



SCHOLAR COACH

Boutique Academic Coaching & Tutoring

AP CHEMISTRY · COURSE REVIEW AND PRACTICE

AP Chemistry Mastery.

Every unit on the exam: concise concept review, worked examples, exam-style writing, practice problems with full explanations, a mixed practice test, and a reference section.

INSIDE

Words in Context · Inferences · Command of Evidence · Central Ideas and Details · Function of a Sentence · Algebra · Advanced Math · Problem-Solving and Data Analysis · Geometry and Trigonometry · Three Full-Length Practice Exams with Explanations



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Course review, practice, and a mixed test.

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Start Here: The Exam, Your Plan, and Your Tools

How the AP Chemistry exam is built, how points are earned, and how to use this book.

F Start Here: The Exam, Your Plan, and Your Tools

How the 2027 AP Chemistry exam is built, how free-response points are earned, and a week-by-week plan with the calculation habits you will use in every unit.

What You Are Preparing For

The exam is **Thursday, May 6, 2027 (Session 2)**. It is a hybrid digital exam: you answer the multiple-choice section on a device and write the free-response answers by hand in a paper booklet. A calculator is permitted and reference information (periodic table, equations, constants) is provided. Always confirm details with your teacher and the official course page in the spring, because exam logistics can change.

Section	Questions	Time	Share of score
I: Multiple choice	60 (discrete questions plus sets that share data or a stimulus)	90 minutes	50%
II: Free response	7 = 3 long (10 points each) + 4 short (4 points each)	105 minutes	50%

Timing is a skill. Multiple choice averages **90 seconds per question**. In Section II, the three long questions deserve roughly 17 minutes each and the short ones about 8 minutes each; that plan leaves about 20 minutes to plan, read carefully and check units and signs.

Unit Weighting

Unit	Title	Approx. share of the exam
1	Atomic Structure and Properties	7-9%
2	Compound Structure and Properties	7-9%
3	Properties of Substances and Mixtures	18-22%
4	Chemical Reactions	7-9%
5	Kinetics	7-9%
6	Thermochemistry	7-9%
7	Equilibrium	7-9%
8	Acids and Bases	11-15%
9	Thermodynamics and Electrochemistry	7-9%

These ranges are the published weightings for the multiple-choice section. Units 3 and 8 together carry about a third of it, so they get the most study time in both plans below. Do not assume the free-response questions follow the same split: any unit can appear in any long or short question, and many questions combine units (for example, equilibrium with acid-base ideas).

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The Six Science Practices

Practice	What it looks like on the exam
1. Models and Representations	Particle diagrams, Lewis diagrams, energy profiles, orbital or geometry sketches
2. Question and Method	Designing or critiquing a procedure; choosing glassware and measurements
3. Representing Data and Phenomena	Reading and drawing graphs and tables: titration curves, linearized kinetics plots, mass spectra, PES
4. Model Analysis	Using a model to predict or explain: Q versus K, collision model, VSEPR, Coulomb's law
5. Mathematical Routines	Calculations with correct setup, units and significant figures
6. Argumentation	Claim-evidence-reasoning written justifications

How Free-Response Points Are Earned

Chief Reader reports, which the exam's scoring leaders publish after each administration, show the same pattern year after year. Learn it and you can gain points without learning any new chemistry.

Long questions (10 points, several parts)

Points are spread across parts. The early, accessible parts (a molarity, an oxidation number, writing an equilibrium expression) are earned most often; sign, ratio and justification parts are earned least often.

Credit comes from a correct **setup with units**, a correct **sign**, and a short **claim, evidence, reasoning** justification. Never skip a part because a later part looks hard; parts are scored independently.

Short questions (4 points, three or four tight tasks)

Each task is narrow, so points are lost mostly through vague reasoning that restates the prompt or answers a different question.

Name the specific quantity or force and tie it to the observation: write "more gas-phase particles" rather than "more disorder," and "overcomes intermolecular forces" rather than "breaks bonds."

A bare number is risky: show the setup so partial credit is possible. Write a justification in three moves: (1) state the claim, (2) cite the specific evidence or quantity, (3) link it to the principle in one sentence.

Your Study Plan

Week	4-week plan (review)	Focus
1	Units 1, 2, 3	Moles, bonding, IMFs, gases, solutions, spectroscopy
2	Units 4, 5, 6	Reactions and titration, rate laws, calorimetry, Hess's law
3	Units 7, 8	Equilibrium, pH, buffers, titration curves
4	Unit 9, mixed test	Entropy, free energy, cells; timed practice and error log

Weeks	8-week plan (full course)	Focus
1	Unit 1 and Unit 2	Do all practice; sketch PES and Lewis diagrams from memory
2	Unit 3, first half	IMFs, solids, gas laws, KMT
3	Unit 3, second half	Solutions, separations, light, Beer-Lambert
4	Units 4 and 5	Net ionic equations, stoichiometry, kinetics
5	Units 6 and 7	Thermochemistry, K and Q
6	Unit 8	Acids, bases, buffers, titrations
7	Unit 9	Thermodynamics and electrochemistry
8	Mixed test and weak spots	Two timed Sections, then review the error log

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How to Use This Book

- 1 **Read Why This Matters**, then study Core Ideas with a pencil; redraw each diagram once.
- 2 **Cover the solution** of each worked example and try it first.
- 3 **Do the Practice set** under mild time pressure, then read every explanation, including those for items you got right.
- 4 **Keep an error log**: for each miss, write the cause (concept, setup, arithmetic, units, wording) and one fix.
- 5 **Rewrite** any justification you scored poorly using the Write It Like a 5 model.

Calculation Habits

- ◆ Write the **formula**, substitute **numbers with units**, then compute. Units that cancel are your error alarm.
- ◆ Convert first: mL to L, degrees C to K (add 273.15), kJ to J. Do not carry 22.4 L/mol outside STP.
- ◆ **Significant figures**: in multiplication and division keep the fewest sig figs; in addition and subtraction keep the fewest decimal places. Do not round mid-problem; round once at the end.
- ◆ For logarithms, the digits after the decimal point in a pH match the sig figs in the concentration.
- ◆ Check reasonableness: a molar mass of 0.5 g/mol or a negative concentration is a signal to recheck.

Quick sig-fig example

A student measures 25.00 mL of 0.1050 M acid. The moles are $0.02500 \text{ L} \times 0.1050 \text{ mol/L} = 2.625 \times 10^{-3} \text{ mol}$. Both factors have four sig figs, so four are kept. Exact counts and conversions such as 1000 mL per L never limit sig figs.

Practice

PRACTICE Start Here Check

Show your work. A calculator is allowed. Justify conclusions.

1. An average multiple-choice question has about how much time under the 60-question, 90-minute Section I?
(A) 45 seconds (B) 90 seconds (C) 1.5 seconds
(D) 15 minutes
2. A student measures 25.00 mL of 0.1050 M NaOH. How many moles of NaOH is that, with the correct number of significant figures?
(A) $2.625 \times 10^{-3} \text{ mol}$ (B) $2.6 \times 10^{-3} \text{ mol}$ (C) $2.63 \times 10^{-3} \text{ mol}$
(D) $2.6250 \times 10^{-3} \text{ mol}$
3. A student dissolves 2.34 g of NaCl (molar mass 58.44 g/mol) in water and dilutes to a total volume of 250.0 mL.
(a) Calculate the molarity of the solution, with correct significant figures.
(b) Identify the glassware that should be used to make the final volume exactly 250.0 mL, and explain why a beaker is not suitable.
4. A student writes: "Ethanol boils at a higher temperature than ethane because the bonds in ethanol are stronger."
(a) Identify the error in this reasoning.
(b) Rewrite the explanation as a claim, evidence and reasoning.

Answers and Explanations

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PRACTICE · START HERE CHECK

1. B. B. 90 minutes is 5400 seconds, and 5400 s divided by 60 questions is 90 s. Choice C is 1.5 minutes written as seconds, and D mixes in the free-response pace.
2. A. A. Both measured factors have four significant figures (25.00 mL and 0.1050 M), so the product keeps four: $0.02500 \text{ L} \times 0.1050 \text{ mol/L} = 0.002625 \text{ mol}$. Choice B rounds to two, as if the volume were 25 mL.
3. (a) $2.34 \text{ g}/58.44 \text{ g/mol} = 0.04004 \text{ mol}$; $M = 0.04004 \text{ mol}/0.2500 \text{ L} = 0.160 \text{ M}$. The mass has three sig figs, so the answer has three. Setup with units and the mL to L conversion earn the credit. (b) A 250 mL volumetric flask: dissolve the solid in less water, transfer quantitatively (rinse the beaker into the flask), then dilute to the mark. A beaker's markings are only approximate, so the final volume would not be known to four significant figures.
4. (a) Boiling overcomes intermolecular forces between molecules; it does not break the covalent bonds within them, so bond strength is not the relevant quantity. (b) Claim: ethanol has the higher boiling point. Evidence: ethanol molecules contain an O-H group and form hydrogen bonds with each other, while ethane molecules (nonpolar) interact only through weaker London dispersion forces. Reasoning: stronger intermolecular forces require more thermal energy to move particles from liquid to gas, so ethanol must be heated to a higher temperature.

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Unit 1: Atomic Structure and Properties

Exam weighting: about 7-9% of the multiple-choice section. Concept review, worked examples, exam-style writing, and 10 practice items, all with full explanations.

1 Atomic Structure and Properties

Moles, mass spectra, composition, electron configuration, PES, and periodic trends, all explained with Coulomb's law and shown the way the exam asks for them.

Why This Matters

Unit 1 carries about 7-9% of the multiple-choice section, but its tools reappear everywhere: moles drive every later calculation, and Coulomb's law explains periodic trends, bonding and intermolecular forces. Students lose points by using the wrong molar mass, skipping the mole ratio in a formula, writing vague "extra shell" arguments, and misreading PES peak heights.

Core Ideas

Moles and Molar Mass

One mole is 6.022×10^{23} particles (Avogadro's number). The molar mass in g/mol is the sum of atomic masses in the formula, so mass, moles and particle count convert in a chain. The subscripts in a formula give particles per formula unit, e.g. one $\text{Ca}(\text{NO}_3)_2$ contains two nitrate ions and six oxygen atoms.

