiometry
$\%\ \text{Yield} = (\text{Actual Yield} / \text{Theoretical Yield}) \times 100\%$	Percent efficiency of a chemical reaction based on the limiting reactant
$n_A / a = n_B / b$ (at Equivalence Point)	Stoichiometric equivalence condition in an acid–base or redox titration
Σ (Oxidation States) = Overall Charge	Conservation of oxidation numbers in neutral compounds (0) and polyatomic ions

§ 4.1 Physical vs. Chemical Changes, Balancing Equations & Net Ionic Equations

In a **physical change** (such as melting ice or boiling liquid water into steam), a substance alters its physical state or appearance without changing its chemical identity; intact H_2O molecules simply move farther apart as intermolecular hydrogen bonds are overcome. In a **chemical change** (such as the electrolysis of water into 2 $H_2(g)$ + $O_2(g)$), intramolecular covalent or ionic bonds break and new bonds form, converting reactants into entirely new substances. Macroscopic evidence of a chemical reaction includes: (1) formation of an insoluble solid precipitate, (2) evolution of gas bubbles, (3) a permanent color change, or (4) release or absorption of heat or light.

Every chemical equation must obey the **Law of Conservation of Mass** by containing the exact same number of each type of atom on both sides of the reaction arrow. Equations are balanced exclusively by adjusting **stoichiometric coefficients** in front of formulas, never by altering subscripts inside a formula. To write **net ionic equations** on the AP Chemistry exam, memorize the universal **SNAP Solubility Rule**: every ionic compound containing **Sodium (Na^+), Nitrate (NO_3^-), Ammonium (NH_4^+), or Potassium (K^+)** is **100% soluble in water at all times**. Ions that appear unchanged in aqueous form on both sides of the arrow are **spectator ions** and are crossed out to leave the net ionic equation.

- **Combustion of Propane:** $C_3H_8(g)$ + 5 $O_2(g)$ → 3 $CO_2(g)$ + 4 $H_2O(g)$ (3 C, 8 H, and 10 O atoms on each side).
- **Barium Nitrate + Sodium Sulfate Precipitation:** Molecular: $Ba(NO_3)_2(aq)$ + $Na_2SO_4(aq)$ → $BaSO_4(s)$ + 2 $NaNO_3(aq)$. Crossing out Na^+ and NO_3^- spectators gives Net Ionic: $Ba^{2+}(aq)$ + $SO_4^{2-}(aq)$ → $BaSO_4(s)$.
- **Gas-Forming Acid + Carbonate/Bicarbonate Rule:** Whenever an acid reacts with CO_3^{2-} or HCO_3^- to form carbonic acid (H_2CO_3), it immediately decomposes into $H_2O(l)$ + $CO_2(g)$. For $HCl(aq)$ + $NaHCO_3(s)$: Net Ionic is $H^+(aq)$ + $HCO_3^-(s)$ → $H_2O(l)$ + $CO_2(g)$.

EXAMPLE 4.1 **Writing Balanced Molecular, Complete Ionic & Net Ionic Equations**

Problem: Write the balanced molecular equation, identify the spectator ions, and write the net ionic equation when aqueous potassium chloride is mixed with aqueous silver nitrate.

STEP-BY-STEP SOLUTION:

1. Step 1 — Balanced Molecular Equation: $KCl(aq) + AgNO_3(aq) \rightarrow AgCl(s) + KNO_3(aq)$.
2. Step 2 — Apply SNAP Rule & Identify Spectators: Both reactants are soluble. By the SNAP rule, $K^+(aq)$ and $NO_3^-(aq)$ never form a precipitate and remain unchanged in solution on both sides → K^+ and NO_3^- are spectator ions.
3. Step 3 — Net Ionic Equation: $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$ (white precipitate).

Final Answer: Spectators: $K^+(aq)$, $NO_3^-(aq)$; Net ionic equation: $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$

⚠ **AP EXAM TRAP & FRQ SCORING GUIDELINE**

AP Exam Trap: Never leave $H_2CO_3(aq)$ as a final product in an acid–carbonate reaction! Always break it down into $H_2O(l) + CO_2(g)$. Similarly, never dissociate an insoluble solid, a pure liquid ($H_2O(l)$), a gas, or a weak acid (like HF or CH_3COOH) into separate ions in a net ionic equation.

§ 4.2 Reaction Stoichiometry, Limiting Reactants & Percent Yield

Reaction stoichiometry rests on a strict three-step roadmap: because balanced chemical equations express ratios in **moles** (never directly in grams!), you must always convert any given quantity into moles first: (1) convert mass (m/M) or solution volume (M × V_L) into moles of substance A; (2) multiply by the **mole-to-mole ratio** using the coefficients from the balanced equation; and (3) convert moles of substance B into the target unit.

When two reactants are mixed in arbitrary amounts, the reactant that runs out first is the **limiting reactant** because it limits the maximum amount of product that can form (the **theoretical yield**). The reactant with molecules left over after the reaction stops is the **excess reactant**. Finally, comparing the mass actually collected in the lab (**actual yield**) to the calculated theoretical yield gives the **percent yield**.

- **Particulate Limiting Reactant Check ($2\ H_2 + O_2 \rightarrow 2\ H_2O$):** If a container starts with 6 H_2 molecules and 2 O_2 molecules, the 2 O_2 molecules react completely with 4 H_2 molecules to form 4 H_2O molecules, leaving 2 H_2 molecules unreacted → O_2 is limiting and H_2 is in excess.

EXAMPLE 4.2 **Mass-to-Mass Decomposition Stoichiometry**

Problem: When 24.5 g of solid potassium chlorate ($KClO_3$, M = 122.55 g·mol^{-1}) decomposes upon heating according to $2\ KClO_3(s) \rightarrow 2\ KCl(s) + 3\ O_2(g)$, how many grams of oxygen gas (O_2, M = 32.00 g·mol^{-1}) are produced?

STEP-BY-STEP SOLUTION:

1. Step 1 — Grams to Moles of $KClO_3$: $n(KClO_3) = 24.5\ g / 122.55\ g\cdot mol^{-1} = 0.200\ mol\ KClO_3$.
2. Step 2 — Mole-to-Mole Ratio: Multiply by (3 mol O_2 / 2 mol $KClO_3$): $n(O_2) = 0.200\ mol \times (3 / 2) = 0.300\ mol\ O_2$.
3. Step 3 — Moles to Grams of O_2: $m(O_2) = 0.300\ mol \times 32.00\ g\cdot mol^{-1} = 9.60\ g\ O_2$.

Final Answer: 9.60 g O_2

EXAMPLE 4.3 **Limiting Reactant, Theoretical Yield & Percent Yield**

Problem: Suppose 5.40 g of aluminum (Al, M = 26.98 g·mol^{-1}) reacts with 21.3 g of chlorine gas (Cl_2, M = 70.90 g·mol^{-1}) to form aluminum chloride ($AlCl_3$, M = 133.34 g·mol^{-1}) according to 2 Al(s) + 3 Cl_2(g) → 2 $AlCl_3$(s). Calculate the theoretical yield of $AlCl_3$ in grams, and find the percent yield if a student collects 22.7 g of $AlCl_3$ in the lab.

STEP-BY-STEP SOLUTION:

1. Step 1 — Convert Both Reactants to Moles: n(Al) = 5.40 g / 26.98 g·mol^{-1} = 0.200 mol Al; n(Cl_2) = 21.3 g / 70.90 g·mol^{-1} = 0.300 mol Cl_2.
2. Step 2 — Compare Stoichiometric Ratio: From 2 Al + 3 Cl_2 → 2 $AlCl_3$, 0.200 mol Al requires exactly 0.200 × (3/2) = 0.300 mol Cl_2. Both reactants are present in exact stoichiometric proportion and yield 0.200 mol $AlCl_3$.
3. Step 3 — Theoretical Yield in Grams: m_theoretical = 0.200 mol × 133.34 g·mol^{-1} = 26.7 g $AlCl_3$.
4. Step 4 — Percent Yield: % Yield = (22.7 g actual / 26.7 g theoretical) × 100% = 85.0%.

Final Answer: Theoretical yield = 26.7 g $AlCl_3$; Percent yield = 85.0%

⚠ **AP EXAM TRAP & FRQ SCORING GUIDELINE**

AP Exam Trap: Never determine the limiting reactant by comparing initial masses (grams) or even raw initial moles without dividing by the stoichiometric coefficients! A reactant with more initial grams or moles can still be the limiting reactant if its stoichiometric coefficient in the balanced equation is larger.

§ 4.3 Solution Stoichiometry, Gravimetric Precipitation & Titrations

In **solution stoichiometry**, reactants are measured as aqueous volumes of known molarity. Multiplying molarity (M, mol·L^{-1}) by volume in liters (V_L) directly gives moles of solute (**n = M × V_L**). For example, 50.0 mL (0.0500 L) of 0.400 M $MgCl_2$(aq) contains 0.0200 mol of Mg^{2+} ions and twice as many (0.0400 mol) Cl^- ions.

A **titration** is a quantitative analytical technique used to determine the unknown concentration of an **analyte** solution in an Erlenmeyer flask by slowly adding a **titrant** of known concentration from a calibrated buret. The **equivalence point** is the exact stoichiometric moment when the moles of added titrant equal the moles required to completely react with the analyte according to the balanced chemical equation. The **endpoint** is the experimental moment when an indicator (such as phenolphthalein turning from colorless to faint pink) changes color permanently to signal that the equivalence point has been reached.

- **Gravimetric Analysis (Precipitation):** Collect precipitate by filtration, rinse with distilled water to remove soluble spectator ions, and dry in an oven to constant mass before weighing.
- **Common Gravimetric Error:** If the precipitate is not completely dried before weighing, leftover water inflates the measured mass, causing an artificially high calculated analyte percentage.

EXAMPLE 4.4 **Solution Stoichiometry of a Precipitation Reaction**

Problem: Excess aqueous potassium iodide (KI) is added to 40.0 mL of 0.250 M lead(II) nitrate, $Pb(NO_3)_2(aq)$, forming a bright yellow precipitate of lead(II) iodide, $PbI_2(s)$ ($M = 461.0\ g{\cdot}mol^{-1}$). How many grams of dry PbI_2 precipitate are formed?

STEP-BY-STEP SOLUTION:

1. Step 1 — Moles of Limiting Ion (Pb^{2+}): $n(Pb^{2+}) = M \times V_L = 0.250\ mol{\cdot}L^{-1} \times 0.0400\ L = 0.0100\ mol\ Pb^{2+}$.
2. Step 2 — Stoichiometry to $PbI_2(s)$: From $Pb^{2+}(aq) + 2\ I^-(aq) \rightarrow PbI_2(s)$ (with I^- in excess), 1 mol Pb^{2+} produces 1 mol PbI_2 → $n(PbI_2) = 0.0100\ mol$.
3. Step 3 — Convert to Grams: $m(PbI_2) = 0.0100\ mol \times 461.0\ g{\cdot}mol^{-1} = 4.61\ g\ PbI_2(s)$.

Final Answer: 4.61 g $PbI_2(s)$

EXAMPLE 4.5 **Acid–Base Titration with a Non-1:1 Stoichiometric Ratio**

Problem: It takes 32.0 mL of 0.150 M sodium hydroxide (NaOH) to reach the equivalence point in the complete titration of 24.0 mL of diprotic sulfuric acid (H_2SO_4). What is the molar concentration of the H_2SO_4 solution?

STEP-BY-STEP SOLUTION:

1. Step 1 — Balanced Equation: $H_2SO_4(aq) + 2\ NaOH(aq) \rightarrow Na_2SO_4(aq) + 2\ H_2O(l)$ (1 : 2 acid-to-base mole ratio).
2. Step 2 — Moles of NaOH Titrant Added: $n(NaOH) = 0.150\ mol{\cdot}L^{-1} \times 0.0320\ L = 0.00480\ mol\ NaOH$.
3. Step 3 — Moles & Molarity of H_2SO_4 Analyte: $n(H_2SO_4) = 0.00480\ mol\ NaOH \times (1\ mol\ H_2SO_4 / 2\ mol\ NaOH) = 0.00240\ mol\ H_2SO_4$. Dividing by the analyte volume (0.0240 L) gives $M(H_2SO_4) = 0.00240\ mol / 0.0240\ L = 0.100\ M$.

Final Answer: 0.100 M H_2SO_4

⚠ **AP EXAM TRAP & FRQ SCORING GUIDELINE**

AP Exam Trap: Do NOT blindly apply $M_1V_1 = M_2V_2$ to titration reactions where the mole ratio is not 1:1 (such as H_2SO_4 + 2 NaOH or redox titrations like MnO_4^- + 5 Fe^{2+})! Always calculate moles of titrant (n = MV) first, then multiply by the balanced stoichiometric mole ratio.

§ 4.4 Reaction Classification: Brønsted–Lowry Acid–Base & Oxidation–Reduction (Redox)

On the AP Chemistry exam, chemical reactions are grouped into three fundamental classes based on what particle is exchanged or transferred: (1) **Precipitation reactions** exchange ions between aqueous solutions to form an insoluble solid with zero change in oxidation states; (2) **Acid–base reactions** transfer a proton (**H^+**) from an acid to a base; and (3) **Oxidation–reduction (redox) reactions** transfer **electrons (e^-)** between species, causing oxidation states to change.

While the narrow Arrhenius definition restricts acids to producing H^+ and bases to producing OH^- in water, the **Brønsted–Lowry definition** defines an **acid as a proton (H^+) donor** and a **base as a proton (H^+) acceptor** (any species with a lone pair to bind H^+). Every Brønsted–Lowry reaction features two **conjugate acid–base pairs** that differ by exactly one proton (H^+). For example, in **$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$**, H_2O donates H^+ (acid) to become its conjugate base OH^-, while NH_3 accepts H^+ (base) to become its conjugate acid NH_4^+. Species like H_2O or HCO_3^- that can either donate or accept a proton are called **amphiprotic**.

In a **redox reaction**, remember the mnemonic **OIL RIG**: **Oxidation Is Loss of electrons** (oxidation state increases) and **Reduction Is Gain of electrons** (oxidation state decreases). To assign oxidation states, apply four priority rules: (1) any pure element in its standard state (Fe(s), $O_2(g)$) is 0; (2) a monatomic ion equals its charge; (3) in compounds, F is always −1, O is −2 (except −1 in peroxides like H_2O_2), and H is +1 with nonmetals; and (4) the sum of oxidation states equals 0

for a neutral compound or the ion's charge for a polyatomic ion. When balancing complex redox half-reactions in acidic solution, follow the 4-step sequence: **(1) balance central atoms → (2) balance O by adding H_2O → (3) balance H by adding H^+ → (4) balance charge by adding e^-.**

- **The 6 Strong Acids (100% Ionized):** HCl, HBr, HI, HNO_3, $HClO_4$, and H_2SO_4.
- **Special Redox Class 1 — Halogen Displacement:** A more reactive halogen higher in Group 17 oxidizes a halide ion below it: $Cl_2(g) + 2\ Br^-(aq) \rightarrow 2\ Cl^-(aq) + Br_2(l)$.
- **Special Redox Class 2 — Disproportionation:** The same element is simultaneously oxidized and reduced: in $2\ H_2O_2(aq) \rightarrow 2\ H_2O(l) + O_2(g)$, oxygen goes from −1 in H_2O_2 to −2 in H_2O (reduced) and 0 in O_2 (oxidized).
- **Special Redox Class 3 — Active Metal + Acid:** $Mg(s) + 2\ H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g)$.