Mole conversions

$$n = \frac{m}{M} \text{ and } N = n \times 6.022 \times 10^{23} \text{ particles/mol.}$$

Always multiply by the subscript when counting a specific ion or atom.

Mass Spectra of Elements

A mass spectrum plots relative abundance against mass-to-charge ratio. Each peak is one isotope (same protons, different neutrons). The average atomic mass is the abundance-weighted mean: $\bar{m} = \sum f_i m_i$, where f_i is the fractional abundance. Because each element's value sits between its isotope masses, it is not a whole number.

Elemental Composition of Pure Substances

Mass percent of an element = (mass of the element in one mole of compound / molar mass) $\times$ 100. A pure compound has a fixed composition (law of definite proportions). The empirical formula is the simplest whole-number mole ratio; combustion analysis finds it by converting all C to CO_2 and all H to H_2O , then finding the remainder (often O) by subtraction. A molecular formula is a whole-number multiple: $M_{\text{molecular}} / M_{\text{empirical}}$.

Composition of Mixtures

In a mixture the components keep their identities and the proportions can vary. Mass percent of a component = (mass of component / total mass) $\times$ 100. Never convert the mass of a mixture straight to moles of one compound; first find the mass of that compound. Purity and percent composition problems are just this ratio, followed by the mole chain.

Atomic Structure and Electron Configuration

Electrons fill subshells in order of increasing energy: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p. Each orbital holds two electrons of opposite spin (Pauli), and degenerate orbitals fill singly first (Hund). Write the noble-gas shorthand, e.g. P is $[\text{Ne}]3s^23p^3$. Two ground-state exceptions: Cr is $[\text{Ar}]4s^13d^5$ and Cu is $[\text{Ar}]4s^13d^{10}$ (half-filled and filled d subshells are stable). Transition-metal cations lose the 4s electrons first, so Fe^{3+} is $[\text{Ar}]3d^5$. A species with unpaired electrons is paramagnetic.

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3 unpaired (Hund)

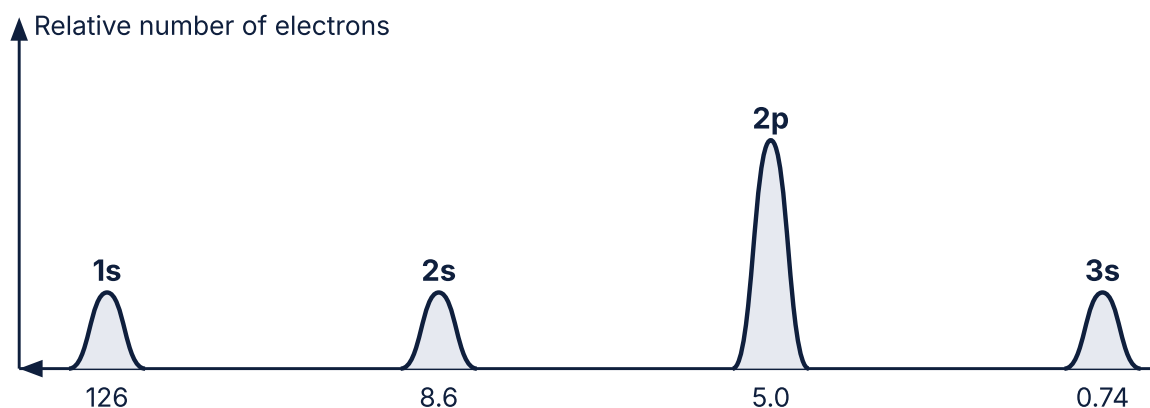


one pair, 2 unpaired

Orbital box diagrams for the 2p subshell. Degenerate orbitals fill singly with parallel spins before any orbital holds a pair.

Photoelectron Spectroscopy

In PES, photons of known energy eject electrons; the binding energy of each is the photon energy minus the electron's measured kinetic energy. Each peak is a subshell; **position** is the binding energy (closer to the nucleus and more charge means a higher energy), **height** is the number of electrons. Peaks for the same subshell sit at higher energy in elements of larger nuclear charge.



Binding energy (MJ/mol); axis not to scale, highest energy at left

PES of magnesium (peak positions are approximate): peak height shows the number of electrons in each subshell, so 2 : 2 : 6 : 2 gives 1s² 2s² 2p⁶ 3s².

Periodic Trends

Explain trends with Coulomb's law

Attraction between the nucleus and an electron grows with effective nuclear charge Z_{eff} and falls with distance (the occupied principal energy level) and with shielding by inner electrons: $F \propto q_1 q_2 / r^2$.

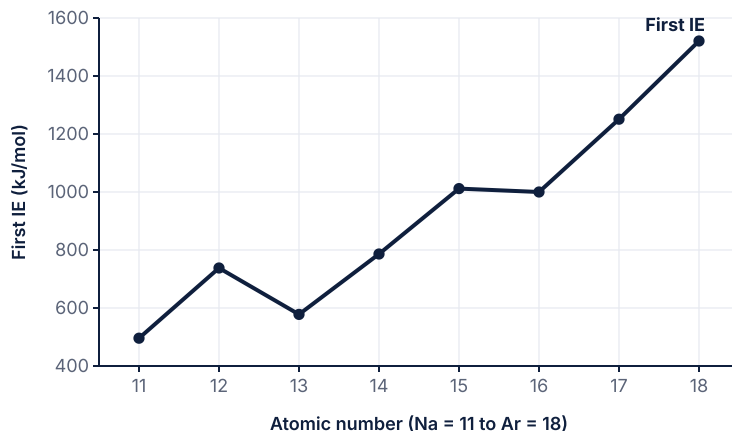
Across a period: same energy level, Z_{eff} rises, so radius falls and IE and electronegativity rise. Down a group: an additional occupied principal energy level means larger radius, lower IE.

Exceptions: IE drops from Be to B (the 2p electron is higher in energy and shielded by 2s) and from N to O (the paired 2p electron feels repulsion). Cations are smaller than their atoms; anions are larger. In an isoelectronic series, more protons means a smaller radius. A large jump in successive ionization energies marks the removal of a core electron, which reveals the number of valence electrons.

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First ionization energy across Period 3 (approximate). The dips at Al and S are the two exceptions to the general rise.

Valence Electrons and Ionic Compounds

Main-group valence electrons equal the group number (1, 2, 13 to 18 as 1, 2, 3 to 8). Metals with low IE lose them and nonmetals with high electron affinity gain them, forming ions that pack into a lattice held by electrostatic attraction. The formula is the lowest whole-number ratio that makes the compound neutral, such as Mg^{2+} with Cl^- giving MgCl_2 .

Worked Examples

EXAMPLE 1: MOLES, IONS AND MIXTURES

A fertilizer mixture has a mass of 10.0 g and contains 8.20 g of calcium nitrate, $\text{Ca}(\text{NO}_3)_2$, (molar mass 164.09 g/mol) plus inert filler. (a) How many nitrate ions are present? (b) What is the mass percent of nitrate ion in the mixture?

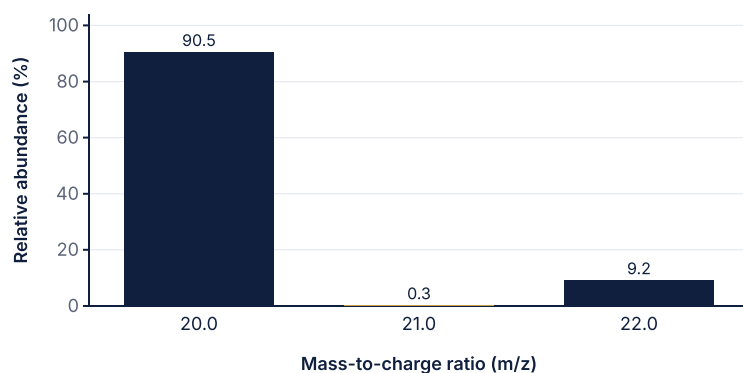
SOLUTION

(a) $n = 8.20/164.09 = 0.04997$ mol of the compound. Each formula unit has 2 nitrate ions: $0.04997 \times 2 \times 6.022 \times 10^{23} = 6.02 \times 10^{22}$ ions.

(b) Moles of nitrate = 0.09995 mol; mass = $0.09995 \times 62.00 = 6.197$ g. Mass percent = $6.197/10.0 \times 100 = 62.0\%$. (Using the 8.20 g alone would give the wrong denominator.)

EXAMPLE 2: MASS SPECTRUM

Calculate the average atomic mass of the element and identify it. Explain what differs among the three isotopes.



Mass spectrum of a gaseous element (all ions carry +1 charge).

SOLUTION

$\bar{m} = 0.905(19.99) + 0.003(20.99) + 0.092(21.99) = 18.09 + 0.063 + 2.023 = 20.18$ amu, matching neon.

The isotopes have the same number of protons (10) and electrons but 10, 11 and 12 neutrons. The average is closest to 20 because that isotope dominates the abundance.

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EXAMPLE 3: COMBUSTION ANALYSIS

Burning 1.000 g of a compound containing only C, H and O gives 1.466 g of CO_2 and 0.600 g of H_2O . The molar mass is 180.2 g/mol. Find the empirical and molecular formulas.

Element	Mass (g)	Moles	Ratio
C	$1.466 \times 12.011/44.009 = 0.4001$	0.03331	1
H	$0.600 \times 2.016/18.015 = 0.0671$	0.0666	2
O	$1.000 - 0.4001 - 0.0671 = 0.5328$	0.03330	1

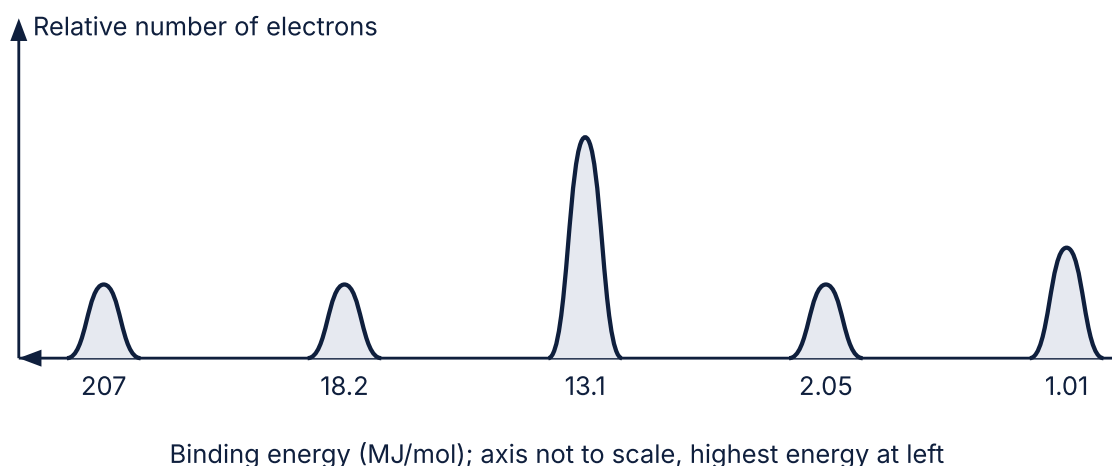
SOLUTION

The ratio C : H : O is 1 : 2 : 1, so the empirical formula is CH_2O (30.03 g/mol).