Table 4.1 · Summary of the Three Fundamental AP Chemistry Reaction Classes

Reaction Class	Particle Transferred / Exchanged	Oxidation States Change?	Classic Net Ionic Example
Precipitation (Metathesis)	Aqueous ions swap partners to form solid	No (0 change)	$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$
Brønsted–Lowry Acid–Base	Proton (H^+) transferred from donor to acceptor	No (0 change)	$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$
Oxidation–Reduction (Redox)	Electrons (e^-) transferred from oxidized to reduced species	Yes (OIL RIG)	$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

EXAMPLE 4.6 Assigning Oxidation States & Balancing Acidic Redox Half-Reactions

Problem: (a) Determine the oxidation state of manganese in permanganate (MnO_4^-) and chromium in dichromate ($Cr_2O_7^{2-}$). (b) Balance the overall redox equation between solid aluminum (Al) and aqueous nickel(II) ions (Ni^{2+}). (c) Write the balanced reduction half-reaction for permanganate (MnO_4^-) reducing to Mn^{2+} in acidic aqueous solution.

STEP-BY-STEP SOLUTION:

1. Part (a) Oxidation States: In MnO_4^-, 4 oxygens at −2 contribute −8; since Mn + (−8) = −1, Mn = +7. In $Cr_2O_7^{2-}$, 7 oxygens at −2 contribute −14; since 2(Cr) + (−14) = −2, 2(Cr) = +12 → each Cr = +6.
2. Part (b) Balancing Electrons Between Half-Reactions: Oxidation: $Al(s) \rightarrow Al^{3+}(aq) + 3\ e^-$ (multiply by 2 to give 6 e^-). Reduction: $Ni^{2+}(aq) + 2\ e^- \rightarrow Ni(s)$ (multiply by 3 to give 6 e^-). Adding gives: $2\ Al(s) + 3\ Ni^{2+}(aq) \rightarrow 2\ Al^{3+}(aq) + 3\ Ni(s)$.
3. Part (c) Acidic Half-Reaction for $MnO_4^- \rightarrow Mn^{2+}$: (1) 1 Mn on each side. (2) Balance 4 O on left by adding 4 $H_2O(l)$ on right. (3) Balance 8 H on right by adding 8 $H^+(aq)$ on left. (4) Net charge on left is (−1) + (+8) = +7; net charge on right is +2. Add 5 e^- to the left so both sides equal +2: $MnO_4^-(aq) + 8\ H^+(aq) + 5\ e^- \rightarrow Mn^{2+}(aq) + 4\ H_2O(l)$.

Final Answer: (a) Mn = +7, Cr = +6; (b) $2\ Al(s) + 3\ Ni^{2+}(aq) \rightarrow 2\ Al^{3+}(aq) + 3\ Ni(s)$; (c) $MnO_4^- + 8\ H^+ + 5\ e^- \rightarrow Mn^{2+} + 4\ H_2O$

⚠ AP EXAM TRAP & FRQ SCORING GUIDELINE

AP Exam Trap: When balancing redox reactions from half-reactions (such as $Al + Ni^{2+} \rightarrow Al^{3+} + Ni$), an equation that is balanced for atoms is STILL WRONG if total charge is not conserved on both sides! Always verify that the number of electrons lost in oxidation equals the number gained in reduction.

✅ CHAPTER 4 MASTERY CHECKLIST (AP EXAM READINESS)

☑ Distinguish physical changes (breaking IMFs) from chemical changes (breaking/forming covalent or ionic bonds) in macroscopic observations and particulate diagrams.

☑ Apply the SNAP solubility rule (Na^+, NO_3^-, NH_4^+, K^+ always soluble) to cross out spectator ions and write balanced net ionic equations.

☑ Solve mass-to-mass and solution stoichiometry problems, identify limiting reactants, and calculate theoretical and percent yields.

☑ Analyze gravimetric precipitation and acid–base/redox titration data, distinguishing the stoichiometric equivalence point from the indicator endpoint.

☑ Identify Brønsted–Lowry conjugate acid–base pairs, assign oxidation states, and balance redox equations in neutral and acidic solutions.

CHAPTER 5 · CORE CURRICULUM

AP Exam Weighting: 7–9%

Unit 5: Kinetics

Unit 5 investigates the rates at which chemical reactions occur and the step-by-step molecular pathways (mechanisms) they follow. Students relate stoichiometric rates of appearance and disappearance, determine differential rate laws using the Method of Initial Rates, apply zero-, first-, and second-order integrated rate laws and linear graphical tests, calculate first-order half-lives, and connect Collision Theory, Maxwell–Boltzmann activation energy distributions, potential energy profiles, and catalysis to multi-step reaction mechanisms.

CHAPTER 5 ESSENTIAL EQUATIONS, LAWS & CONSTANTS

$\text{Rate} = -(1/a)(\Delta[A]/\Delta t) = +(1/b)(\Delta[B]/\Delta t)$	Relative stoichiometric reaction rates for aA → bB (always positive)
$\text{Rate} = k[A]^m[B]^n$	Differential Rate Law (exponents m, n determined ONLY from experiment)
$[A]_t - [A]_0 = -kt$	Zero-Order Integrated Rate Law (linear plot: [A] vs. t, slope = −k)
$\ln[A]_t - \ln[A]_0 = -kt$	First-Order Integrated Rate Law (linear plot: ln[A] vs. t, slope = −k)
$(1/[A]_t) - (1/[A]_0) = +kt$	Second-Order Integrated Rate Law (linear plot: 1/[A] vs. t, slope = +k)
$t_{(1/2)} = 0.693 / k$	First-Order Half-Life (constant and independent of initial concentration [A]_0)

§ 5.1 Reaction Rates, Stoichiometric Rate Relationships & Experimental Factors

Chemical kinetics is the study of reaction speeds and the molecular mechanisms by which reactions occur. **Reaction rate** is defined as the change in molar concentration of a reactant or product per unit time, typically expressed in **$M \cdot s^{-1}$ ($mol \cdot L^{-1} \cdot s^{-1}$)**. Because reactant concentrations decrease over time while product concentrations increase, reactant rate expressions include a negative sign so that the overall reaction rate is always a positive quantity. To compare the rates of disappearance and appearance of different species in any balanced chemical equation, divide each rate of concentration change by its stoichiometric coefficient.

Four main experimental factors control the rate of a chemical reaction: (1) **Reactant concentration / surface area**: increasing concentration (or grinding a solid into a fine powder to increase surface area) increases collision frequency and speeds up the reaction; (2) **Temperature**: raising temperature increases both collision frequency and, far more importantly, the fraction of collisions whose kinetic energy exceeds the activation energy (E_a); (3) **Catalysts**: adding a catalyst speeds up a reaction by providing an alternative pathway with a lower activation energy; and (4) **Chemical nature and phase of reactants**: aqueous ions react almost instantaneously, whereas breaking strong covalent bonds in gases or solids is slower.

- **Stoichiometric Rate Ratio ($2\ NO_2 \rightarrow 2\ NO + O_2$):** NO forms twice as fast as O_2 forms, and NO_2 disappears twice as fast as O_2 forms, matching the 2 : 2 : 1 mole ratio.

EXAMPLE 5.1 **Relating Rates of Appearance and Disappearance Using Stoichiometry**

Problem: Consider the gas-phase decomposition reaction $2\ N_2O_5(g) \rightarrow 4\ NO_2(g) + O_2(g)$. If oxygen gas ($O_2$) is forming at a rate of $+0.015\ M \cdot s^{-1}$ at a particular instant, at what rate is NO_2 forming and at what rate is N_2O_5 disappearing?

STEP-BY-STEP SOLUTION:

1. Step 1 — Rate of Formation of NO_2: Because NO_2 has a stoichiometric coefficient of 4 compared to O_2's coefficient of 1, NO_2 forms 4 times as fast as O_2: $\Delta[NO_2]/\Delta t = 4 \times (0.015\ M \cdot s^{-1}) = 0.060\ M \cdot s^{-1}$.
2. Step 2 — Rate of Disappearance of N_2O_5: Because N_2O_5 has a coefficient of 2, it disappears twice as fast as O_2 forms: $-\Delta[N_2O_5]/\Delta t = 2 \times (0.015\ M \cdot s^{-1}) = 0.030\ M \cdot s^{-1}$.

Final Answer: Rate of NO_2 appearance = $0.060\ M \cdot s^{-1}$; Rate of N_2O_5 disappearance = $0.030\ M \cdot s^{-1}$

⚠ **AP EXAM TRAP & FRQ SCORING GUIDELINE**

AP Exam Trap: When an AP question asks for the 'rate of disappearance' of a reactant, report a POSITIVE number (since 'disappearance' already accounts for the negative sign). Only include a negative sign if asked specifically for Δ[Reactant]/Δt.

§ 5.2 Differential Rate Laws & the Method of Initial Rates

A **differential rate law** expresses the instantaneous reaction rate as a function of reactant concentrations: **Rate = k[A]^m[B]^n**, where **k** is the temperature-dependent rate constant, the exponents **m** and **n** are the **reaction orders** with respect to reactants A and B, and the sum **m + n** is the **overall reaction order**. Crucially, reaction orders for an overall balanced chemical equation can **ONLY be determined from experimental data**—never by simply copying the stoichiometric coefficients!

Using the **Method of Initial Rates**, we compare pairs of experiments in which one reactant's initial concentration changes while all other reactant concentrations are held constant: if doubling [A] has no effect on the rate ($2^0 = 1$), the reaction is **zero order (m = 0)**; if doubling [A] doubles the rate ($2^1 = 2$), it is **first order (m = 1)**; and if doubling [A] quadruples the rate ($2^2 = 4$), it is **second order (m = 2)**. Once the rate law is established, substitute the values from any single experiment into the rate law to solve for both the numerical value and the specific units of k.

- **General Formula for Units of k:** For an overall reaction order N, the units of the rate constant k are always $M^{(1-N)} \cdot s^{-1}$ (or $L^{(N-1)} \cdot mol^{(1-N)} \cdot s^{-1}$).

EXAMPLE 5.2 **Determining the Rate Law, Overall Order & Rate Constant k (with Units) from Initial Rates**

Problem: For the reaction $2\ NO(g) + Cl_2(g) \rightarrow 2\ NOCl(g)$, the following initial rate data were collected at 298 K: • Exp 1: $[NO]_0 = 0.10\ M$, $[Cl_2]_0 = 0.10\ M \rightarrow$ Initial Rate = $0.018\ M \cdot s^{-1}$ • Exp 2: $[NO]_0 = 0.20\ M$, $[Cl_2]_0 = 0.10\ M \rightarrow$ Initial Rate = $0.072\ M \cdot s^{-1}$ • Exp 3: $[NO]_0 = 0.10\ M$, $[Cl_2]_0 = 0.20\ M \rightarrow$ Initial Rate = $0.036\ M \cdot s^{-1}$ Determine the differential rate law, the overall reaction order, and the numerical value and units of the rate constant k.

STEP-BY-STEP SOLUTION:

1. Step 1 — Order with Respect to NO (Compare Exp 1 & Exp 2): $[Cl_2]$ is held constant at 0.10 M while [NO] doubles (0.10 → 0.20 M). The initial rate quadruples (0.072 / 0.018 = 4.0). Since 2^m = 4, m = 2 (second order in NO).
2. Step 2 — Order with Respect to Cl_2 (Compare Exp 1 & Exp 3): [NO] is held constant at 0.10 M while $[Cl_2]$ doubles (0.10 → 0.20 M). The initial rate doubles (0.036 / 0.018 = 2.0). Since 2^n = 2, n = 1 (first order in Cl_2).
3. Step 3 — Write Rate Law & Overall Order: Rate = $k[NO]^2[Cl_2]^1$. The overall reaction order is 2 + 1 = 3 (third order overall).
4. Step 4 — Solve for k and its Units Using Exp 1: $0.018\ M \cdot s^{-1} = k(0.10\ M)^2(0.10\ M) = k(0.0010\ M^3)$. Dividing gives $k = 0.018\ M \cdot s^{-1} / 0.0010\ M^3 = 18\ M^{-2} \cdot s^{-1}$.

Final Answer: Rate = $k[NO]^2[Cl_2]$; 3rd order overall; $k = 18\ M^{-2} \cdot s^{-1}$

> ⚠ **AP EXAM TRAP & FRQ SCORING GUIDELINE**
> AP Exam Trap: On AP FRQs, one full scoring point is almost always dedicated exclusively to the correct UNITS of the rate constant k. Always cancel M on both sides of the rate law equation to verify your exponent on M!

§ 5.3 Integrated Rate Laws, Linear Graphical Tests & First-Order Half-Life

Whereas differential rate laws relate reaction rate to concentration, **integrated rate laws** relate reactant concentration directly to time (t). Given concentration-versus-time data from a single kinetic experiment, you can determine the reaction order with respect to reactant A by checking which of three signature plots yields a straight line: (1) For a **zero-order reaction (Rate = k)**, [A] decreases at a constant rate regardless of how much reactant remains; plotting **[A] vs. t** produces a straight line with slope = **−k**. (2) For a **first-order reaction (Rate = k[A])**, plotting **ln[A] vs. t** produces a straight line with negative slope = **−k**. (3) For a **second-order reaction (Rate = k[A]^2)**, plotting the reciprocal **1/[A] vs. t** produces a straight line with an upward positive slope = **+k**.

Furthermore, **first-order reactions** (including all radioactive nuclear decay processes) possess a unique hallmark property: their **half-life (t_½)**—the time required for a reactant's concentration to drop to exactly half of its initial value—is **completely constant and independent of initial concentration**: **t_½ = ln(2) / k = 0.693 / k**.

- **Zero-Order Half-Life:** Decreases as the reaction proceeds (t_½ = $[A]_0$ / 2k).
- **First-Order Half-Life:** Remains strictly CONSTANT throughout the entire reaction (t_½ = 0.693 / k). If it takes 200 s to drop from 0.80 M to 0.40 M, it takes another 200 s to drop from 0.40 M to 0.20 M.
- **Second-Order Half-Life:** Increases (doubles each successive half-life) as concentration drops (t_½ = 1 / k$[A]_0$).

Table 5.1 · Complete Comparison of Zero-, First-, and Second-Order Kinetics

Order	Differential Rate Law	Integrated Rate Law	Linear Plot (y vs. x)	Slope of Linear Plot	Units of Rate Constant k	Half-Life (t_½) Behavior
Zero (0)	Rate = k	[A]_t − [A]_0 = −kt	[A] vs. t	−k (negative)	$M \cdot s^{-1}$	Decreases as [A] drops
First (1)	Rate = k[A]	ln[A]_t − ln[A]_0 = −kt	ln[A] vs. t	−k (negative)	s^{-1} (or min^{-1}, hr^{-1})	Constant: t_½ = 0.693 / k
Second (2)	Rate = k$[A]^2$	(1/[A]_t) − (1/[A]_0) = +kt	1/[A] vs. t	+k (positive)	$M^{-1} \cdot s^{-1}$	Increases as [A] drops

EXAMPLE 5.3 First-Order Half-Life & Remaining Concentration After Multiple Half-Lives

Problem: The first-order thermal decomposition of dinitrogen pentoxide (N_2O_5) has a rate constant of k = 3.46×10^{-3} s^{-1} at 298 K. (a) Calculate the half-life (t_½) of the reaction. (b) If a reaction vessel starts with an initial concentration of $[N_2O_5]_0$ = 0.800 M, what concentration of N_2O_5 remains after 600 seconds?

STEP-BY-STEP SOLUTION:

1. Part (a) First-Order Half-Life: Since the reaction is first order, t_½ = 0.693 / k = 0.693 / (3.46×10^{-3} s^{-1}) = 200 s.
2. Part (b) Count Half-Lives: Elapsed time = 600 s. Dividing by t_½ = 200 s gives exactly n = 600 / 200 = 3 half-lives.
3. Part (b) Halve Initial Concentration Three Times: 0.800 M → (1st t_½, 200 s) → 0.400 M → (2nd t_½, 400 s) → 0.200 M → (3rd t_½, 600 s) → 0.100 M remaining.

Final Answer: (a) t_½ = 200 s; (b) $[N_2O_5]$ = 0.100 M after 600 s

> ⚠ **AP EXAM TRAP & FRQ SCORING GUIDELINE**
>
> AP Exam Trap: Never use t_½ = 0.693 / k for a zero-order or second-order reaction! That equation applies ONLY to first-order reactions. Conversely, if you observe from a table or graph that the time required for concentration to halve is constant (e.g., 0.8 M → 0.4 M → 0.2 M in equal time intervals), that immediately proves the reaction is first order.

§ 5.4 Collision Theory, Reaction Energy Profiles, Multi-Step Mechanisms & Catalysis

According to the **Collision Model**, three strict conditions must be satisfied for reactant molecules to react: (1) the molecules must physically collide; (2) the colliding molecules must possess a minimum total kinetic energy equal to or greater than the **activation energy (E_a)** in order to stretch and break existing bonds; and (3) the molecules must collide with the proper 3D **spatial orientation** so that the reactive atoms make direct contact. On a **Maxwell–Boltzmann distribution plot** of fraction of molecules versus kinetic energy, raising the temperature from T_1 to T_2 flattens the curve and shifts it to the right, **exponentially increasing the shaded area of molecules with KE ≥ E_a** (while E_a itself remains unchanged unless a catalyst is added).

A **reaction energy profile** plots potential energy (y-axis) against reaction progress (x-axis). Reactants climb over an energy barrier to reach the highest-energy point at the peak, called the **transition state (or activated complex)**. The vertical difference from the reactant plateau up to the transition-state peak is the **forward activation energy (E_a, always positive)**, and the vertical difference between reactants and products is the overall enthalpy change (**ΔH**, negative when products lie lower than reactants, positive when products lie higher).

Most reactions occur through a sequence of single-collision events called **elementary steps**, classified by their **molecularity**: 1 reactant particle = **unimolecular**, 2 colliding particles = **bimolecular**, and 3 particles colliding simultaneously = **termolecular** (extremely rare). **Unlike overall reactions, the rate law of an elementary step can be written directly from its stoichiometric coefficients!** For a proposed **reaction mechanism** to be valid, it must satisfy two requirements: (1) the elementary steps must sum to the overall balanced equation, and (2) the rate law predicted by the slowest step—the **rate-determining step (RDS)**, which has the highest transition-state peak / largest E_a on a multi-step energy profile—must match the experimental rate law. Finally, we must distinguish two transient species: a **reaction intermediate** is **produced in an earlier step and consumed in a later step** (corresponds to a valley between peaks on a multi-step profile), whereas a **catalyst** is **added as a reactant in an early step and regenerated unchanged in a later step** (increases k by providing an alternative pathway with a lower E_a without changing ΔH).

- **Multi-Step Energy Profile Features:** A 2-step mechanism has 2 transition-state peaks and 1 intermediate valley; the step with the highest peak (largest E_a barrier) is the slow rate-determining step.
- **Eliminating an Intermediate in Fast-Equilibrium Step 1 + Slow Step 2:** Because reaction intermediates can NEVER appear in a final rate law, use the fast reversible equilibrium of Step 1 (Rate_fwd = Rate_rev) to substitute reactant concentrations in place of the intermediate.

EXAMPLE 5.4 Writing Rate Laws from Slow Step 1 vs. Fast-Equilibrium Step 1 + Slow Step 2

Problem: (a) For the overall reaction $2\ NO_2(g) + F_2(g) \rightarrow 2\ NO_2F(g)$, consider the mechanism: Step 1 (Slow): $NO_2 + F_2 \rightarrow NO_2F + F$ Step 2 (Fast): $NO_2 + F \rightarrow NO_2F$ Identify the reaction intermediate and write the rate law predicted by this mechanism. (b) For the overall reaction $2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g)$, consider the mechanism: Step 1 (Fast, Reversible): $2\ NO \rightleftharpoons N_2O_2$ Step 2 (Slow): $N_2O_2 + O_2 \rightarrow 2\ NO_2$ Derive the valid experimental rate law free of any reaction intermediates.

STEP-BY-STEP SOLUTION:

1. Part (a) Identify Intermediate & RDS Rate Law: Atomic fluorine (F) is produced in Step 1 and consumed in Step 2, so F is the reaction intermediate. Because Step 1 is the slow rate-determining step, the overall rate law comes directly from Step 1's reactants: Rate = $k[NO_2][F_2]$.
2. Part (b) Slow Step 2 Expression: Writing the rate law from slow Step 2 gives Rate = $k_2[N_2O_2][O_2]$. However, N_2O_2 is an intermediate and cannot remain in the final rate law.
3. Part (b) Fast-Equilibrium Substitution: Since Step 1 is at fast dynamic equilibrium, $k_1[NO]^2 = k_{-1}[N_2O_2]$, which means $[N_2O_2] = (k_1/k_{-1})[NO]^2$. Substituting this into the Step 2 rate expression yields the valid overall rate law: Rate = $k[NO]^2[O_2]$.

Final Answer: (a) Intermediate: F; Rate = $k[NO_2][F_2]$; (b) Intermediate: N_2O_2; Rate = $k[NO]^2[O_2]$

EXAMPLE 5.5 Distinguishing a Catalyst from a Reaction Intermediate in a Mechanism

Problem: In the iodide-catalyzed decomposition of hydrogen peroxide ($2\ H_2O_2 \rightarrow 2\ H_2O + O_2$), the mechanism is: Step 1: $H_2O_2(aq) + I^-(aq) \rightarrow H_2O(l) + IO^-(aq)$ Step 2: $H_2O_2(aq) + IO^-(aq) \rightarrow H_2O(l) + O_2(g) + I^-(aq)$ Identify the catalyst and the reaction intermediate, and justify each choice.

STEP-BY-STEP SOLUTION:

1. Step 1 — Identify the Reaction Intermediate: Hypoiodite ion (IO^-) is produced as a product in Step 1 and consumed as a reactant in Step 2; therefore, IO^- is the reaction intermediate.
2. Step 2 — Identify the Catalyst: Iodide ion (I^-) is present initially as a reactant in Step 1 and is regenerated unchanged as a product at the end of Step 2; therefore, I^- is the catalyst.

Final Answer: Catalyst: $I^-(aq)$ (consumed in Step 1, regenerated in Step 2); Intermediate: $IO^-(aq)$ (produced in Step 1, consumed in Step 2)

⚠ AP EXAM TRAP & FRQ SCORING GUIDELINE

AP Exam Trap: Never include a reaction intermediate in an overall rate law! Conversely, a homogeneous catalyst CAN appear in the rate law (for example, Rate = $k[H_2O_2][I^-]$ in Example 5.5 because I^- is a reactant in the slow first step).

✅ CHAPTER 5 MASTERY CHECKLIST (AP EXAM READINESS)

☑ Relate rates of disappearance of reactants and appearance of products using balanced stoichiometric coefficients.

☑ Determine reaction orders (0, 1, 2), overall order, and the numerical value and units of k using the Method of Initial Rates.

☑ Identify zero-, first-, and second-order reactions from linear plots ([A], ln[A], or 1/[A] vs. t), slope signs, and constant first-order half-life ($t_{½} = 0.693/k$).

☑ Explain how temperature and catalysts affect reaction rates using Collision Theory, Maxwell–Boltzmann curves, and potential energy profiles.

☑ Validate multi-step mechanisms, derive rate laws when Step 1 is slow or when Step 1 is a fast equilibrium before a slow Step 2, and distinguish intermediates from catalysts.

CHAPTER 6 · CORE CURRICULUM

AP Exam Weighting: 7–9%

Unit 6: Thermochemistry

Unit 6 applies the First Law of Thermodynamics (conservation of energy) to chemical and physical processes. Students distinguish the chemical system from the surroundings, analyze endothermic and exothermic enthalpy changes (ΔH), interpret heating curves and phase-change plateaus, and master all four AP Chemistry methods for determining ΔH°_rxn: (1) coffee-cup calorimetry (q = mcΔT), (2) average bond enthalpies, (3) standard enthalpies of formation (ΔH°_f), and (4) Hess's Law.

CHAPTER 6 ESSENTIAL EQUATIONS, LAWS & CONSTANTS

$\Delta E = q + w$	First Law of Thermodynamics: Internal energy change = heat (q) + work (w = −PΔV)
$q = m \times c \times \Delta T$	Calorimetry heat transfer: mass (g) × specific heat ($J \cdot g^{-1} \cdot °C^{-1}$) × (T_final − T_initial)
$q_{system} = -q_{surroundings}$	Conservation of heat in an insulated coffee-cup calorimeter
$\Delta H_{rxn} = -q_{water} / n_{limiting}$	Molar enthalpy of reaction or dissolution from calorimetry data
$\Delta H°_{rxn} = \Sigma\ BE(\text{bonds broken}) - \Sigma\ BE(\text{bonds formed})$	Method 2: Enthalpy of reaction from average bond enthalpies (Broken − Formed)
$\Delta H°_{rxn} = \Sigma\ n \cdot \Delta H°_f(\text{products}) - \Sigma\ m \cdot \Delta H°_f(\text{reactants})$	Method 3: Enthalpy of reaction from standard enthalpies of formation (Products − Reactants)

§ 6.1 First Law of Thermodynamics, System vs. Surroundings & Enthalpy (ΔH)

The **First Law of Thermodynamics** states that the total energy of the universe is constant: energy can be transferred or transformed, but never created or destroyed. In thermochemistry, we divide the universe into two parts: the **system** (which consists strictly of the specific atoms, molecules, and ions participating in the chemical reaction or phase change) and the **surroundings** (everything else—the beaker, the air in the room, the thermometer, and, crucially, **even the water solvent inside the beaker** during an aqueous reaction!).

Energy enters or leaves a chemical system as **heat (q)** and **work (w)**: **ΔE = q + w**. When heat flows into the system, **q > 0**; when heat escapes from the system, **q < 0**. When work is done ON the system by compressing a gas, **w > 0**; when an expanding gas does work ON the surroundings, **w < 0**. For reactions occurring at constant pressure, heat flow is called the **enthalpy change (ΔH)**: in an **exothermic reaction (ΔH < 0)**, reactants drop to lower-energy products and release heat into the surroundings (so the water/beaker warms up and T rises); in an **endothermic reaction (ΔH > 0)**, reactants absorb heat from the surroundings to climb to higher-energy products (so the water/beaker cools down and T drops).

Temperature measures the average kinetic energy of particles in a sample. When a hot piece of metal (e.g., at 90 °C) is placed into cool water (at 20 °C), faster-moving metal atoms collide with slower water molecules at the boundary, transferring kinetic energy spontaneously from hot to cold until both reach the exact same final temperature—a state called **thermal equilibrium**, where particles share the same average kinetic energy.

- **Stoichiometric Enthalpy Rules:** In 2 Na(s) + Cl_2(g) → 2 NaCl(s), ΔH° = −822 $kJ \cdot mol_rxn^{-1}$ means 822 kJ of heat are released per 2 moles of NaCl formed. Reversing the reaction flips the sign to +822 $kJ \cdot mol_rxn^{-1}$.

EXAMPLE 6.1 **Stoichiometric Heat Released from a Thermochemical Equation**

Problem: Given the thermochemical equation 2 Na(s) + Cl_2(g) → 2 NaCl(s) with ΔH°_rxn = −822 kJ·mol_rxn^{-1}, calculate the heat change (q) when 10.0 g of solid NaCl (M = 58.44 g·mol^{-1}) is produced.

STEP-BY-STEP SOLUTION:

1. Step 1 — Convert Grams of NaCl to Moles: n(NaCl) = 10.0 g / 58.44 g·mol^{-1} = 0.1711 mol NaCl.
2. Step 2 — Multiply by Stoichiometric Enthalpy Ratio: Because −822 kJ corresponds to 2 moles of NaCl formed, q = 0.1711 mol NaCl × (−822 kJ / 2 mol NaCl) = −70.3 kJ.

Final Answer: q = −70.3 kJ (70.3 kJ of heat is released)

⚠ **AP EXAM TRAP & FRQ SCORING GUIDELINE**

AP Exam Trap: When an aqueous reaction in a beaker or coffee-cup calorimeter causes the thermometer reading to DROP, students often think the reaction lost heat (exothermic). Remember: the thermometer is in the SURROUNDINGS (the water)! If the water gets colder, the chemical system ABSORBED heat from the water, so the reaction is ENDOTHERMIC (ΔH > 0).

§ 6.2 Calorimetry (q = mcΔT), Heating Curves & Phase-Change Plateaus

To calculate the heat absorbed or released when a substance changes temperature without changing phase, we use **q = mcΔT**, where *m* is mass in grams, *c* is specific heat capacity in J·g^{-1}·°C^{-1}, and ΔT = T_final − T_initial. Liquid water has an unusually high specific heat capacity (**c = 4.184 J·g^{-1}·°C^{-1}**) due to extensive hydrogen bonding, whereas metals like aluminum (0.897 J·g^{-1}·°C^{-1}) and copper (0.385 J·g^{-1}·°C^{-1}) have much lower specific heats and heat up rapidly. In a nested Styrofoam **coffee-cup calorimeter** at constant atmospheric pressure, any heat released or absorbed by the chemical reaction is exchanged with the solution: **q_rxn = −q_solution = −(m_total × c × ΔT)**, and dividing q_rxn (in kJ) by the moles of limiting reactant gives **ΔH_rxn (in kJ·mol^{-1})**.

On a **heating curve** (Temperature vs. Heat Added), two distinct regimes appear: (1) along the **three slanted segments** (warming solid ice, warming liquid water, and warming steam), added heat increases the **average kinetic energy** of the molecules, so temperature rises and we use **q = mcΔT**; (2) along the **two flat horizontal plateaus** (melting at 0 °C and boiling at 100 °C for water), the temperature stays **completely constant (ΔT = 0)** because all added heat goes into increasing **potential energy** by overcoming intermolecular forces! During a phase-change plateau, calculate heat using **q = n × ΔH_fus** or **q = n × ΔH_vap**. Notice that water's heat of vaporization (**ΔH_vap = 40.7 kJ·mol^{-1}**) is nearly 7 times larger than its heat of fusion (**ΔH_fus = 6.01 kJ·mol^{-1}** or 334 J·g^{-1}) because boiling completely separates molecules against hydrogen bonds, so the boiling plateau is much longer than the melting plateau.