$180.2/30.03 = 6.00$, so the molecular formula is $\text{C}_6\text{H}_{12}\text{O}_6$.

EXAMPLE 4: READING PES

(a) Identify X and write its configuration. (b) Explain why the peak at 207 MJ/mol is at the highest energy. (c) Predict how the spectrum of sulfur differs.



PES of an unknown element X.

SOLUTION

(a) Heights 2 : 2 : 6 : 2 : 3 give $1s^2 2s^2 2p^6 3s^2 3p^3$ (15 electrons), so X is phosphorus.

(b) The 1s electrons are in the lowest principal energy level, closest to the nucleus and least shielded, so Coulomb attraction is greatest and the most energy is needed to remove them.

(c) Sulfur has one more proton and one more electron: the five peaks appear at slightly higher energies (larger Z_{eff}) and the last peak, 3p, has relative height 4 instead of 3.

Write It Like a 5**Model Response**

Prompt: The first ionization energy of aluminum (578 kJ/mol) is lower than that of magnesium (738 kJ/mol). Explain.

Response: Aluminum's outermost electron is in a 3p subshell, while magnesium's is in 3s. The 3p electron is, on average, farther from the nucleus and is shielded by the 3s electrons, so even though aluminum has a larger nuclear charge, the Coulombic attraction on that electron is weaker and less energy is needed to remove it.

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What the grader looks for

(1) Names the correct subshells for each outermost electron. (2) Compares distance and shielding, not just "stability". (3) Links to Coulomb's law, and states the direction of the comparison clearly.

Coach's Playbook

- ◆ Write molar masses to two decimals and show each unit on every line.
- ◆ Say "an additional occupied principal energy level" instead of "an extra shell."
- ◆ For PES: count peaks (subshells), read heights (electrons), then read positions (energy).
- ◆ Draw an orbital box diagram before deciding paramagnetic or diamagnetic.

Common traps

(1) Using the wrong molar mass or forgetting a mole ratio from subscripts. (2) Treating a mixture's total mass as the mass of one compound. (3) Removing 3d electrons before 4s when forming a transition-metal ion. (4) Explaining radius or IE with shells but no Coulomb's law, or mixing up peak height and position in PES.

Quick Check

1) How many oxygen atoms are in 0.50 mol of $\text{Ca}(\text{NO}_3)_2$? (A: $0.50 \times 6 \times 6.022 \times 10^{23} = 1.8 \times 10^{24}$.) 2) Which has the larger radius, S^{2-} or Cl^- ? (A: sulfide, fewer protons for the same 18 electrons.) 3) What does a PES peak height show? (A: the relative number of electrons in that subshell.)

Challenge Corner

A 4.00 g sample of a mixture of NaCl (58.44 g/mol) and an inert solid contains 0.0210 mol of chloride ion. **Find the mass percent of NaCl.** Mass of NaCl = $0.0210 \times 58.44 = 1.227$ g; mass percent = $1.227/4.00 \times 100 = 30.7\%$.

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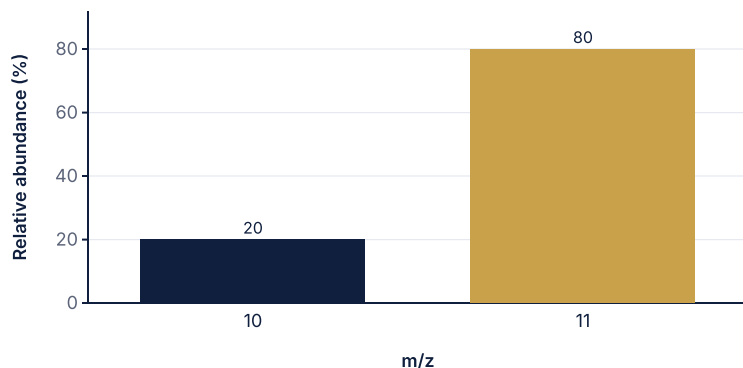
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Practice

PRACTICE Unit 1 Practice

Show your work. A calculator is allowed. Justify conclusions.

- Which 10.0 g sample contains the greatest number of oxygen atoms?
 (A) H_2O (B) CO_2 (C) O_2 (D) SO_2
- What is the average atomic mass of an element whose mass spectrum shows 20% at $m/z = 10$ and 80% at $m/z = 11$?



Mass spectrum of a boron-like element.

- What is the ground-state electron configuration of Fe^{3+} ?
 (A) $[\text{Ar}] 3d^5$ (B) $[\text{Ar}] 4s^2 3d^3$ (C) $[\text{Ar}] 4s^1 3d^4$ (D) $[\text{Ar}] 3d^6$
- A PES of element Z shows five peaks with relative heights 2 : 2 : 6 : 2 : 1. Which element is Z?

Binding energy (MJ/mol)	150	11.4	7.1	1.1	0.58
Relative peak height	2	2	6	2	1

- (A) Mg (B) B (C) Si (D) Al
- The first ionization energy of sulfur is slightly lower than that of phosphorus. Which statement best explains this?
 (A) S has a larger atomic radius than P
 (B) S has a smaller nuclear charge than P
 (C) Repulsion between the two electrons in one 3p orbital of S makes one easier to remove
 (D) S has more shielding electrons than P
- Which species has the largest radius?
 (A) F^- (B) Na^+ (C) Mg^{2+} (D) O^{2-}
- A mass spectrum of copper shows 69.2% at 62.93 amu and 30.8% at 64.93 amu.
 (a) Calculate the average atomic mass, with correct significant figures.
 (b) Explain, in terms of subatomic particles, why the spectrum has two peaks.
 (c) Explain why the average atomic mass is not a whole number.
- A student heats 2.456 g of hydrated magnesium sulfate, $\text{MgSO}_4 \cdot x\text{H}_2\text{O}$, until its mass is constant at 1.200 g.
 (a) Calculate x.
 (b) Why must the student heat, cool and reweigh until two masses agree?
 (c) Predict the effect on x if the sample is not heated long enough, and justify.
- A student reports the successive ionization energies (kJ/mol) of element Q: $\text{IE}_1 = 738$, $\text{IE}_2 = 1451$, $\text{IE}_3 = 7733$, $\text{IE}_4 = 10540$.
 (a) State how many valence electrons Q has and justify your answer.
 (b) Identify the group of Q and give the formula of its oxide.
 (c) Explain why IE_1 of Q is greater than that of the element just below it in the same group.

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10. (a) Write the full ground-state electron configuration of the chloride ion.
(b) Sketch (describe peaks and relative heights) the PES of a chlorine atom, from highest to lowest binding energy.
(c) Justify why the radius of Cl^- is greater than that of a Cl atom.
(d) Is the Cl atom paramagnetic? Justify.

Answers Unit 1: Answers and Explanations

Read every explanation, including the ones for problems you answered correctly.

1 Atomic Structure and Properties

PRACTICE · UNIT 1 PRACTICE

1. C. Moles of O atoms: O_2 0.625, H_2O 0.555, CO_2 0.454, SO_2 0.312. Water is tempting because it has the smallest molar mass of the compounds, but each molecule has only one O while each O_2 molecule has two and a lower molar mass than CO_2 and SO_2 .
2. B. $0.20(10) + 0.80(11) = 10.8$. The value 10.5 is the unweighted mean of 10 and 11, and 10.2 reverses the abundances.
3. A. Iron is $[\text{Ar}]4s^23d^6$. A transition-metal cation loses 4s electrons first, then 3d, so removing three electrons gives $3d^5$. The $4s^23d^3$ option wrongly removes 3d electrons first, and $3d^6$ removes only two electrons.
4. D. Heights give $1s^22s^22p^63s^23p^1$, 13 electrons: aluminum. Mg stops at 3s2 (12 electrons); Si would show 3p2.
5. C. P is $3p^3$ (all singly occupied); S is $3p^4$ with one doubly occupied orbital, so the paired electron feels extra repulsion. S does not have a larger radius or a smaller nuclear charge; it has 16 protons versus 15.
6. D. All four have 10 electrons (isoelectronic), so the one with the fewest protons (8) has the weakest pull per electron and the largest radius. Students often choose Mg^{2+} because Mg atoms are large.
7. (a) $0.692(62.93) + 0.308(64.93) = 43.55 + 20.00 = 63.55$ amu. (b) Two isotopes exist: both have 29 protons, but they have different numbers of neutrons (34 and 36), so their masses differ. (c) The value is a weighted average of isotope masses with fractional abundances, so it lies between 62.93 and 64.93 and does not equal either one.
8. (a) Water lost = $2.456 - 1.200 = 1.256$ g; $1.256/18.015 = 0.06972$ mol. MgSO_4 : $1.200/120.37 = 0.009970$ mol. $x = 0.06972/0.009970 = 6.99 \approx 7$. (b) A constant mass shows all water has left; if the mass were still falling, some water would remain. (c) x would be too small: undried water stays in the residue, so the measured mass lost and the calculated moles of water are smaller while the residue mass is too large.
9. (a) Two. The large jump between IE2 (1451) and IE3 (7733) shows the third electron is removed from a lower principal energy level (core), which is closer to the nucleus and unshielded by the two valence electrons, so it is held much more strongly. (b) Group 2; the ion is Q^{2+} and the oxide is QO (Q is magnesium). (c) The element below has an additional occupied principal energy level, so its valence electrons are farther from the nucleus and more shielded; Coulomb attraction is smaller, so less energy is needed for IE1.
10. (a) $1s^22s^22p^63s^23p^6$ (18 electrons). (b) Five peaks: 1s (height 2), 2s (2), 2p (6), 3s (2) and 3p (5), in order of decreasing binding energy; 1s is at the far left. (c) The anion has the same nuclear charge (17 protons) but one more electron, so electron-electron repulsion increases and the same nuclear attraction is shared among more electrons, so the electron cloud expands. (d) Yes: $3p^5$ has one unpaired electron, so the atom is paramagnetic.