- **Total Mass Rule in Coffee-Cup Calorimetry:** When a solid salt dissolves in water, m_total = m_water + m_salt (unless told to neglect solute mass). When two aqueous solutions are mixed, add both solution volumes/masses together!

EXAMPLE 6.2 Specific Heat Calculation & Phase-Change Plateau Heat

Problem: (a) A 60.0 g piece of aluminum metal (c = 0.897 $J \cdot g^{-1} \cdot °C^{-1}$) is heated from 20.0 °C to 52.5 °C. How much heat energy (in J) is absorbed? (b) Given that the enthalpy of fusion of ice is 334 $J \cdot g^{-1}$ (6.01 $kJ \cdot mol^{-1}$), how many kilojoules of heat are required to completely melt a 1,814 g block of ice at 0 °C?

STEP-BY-STEP SOLUTION:

1. Part (a) Warming Metal ($q = mc\Delta T$): ΔT = 52.5 °C − 20.0 °C = +32.5 °C. Substituting gives q = (60.0 g)(0.897 $J \cdot g^{-1} \cdot °C^{-1}$)(32.5 °C) = +1,750 J.
2. Part (b) Melting Ice Plateau (Constant T = 0 °C): Because temperature does not change during melting, multiply mass by heat of fusion: q = 1,814 g × 334 $J \cdot g^{-1}$ = 606,000 J = +606 kJ.

Final Answer: (a) +1,750 J; (b) +606 kJ

EXAMPLE 6.3 Coffee-Cup Calorimetry: Dissolution of a Salt & Mixing Two Aqueous Solutions

Problem: (a) When 10.00 g of solid $CaCl_2$ (M = 110.98 $g \cdot mol^{-1}$) dissolves in 500.0 g of water in a coffee-cup calorimeter, the temperature of the combined solution (c = 4.184 $J \cdot g^{-1} \cdot °C^{-1}$) rises from 23.50 °C to 27.00 °C. Calculate $\Delta H°_{soln}$ in $kJ \cdot mol^{-1}$. (b) When 30.0 mL of 0.50 M $AgNO_3$(aq) is mixed with 30.0 mL of 0.50 M KCl(aq) in a calorimeter, the temperature of the 60.0 g combined solution (c = 4.184 $J \cdot g^{-1} \cdot °C^{-1}$) rises by +3.80 °C as AgCl(s) precipitates. Calculate $\Delta H°_{rxn}$ in kJ per mole of AgCl formed.

STEP-BY-STEP SOLUTION:

1. Part (a) Step 1 — Heat Absorbed by Solution: Total solution mass m = 500.0 g + 10.00 g = 510.0 g; ΔT = 27.00 − 23.50 = +3.50 °C. Thus q_{soln} = (510.0 g)(4.184 $J \cdot g^{-1} \cdot °C^{-1}$)(3.50 °C) = +7,468 J = +7.468 kJ.
2. Part (a) Step 2 — Flip Sign & Divide by Moles of $CaCl_2$: Since the water warmed up, dissolution is exothermic: q_{rxn} = −7.468 kJ. Moles of $CaCl_2$ = 10.00 g / 110.98 $g \cdot mol^{-1}$ = 0.09011 mol. Thus $\Delta H°_{soln}$ = −7.468 kJ / 0.09011 mol = −82.9 $kJ \cdot mol^{-1}$.
3. Part (b) Step 1 — Heat Absorbed by 60.0 g Mixed Solution: q_{soln} = (60.0 g)(4.184 $J \cdot g^{-1} \cdot °C^{-1}$)(3.80 °C) = +954 J = +0.954 kJ → q_{rxn} = −0.954 kJ.
4. Part (b) Step 2 — Moles of AgCl Precipitate & $\Delta H°_{rxn}$: $n(Ag^+) = n(Cl^-)$ = 0.50 M × 0.0300 L = 0.0150 mol AgCl formed. Dividing gives $\Delta H°_{rxn}$ = −0.954 kJ / 0.0150 mol = −63.6 $kJ \cdot mol^{-1}$.

Final Answer: (a) $\Delta H°_{soln}$ = −82.8 to −82.9 $kJ \cdot mol^{-1}$; (b) $\Delta H°_{rxn}$ = −63.6 $kJ \cdot mol^{-1}$

⚠ AP EXAM TRAP & FRQ SCORING GUIDELINE

AP Exam Trap: When two 30.0 mL solutions are mixed in a calorimeter, students often use m = 30.0 g in $q = mc\Delta T$ and use n = (0.50 M)(0.060 L) for moles! That is double-backwards: use the COMBINED mass (30.0 + 30.0 = 60.0 g) in $q = mc\Delta T$ because the heat warms all 60.0 g of water, and use the INDIVIDUAL reactant volume (0.0300 L × 0.50 M = 0.0150 mol) to find moles of limiting reactant!

§ 6.3 Average Bond Enthalpies & Standard Enthalpies of Formation ($\Delta H°_f$)

Beyond calorimetry (Method 1), the AP Chemistry exam tests two tabular methods for calculating $\Delta H°_{rxn}$: **Method 2 — Average Bond Enthalpies**: Remember the golden rule of chemical bonding: **breaking existing bonds ALWAYS requires an input of energy (endothermic, +)**, and **forming new bonds ALWAYS releases energy (exothermic, −)**. Therefore, **$\Delta H°_{rxn}$ = Σ BE(bonds broken in reactants) − Σ BE(bonds formed in products)**.

Method 3 — Standard Enthalpies of Formation ($\Delta H°_f$): The standard enthalpy of formation is the heat change when **exactly 1 mole of a compound** is formed from its pure elements in their natural standard states at 25 °C (298 K) and 1 atm. By definition, **$\Delta H°_f$ of any pure element in its standard state (such as O_2(g), N_2(g), H_2(g), C(s, graphite), or**

Na(s)) is exactly 0 kJ·mol^{-1}. Using formation enthalpies, **$\Delta H°_{rxn} = \Sigma\, n \cdot \Delta H°_f(\text{products}) - \Sigma\, m \cdot \Delta H°_f(\text{reactants})$** (Notice: Products minus Reactants—the exact opposite order of bond enthalpies!).

- **BARF Mnemonic for Bond Enthalpies:** Break = Absorb (+), Release = Form (−). Always draw Lewis structures first so you don't miss double/triple bonds or multiple O–H bonds per H_2O molecule!
- **Why Bond Enthalpies & $\Delta H°_f$ Order Are Opposite:** Bond enthalpies are positive energies required to BREAK bonds (Reactants − Products), whereas $\Delta H°_f$ values are enthalpies of FORMING compounds (Products − Reactants).

EXAMPLE 6.4 **Calculating $\Delta H°_{rxn}$ for Methane Combustion Using Both Bond Enthalpies & $\Delta H°_f$**

Problem: Consider the combustion of methane: $CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(g)$. (a) Estimate $\Delta H°_{rxn}$ using average bond enthalpies (kJ·mol^{-1}): C–H = 413, O=O = 495, C=O (in CO_2) = 799, O–H = 467. (b) Calculate $\Delta H°_{rxn}$ using standard enthalpies of formation $\Delta H°_f$ (kJ·mol^{-1}): $CH_4(g) = -75$, $O_2(g) = 0$, $CO_2(g) = -394$, $H_2O(g) = -242$.

STEP-BY-STEP SOLUTION:

1. Part (a) Bond Enthalpies (Broken − Formed): Reactant bonds broken = 4(C–H) + 2(O=O) = 4(413) + 2(495) = 1,652 + 990 = +2,642 kJ. Product bonds formed = 2(C=O) + 4(O–H) = 2(799) + 4(467) = 1,598 + 1,868 = 3,466 kJ. Thus $\Delta H°_{rxn}$ = 2,642 − 3,466 = −824 kJ·mol$_{rxn}^{-1}$.
2. Part (b) Enthalpies of Formation (Products − Reactants): $\Sigma\, \Delta H°_f(\text{products}) = [1(-394) + 2(-242)] = -878$ kJ. $\Sigma\, \Delta H°_f(\text{reactants}) = [1(-75) + 2(0)] = -75$ kJ. Thus $\Delta H°_{rxn} = (-878) - (-75) = -803$ kJ·mol$_{rxn}^{-1}$.

Final Answer: (a) −824 kJ·mol$_{rxn}^{-1}$ (from average bond enthalpies); (b) −803 kJ·mol$_{rxn}^{-1}$ (from exact $\Delta H°_f$)

⚠ **AP EXAM TRAP & FRQ SCORING GUIDELINE**

AP Exam Trap: The #1 student error in Unit 6 is mixing up the subtraction order between Bond Enthalpies (Reactants Broken − Products Formed) and Standard Enthalpies of Formation (Products − Reactants). Always write the words 'Broken − Formed' or 'Products − Reactants' before plugging in numbers!

§ 6.4 Hess's Law & Synthesis of the Four AP Enthalpy Methods

Method 4 — Hess's Law: Because enthalpy (H) is a **state function**, the overall enthalpy change of a chemical reaction depends only on the initial reactants and final products, regardless of how many intermediate steps the pathway takes. Two simple algebraic rules govern Hess's Law: (1) if you **reverse** a chemical equation, you must **flip the sign of ΔH°**; and (2) if you **multiply** the coefficients of an equation by a factor *k*, you must **multiply ΔH° by that exact same factor *k***.

When solving a Hess's Law problem on the AP exam, work systematically by focusing on one unique reactant or product from the target equation at a time: align the given step so that species appears on the correct side of the arrow with the exact target coefficient, adjust its ΔH° accordingly, and then sum all manipulated equations to verify that intermediate species cancel completely.

- **Rule 1 (Reversing an Equation):** A → B (ΔH° = +X) becomes B → A (ΔH° = −X).
- **Rule 2 (Scaling Coefficients):** Multiplying all coefficients by n multiplies ΔH° by n (because enthalpy is an extensive property).

Table 6.1 · Master Summary of the Four AP Chemistry Methods for Determining ΔH°_rxn

Method	Core Formula	Subtraction Order / Key Rule	Critical Exam Pitfall to Avoid
1. Calorimetry	q_water = mcΔT; ΔH = −q_water / n	Flip sign of q_water to get q_rxn	Convert J to kJ (÷ 1,000) before dividing by moles n
2. Bond Enthalpies	ΔH° = Σ BE(broken) − Σ BE(formed)	REACTANTS − PRODUCTS	In 2 H_2O, there are 2 × 2 = 4 O–H bonds; CO_2 has two C=O double bonds
3. Enthalpies of Formation	ΔH° = Σ n·ΔH°_f(prod) − Σ m·ΔH°_f(react)	PRODUCTS − REACTANTS	ΔH°_f = 0 for pure elements (O_2(g), C(graphite)); check phase (H_2O(l) vs. H_2O(g))
4. Hess's Law	ΔH°_total = $\Delta H°_1$ + $\Delta H°_2$ + …	Reverse eq → flip sign; ×k → ×k	Verify intermediate species cancel completely when equations are added

EXAMPLE 6.5 **Applying Hess's Law to a Multi-Step Reaction Target**

> **Problem:** Calculate ΔH°_rxn for the target reaction: N_2O_4(g) → 2 NO(g) + O_2(g), given the following two reactions: Reaction 1: N_2O_4(g) → 2 NO_2(g) $\Delta H°_1$ = +57.9 kJ Reaction 2: NO(g) + ½ O_2(g) → NO_2(g) $\Delta H°_2$ = −56.6 kJ

STEP-BY-STEP SOLUTION:

1. Step 1 — Align Reaction 1 with Target: The target equation has 1 mol N_2O_4(g) on the reactant side. Reaction 1 already has 1 mol N_2O_4(g) on the left, so keep Reaction 1 as written: N_2O_4(g) → 2 NO_2(g), $\Delta H°_1$ = +57.9 kJ.
2. Step 2 — Manipulate Reaction 2: The target equation requires 2 mol NO(g) and 1 mol O_2(g) on the product side. Reverse Reaction 2 and multiply all coefficients by 2: 2 NO_2(g) → 2 NO(g) + O_2(g). Flip the sign of $\Delta H°_2$ and multiply by 2: $\Delta H°_{2,new}$ = 2 × (+56.6 kJ) = +113.2 kJ.
3. Step 3 — Sum Equations & Enthalpies: Adding the two equations cancels the 2 NO_2(g) intermediate on both sides and yields ΔH°_target = +57.9 kJ + 113.2 kJ = +171.1 kJ·mol_rxn^{-1}.

Final Answer: +171.1 kJ·mol_rxn^{-1}

⚠ **AP EXAM TRAP & FRQ SCORING GUIDELINE**

AP Exam Trap: Contrast how scaling a reaction affects ΔH° (Unit 6), K (Unit 7), and E° (Unit 9): when you multiply an equation by 2, you multiply ΔH° by 2, you SQUARE K (K^2), and you DO NOT CHANGE E° at all!

✅ **CHAPTER 6 MASTERY CHECKLIST (AP EXAM READINESS)**

☑ Distinguish the chemical system from the surroundings (including the water solvent) and relate exothermic/endothermic ΔH signs to temperature changes of the water.

☑ Calculate heat transfer using q = mcΔT on slanted heating segments and q = n·ΔH_fus or n·ΔH_vap on constant-temperature phase-change plateaus.

☑ Determine molar enthalpy of reaction or dissolution (ΔH°_rxn in kJ·mol^{-1}) from coffee-cup calorimetry experiments.

☑ Calculate ΔH°_rxn from average bond enthalpies (Broken − Formed) and from standard enthalpies of formation (Products − Reactants, with ΔH°_f = 0 for elements).

☑ Apply Hess's Law by reversing and scaling intermediate thermochemical equations to find ΔH° of a target reaction.

CHAPTER 7 · CORE CURRICULUM

AP Exam Weighting: 7–9%

Unit 7: Equilibrium

Unit 7 examines reversible chemical processes and dynamic chemical equilibrium. Students interpret rate-versus-time and concentration-versus-time equilibrium graphs, write K_c, K_p, and K_sp equilibrium expressions (omitting pure solids and pure liquids), manipulate K values algebraically, solve ICE tables using the 5% small-x approximation, compare the reaction quotient Q to K to predict shift direction, apply Le Chatelier's Principle, and calculate molar solubility and the common-ion effect.

CHAPTER 7 ESSENTIAL EQUATIONS, LAWS & CONSTANTS

$K_c = ([C]^c [D]^d) / ([A]^a [B]^b)$	Equilibrium constant expression for aA + bB ⇌ cC + dD (omit pure (s) and (l); unitless)
$K_{rev} = 1/K$; $K_{new} = K^n$; $K_{total} = K_1 \times K_2$	Algebraic manipulation of K when reversing, scaling by n, or adding reactions
$Q < K \rightarrow$ Shift Right; $Q = K \rightarrow$ Equilibrium; $Q > K \rightarrow$ Shift Left	Reaction Quotient (Q) comparison using initial concentrations/pressures
$K_{sp} = [M^{(y+)}]^x [X^{(x-)}]^y$	Solubility Product Constant for a slightly soluble salt $M_x X_y(s) \rightleftharpoons x\, M^{(y+)}(aq) + y\, X^{(x-)}(aq)$

§ 7.1 Dynamic Equilibrium, K_c & K_p Expressions & Algebraic Manipulation of K

In a closed container, many chemical reactions are **reversible**: reactants form products while products simultaneously turn back into reactants. **Chemical equilibrium** is reached when the **rate of the forward reaction equals the rate of the reverse reaction (Rate_fwd = Rate_rev)**. Because both reactions continue occurring at the exact same speed, chemical equilibrium is **dynamic, not static**. On a **rate vs. time graph**, the forward rate drops and the reverse rate rises until the two curves **merge into a single flat line** (rates are equal). On a **concentration vs. time graph**, reactant and product concentrations level off into **horizontal lines**: at equilibrium, concentrations remain **constant**, but they do NOT have to be equal!

We quantify equilibrium using the **equilibrium constant K** (reported without units): products over reactants, each raised to the power of its stoichiometric coefficient. **Crucially, never include pure solids (s) or pure liquids (l) in an equilibrium expression (K or Q)—only gases (g) and aqueous species (aq) appear!** The magnitude of K reveals the composition at equilibrium: when **K >> 1** (e.g., 1.3×10^{8}), the numerator dominates and equilibrium lies far to the right (mostly products); when **K << 1** (e.g., 1.49×10^{-10}), the denominator dominates and equilibrium lies far to the left (mostly unreacted reactants).

When we algebraically manipulate a balanced equation, K transforms according to three rules: (1) **Reversing a reaction** inverts K (**K_rev = 1 / K**); (2) **Multiplying coefficients by a factor n** raises K to the nth power (**K_new = K^n**); and (3) **Adding two or more reactions together** multiplies their equilibrium constants (**$K_{total} = K_1 \times K_2$**).

- **Haber Process Expression ($N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$):** $K_c = [NH_3]^2 / ([N_2][H_2]^3)$.
- **Particulate Equilibrium Diagram ($A(g) \rightleftharpoons B(g)$):** If an equilibrium box shows 2 molecules of A and 8 molecules of B, then K_c = 8 / 2 = 4.0 (confirming K > 1). Each gas's partial pressure is P_i = (N_i / N_total) × P_total.

EXAMPLE 7.1 **Calculating K_c and Interpreting Large vs. Small Equilibrium Constants**

Problem: (a) For the synthesis of ammonia, $N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$, an equilibrium mixture at 350 K contains $[NH_3] = 1.98$ M, $[N_2] = 0.031$ M, and $[H_2] = 0.010$ M. Calculate K_c. (b) For $N_2(g) + O_2(g) \rightleftharpoons 2\ NO(g)$ at 300 K, equilibrium concentrations are $[NO] = 1.22 \times 10^{-5}$ M, $[N_2] = 1.0$ M, and $[O_2] = 1.0$ M. Calculate K_c and state whether reactants or products dominate in each system.

STEP-BY-STEP SOLUTION:

1. Part (a) Ammonia K_c: $K_c = [NH_3]^2 / ([N_2][H_2]^3) = (1.98)^2 / [(0.031)(0.010)^3] = 3.9204 / (3.1 \times 10^{-5}) = 1.3 \times 10^5$ (or if $[H_2] = 0.0010$ M, 1.3×10^8; since K >> 1, products strongly dominate at equilibrium).
2. Part (b) Nitric Oxide K_c: $K_c = [NO]^2 / ([N_2][O_2]) = (1.22 \times 10^{-5})^2 / [(1.0)(1.0)] = 1.49 \times 10^{-10}$. Because K << 1, the mixture consists almost entirely of unreacted N_2 and O_2 reactants.

Final Answer: (a) K_c >> 1 (products dominate); (b) $K_c = 1.49 \times 10^{-10}$ (reactants dominate)

⚠ **AP EXAM TRAP & FRQ SCORING GUIDELINE**

AP Exam Trap: In heterogeneous equilibria such as $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$, students frequently write $CaCO_3$ and CaO in the K expression. Because pure solids and pure liquids have constant density/activity (set to 1), the correct expression is simply $K_c = [CO_2]$ and $K_p = P_{CO_2}$!

§ 7.2 ICE Tables, the 5% Small-x Approximation & Reaction Quotient (Q vs. K)

When given initial concentrations and asked to determine equilibrium concentrations or K, we organize our stoichiometric data using an **ICE Table (Initial, Change, Equilibrium)**. The entries in the **Change (C)** row must always obey the exact mole ratios of the balanced chemical equation (e.g., −2x, −x, +2x). When K is very small (typically $K < 10^{-4}$), the amount of reactant that dissociates (x) is negligible compared to the initial concentration $[A]_0$, allowing us to apply the **5% small-x approximation** (setting $[A]_0 - ax \approx [A]_0$) to avoid the quadratic formula.

To test whether a non-equilibrium mixture will shift forward (right) or reverse (left) to reach equilibrium, we calculate the **Reaction Quotient (Q)** using the exact same formula as K, but plugging in **current/initial concentrations**: (1) if **Q < K**, the product-to-reactant ratio is too small (too many reactants), so the net reaction **shifts right (forward)** to form more products; (2) if **Q = K**, the system is already at dynamic equilibrium; and (3) if **Q > K** (e.g., Q = 1.8 when K_c = 0.18), there are too many products, so the net reaction **shifts left (reverse)** to form more reactants.

- **ICE Table Change Row Rule:** Reactants decrease (− coefficient × x) and products increase (+ coefficient × x) whenever Q < K (or when starting with zero products).

EXAMPLE 7.2 Using an ICE Table to Find K_c from Initial and Equilibrium Concentrations

Problem: For the reaction $2\ NO(g) + 2\ H_2(g) \rightleftharpoons N_2(g) + 2\ H_2O(g)$, a 2.0 L vessel initially holds $[NO]_0 = 0.100$ M, $[H_2]_0 = 0.050$ M, $[N_2]_0 = 0$ M, and $[H_2O]_0 = 0.100$ M. At equilibrium, [NO]_eq is measured to be 0.060 M. Determine the equilibrium concentrations of all species and calculate K_c.

STEP-BY-STEP SOLUTION:

1. Step 1 — Determine the Change in [NO]: Since [NO] dropped from 0.100 M to 0.060 M, $\Delta[NO] = -2x = -0.040$ M → $x = 0.020$ M.
2. Step 2 — Apply the 2 : 2 : 1 : 2 Mole Ratio Across the Change Row: $\Delta[H_2] = -2x = -0.040$ M; $\Delta[N_2] = +x = +0.020$ M; $\Delta[H_2O] = +2x = +0.040$ M.
3. Step 3 — Sum Initial + Change to Find Equilibrium Row: $[NO]_{eq} = 0.060$ M; $[H_2]_{eq} = 0.050 - 0.040 = 0.010$ M; $[N_2]_{eq} = 0 + 0.020 = 0.020$ M; $[H_2O]_{eq} = 0.100 + 0.040 = 0.140$ M.
4. Step 4 — Substitute into K_c: $K_c = ([N_2][H_2O]^2) / ([NO]^2[H_2]^2) = [(0.020)(0.140)^2] / [(0.060)^2(0.010)^2] = (3.92 \times 10^{-4}) / (3.6 \times 10^{-7}) = 1.1 \times 10^3$.

Final Answer: $[NO] = 0.060$ M, $[H_2] = 0.010$ M, $[N_2] = 0.020$ M, $[H_2O] = 0.140$ M; $K_c = 1.1 \times 10^3$

EXAMPLE 7.3 ICE Table Calculation Using the Small-x Approximation

Problem: For the decomposition $2\ SO_3(g) \rightleftharpoons 2\ SO_2(g) + O_2(g)$, $K_c = 5.9 \times 10^{-9}$ at a certain temperature. If a rigid container is initially charged with 1.00 M $SO_3(g)$ and no products, what is the equilibrium concentration of $O_2(g)$?

STEP-BY-STEP SOLUTION:

1. Step 1 — Set Up ICE Expressions: $[SO_3]_{eq} = 1.00 - 2x$; $[SO_2]_{eq} = 2x$; $[O_2]_{eq} = x$.
2. Step 2 — Apply Small-x Approximation: Because $K_c = 5.9 \times 10^{-9}$ is extremely small, $2x << 1.00$, so approximate $1.00 - 2x \approx 1.00$.
3. Step 3 — Solve for x: $K_c = ([SO_2]^2[O_2]) / [SO_3]^2 \approx (2x)^2(x) / (1.00)^2 = 4x^3 = 5.9 \times 10^{-9}$. Dividing by 4 gives $x^3 = 1.475 \times 10^{-9}$, and taking the cube root yields $x = [O_2]_{eq} = 1.14 \times 10^{-3}$ M.

Final Answer: $[O_2]_{eq} = 1.14 \times 10^{-3}$ M

⚠ AP EXAM TRAP & FRQ SCORING GUIDELINE

AP Exam Trap: In Example 7.3, notice that $[SO_2]_{eq} = 2x$, so when substituted into $[SO_2]^2[O_2]$ it becomes $(2x)^2(x) = 4x^3$, NOT $2x^3$! Always put parentheses around stoichiometric terms like $(2x)^2$ or $(3x)^3$ before squaring or cubing.

§ 7.3 Le Chatelier's Principle &Graphical Stress Analysis

Le Chatelier's Principle states that when a chemical system at equilibrium is disturbed by an external stress (a change in concentration, partial pressure/volume, or temperature), the system shifts in the direction that partially counteracts the imposed stress: (1) **Adding or removing a reactant/product**: adding a species shifts the reaction to the opposite side to consume it; removing a species shifts the reaction toward that same side to replace it (understand via Q vs. K!). (2) **Changing container volume / pressure of a gas mixture**: decreasing volume increases total pressure and shifts the reaction toward the side with **fewer total moles of gas**; increasing volume lowers pressure and shifts toward the side with **more total moles of gas**. (3) **Changing temperature**: write **'Heat'** directly into the equation as a **product for exothermic reactions (ΔH < 0)** or as a **reactant for endothermic reactions (ΔH > 0)**. Heating shifts the equilibrium away from Heat; cooling shifts toward Heat. **Crucially, TEMPERATURE is the ONLY factor that actually changes the numerical value of the equilibrium constant K!**

On a **concentration vs. time graph** (such as for $N_2 + 3\ H_2 \rightleftharpoons 2\ NH_3$), you can diagnose the exact stress from the shape of the discontinuity: a **sharp vertical spike on ONLY ONE curve** (e.g., $[N_2]$ jumping straight up) proves that extra N_2 gas was injected into the vessel, after which $[N_2]$ and $[H_2]$ gradually curve downward while $[NH_3]$ curves upward to a new equilibrium plateau. By contrast, if **ALL gas concentrations jump vertically at the same instant**, the container volume was suddenly compressed!

- **Three Disturbances That Cause ZERO Shift in Equilibrium:** (1) Adding or removing a pure solid (s) or pure liquid (l) (as long as some remains); (2) adding an inert noble gas (such as He or Ar) at constant volume (partial pressures of reacting gases do not change); (3) adding a catalyst (speeds up forward and reverse rates equally so equilibrium is reached faster, with zero change in equilibrium concentrations or K).

Table 7.1 · Complete Le Chatelier's Principle Stress, Shift Direction & Effect on K Summary

External Stress Applied	Q vs. K Justification	Direction of Net Shift	Effect on Numerical Value of K
Add Reactant / Remove Product	Decreases Q (Q < K)	Shifts Right (Forward →)	No change in K
Add Product / Remove Reactant	Increases Q (Q > K)	Shifts Left (Reverse ←)	No change in K
Decrease Volume (Increase P)	Gas concentrations rise	Toward side with FEWER moles of gas	No change in K
Increase Volume (Decrease P)	Gas concentrations drop	Toward side with MORE moles of gas	No change in K
Increase T (Exothermic, $\Delta H < 0$)	Heat is a product	Shifts Left (←)	K DECREASES
Increase T (Endothermic, $\Delta H > 0$)	Heat is a reactant	Shifts Right (→)	K INCREASES
Add Pure Solid, Inert Gas (const V), or Catalyst	Q = K remains unchanged	NO SHIFT	No change in K

EXAMPLE 7.3B **Predicting Equilibrium Shifts & Diagnosing Concentration-Time Graph Spikes**

Problem: Consider the exothermic Haber synthesis of ammonia: $N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$, $\Delta H° = -92\ kJ{\cdot}mol_rxn^{-1}$. (a) Predict the direction of shift and the effect on K_c when (i) the vessel volume is compressed to half its original value at constant T, and (ii) the temperature of the vessel is increased. (b) On a concentration-vs.-time graph at equilibrium, $[N_2]$ suddenly jumps vertically upward while $[H_2]$ and $[NH_3]$ show no vertical jump at that instant. What stress occurred, and how do the three curves respond afterward?

STEP-BY-STEP SOLUTION:

1. Part (a)(i) Volume Compression: Decreasing container volume increases total gas pressure and shifts the equilibrium toward the side with fewer moles of gas. The reactant side has 1 + 3 = 4 moles of gas while the product side has 2 moles of gas → Shifts RIGHT (toward 2 NH_3). Because T is constant, K_c is unchanged.
2. Part (a)(ii) Temperature Increase: Since $\Delta H° < 0$ (exothermic), write 'Heat' as a product. Raising temperature shifts the equilibrium away from Heat → Shifts LEFT (toward reactants), and the numerical value of K_c DECREASES.
3. Part (b) Single Vertical Spike Diagnosis: A sharp vertical spike on only the $[N_2]$ curve indicates that extra $N_2(g)$ was injected into the rigid vessel. Immediately after the spike (Q < K), the reaction shifts right: $[N_2]$ and $[H_2]$ gradually decrease (in a 1:3 slope ratio) while $[NH_3]$ increases (with slope 2) until a new flat equilibrium plateau is established.

Final Answer: (a)(i) Shifts right, K_c unchanged; (a)(ii) Shifts left, K_c decreases; (b) Extra N_2 injected → shifts right

⚠ **AP EXAM TRAP & FRQ SCORING GUIDELINE**

AP Exam Trap: On AP FRQs, invoking 'Le Chatelier's principle' as a buzzword without explaining Q vs. K often loses credit. When explaining why adding a reactant shifts equilibrium right, state: 'Adding reactant increases the denominator of the reaction quotient Q, making Q < K; therefore, the forward reaction proceeds until Q increases back to equal K.'

§ 7.4 Solubility Equilibria (K_sp), Precipitation (Q_sp vs. K_sp) & the Common-Ion Effect

Even an 'insoluble' ionic salt such as lead(II) chloride ($PbCl_2$) or iron(II) sulfide (FeS) dissolves to a tiny extent in a saturated aqueous solution: **$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\ Cl^-(aq)$**. Because the pure solid is omitted, the **solubility product constant (K_sp)** expression is **$K_{sp} = [Pb^{2+}][Cl^-]^2$**. While K_sp is the unitless equilibrium constant, a salt's **molar solubility (s)** is the number of moles of solid salt that dissolve per liter of solution (in $mol \cdot L^{-1}$) to reach saturation. For a 1:1 salt (MX, like AgCl or FeS), **$K_{sp} = s^2$**; for a 1:2 or 2:1 salt (MX_2 or M_2X, like $PbCl_2$, MgF_2, or Ag_2CrO_4), **$K_{sp} = (s)(2s)^2 = 4s^3$**.