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Unit 2: Compound Structure and Properties

Exam weighting: about 7-9% of the multiple-choice section. Concept review, worked examples, exam-style writing, and 10 practice items, all with full explanations.

2 Compound Structure and Properties

Bond types, potential energy curves, ionic and metallic structure, Lewis diagrams, resonance, formal charge, VSEPR and hybridization, explained with Coulomb's law.

Why This Matters

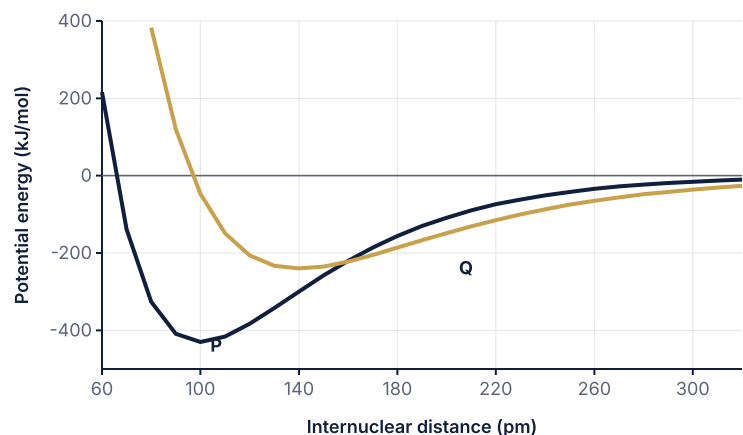
Unit 2 is about 7-9% of the multiple-choice section and feeds Unit 3 (geometry decides polarity, polarity decides intermolecular forces). The exam asks you to draw Lewis diagrams with the right electron count, to count electron domains, and to justify properties of ionic, metallic and covalent substances. Most lost points come from mixing up electron geometry with molecular geometry and from arguing with bond strength when the question is about intermolecular forces.

Core Ideas

Types of Chemical Bonds

Bonding is a continuum set by the difference in electronegativity (ΔEN). Nonmetal pairs with ΔEN near 0 form nonpolar covalent bonds (shared electrons); intermediate differences form polar covalent bonds with partial charges (δ^+ , δ^-) toward the more electronegative atom; a metal with a nonmetal (large ΔEN) forms ionic bonds. Metals bond metallically: cations in a sea of delocalized valence electrons.

Intramolecular Force and Potential Energy



Potential energy of two bonded atoms versus separation. The minimum gives the bond length; the depth below zero gives the bond energy (P: 100 pm, 430 kJ/mol; Q: 140 pm, 240 kJ/mol).

At large separation there is little interaction. As atoms approach, attraction (nucleus to the other atom's electrons) lowers the energy; at very short distance, nucleus-nucleus and electron-electron repulsion raises it steeply. The minimum is the bond length and its depth is the bond energy. Multiple bonds between the same atoms (higher bond order) are shorter and stronger. Coulomb's law connects this to charge and distance.

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Structure of Ionic Solids

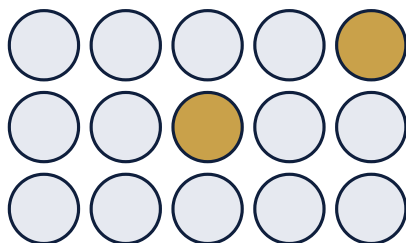
Lattice energy and Coulomb's law

The strength of ionic attraction scales as q_1q_2/r for energy ($1/r^2$ for force), where r is the distance between ion centers.

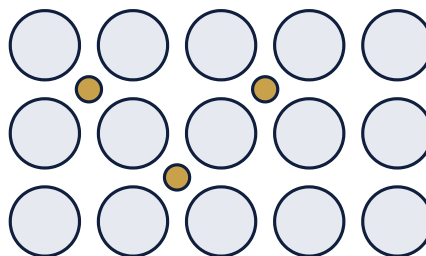
Greater ion charge and smaller ion radii give a stronger lattice: higher melting point and hardness. Ionic solids are brittle (shifting layers brings like charges together), do not conduct as solids, and conduct when molten or dissolved because ions can move.

Structure of Metals and Alloys

Metals conduct and are malleable and ductile because the delocalized electrons move freely and layers of cations can slide without breaking bonds. Alloys are mixtures of metals (or a metal with a small nonmetal). Atoms of similar radius form **substitutional** alloys (brass); a much smaller atom fits in holes to form an **interstitial** alloy (steel with carbon), which usually is harder because the layers cannot slide as easily.



Substitutional: similar radii



Interstitial: small atoms in gaps

Alloy structures. Substitutional alloys replace host atoms with atoms of similar radius; interstitial alloys place much smaller atoms in the holes.

Lewis Diagrams

- 1 Count valence electrons (add one per negative charge, subtract one per positive charge).
- 2 Connect atoms with single bonds, using the least electronegative atom (not H) as the center.
- 3 Complete octets on outer atoms, then place leftovers on the center.
- 4 Make double or triple bonds from lone pairs until the center has an octet.

Exceptions: H holds 2; Be and B can have fewer than 8; period-3 and larger central atoms may have more than 8; odd-electron species have an unpaired electron (not a lone pair).

Resonance and Formal Charge

Formal charge

$FC = V - N - B$, where V = valence electrons, N = nonbonding electrons, B = number of bonds (shared electrons / 2).

The best Lewis structure has formal charges closest to zero, with negative charge on the more electronegative atom. Resonance structures differ only in electron placement; the real structure is an average, with bond order = total bonds / number of equivalent positions.

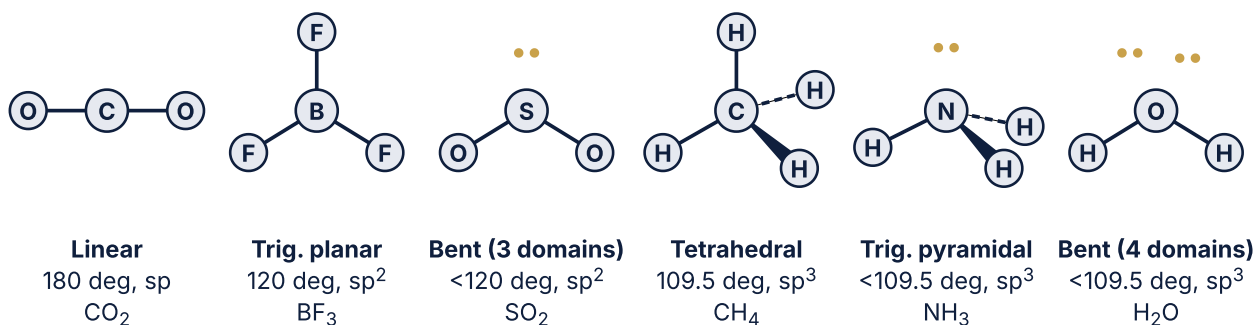
VSEPR and Hybridization

Electron domains (bonds, lone pairs and each multiple bond count as one) repel and arrange themselves as far apart as possible; the **electron geometry** counts all domains, while the **molecular geometry** names only the atoms. Hybridization follows the domain count: 2 is sp , 3 is sp^2 and 4 is sp^3 . A double bond is one sigma and one pi bond; a triple is one sigma and two pi. Lone pairs repel more than bonding pairs, so bond angles shrink. A molecule is polar only if it has polar bonds and an asymmetric shape; bond angle differences come from lone pairs, not polarity.

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Molecular geometries for 2, 3 and 4 electron domains. Solid wedge: toward viewer; dashed: away; gold dots: lone pairs.

Domains	Lone pairs	Molecular shape	Angle	Hybrid	Example
2	0	Linear	180	sp	CO ₂
3	0	Trigonal planar	120	sp ²	BF ₃
3	1	Bent	<120	sp ²	SO ₂
4	0	Tetrahedral	109.5	sp ³	CH ₄
4	1	Trigonal pyramidal	<109.5	sp ³	NH ₃
4	2	Bent	<109.5	sp ³	H ₂ O

Species with five or six domains (expanded octets) also occur; confirm with your teacher whether your course tests them.

Worked Examples

EXAMPLE 1: BOND TYPE FROM ELECTRONEGATIVITY

Using the electronegativities given, classify each bond and state which atom carries the partial negative charge.

Bond	Electronegativities	Delta EN	Type
Na-Cl	0.93 and 3.16	2.23	Ionic
O-H	3.44 and 2.20	1.24	Polar covalent, O is δ ⁻
C-H	2.55 and 2.20	0.35	Nearly nonpolar covalent
Cl-Cl	3.16 and 3.16	0.00	Nonpolar covalent

SOLUTION

Subtract the values for each pair and compare with the continuum above; the larger the difference, the greater the charge separation.

Na-Cl is the metal-nonmetal pair, so electrons are transferred (ionic). Among covalent bonds, O-H is the most polar and O is the negative end.

EXAMPLE 2: RESONANCE AND FORMAL CHARGE

Draw the Lewis diagram for NO₃⁻, assign formal charges, and find the N-O bond order.

SOLUTION

Valence electrons: 5 + 3(6) + 1 = 24. Place N in the center with three O atoms; use one N=O double bond and two N-O single bonds, with lone pairs to give every atom an octet.

Formal charges: N is 5 - 0 - 4 = +1; the double-bonded O is 6 - 4 - 2 = 0; each single-bonded O is 6 - 6 - 1 = -1. The total is +1 + 0 - 1 - 1 = -1, matching the ion.

The double bond can be placed on any of the three O atoms (three resonance structures). Bond order = 4 bonds / 3 positions = 1.33, so each N-O bond is identical and between single and double in length.

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EXAMPLE 3: VSEPR AND HYBRIDIZATION

For PCl_3 and CH_2O (C is central), give the electron domains, molecular geometry, hybridization and polarity.

SOLUTION

PCl_3 : $5 + 21 = 26$ electrons; P has three bonds and one lone pair, so 4 domains: electron geometry tetrahedral, molecular geometry **trigonal pyramidal**, sp^3 . Polar bonds do not cancel because the lone pair makes the shape asymmetric, so the molecule is polar.