To determine whether a precipitate will form when two aqueous solutions are mixed, calculate the diluted ion concentrations using the combined total volume and evaluate the ion-product reaction quotient **Q_sp**: if **Q_sp > K_sp**, the solution is supersaturated and a **solid precipitate forms** until Q_sp drops to K_sp; if **Q_sp ≤ K_sp**, no precipitate forms.

Finally, the **Common-Ion Effect** describes the dramatic decrease in molar solubility of a slightly soluble salt when it is dissolved in a solution that already contains one of its constituent ions (e.g., adding soluble NaCl to a saturated AgCl solution, or dissolving MgF_2 in 0.10 M NaF). By Le Chatelier's Principle, the high initial concentration of the common ion shifts the dissolution equilibrium to the left, suppressing ionization and reducing molar solubility by orders of magnitude (without changing K_sp).

- **1:1 Salt Formula (FeS, $K_{sp} = 8.0 \times 10^{-28}$):** $K_{sp} = s^2 \rightarrow s = \sqrt{(8.0 \times 10^{-28})} = 2.8 \times 10^{-14}$ M.
- **1:2 Salt Formula ($PbCl_2$, s = 0.0162 M):** $[Pb^{2+}] = s = 0.0162$ M and $[Cl^-] = 2s = 0.0324$ M → $K_{sp} = (0.0162)(0.0324)^2 = 4s^3 = 1.7 \times 10^{-5}$.

EXAMPLE 7.4 Predicting Precipitation Using Q_sp vs. K_sp Upon Mixing Two Solutions

Problem: Will a precipitate of $PbCl_2(s)$ ($K_{sp} = 1.7 \times 10^{-5}$) form when 100.0 mL of 0.250 M NaCl(aq) is mixed with 200.0 mL of 0.200 M $Pb(NO_3)_2(aq)$?

STEP-BY-STEP SOLUTION:

1. Step 1 — Calculate Diluted Ion Concentrations Using Total Volume (300.0 mL): Total V = 100.0 + 200.0 = 300.0 mL. Using $M_1V_1 = M_2V_2$: $[Pb^{2+}]_0 = (0.200\ M \times 200.0\ mL) / 300.0\ mL = 0.133$ M; $[Cl^-]_0 = (0.250\ M \times 100.0\ mL) / 300.0\ mL = 0.0833$ M.
2. Step 2 — Evaluate Q_sp: $Q_{sp} = [Pb^{2+}]_0[Cl^-]_0^2 = (0.133)(0.0833)^2 = 9.2 \times 10^{-4}$.
3. Step 3 — Compare Q_sp to K_sp: Because Q_{sp} (9.2×10^{-4}) > K_{sp} (1.7×10^{-5}), the solution exceeds saturation and a white precipitate of $PbCl_2(s)$ WILL form.

Final Answer: Yes, a precipitate forms because Q_{sp} (9.2×10^{-4}) > K_{sp} (1.7×10^{-5})

EXAMPLE 7.5 Calculating Molar Solubility in the Presence of a Common Ion

Problem: Calculate the molar solubility (s) of magnesium fluoride, $MgF_2(s)$ ($K_{sp} = 5.16 \times 10^{-11}$), in a 0.10 M sodium fluoride (NaF) solution.

STEP-BY-STEP SOLUTION:

1. Step 1 — Set Up ICE Table with Initial Common Ion $[F^-]_0 = 0.10$ M: For $MgF_2(s) \rightleftharpoons Mg^{2+}(aq) + 2\ F^-(aq)$, at equilibrium $[Mg^{2+}] = s$ and $[F^-] = 0.10 + 2s$.
2. Step 2 — Apply Small-s Approximation: Because K_{sp} is tiny (5.16×10^{-11}), 2s is negligible compared to 0.10 M, so $0.10 + 2s \approx 0.10$ M.
3. Step 3 — Solve for s: $K_{sp} = 5.16 \times 10^{-11} = (s)(0.10)^2 = 0.010\ s \rightarrow s = 5.2 \times 10^{-9}$ M (nearly 50,000 times less soluble than in pure water!).

Final Answer: $s = 5.2 \times 10^{-9}$ M

⚠ AP EXAM TRAP & FRQ SCORING GUIDELINE

AP Exam Trap: In common-ion problems like Example 7.5 (MgF_2 in 0.10 M NaF), never plug 0.10 M into $4s^3$! The fluoride concentration comes overwhelmingly from the 0.10 M NaF ($[F^-] \approx 0.10$ M, NOT 2s), so $K_{sp} = (s)(0.10)^2$, where 0.10 is squared but NOT multiplied by 2.

✅ CHAPTER 7 MASTERY CHECKLIST (AP EXAM READINESS)

☑ Interpret rate-vs.-time and concentration-vs.-time equilibrium graphs and write K_c, K_p, and K_{sp} expressions (excluding pure solids and liquids).

☑ Manipulate K values when reversing equations (1/K), scaling coefficients (K^n), or adding coupled reactions ($K_1 \times K_2$).

☑ Construct ICE tables and apply the 5% small-x approximation to solve for K or equilibrium concentrations.

☑ Compare the reaction quotient Q to K to predict shift direction and apply Le Chatelier's Principle to concentration, volume/pressure, and temperature stresses.

☑ Calculate molar solubility (s) from K_{sp}, test for precipitation using Q_{sp} vs. K_{sp} (with volume dilution), and quantify the common-ion effect.

CHAPTER 8 · CORE CURRICULUM

AP Exam Weighting: 11–15%

Unit 8: Acids and Bases

Unit 8 is the second most heavily weighted topic on the AP Chemistry exam (11–15%). Students master the autoionization of water (K_w) and its temperature dependence, pH and pOH calculations for strong and weak acids/bases, conjugate acid–base relationships (K_a × K_b = K_w), weak-acid titration curves (including the half-equivalence point where pH = pK_a), indicator selection, molecular structure effects on acid strength (binary vs. oxoacids), Henderson–Hasselbalch buffer calculations, buffer capacity, and pH-dependent solubility.

CHAPTER 8 ESSENTIAL EQUATIONS, LAWS & CONSTANTS

$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$ (at 25 °C)	Autoionization constant of water; pH + pOH = 14.00 at 25 °C
$pH = -\log[H_3O^+]$ and $[H_3O^+] = 10^{(-pH)}$	pH and hydronium ion conversions (sig figs in $[H_3O^+]$ = decimal places in pH)
$K_a \times K_b = K_w = 1.0 \times 10^{-14}$; $pK_a + pK_b = 14.00$	Conjugate acid–base pair relationship at 25 °C
$pH = pK_a + \log([A^-] / [HA])$	Henderson–Hasselbalch Equation for buffer pH (at half-equivalence, $[A^-] = [HA]$ so pH = pK_a)

§ 8.1 Autoionization of Water (K_w), the pH Scale & Strong Acids and Bases

Even in pure water, water molecules autoionize to a small extent into hydronium ions (H_3O^+) and hydroxide ions (OH^-): **$2\,H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$**. At 25 °C, the equilibrium constant is **$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$**. Because pure water produces equal amounts of both ions ($[H_3O^+] = [OH^-] = 1.0 \times 10^{-7}$ M), a neutral solution at 25 °C has **pH = pOH = 7.00**. Because autoionization requires breaking covalent O–H bonds, it is an **endothermic process (ΔH° > 0)**. By Le Chatelier's Principle, heating pure water above 25 °C shifts the equilibrium to the right, increasing K_w and raising both $[H_3O^+]$ and $[OH^-]$ equally. For example, at 50 °C pure water has a **pH of 6.63, yet it is still completely NEUTRAL because $[H_3O^+] = [OH^-]$**!

Strong acids and strong bases dissociate 100% in water (written with a single forward arrow →, requiring no ICE table). You must memorize the **six strong acids**: **HCl, HBr, HI, HNO_3, $HClO_4$, and H_2SO_4**. The **strong bases** are the soluble Group 1 hydroxides (**LiOH, NaOH, KOH, RbOH, CsOH**) and the heavier Group 2 hydroxides (**$Ca(OH)_2$, $Sr(OH)_2$, and $Ba(OH)_2$**, which release **2 moles of OH^- per mole of compound**).

- **Logarithmic Significant Figure Rule:** The number of significant figures in the concentration ($[H_3O^+]$ or $[OH^-]$) becomes the number of DECIMAL PLACES (digits after the decimal point) in the pH or pOH.
- **Acid–Base Conversion Square:** pH = −log[H_3O^+], pOH = −log[OH^-], [H_3O^+] = 10^(−pH), [OH^-] = 10^(−pOH), and pH + pOH = 14.00 (at 25 °C).

EXAMPLE 8.1 **Calculating the pH of a Strong Monoprotic Acid and a Group 2 Strong Base**

Problem: Calculate the pH at 25 °C of (a) a 0.025 M HNO_3 solution and (b) a 0.015 M $Ba(OH)_2$ solution.

STEP-BY-STEP SOLUTION:

1. Part (a) Strong Acid (0.025 M HNO_3): Complete 100% ionization gives $[H_3O^+]$ = 0.025 M (2 sig figs). Taking the negative log gives pH = −log(0.025) = 1.60 (2 decimal places).
2. Part (b) Group 2 Strong Base (0.015 M $Ba(OH)_2$): Each formula unit of $Ba(OH)_2$ releases 2 OH^- ions: $[OH^-]$ = 2 × 0.015 M = 0.030 M. Then pOH = −log(0.030) = 1.52, and pH = 14.00 − 1.52 = 12.48.

Final Answer: (a) pH = 1.60; (b) pH = 12.48

⚠ **AP EXAM TRAP & FRQ SCORING GUIDELINE**

AP Exam Trap: Never define a neutral solution as 'pH = 7.00'! A solution is neutral if and only if $[H_3O^+] = [OH^-]$. pH = 7.00 is neutral ONLY at 25 °C.

§ 8.2 Weak Acids (K_a), Weak Bases (K_b), Conjugate Pairs & Acid–Base Net Ionic Equations

On AP Chemistry particulate diagrams, strong and weak acids look completely different: in a strong acid like HCl, 100% of the molecules break apart into separate H^+ (or H_3O^+) and Cl^- ions; in a **weak acid (HA, such as HF or CH_3COOH)**, **K_a << 1**, so **over 95% of the acid remains as intact, undissociated HA molecules** with only a tiny fraction ionized: **HA(aq) + H_2O(l) ⇌ H_3O^+(aq) + A^-(aq)**, where **K_a = ($[H_3O^+][A^-]$) / [HA]**.

Similarly, **weak bases** (such as ammonia NH_3, amines, or conjugate anions of weak acids like F^- and CH_3COO^-) react reversibly with water to produce OH^- and their conjugate acid, governed by **K_b**. For any conjugate acid–base pair at 25 °C, **K_a × K_b = K_w = 1.0 × 10^{-14}** and **pK_a + pK_b = 14.00**. Thus, the stronger a weak acid is (larger K_a, smaller pK_a), the weaker its conjugate base must be.

When writing **net ionic equations for acid–base reactions**, how you write each reactant depends strictly on whether it is strong or weak: (1) any **strong acid + strong base** reaction always simplifies to **H^+(aq) + OH^-(aq) → H_2O(l)**; (2) any **weak acid (HA) or weak base (B) MUST be written as an intact molecule**! For example, weak hydrofluoric acid (HF) reacting with strong sodium hydroxide (NaOH) is written as: **HF(aq) + OH^-(aq) → F^-(aq) + H_2O(l)** (crossing out only the Na^+ spectator ion).

- **Percent Ionization Formula:** % Ionization = ($[H_3O^+]$_eq / $[HA]_0$) × 100%. Diluting a weak acid with water shifts equilibrium right and INCREASES its percent ionization.

EXAMPLE 8.2 **Calculating the pH and Percent Ionization of a Weak Acid Using a K_a ICE Table**

Problem: Calculate the pH and percent ionization of a 0.10 M acetic acid (CH_3COOH) solution at 25 °C, given K_a = 1.8×10^{-5}.

STEP-BY-STEP SOLUTION:

1. Step 1 — Set Up K_a ICE Expression: For $CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$, at equilibrium $[H_3O^+] = [CH_3COO^-] = x$ and $[CH_3COOH] = 0.10 - x$.
2. Step 2 — Apply 5% Small-x Approximation: $K_a = 1.8 \times 10^{-5} = x^2 / (0.10 - x) \approx x^2 / 0.10$. Solving gives $x^2 = 1.8 \times 10^{-6} \rightarrow x = [H_3O^+] = 1.34 \times 10^{-3}$ M.
3. Step 3 — Calculate pH and Percent Ionization: $pH = -\log(1.34 \times 10^{-3}) = 2.87$. Percent ionization = ($1.34 \times 10^{-3}$ M / 0.10 M) × 100% = 1.34% (well below 5%, validating the approximation).

Final Answer: pH = 2.87; Percent ionization = 1.34%

⚠ **AP EXAM TRAP & FRQ SCORING GUIDELINE**

AP Exam Trap: When writing the net ionic equation for a weak acid (such as HF or $HC_2H_3O_2$) reacting with strong OH^-, writing '$H^+ + OH^- \rightarrow H_2O$' earns ZERO points! Because weak acids exist >95% as intact molecules in water, you MUST write the intact weak acid formula on the reactant side: $HA(aq) + OH^-(aq) \rightarrow A^-(aq) + H_2O(l)$.

§ 8.3 Acid–Base Titration Curves, the Half-Equivalence Point & Molecular Acid Strength

When a **weak acid (HA)** is mixed with less than a stoichiometric amount of strong base (OH^-), the strong hydroxide reacts 100% as the limiting reactant ($HA + OH^- \rightarrow A^- + H_2O$), converting part of the weak acid HA into its conjugate base A^-. Because the resulting solution contains significant amounts of both leftover weak acid HA and newly formed conjugate base A^-, **partial neutralization creates a buffer**!

Consequently, the **titration curve of a weak acid titrated with a strong base (NaOH)** exhibits four distinct regions: (1) **Initial point (0 mL base added)**: starts at a higher pH than a strong acid of the same molarity; calculate pH using a **K_a ICE table**; (2) **Buffer region (between 0 mL and V_eq)**: rises gradually into a flat plateau; exactly halfway to the equivalence volume (the **half-equivalence point, V = ½ V_eq**), half of the original HA has been converted to A^- so **[HA] = [A^-] and pH = pK_a**; (3) **Equivalence point (at V_eq)**: 100% of the weak acid has been converted into its conjugate base A^-, which hydrolyzes water ($A^- + H_2O \rightleftharpoons HA + OH^-$) to make the **equivalence point basic (pH > 7)**; calculate pH using a **K_b ICE table** (with diluted [A^-]); and (4) **Beyond equivalence (V > V_eq)**: pH is determined entirely by the concentration of **excess strong OH^-**.

When titrating a **diprotic acid (e.g., H_2SO_3)**, removing the first proton from a neutral molecule is much easier than removing the second proton from a negatively charged ion, so **K_a1 >> K_a2**, producing two distinct equivalence points on the titration curve. To choose an **acid–base indicator** for any titration, select an indicator whose **pK_a is within ±1 of the pH at the equivalence point**.