CH_2O : $4 + 2 + 6 = 12$ electrons; C has two C-H bonds and a C=O double bond, which counts as one domain, so 3 domains: **trigonal planar**, sp^2 , about 120 degrees. The C=O has one sigma and one pi bond. The molecule is polar (C=O is polar, the shape is not symmetric).

EXAMPLE 4: COULOMB'S LAW AND LATTICE ENERGY

Compare the attraction between ions in MgO and NaF using the radii given, and justify which has the higher melting point.

Ion	Charge	Radius (pm)
Mg^{2+}	+2	72
O^{2-}	-2	140
Na^+	+1	102
F^-	-1	133

SOLUTION

Distances: MgO $72 + 140 = 212$ pm; NaF $102 + 133 = 235$ pm.

Relative energy $\propto (q_1 q_2)/r$: MgO $4/212 = 0.0189$; NaF $1/235 = 0.00426$; the ratio is **4.43**.

MgO has the stronger lattice: it has doubly charged ions (four times the charge product) and a smaller distance, so more energy is needed to separate the ions and its melting point is higher.

Write It Like a 5**Model Response**

Prompt: Explain why the bond angle in NH_3 (107 degrees) is smaller than in CH_4 (109.5 degrees). **Response:** Both central atoms have four electron domains, so the electron geometry is tetrahedral. In CH_4 all four domains are bonding pairs. In NH_3 one domain is a lone pair, which occupies more space near the nucleus and repels the bonding pairs more strongly than they repel each other, pushing the N-H bonds closer together and reducing the angle.

What the grader looks for

(1) Counts four domains for both. (2) Identifies the lone pair as the difference. (3) States that lone-pair repulsion is greater than bonding-pair repulsion. (4) Does not cite polarity or electronegativity as the cause of the angle.

Coach's Playbook

- ◆ Always compute total valence electrons first and check your final diagram uses exactly that many.
- ◆ Count a double or triple bond as one electron domain.
- ◆ Answer what is asked: electron geometry, molecular geometry, hybridization and bond angle are four different answers.
- ◆ For ionic comparisons, write charges and distances; for covalent bonds, discuss bond order and length.

Common traps

(1) Wrong electron count, such as adding an electron to form a cation (a cation has fewer). (2) Confusing an unpaired electron with a lone pair. (3) Counting three domains instead of four on atoms with a lone pair, which gives the wrong hybridization. (4) Giving bond angle or hybridization when molecular geometry was asked, and the reverse.

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Quick Check

1) Hybridization of C in CO_2 ? (A: two domains, sp .) 2) Formal charge of N in NH_4^+ ? (A: $5 - 0 - 4 = +1$.) 3) Why is brass harder than pure copper? (A: Zn atoms of different size disturb the layers so they slide less easily.)

Challenge Corner

The NO_2^+ ion has 16 valence electrons. **Give its Lewis structure, geometry and hybridization.** N is central with two $\text{N}=\text{O}$ double bonds and no lone pair on N: $[\text{O}=\text{N}=\text{O}]^+$. Formal charges: N is $5 - 0 - 4 = +1$, each O is $6 - 4 - 2 = 0$. Two domains give a **linear** shape and sp hybridization, 180 degrees.

Practice

PRACTICE Unit 2 Practice

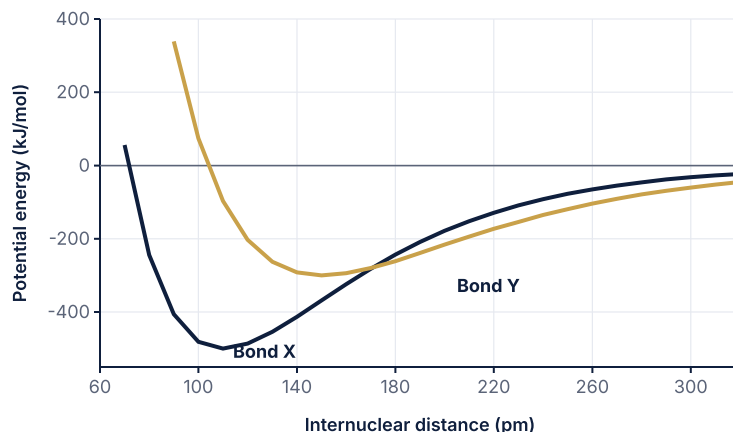
Show your work. A calculator is allowed. Justify conclusions.

1. Using the electronegativity values in the table, which bond is the most polar?

Element	H	C	N	O	S
Electronegativity	2.20	2.55	3.04	3.44	2.58

(A) C-H (B) N-H (C) O-H (D) S-H

2. The graph shows potential energy versus internuclear distance for two bonds. Which statement is correct?



- (A) Bond X is shorter and has the greater bond energy
 (B) Bond Y is shorter and has the greater bond energy
 (C) Bond X is longer and has the lesser bond energy
 (D) Bond Y is shorter and has the lesser bond energy
3. How many valence electrons must appear in the Lewis diagram of the sulfite ion, SO_3^{2-} ?
 (A) 24 (B) 28 (C) 18 (D) 26
4. Which pairing of molecular geometry and central-atom hybridization is correct for H_2O ?
 (A) Linear, sp (B) Bent, sp^3 (C) Bent, sp^2
 (D) Tetrahedral, sp^3
5. Alloy 1 is made from Cu atoms (radius 128 pm) and Zn atoms (134 pm). Alloy 2 is made from Fe atoms (126 pm) and C atoms (77 pm). Which classification is correct?
 (A) Alloy 1 is interstitial and Alloy 2 is substitutional
 (B) Both alloys are substitutional
 (C) Alloy 1 is substitutional and Alloy 2 is interstitial
 (D) Both alloys are interstitial

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6. Which compound is expected to have the largest lattice energy magnitude? Ionic radii: Mg^{2+} 72 pm, O^{2-} 140 pm, Ca^{2+} 100 pm, S^{2-} 184 pm, Na^{+} 102 pm, Cl^{-} 181 pm.
- (A) MgO (B) CaS (C) NaCl (D) They are all equal
7. A student tests four unlabeled solids and records the data below.
- Solid A: melting point 801 degrees C; does not conduct as a solid; conducts when molten or dissolved; brittle; soluble in water.
- Solid B: 1085 degrees C; conducts as a solid and when molten; malleable; insoluble.
- Solid C: 1710 degrees C; does not conduct in any state; very hard; insoluble.
- Solid D: 43 degrees C; does not conduct; soft; dissolves in hexane.
- (a) Classify each as ionic, metallic, molecular or covalent network and justify with the evidence.
- (b) Design a two-step test that would distinguish solid A from a metal if the label fell off.
8. Consider the cyanate ion, OCN^{-} (atoms in the order O, C, N).
- (a) Draw two Lewis structures: one with an O-C single bond and a C-N triple bond, and one with two double bonds.
- (b) Calculate the formal charge on each atom in both structures.
- (c) Identify which structure contributes more and justify.
- (d) State the geometry and the hybridization of carbon.
9. Boron trifluoride, ammonia and methane are compared.
- (a) Give the molecular geometry, hybridization and bond angle of BF_3 , NH_3 and CH_4 .
- (b) Explain, in terms of electron domains, why the H-N-H angle (107 degrees) is smaller than the H-C-H angle (109.5 degrees).
- (c) Predict whether each molecule is polar and justify.
- (d) Explain why the H-O-H angle in water (104.5 degrees) is smaller than in ammonia.
10. MgO melts at about 2850 degrees C and NaF at about 990 degrees C. The ionic radii are Mg^{2+} 72 pm, O^{2-} 140 pm, Na^{+} 102 pm and F^{-} 133 pm.
- (a) Calculate the ratio of the Coulombic energy factor q_1q_2/r for MgO to that of NaF.
- (b) Use your result to explain the melting-point difference.
- (c) Sketch or describe how the potential energy curve for the Mg-O attraction compares with one for Na-F.

Answers Unit 2: Answers and Explanations

Read every explanation, including the ones for problems you answered correctly.

2 Compound Structure and Properties

PRACTICE · UNIT 2 PRACTICE

- C. Delta EN: C-H 0.35, N-H 0.84, O-H 1.24, S-H 0.38. The largest difference is O-H. N-H is a common wrong pick because N is highly electronegative, but oxygen is higher still.
- A. The minimum for X is at about 110 pm and 500 kJ/mol deep; Y's minimum is at 150 pm and about 300 kJ/mol deep. A shorter bond sits at the smaller distance, and a deeper well means more energy is required to break it.
- D. Sulfur contributes 6, three oxygen atoms contribute 18, and the 2- charge adds 2 more: $6 + 18 + 2 = 26$. Choosing 24 ignores the charge, and 28 adds four electrons for the charge instead of two.
- B. Oxygen has four electron domains (two bonds and two lone pairs), so it is sp^3 , and the two lone pairs make the molecular geometry bent. Tetrahedral is the electron geometry, not the molecular geometry.
- C. Cu and Zn have nearly equal radii, so Zn atoms replace Cu atoms in the lattice (substitutional). C atoms are much smaller than Fe atoms, so they fit in the holes (interstitial). Atomic mass is not the criterion.
- A. MgO has charge product 4 at 212 pm; CaS has the same charge product but a distance of 284 pm; NaCl has charge product 1 at 283 pm. The largest q_1q_2/r belongs to MgO.
- (a) A is ionic: high melting point, brittle, nonconductor as a solid but conducts when ions are free to move. B is metallic: conducts as a solid because of delocalized electrons and is malleable. C is covalent network: very high melting point, hard, no mobile charges. D is molecular: low melting point because only weak intermolecular forces hold molecules together, and it dissolves in a nonpolar solvent. (b) Test 1: measure conductivity of the solid; a metal conducts and A does not. Test 2: dissolve a sample in water and test conductivity; A forms a conducting solution of mobile ions, while a metal is insoluble. Each result is stated with the observation and its meaning.
- (a) Valence electrons: $6 + 4 + 5 + 1 = 16$. Structure 1: O with a single bond and three lone pairs, C triple-bonded to N, N with one lone pair. Structure 2: $\text{O}=\text{C}=\text{N}$ with two lone pairs on O and two on N. (b) Structure 1: $\text{O} = 6 - 6 - 1 = -1$, $\text{C} = 4 - 0 - 4 = 0$, $\text{N} = 5 - 2 - 3 = 0$. Structure 2: $\text{O} = 6 - 4 - 2 = 0$, $\text{C} = 0$, $\text{N} = 5 - 4 - 2 = -1$. (c) Structure 1 contributes more because the negative formal charge sits on O, the more electronegative atom. (d) Two electron domains on C: linear, sp .