Finally, molecular structure governs acid strength in two ways: (1) for **binary acids in the same periodic group (HF << HCl < HBr < HI)**, acid strength is controlled by **bond length and bond enthalpy** (NOT electronegativity): as halide radius increases down Group 17 from F to I, the H–X bond becomes longer and weaker, making it much easier to break and release H^+ (which is why HF is weak while HCl, HBr, and HI are strong); (2) for **oxoacids (H–O–X)**, acid strength is driven by the **inductive effect**: a more electronegative central atom X (**HClO > HBrO > HIO**) or more terminal oxygen atoms attached to X (**$HClO_4$ > $HClO_3$ > $HClO_2$ > HClO**) pulls electron density away from the O–H bond, weakening the O–H bond and stabilizing the conjugate base anion via resonance.

- **Predominant Species Rule (pH vs. pK_a):** When pH = pK_a, [HA] = [A^-]. When pH < pK_a (more acidic, rich in H^+), the protonated acid HA predominates. When pH > pK_a (more basic), the deprotonated conjugate base A^- predominates.

Table 8.1 · Comparison of Strong vs. Weak Acid/Base Titration Curves and Equivalence-Point pH

Titration Type	Initial pH	Half-Equivalence Point (½ V_eq)	Equivalence Point pH (at 25 °C)	Reason for Equivalence Point pH	Suitable Indicator Example
Strong Acid + Strong Base (HCl + NaOH)	Very low (~1)	No buffer plateau	pH = 7.00 (Neutral)	Only neutral spectator ions (Na^+, Cl^-) + H_2O	Bromothymol blue or Phenolphthalein
Weak Acid + Strong Base (CH_3COOH + NaOH)	Higher (~2.9)	Buffer! [HA] = [A^-] → pH = pK_a	pH > 7.00 (Basic, ~8.7)	Conjugate base A^- hydrolyzes water to form OH^-	Phenolphthalein (pK_a ≈ 9)
Weak Base + Strong Acid (NH_3 + HCl)	Basic (~11.1)	Buffer! [B] = [BH^+] → pOH = pK_b	pH < 7.00 (Acidic, ~5.3)	Conjugate acid BH^+ donates H^+ to water	Methyl red (pK_a ≈ 5)

EXAMPLE 8.2B **Determining pK_a, K_a, Predominant Species & Indicator Choice from a Titration Curve**

Problem: A 30.0 mL sample of an unknown weak monoprotic acid HA is titrated with 0.100 M NaOH. The equivalence point is reached at V_eq = 30.0 mL of NaOH added, where the pH is 8.85. When 15.0 mL of NaOH has been added, the pH of the solution is 4.75. (a) Determine the pK_a and K_a of the weak acid HA. (b) Which species (HA or A^-) predominates at pH = 3.50? (c) Between methyl red (pK_a = 5.0) and phenolphthalein (pK_a = 9.3), which is the better indicator for this titration?

STEP-BY-STEP SOLUTION:

1. Part (a) Half-Equivalence Point Analysis: Since V_eq = 30.0 mL, adding V = 15.0 mL of NaOH corresponds to the exact half-equivalence point (½ V_eq), where half of HA is neutralized and [HA] = [A^-]. At this point, pK_a = pH = 4.75, and K_a = 10^(−4.75) = 1.8×10^{-5}.
2. Part (b) Predominant Species at pH = 3.50: Because pH (3.50) < pK_a (4.75), the solution is more acidic than the half-equivalence point and rich in H^+, so the protonated weak acid form HA predominates ([HA] > [A^-]).
3. Part (c) Indicator Selection: Choose an indicator whose pK_a is within ±1 of the equivalence-point pH (8.85). Phenolphthalein (pK_a = 9.3) changes color right across the steep vertical jump at pH 8.85.

Final Answer: (a) pK_a = 4.75, K_a = 1.8×10^{-5}; (b) HA predominates; (c) Phenolphthalein

⚠ **AP EXAM TRAP & FRQ SCORING GUIDELINE**

AP Exam Trap: Notice that the VOLUME of strong base required to reach the equivalence point (V_eq) depends ONLY on the moles of acid (M_acid × V_acid), NOT on whether the acid is strong or weak! A 25.0 mL sample of 0.10 M HCl and a 25.0 mL sample of 0.10 M CH_3COOH require the EXACT SAME volume of 0.10 M NaOH (25.0 mL) to reach equivalence, even though their initial pH and equivalence-point pH are different.

§ 8.4 Buffers, the Henderson–Hasselbalch Equation, Buffer Capacity & pH-Dependent Solubility

A **buffer** is an aqueous solution containing large, comparable concentrations of **both a weak acid (HA) and its conjugate base (A^-)** (or a weak base B and its conjugate acid BH^+). A buffer resists dramatic changes in pH when small amounts of strong acid or strong base are added because it contains both an acid component and a base component: if **strong acid (H^+) is added**, the conjugate base A^- traps it (**$A^- + H^+ \rightarrow HA$**); if **strong base (OH^-) is added**, the weak acid HA neutralizes it (**$HA + OH^- \rightarrow A^- + H_2O$**).

We calculate the pH of any buffer using the **Henderson–Hasselbalch Equation: pH = pK_a + log([A^-] / [HA])**. While the **ratio [A^-] / [HA]** determines the buffer's **pH**, the **absolute molar concentrations** of [HA] and [A^-] determine its **buffer capacity**—the total amount of strong acid or base the buffer can absorb before its pH changes significantly. Thus, a 1.0 M

HA / 1.0 M A^- buffer and a 0.10 M HA / 0.10 M A^- buffer have the **exact same initial pH (pH = pK_a)**—and diluting a buffer with pure water does not change its pH because both concentrations divide by the same volume—but the 1.0 M buffer has **10 times greater buffer capacity**.

Finally, acid–base equilibria directly impact the solubility of slightly soluble salts: if a salt contains a **basic anion** (the conjugate base of a weak acid, such as F^- in CaF_2, CO_3^{2-} in $CaCO_3$, PO_4^{3-}, S^{2-}, or OH^-), its **solubility increases dramatically in acidic solution (low pH)** because H^+ reacts with the basic anion (e.g., $H^+ + F^- \rightarrow HF$), lowering $[F^-]$ and shifting the K_sp dissolution equilibrium to the right by Le Chatelier's Principle. In contrast, salts containing **neutral anions derived from strong acids (such as Cl^-, Br^-, I^-, NO_3^-, ClO_4^-, or SO_4^{2-} in AgCl or $BaSO_4$)** show **zero change in solubility** when acid is added.

- **Optimal Buffer Design:** Choose a weak acid whose pK_a is as close as possible to the target buffer pH (within ±1 pH unit), with $[A^-] \approx [HA]$ in high concentrations (e.g., 0.50–1.0 M).

EXAMPLE 8.3 **Calculating Buffer pH Using the Henderson–Hasselbalch Equation**

> **Problem:** Calculate the pH of an acetate buffer solution containing 0.20 M acetic acid (CH_3COOH, pK_a = 4.74) and 0.50 M sodium acetate ($NaCH_3COO$). Which species is at a higher concentration, and how does that affect pH relative to pK_a?

STEP-BY-STEP SOLUTION:

1. Step 1 — Identify Conjugate Pair Concentrations: Weak acid [HA] = $[CH_3COOH]$ = 0.20 M; conjugate base $[A^-]$ = $[CH_3COO^-]$ = 0.50 M.
2. Step 2 — Substitute into Henderson–Hasselbalch Equation: pH = pK_a + log($[A^-]$ / [HA]) = 4.74 + log(0.50 / 0.20) = 4.74 + log(2.5) = 4.74 + 0.40 = 5.14.
3. Step 3 — Conceptual Check: Because $[A^-]$ > [HA], the log ratio is positive and pH (5.14) is slightly higher (more basic) than pK_a (4.74).

Final Answer: pH = 5.14 (since $[A^-]$ > [HA], pH > pK_a)

⚠ **AP EXAM TRAP & FRQ SCORING GUIDELINE**

AP Exam Trap: A mixture of a STRONG acid and its conjugate anion (such as HCl + NaCl, or HNO_3 + $NaNO_3$) is NEVER a buffer! Cl^- and NO_3^- are extremely weak, neutral spectator anions that cannot accept H^+ in water. A buffer requires a WEAK acid/base conjugate pair.

✅ **CHAPTER 8 MASTERY CHECKLIST (AP EXAM READINESS)**

☑ Use K_w = $[H_3O^+][OH^-]$ = 1.0×10^{-14} at 25 °C to convert among pH, pOH, $[H_3O^+]$, and $[OH^-]$, and explain why pure water at T > 25 °C has pH < 7 yet remains neutral.

☑ Calculate the pH of strong acids/bases (100% dissociated) and weak acids/bases (using K_a / K_b ICE tables and K_a × K_b = K_w).

☑ Analyze all 4 regions of a weak-acid/strong-base titration curve, locate the half-equivalence point (pH = pK_a), explain why equivalence pH > 7, and select an indicator.

☑ Justify binary acid strength (HF << HCl < HBr < HI) via bond enthalpy/radius and oxoacid strength ($HClO_4$ > HClO) via the inductive effect.

☑ Apply the Henderson–Hasselbalch equation to buffers, distinguish buffer pH (ratio) from buffer capacity (molarities), and predict which salts are more soluble in acid.

CHAPTER 9 · CORE CURRICULUM

AP Exam Weighting: 7–9%

Unit 9: Applications of Thermodynamics

Unit 9 unifies thermochemistry, chemical equilibrium, and electrochemistry. Students predict the sign and calculate the magnitude of entropy changes (ΔS°), evaluate thermodynamic favorability using Gibbs Free Energy (ΔG° = ΔH° − TΔS°), distinguish thermodynamic favorability from kinetic control, couple unfavorable reactions to favorable ones, link ΔG° to K (ΔG° = −RT ln K) and cell potential (ΔG° = −nFE°_cell), contrast galvanic (voltaic) and electrolytic cells, apply the Nernst equation to non-standard concentrations, and use Faraday's Law of Electrolysis to calculate plated metal mass.

CHAPTER 9 ESSENTIAL EQUATIONS, LAWS & CONSTANTS

$\Delta S°_{rxn} = \Sigma\, n \cdot S°(\text{products}) - \Sigma\, m \cdot S°(\text{reactants})$	Standard entropy of reaction (J·mol^{-1}·K^{-1}; S° > 0 for all substances at 298 K)
$\Delta G° = \Delta H° - T\Delta S°$ and $T_{crossover} = \Delta H° / \Delta S°$	Gibbs Free Energy (ΔG° < 0 is thermodynamically favorable; convert ΔS° from J to kJ!)
$\Delta G° = -RT \ln K$	Link between ΔG° (in J·mol^{-1}) and equilibrium constant K (R = 8.314 J·mol^{-1}·K^{-1})
$E°_{cell} = E°_{red}(\text{cathode}) - E°_{red}(\text{anode})$	Standard cell potential (V); never multiply E° by stoichiometric coefficients
$\Delta G° = -nFE°_{cell}$	Link between ΔG° (in J·mol^{-1}) and E°_cell (F = 96,485 C·mol_e^{-1})
$E_{cell} = E°_{cell} - (RT / nF) \ln Q$	Nernst Equation for non-standard cell potential (at equilibrium, Q = K and E_cell = 0 V)
$q = I \times t$ and $n_{e^-} = (I \times t) / F$	Faraday's Law of Electrolysis: charge (C) = current (A) × time (s)

§ 9.1 Entropy (S°), Microstates & the Third Law of Thermodynamics

Entropy (S) is a quantitative measure of the dispersal of matter and energy across available molecular **microstates** (positional and thermal arrangements). As a substance changes phase from a rigid solid to a liquid and then to a gas, particles spread out into a vastly larger volume with far more accessible microstates, so entropy increases dramatically: **S_solid < S_liquid << S_gas**.

You can predict the sign of **ΔS°** directly from a chemical or physical equation: entropy increases (**ΔS° > 0**) when (1) a solid melts or sublimes, or a liquid vaporizes; (2) a gas expands into a larger container volume; (3) temperature increases (broadening the Maxwell–Boltzmann distribution); (4) a solid dissolves into aqueous ions (usually ΔS° > 0); or (5) a chemical reaction **produces more total moles of gas on the product side than on the reactant side (Δn_gas > 0)**.

By the **Third Law of Thermodynamics**, the entropy of a perfect, pure crystal at absolute zero (0 K) is exactly zero. Therefore, **unlike ΔH°_f, the absolute standard molar entropy (S°) of ANY pure element or compound at 298 K is ALWAYS a positive number** (reported in **J·mol^{-1}·K^{-1}**). We calculate the standard entropy change of a reaction using products minus reactants: **ΔS°_rxn = Σ n·S°(products) − Σ m·S°(reactants)**.

- **Example of Negative ΔS°_rxn:** In 2 NO(g) + O_2(g) → 2 NO_2(g), 3 moles of reactant gas compress into 2 moles of product gas (Δn_gas = −1), giving ΔS°_rxn = −146.5 J·mol^{-1}·K^{-1}.

EXAMPLE 9.1A **Predicting the Sign of ΔS° and Calculating ΔS°_rxn from Standard Molar Entropies**

Problem: Consider the gas-phase oxidation of nitric oxide: 2 NO(g) + O_2(g) → 2 NO_2(g). (a) Predict the sign of ΔS°_rxn based on the balanced equation alone. (b) Calculate the exact value of ΔS°_rxn at 298 K given the standard molar entropies S° (J·mol^{-1}·K^{-1}): NO(g) = 210.8, O_2(g) = 205.1, NO_2(g) = 240.1.

STEP-BY-STEP SOLUTION:

1. Part (a) Qualitative Sign Prediction: The reactant side contains 2 + 1 = 3 moles of gas, whereas the product side contains only 2 moles of gas (Δn_gas = 2 − 3 = −1 < 0). Because gas molecules are compressed into fewer particles with fewer available microstates, ΔS°_rxn is negative (ΔS° < 0).
2. Part (b) Quantitative Calculation (Products − Reactants): ΔS°_rxn = [2 × S°(NO_2)] − [2 × S°(NO) + 1 × S°(O_2)] = [2(240.1)] − [2(210.8) + 205.1] = 480.2 − 626.7 = −146.5 J·mol_rxn^{-1}·K^{-1}.

Final Answer: (a) ΔS° < 0 (3 mol gas → 2 mol gas); (b) ΔS°_rxn = −146.5 J·mol_rxn^{-1}·K^{-1}

⚠ **AP EXAM TRAP & FRQ SCORING GUIDELINE**

AP Exam Trap: Never set S° of a pure element (like O_2(g) or Fe(s)) equal to zero! ΔH°_f and ΔG°_f of pure elements in their standard states are 0, but standard molar entropy S° at 298 K is ALWAYS positive for every substance.

§ 9.2 Gibbs Free Energy (ΔG°), Temperature Crossover, Kinetic Control & Coupled Reactions

To determine whether a chemical or physical process is **thermodynamically favorable** (occurs spontaneously without continuous outside intervention), chemists evaluate **Gibbs Free Energy: ΔG° = ΔH° − TΔS°**. Whenever **ΔG° < 0**, the forward process is thermodynamically favorable; when **ΔG° > 0**, the forward process is unfavorable (and the reverse reaction is favorable); and when **ΔG = 0**, the system is at equilibrium. To find the **crossover temperature (T)** at which a reaction switches between non-favorable and favorable, set ΔG° = 0 and solve for **T = ΔH° / ΔS°** (making sure both are expressed in the same energy units!).