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9. (a) BF_3 : trigonal planar, sp^2 , 120 degrees. NH_3 : trigonal pyramidal, sp^3 , about 107 degrees. CH_4 : tetrahedral, sp^3 , 109.5 degrees. (b) Both have four domains, but N has one lone pair; a lone pair repels bonding pairs more strongly than bonding pairs repel each other, squeezing the N-H bonds together. (c) BF_3 is nonpolar (symmetric, polar bond dipoles cancel); NH_3 is polar (pyramidal and asymmetric; the lone pair side is negative); CH_4 is nonpolar (symmetric tetrahedron with weakly polar bonds). (d) Oxygen has two lone pairs instead of one, so there is more lone-pair repulsion pushing the bonding pairs closer together.
10. (a) $r_{\text{MgO}} = 212 \text{ pm}$, $r_{\text{NaF}} = 235 \text{ pm}$. Ratio = $(2 \times 2/212)/(1 \times 1/235) = 4.43$. (b) The electrostatic attraction in MgO is about 4.4 times stronger because of the larger charges and the smaller interionic distance, so much more thermal energy is needed to disrupt the lattice and melt it. (c) The Mg-O well is deeper (more negative at its minimum) and its minimum is at a slightly shorter distance than for Na-F, indicating a stronger bond and shorter separation.

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Unit 3: Properties of Substances and Mixtures

Exam weighting: about 18-22% of the multiple-choice section. Concept review, worked examples, exam-style writing, and 10 practice items, all with full explanations.

3 Properties of Substances and Mixtures

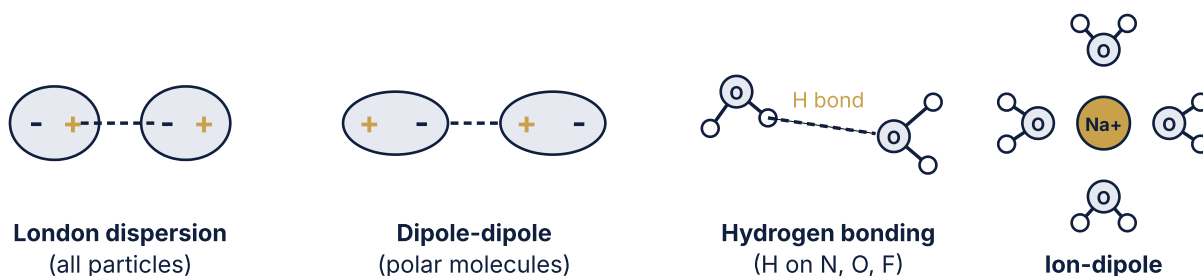
Intermolecular forces, solids, gas laws, kinetic molecular theory, solutions, separations, spectroscopy and the Beer-Lambert law, the heaviest unit on the exam.

Why This Matters

Unit 3 is the heaviest unit, about 18-22% of the multiple-choice section, and it shows up in nearly every free-response set. Students lose points by justifying with molar mass alone, saying boiling "breaks bonds," using 22.4 L/mol off STP, mixing Celsius and kelvin, and drawing solution diagrams whose ions are not separated.

Core Ideas

Intermolecular and Interparticle Forces



Intermolecular and interparticle forces (schematic). Water's O end, partly negative, points toward a cation.

For similar-sized molecules, strength increases roughly as London dispersion < dipole-dipole < hydrogen bonding < ion-dipole < ionic bonding. **London dispersion forces (LDF)** act between all particles; they grow with the number of electrons (polarizability) and surface contact. Dipole-dipole acts between polar molecules; hydrogen bonding needs H bonded to N, O or F and a lone pair on a neighboring N, O or F. Ion-dipole forces act between ions and polar molecules. Phase changes overcome intermolecular forces; they do not break covalent bonds.

Properties of Solids

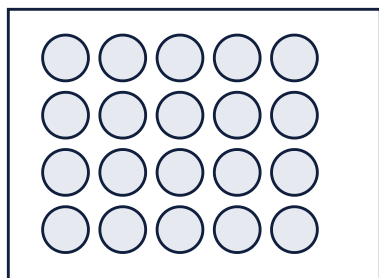
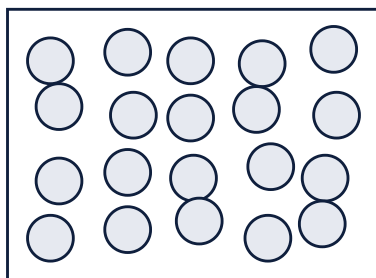
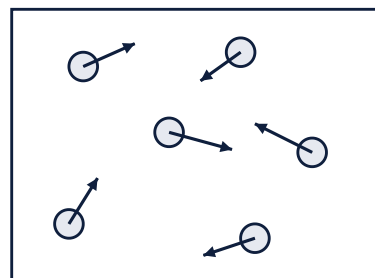
Type	Particles / forces	Melting point	Conducts?
Ionic	Ions, electrostatic	High	Only molten or dissolved
Metallic	Cations, delocalized electrons	Varies	Solid and liquid
Covalent network	Atoms, covalent bonds throughout (diamond, quartz)	Very high	No (graphite conducts)
Molecular	Molecules, IMFs	Low	No

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Solids, Liquids, and Gases

**Solid****Liquid****Gas**

Particle diagrams. Solid: fixed positions, touching. Liquid: touching but able to move past each other. Gas: far apart, moving fast (longer line = faster particle).

In solids and liquids the particles touch; in gases they are far apart, so a gas is easily compressed. At a given temperature, the stronger the IMFs, the lower the vapor pressure and the higher the boiling point; a liquid boils when its vapor pressure equals the external pressure.

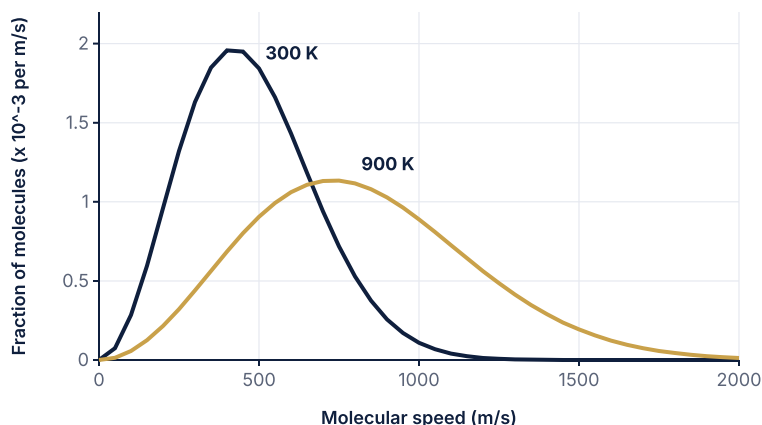
Ideal Gas Law

Gas equations

$PV = nRT$ with $R = 0.08206 \text{ L atm/(mol K)} = 8.314 \text{ J/(mol K)}$, T in kelvin ($K = ^\circ\text{C} + 273.15$). Density: $d = PM/RT$.

Dalton's law: $P_A = X_A P_{\text{total}}$, with $X_A = n_A/n_{\text{total}}$. For a fixed amount: $P_1 V_1/T_1 = P_2 V_2/T_2$. Use 22.4 L/mol only at exactly STP.

Kinetic Molecular Theory



Maxwell-Boltzmann distributions for the same gas (N_2 , 28.0 g/mol). Both areas are equal; the higher temperature curve is lower, broader, and shifted right.

KMT assumes point-like particles in random motion with no attractions and elastic collisions. Temperature is proportional to average kinetic energy, $KE_{\text{avg}} = \frac{3}{2}k_B T$, the same for all gases at the same temperature, so lighter molecules move faster: $u_{\text{rms}} = \sqrt{3RT/M}$ (M in kg/mol). Raising T moves the peak right, flattens the curve and keeps the area fixed. Pressure rises with T because particles hit the walls harder and more often.

Deviation from Ideal Gas Law

Real gases deviate at high pressure (particle volume is no longer negligible, so $PV/nRT > 1$) and low temperature (attractions pull molecules together and reduce pressure on the walls, so $PV/nRT < 1$). Small, nonpolar gases such as He and H_2 stay nearly ideal; large or polar molecules deviate more.

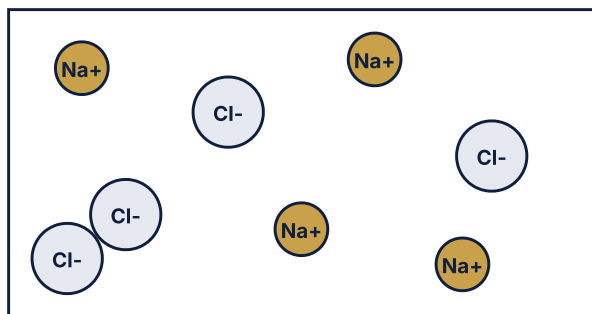
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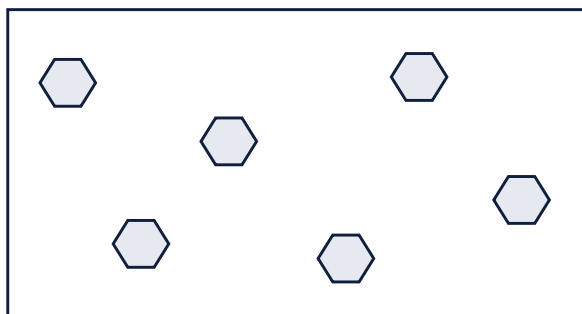
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Solutions and Mixtures

Molarity $M = n_{\text{solute}}/V_{\text{solution}}$ (liters of solution, not solvent). Dilution: $M_1V_1 = M_2V_2$. A solution is a homogeneous mixture; its particles do not settle or scatter much light. "Like dissolves like": polar and ionic solutes dissolve in polar water through ion-dipole or hydrogen bonding; nonpolar solutes dissolve in nonpolar solvents through dispersion forces. Quick solubility rules: salts of Group 1, ammonium, nitrate and acetate are soluble; most chlorides, bromides and iodides are soluble except Ag^+ , Pb^{2+} and Hg_2^{2+} ; most sulfates are soluble except Ba^{2+} and Pb^{2+} ; most hydroxides, carbonates, phosphates and sulfides are insoluble unless paired with Group 1 or ammonium.



NaCl(aq): separate ions



Glucose(aq): intact molecules

Particle representations of solutions (water molecules not drawn). The ionic solute separates into ions; the molecular solute stays as whole molecules.

Separation of Solutions and Mixtures

Filtration separates a solid from a liquid. Simple distillation separates miscible liquids with different boiling points: the lower-boiling liquid evaporates first and is condensed. Chromatography separates components by their different attractions to a stationary phase and a mobile phase; $R_f = d_{\text{spot}}/d_{\text{solvent front}}$. A compound with less attraction to the stationary phase and more to the mobile phase moves farther; say "moved less," never "did not move."

Spectroscopy, Photons, and the Beer-Lambert Law

Region	Wavelength (approx.)	Interaction with matter
Microwave	1 mm to 1 m	Molecular rotation
Infrared	700 nm to 1 mm	Bond vibration
Visible	400 to 700 nm	Valence electron transitions
Ultraviolet	10 to 400 nm	Valence electron transitions
X-ray	0.01 to 10 nm	Core electron ejection

Photons and absorbance

$E = h\nu$ and $c = \lambda\nu$, with $h = 6.626 \times 10^{-34} \text{ J s}$ and $c = 3.00 \times 10^8 \text{ m/s}$. Higher frequency means shorter wavelength and more energy per photon.

Beer-Lambert: $A = abc$ (a molar absorptivity, b path length, c concentration). A graph of A versus c at the wavelength of maximum absorbance is a straight line through the origin.

Worked Examples

EXAMPLE 1: MOLAR MASS FROM GAS DATA

A 1.22 g sample of a gas occupies 0.750 L at 1.00 atm and 27 degrees C. Find its molar mass and identify the gas from the options argon (39.95 g/mol), neon (20.18 g/mol) and krypton (83.80 g/mol).

SOLUTION

$T = 27 + 273 = 300. \text{ K}$ and $n = PV/RT = (1.00)(0.750)/(0.08206 \times 300.) = 0.03046 \text{ mol}$.

$M = m/n = 1.22 \text{ g}/0.03046 \text{ mol} = 40.0 \text{ g/mol}$, which is argon.

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EXAMPLE 2: MAXWELL-BOLTZMANN REASONING

Use the 300 K and 900 K curves for N₂ above. (a) Which curve is 900 K and why? (b) Compare the rms speeds. (c) Are there more fast molecules at the higher temperature?

SOLUTION

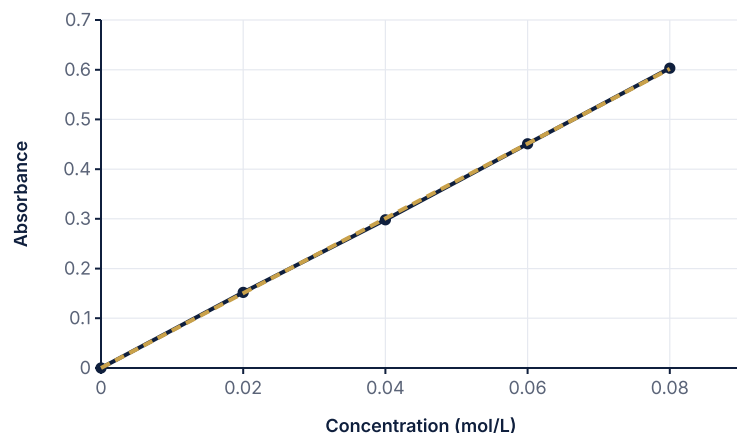
(a) The 900 K curve has the peak at higher speed, lower height and a broader spread. Its area is the same because the total number of molecules is fixed.

(b) $u_{\text{rms}} = \sqrt{3RT/M}$: at 300 K, $\sqrt{3(8.314)(300)/0.028013} = 517$ m/s; at 900 K, 895 m/s. The ratio is $\sqrt{3} = 1.73$.

(c) The fraction with speeds above 1500 m/s is much larger at 900 K because more molecules have the high kinetic energy in the tail.

EXAMPLE 3: BEER-LAMBERT CALIBRATION

Using the calibration line, find the concentration of an unknown whose absorbance is 0.375, and state the slope with units.



Calibration data at the wavelength of maximum absorbance, $b = 1.00$ cm. Dots are standards; the dashed line is the best fit through the origin.

SOLUTION

Best-fit slope through the origin: $\sum cA / \sum c^2 = 7.52$ L/mol, so $A = 7.52c$ and $ab = 7.52$ L/mol, which gives $a = 7.52$ L/(mol cm).

$c = 0.375/7.52 = 0.0499$ mol/L. The reading lies within the range of the standards, so interpolation is valid.

EXAMPLE 4: JUSTIFY A BOILING-POINT RANKING

Ethanol, dimethyl ether and propane have nearly equal molar masses (46, 46 and 44 g/mol). Their boiling points are 78 degrees C, -25 degrees C and -42 degrees C. Explain the order.

Substance	Formula	Polar?	Strongest IMF	bp (degrees C)
Ethanol	CH ₃ CH ₂ OH	Yes	Hydrogen bonding	78
Dimethyl ether	CH ₃ OCH ₃	Yes	Dipole-dipole	-25
Propane	C ₃ H ₈	No	London dispersion	-42

SOLUTION

Because the molar masses (and so dispersion forces) are nearly equal, the difference must come from other forces.

Ethanol has an O-H bond, so its molecules hydrogen-bond; this is the strongest attraction and requires the most energy to overcome. Dimethyl ether has polar C-O bonds but no H on O, so only dipole-dipole forces act. Propane is nonpolar, with only dispersion forces. Vaporization overcomes these intermolecular forces, not the covalent bonds.

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Model Response

Prompt: At 300 K and 200 atm a sample of ammonia gas shows $PV/nRT = 0.78$, while helium under the same conditions shows 1.10. Explain both. **Response:** At high pressure the molecules are close together. Ammonia molecules are polar and hydrogen-bond, so attractions between them reduce the force of collisions with the walls and the measured pressure is less than ideal, giving a ratio below 1. Helium atoms have almost no attraction, so the dominant deviation is the volume of the atoms themselves, which leaves less free volume; the pressure is greater than ideal and the ratio is above 1.

What the grader looks for

(1) Names the intermolecular force for each gas. (2) Connects attraction to lower wall pressure and finite particle volume to higher pressure. (3) Links each effect to the direction of the ratio. (4) Uses particle-level language, not just "nonideal."

Coach's Playbook

- 1 Convert units first: mL to L, degrees C to K, kJ to J.
- 2 Pick the correct equation: ideal gas, dilution, Dalton or Beer-Lambert.
- 3 Identify the IMFs in every substance named, before comparing.
- 4 Check that a particle diagram preserves the number of particles.

Common traps

(1) Using 22.4 L/mol when conditions are not STP, or Celsius in $PV = nRT$. (2) Justifying a boiling point with only molar mass or with "stronger bonds". (3) Writing dipole-dipole where ion-dipole applies. (4) Assuming a higher boiling point means higher vapor pressure; at a given temperature it is the opposite.

Quick Check

1) A mixture has 0.60 mol He and 0.40 mol Ne at 2.0 atm total. P_{He} ? (A: $0.60 \times 2.0 = 1.2$ atm.) 2) Which has greater u_{rms} at 300 K, He or Ar? (A: He, smaller M.) 3) Which photon has more energy, 400 nm or 700 nm? (A: 400 nm.)

Challenge Corner

A 5.00 L tank holds 3.00 mol of gas at 25 degrees C. **Find the pressure and the new pressure if heated to 100 degrees C.** $P = nRT/V = (3.00)(0.08206)(298.15)/5.00 = 14.7$ atm. At 373.15 K, $P = 18.4$ atm (volume and moles are fixed, so $P \propto T$).

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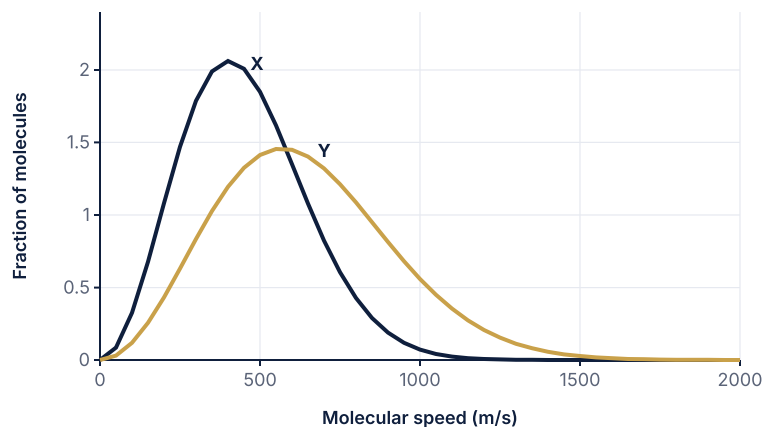
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Practice

PRACTICE Unit 3 Practice

Show your work. A calculator is allowed. Justify conclusions.

- Which statement best explains why HF (boiling point 20 degrees C) boils at a higher temperature than HCl (-85 degrees C)?
(A) HF has a greater molar mass than HCl
(B) Hydrogen bonds form between HF molecules but not between HCl molecules
(C) The H-F covalent bond is stronger than the H-Cl bond
(D) HF has stronger London dispersion forces than HCl
- A rigid 4.00 L vessel contains 0.200 mol of gas at 350 K. What is the pressure? ($R = 0.08206 \text{ L atm/(mol K)}$)
(A) 1.44 atm (B) 5.74 atm (C) 0.316 atm (D) 0.696 atm
- The graph shows the speed distribution of the same gas at two temperatures. Which statement is correct?