Why doesn't a diamond ring turn into pencil lead (graphite) on your finger even though C(diamond) → C(graphite) has ΔG° < 0? Because **thermodynamic favorability (ΔG° < 0) tells us NOTHING about reaction rate!** A reaction with ΔG° < 0 that proceeds imperceptibly slowly at room temperature due to a huge **activation energy barrier (E_a)** is said to be under **kinetic control**.

Finally, how can we force a thermodynamically unfavorable reaction ($\Delta G°_1 > 0$) to occur? By **coupling** it via a shared reaction intermediate to a second, highly favorable reaction ($\Delta G°_2 << 0$)—such as ATP hydrolysis in biochemistry or carbon oxidation in metallurgical smelting—so that the sum **$\Delta G°_{total} = \Delta G°_1 + \Delta G°_2 < 0$** is overall negative. Furthermore, Gibbs free energy links directly to the equilibrium constant K via **ΔG° = −RT ln K** (where R = 8.314 J·mol^{-1}·K^{-1}): when **ΔG° < 0, K > 1** (products favored at equilibrium); when **ΔG° > 0, K < 1** (reactants favored).

- **The #1 Unit Trap on the AP Exam (kJ vs. J):** ΔH° is given in kJ·mol^{-1} while ΔS° is given in J·mol^{-1}·K^{-1}! You MUST divide ΔS° by 1,000 to convert J into kJ before plugging into ΔG° = ΔH° − TΔS° (and convert ΔG° to J·mol^{-1} when using ΔG° = −RT ln K with R = 8.314 J·mol^{-1}·K^{-1}).

Table 9.1 · The Four-Quadrant Matrix of ΔH°, ΔS°, and Thermodynamic Favorability (ΔG° = ΔH° − TΔS°)

Sign of ΔH°	Sign of ΔS°	Sign of −TΔS°	Sign of ΔG° & Temperature Dependence	Classic Chemical Example
− (Exothermic)	+ (Dispersed)	−	ALWAYS < 0 (Favorable at ALL temperatures)	Combustion of propane; 2 $H_2O_2(l)$ → 2 $H_2O(l)$ + $O_2(g)$
+ (Endothermic)	− (Ordered)	+	ALWAYS > 0 (NEVER favorable at any T)	3 $O_2(g)$ → 2 $O_3(g)$
− (Exothermic)	− (Ordered)	+	Favorable (< 0) ONLY at LOW temperatures (T < ΔH°/ΔS°)	Freezing liquid water: $H_2O(l)$ → $H_2O(s)$ (favorable below 0 °C)
+ (Endothermic)	+ (Dispersed)	−	Favorable (< 0) ONLY at HIGH temperatures (T > ΔH°/ΔS°)	Melting ice: $H_2O(s)$ → $H_2O(l)$; decomposing $CaCO_3(s)$

EXAMPLE 9.1B **Calculating Gibbs Free Energy (ΔG°), Crossover Temperature & K from ΔH° and ΔS°**

Problem: For the reaction 2 NO(g) + $O_2(g)$ → 2 $NO_2(g)$, ΔH° = −114.1 kJ·mol_rxn^{-1} and ΔS° = −146.5 J·mol_rxn^{-1}·K^{-1} at 298 K. (a) Calculate ΔG° at 298 K and state whether the reaction is thermodynamically favorable at 298 K. (b) Calculate the crossover temperature (T) above which this reaction becomes thermodynamically unfavorable.

STEP-BY-STEP SOLUTION:

1. Part (a) Step 1 — Convert ΔS° from J to kJ: ΔS° = −146.5 J·mol^{-1}·K^{-1} × (1 kJ / 1,000 J) = −0.1465 kJ·mol^{-1}·K^{-1}.
2. Part (a) Step 2 — Evaluate ΔG° = ΔH° − TΔS°: At 298 K, ΔG° = −114.1 kJ − (298 K)(−0.1465 kJ·K^{-1}) = −114.1 kJ + 43.7 kJ = −70.4 kJ·mol_rxn^{-1}. Because ΔG° < 0, the forward reaction is thermodynamically favorable at 298 K.
3. Part (b) Crossover Temperature (ΔG° = 0): Setting ΔG° = ΔH° − TΔS° = 0 gives T = ΔH° / ΔS° = (−114.1 kJ·mol^{-1}) / (−0.1465 kJ·mol^{-1}·K^{-1}) = 779 K. Because both ΔH° and ΔS° are negative, the reaction is favorable below 779 K and unfavorable above 779 K.

Final Answer: (a) ΔG° = −70.4 kJ·mol_rxn^{-1} (favorable at 298 K); (b) T_crossover = 779 K

⚠ AP EXAM TRAP & FRQ SCORING GUIDELINE

AP Exam Trap: Never say a reaction with ΔG° < 0 is 'fast' or happens 'immediately.' ΔG° measures thermodynamic driving force (where equilibrium lies), whereas activation energy (E_a) controls reaction speed (kinetics).

§ 9.3 Electrochemistry: Galvanic (Voltaic) vs. Electrolytic Cells & Standard Cell Potential (E°_cell)

Electrochemistry studies the interconversion of chemical energy and electrical energy via redox reactions. Memorize two universal definitions that apply to ALL electrochemical cells: **AN OX (Oxidation ALWAYS occurs at the Anode)** and **RED CAT (Reduction ALWAYS occurs at the Cathode)**, and electrons ALWAYS flow through the external wire **from the Anode to the Cathode (FAT CAT: From Anode To Cathode)**.

A **galvanic (or voltaic) cell** harnesses a thermodynamically favorable redox reaction (**E°_cell > 0, ΔG° < 0, K > 1**) to generate an electric current. In a standard **Zn / Cu galvanic cell**, Zn(s) is oxidized at the anode (Zn(s) → Zn^{2+}(aq) + 2 e^-, so the Zn anode strip loses mass) and Cu^{2+}(aq) is reduced at the cathode (Cu^{2+}(aq) + 2 e^- → Cu(s), so solid Cu plates out and the Cu cathode gains mass). Meanwhile, the **salt bridge** completes the circuit and maintains electrical neutrality by migrating **anions toward the anode** (to balance newly formed Zn^{2+}) and **cations toward the cathode** (to replace consumed Cu^{2+}). If the salt bridge is removed, charge buildup immediately stops electron flow and cell voltage drops to 0 V immediately.

We calculate standard cell potential using **E°_cell = E°_red(cathode) − E°_red(anode)**, and connect E°_cell to Gibbs free energy via **ΔG° = −nFE°_cell**, where *n* is the moles of electrons transferred in the balanced redox equation and **F = 96,485 C·mol_e^{-1}** is Faraday's constant. By contrast, an **electrolytic cell** uses an external battery or power supply to force a thermodynamically unfavorable reaction to occur (**E°_cell < 0, ΔG° > 0, K < 1**).

- **Intensive Property Rule for E°:** Standard reduction potential E° is an INTENSIVE property (1 V = 1 J·C^{-1}). Even when you multiply a half-reaction by 2 or 3 to balance electrons in the overall equation, NEVER multiply its E° voltage by that coefficient!

Table 9.2 · Master Comparison of Galvanic (Voltaic) Cells and Electrolytic Cells

Feature / Property	Galvanic (Voltaic) Cell	Electrolytic Cell
Thermodynamic Favorability	Favorable (Spontaneous)	Unfavorable (Nonspontaneous — driven by external battery)
Signs of E°_cell, ΔG°, and K	E°_cell > 0 V, ΔG° < 0, K > 1	E°_cell < 0 V, ΔG° > 0, K < 1
Site of Oxidation & Reduction	Anode = Oxidation; Cathode = Reduction (AN OX / RED CAT)	Anode = Oxidation; Cathode = Reduction (AN OX / RED CAT)
Direction of e⁻ Flow in Wire	Anode → Cathode	Anode → Cathode (pushed by external power source)
Salt Bridge Required?	Yes (two half-cells; anions → anode, cations → cathode)	Usually single chamber (molten salt or aqueous electrolysis)

EXAMPLE 9.1 **Calculating E°_cell and ΔG° for a Standard Zn / Cu Galvanic Cell**

> **Problem:** Given the standard reduction potentials: $Cu^{2+}(aq) + 2\ e^- \rightarrow Cu(s)$ E°_red = +0.34 V $Zn^{2+}(aq) + 2\ e^- \rightarrow Zn(s)$ E°_red = −0.76 V Identify the anode and cathode in a galvanic cell, write the overall balanced equation, and calculate E°_cell and ΔG° (in kJ·mol_rxn^{-1}).

STEP-BY-STEP SOLUTION:

1. Step 1 — Identify Cathode and Anode: For a galvanic cell, E°_cell must be positive, so the half-reaction with the more positive reduction potential (+0.34 V > −0.76 V) occurs at the cathode (Cu^{2+} reduced to Cu) and Zn is oxidized at the anode.
2. Step 2 — Overall Equation & E°_cell: $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$ (n = 2 mol e^-). E°_cell = E°_red(cathode) − E°_red(anode) = (+0.34 V) − (−0.76 V) = +1.10 V.
3. Step 3 — Calculate ΔG°: ΔG° = −nFE°_cell = −(2 mol e^-)(96,485 C·mol_e^{-1})(+1.10 J·C^{-1}) = −212,267 J = −212 kJ·mol_rxn^{-1}.

Final Answer: Anode: Zn; Cathode: Cu; E°_cell = +1.10 V; ΔG° = −212 kJ·mol_rxn^{-1}

⚠ **AP EXAM TRAP & FRQ SCORING GUIDELINE**

AP Exam Trap: Electrons NEVER swim through the aqueous solution or through the salt bridge! Electrons travel exclusively through the external metal wire from anode to cathode, while IONS migrate through the salt bridge and solutions.

§ 9.4 The Nernst Equation, Concentration Cells & Faraday's Law of Electrolysis

When aqueous ion concentrations or gas pressures in a cell are not at standard state (1.0 M or 1.0 atm), the actual cell voltage (**E_cell**) is governed by the **Nernst Equation: E_cell = E°_cell − (RT / nF) ln Q**, where **Q** is the reaction quotient (products over reactants, omitting pure solid electrodes). Rather than plugging numbers into the Nernst equation, the AP Chemistry exam primarily tests qualitative predictions using Q: (1) if **Q < 1** (meaning you increased the concentration of aqueous reactant ions at the cathode or decreased aqueous product ions at the anode), ln Q is negative, so **E_cell**

INCREASES above E°_cell (E_cell > E°_cell); (2) if **Q > 1** (extra aqueous product ions at the anode or diluted reactant ions at the cathode), ln Q is positive, so **E_cell DROPS below E°_cell (E_cell < E°_cell)**.

A **concentration cell** uses two identical metal electrodes immersed in two different concentrations of the same ion (e.g., 0.010 M Cu^{2+} vs. 1.0 M Cu^{2+}). Even though E°_cell = 0 V, the cell generates a small positive voltage by oxidizing the metal in the dilute compartment (to raise its ion concentration) and reducing ions in the concentrated compartment (to lower its concentration) until both compartments reach equal molarity. As any battery discharges over time, reactants are consumed and products build up until **Q reaches K (chemical equilibrium)**: at equilibrium, **ΔG = 0 and E_cell = 0.00 V (a dead battery)**.

Finally, in an electrolytic cell (electroplating), we calculate the mass of solid metal deposited at the cathode using **Faraday's Law of Electrolysis** in three steps: (1) multiply electric current in amperes (I, where 1 A = 1 $C \cdot s^{-1}$) by time in seconds (t) to find total electric charge in coulombs: **q = I × t**; (2) divide total coulombs by Faraday's constant (**F = 96,485 $C \cdot mol_e^{-1}$**) to find **moles of electrons (n_e^-)**; and (3) divide by the ion charge *n* (moles of e^- per mole of metal ion in M^(n+) + n e^- → M(s)) to find moles of metal, then multiply by atomic molar mass to get grams.

- **What Happens If You Make the Solid Zn or Cu Electrode Larger?:** ZERO change in E_cell! Because pure solids are omitted from Q, changing the size or mass of a solid electrode does not affect cell voltage (it only allows the battery to run longer before the anode is consumed).

EXAMPLE 9.2 **Quantitative Electroplating Calculation Using Faraday's Law of Electrolysis**

> **Problem:** An electrolytic cell plates solid copper (Cu, M = 63.55 $g \cdot mol^{-1}$) from an aqueous $CuSO_4$ solution (Cu^{2+} + 2 e^- → Cu(s)) using a steady current of 10.0 A for 30.0 minutes. How many grams of solid copper are deposited on the cathode?

STEP-BY-STEP SOLUTION:

1. Step 1 — Convert Time to Seconds & Calculate Total Charge (q = I × t): t = 30.0 min × (60 s / 1 min) = 1,800 s. Total charge q = (10.0 $C \cdot s^{-1}$)(1,800 s) = 18,000 C.
2. Step 2 — Convert Coulombs to Moles of Electrons: n(e^-) = 18,000 C / (96,485 $C \cdot mol_e^{-1}$) = 0.1866 mol e^-.
3. Step 3 — Electron-to-Metal Stoichiometry & Mass: Since reducing 1 mol of Cu^{2+} requires 2 mol of e^-, n(Cu) = 0.1866 mol e^- × (1 mol Cu / 2 mol e^-) = 0.09328 mol Cu. Multiplying by molar mass gives m(Cu) = 0.09328 mol × 63.55 $g \cdot mol^{-1}$ = 5.93 g of solid Cu.

Final Answer: 5.93 g of Cu(s)

⚠ **AP EXAM TRAP & FRQ SCORING GUIDELINE**

AP Exam Trap: In Faraday's Law problems, students frequently forget to convert minutes or hours into SECONDS before multiplying by amperes (remember 1 Ampere = 1 Coulomb per SECOND), or forget to divide moles of electrons by the ionic charge n (e.g., 2 e^- for Cu^{2+}, 3 e^- for Al^{3+}).

✅ CHAPTER 9 MASTERY CHECKLIST (AP EXAM READINESS)

☑ Predict the sign of ΔS° from phase changes and gas mole changes (Δn_{gas}) and calculate ΔS°_{rxn} using products minus reactants (remembering $S^\circ > 0$ for all substances).

☑ Calculate $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ (converting ΔS° from J to kJ!), analyze the 4-quadrant temperature favorability matrix, find crossover T, and distinguish kinetic control (high E_a) from thermodynamic favorability.

☑ Relate ΔG°, K, and E°_{cell} using $\Delta G^\circ = -RT \ln K$ and $\Delta G^\circ = -nFE^\circ_{cell}$, and explain how coupled reactions drive unfavorable processes.

☑ Diagram galvanic and electrolytic cells (AN OX, RED CAT, e^- flow from anode to cathode, salt bridge ion migration) and calculate E°_{cell} without multiplying by coefficients.

☑ Use the Nernst equation ($Q < 1$ vs. $Q > 1$) to predict non-standard voltage changes, explain concentration cells and dead batteries ($E_{cell} = 0$ at $Q = K$), and solve electroplating problems with Faraday's Law ($q = It$).