- (A) Y is the higher temperature because it contains more molecules
(B) X is the higher temperature because its peak is taller
(C) Y is the lower temperature because its curve is broader
(D) Y is the higher temperature because its peak is at a greater speed and the areas under the curves are equal
- A 25.0 mL sample of 0.800 M NaCl is diluted with water to a final volume of 100.0 mL. What is the final concentration?
(A) 0.267 M (B) 0.200 M (C) 0.800 M (D) 3.20 M
- A solution in a 1.00 cm cuvette has absorbance 0.540. What is the absorbance of the same solution in a 2.00 cm cuvette?
(A) 0.270 (B) 0.540 (C) 1.08 (D) 2.16
- In paper chromatography, the paper is polar and the solvent is nonpolar. Which compound will have the largest R_f value?
(A) The nonpolar compound, which is attracted to the solvent more than to the paper
(B) The ionic compound, which is attracted to the paper
(C) The compound with the greatest molar mass
(D) The polar compound, which hydrogen bonds to the paper
- A student prepares 250.0 mL of 0.100 M copper(II) sulfate from solid $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (molar mass 249.69 g/mol).
 - Calculate the mass of solid required.
 - Describe the procedure, naming the glassware.
 - Describe how water molecules arrange themselves around a Cu^{2+} ion and name the force.
 - Explain why NaCl dissolves in water but not in hexane, whereas iodine (I_2) dissolves in hexane.
- A student measures the absorbance of four solutions of a colored compound at its wavelength of maximum absorbance in a 1.00 cm cuvette: 0.0200 M, $A = 0.152$; 0.0400 M, $A = 0.298$; 0.0600 M, $A = 0.451$; 0.0800 M, $A = 0.603$. An unknown has $A = 0.375$.
 - Determine the slope of the best-fit line through the origin, with units.
 - Calculate the concentration of the unknown.
 - Explain why the measurement is made at the wavelength of maximum absorbance.
 - Fingerprints are on the cuvette when the unknown is measured. Predict the effect on the calculated concentration.

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9. The ratio PV/nRT was measured at 300 K for two gases (fictional data).
 Gas X: 1.00 at 1 atm, 1.03 at 50 atm, 1.12 at 200 atm.
 Gas Y: 0.99 at 1 atm, 0.90 at 50 atm, 0.78 at 200 atm.
 (a) Which gas is more likely He and which is NH_3 ? Justify.
 (b) Explain, at the particle level, why the ratio for X rises above 1.
 (c) Explain why the ratio for Y falls below 1.
 (d) Predict the effect of raising the temperature of Y to 600 K at 200 atm and justify.
10. A green laser emits light of wavelength 532 nm.
 (a) Calculate the frequency.
 (b) Calculate the energy of one photon and the energy per mole of photons in kJ/mol.
 (c) A C-C bond requires about 350 kJ/mol to break. Could a 532 nm photon break it? Could a 250 nm photon?
 (d) An infrared photon of wavelength 10.0 micrometers is absorbed by a sample. How does its energy compare with the 532 nm photon, and what molecular motion is probed?

Answers Unit 3: Answers and Explanations

Read every explanation, including the ones for problems you answered correctly.

3 Properties of Substances and Mixtures

PRACTICE · UNIT 3 PRACTICE

1. B. HF has H bonded to the highly electronegative F and a lone pair on a neighboring F, so it forms hydrogen bonds. HCl is heavier (so dispersion forces are larger in HCl, not HF), and covalent bond strength is irrelevant because boiling does not break the H-F bond.
2. A. $P = nRT/V = (0.200)(0.08206)(350)/4.00 = 1.44$ atm. 5.74 atm forgets to divide by volume; 0.316 atm uses 77 degrees C instead of kelvin; 0.696 atm inverts the expression.
3. D. At higher temperature the average kinetic energy increases, so the peak shifts to greater speed and the curve broadens and flattens. The areas are equal because both curves represent the same number of molecules, so taller does not mean hotter.
4. B. $M_2 = M_1V_1/V_2 = (0.800)(25.0)/(100.0) = 0.200$ M. 0.267 M divides by the 75.0 mL of water added instead of the final volume; 3.20 M inverts the volume ratio.
5. C. $A = abc$ is proportional to path length, so doubling b doubles A to 1.08. Halving it is the inverse relationship; 2.16 would double twice.
6. A. Compounds that interact least with the stationary phase and most with the mobile phase travel farthest. The nonpolar compound has the weakest attraction to the polar paper, so it moves the greatest distance relative to the solvent front. Molar mass alone does not decide.
7. (a) $0.2500 \text{ L} \times 0.100 \text{ mol/L} = 0.0250 \text{ mol}$; $0.0250 \times 249.69 = 6.24 \text{ g}$. (b) Weigh 6.24 g on a balance, dissolve it in less than 250 mL of distilled water in a beaker, transfer quantitatively (rinsing the beaker into the flask) to a 250.0 mL volumetric flask, add water to the mark, stopper and invert to mix. (c) The partially negative O atoms of the water molecules point toward the Cu^{2+} ; the force is ion-dipole. (d) NaCl is ionic: ion-dipole attractions with water compensate for separating the ions, but hexane (nonpolar) offers only weak dispersion forces. I_2 is nonpolar, so dispersion forces between I_2 and hexane are comparable to those in the pure substances, and it dissolves.
8. (a) $\text{Slope} = \sum cA / \sum c^2 = 7.52 \text{ L/mol}$ (this equals ab ; with $b = 1.00 \text{ cm}$, $a = 7.52 \text{ L/(mol cm)}$). (b) $c = 0.375/7.52 = 0.0499 \text{ M}$. (c) At the maximum, absorbance is largest for a given concentration (greatest sensitivity) and changes least with small wavelength errors, so the calibration line is steeper and more precise. (d) Fingerprints scatter and absorb light, so the measured absorbance is falsely high, and the calculated concentration is too high.
9. (a) X is He (small, nonpolar, almost no attractions); Y is NH_3 (polar, hydrogen bonds). (b) At high pressure the atoms occupy a significant fraction of the container volume, so the free volume is less than V and the pressure is greater than the ideal value. (c) Attractions between molecules pull them together before they hit the wall, reducing the force of collisions and the measured pressure. (d) The ratio moves closer to 1 (rises): at 600 K the molecules have greater kinetic energy, which makes the attractions less important relative to motion.
10. (a) $\nu = c/\lambda = 3.00 \times 10^8/532 \times 10^{-9} = 5.64 \times 10^{14} \text{ Hz}$. (b) $E = h\nu = 6.626 \times 10^{-34} \times 5.64 \times 10^{14} = 3.74 \times 10^{-19} \text{ J per photon}$; times 6.022×10^{23} gives 225 kJ/mol. (c) 225 kJ/mol is less than 350 kJ/mol, so a single 532 nm photon cannot break the bond. At 250 nm, $E = 7.95 \times 10^{-19} \text{ J} = 479 \text{ kJ/mol}$, which is enough. (d) $E_{\text{IR}} = 1.99 \times 10^{-20} \text{ J}$, which is $532/10000 = \text{about } 1/19$ as large as the green photon. IR photons match the energy of bond vibrations.

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Unit 4: Chemical Reactions

Exam weighting: about 7-9% of the multiple-choice section. Concept review, worked examples, exam-style writing, and 10 practice items, all with full explanations.

4 Chemical Reactions

Master net ionic equations, stoichiometry with limiting reactants, titration, and redox: the quantitative core that every later chemistry unit builds on.

Why This Matters

Unit 4 is worth 7 to 9 percent of the multiple-choice section, but its skills (moles, mole ratios, net ionic equations, oxidation numbers) are used in nearly every free-response question about equilibrium, acids, and electrochemistry. Students lose points here by skipping a mole ratio, forgetting a coefficient, and writing molecular equations when a net ionic one is asked.

Core Ideas

4.1 Introduction to Reactions and 4.4 Physical and Chemical Changes

A **chemical change** forms new substances: atoms are rearranged, bonds break and form. A **physical change** (melting, dissolving a molecular solid, evaporating) leaves the same particles with only their arrangement or spacing altered. Evidence such as color change or gas formation suggests a chemical change; the proof is a new substance. Dissolving NaCl separates existing ions, so it is physical; burning magnesium makes MgO, so it is chemical.

4.2 Net Ionic Equations and 4.3 Representations of Reactions

Writing a net ionic equation

1. Write the balanced molecular equation with states.
2. Split strong electrolytes (soluble ionic compounds, strong acids and bases) into ions. Leave solids, liquids, gases, weak acids, weak bases, and molecular compounds whole.
3. Cancel spectator ions that appear unchanged on both sides.
4. Check that atoms and charge both balance.

Example: $\text{Pb}(\text{NO}_3)_2(\text{aq}) + 2\text{KI}(\text{aq}) \rightarrow \text{PbI}_2(\text{s}) + 2\text{KNO}_3(\text{aq})$ has net ionic equation $\text{Pb}^{2+}(\text{aq}) + 2\text{I}^{-}(\text{aq}) \rightarrow \text{PbI}_2(\text{s})$; K^{+} and NO_3^{-} are spectators. A reaction may be shown as an equation, a particle diagram, or a table of amounts, and all must conserve atoms. In particle diagrams, count particles, not their drawn size.

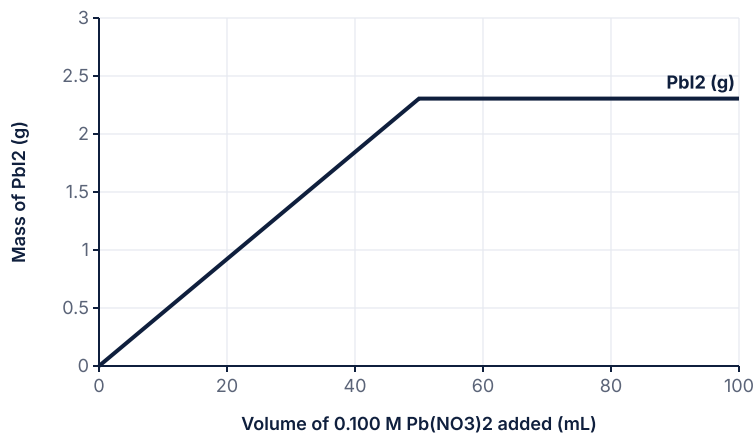
4.5 Stoichiometry

Coefficients give mole ratios, never mass ratios. The route is always grams, then moles (divide by molar mass), then the ratio from the balanced equation, then grams or liters. The **limiting reactant** is the one that would produce the least product; compare moles divided by coefficient. **Percent yield** is actual yield divided by theoretical yield, times 100.

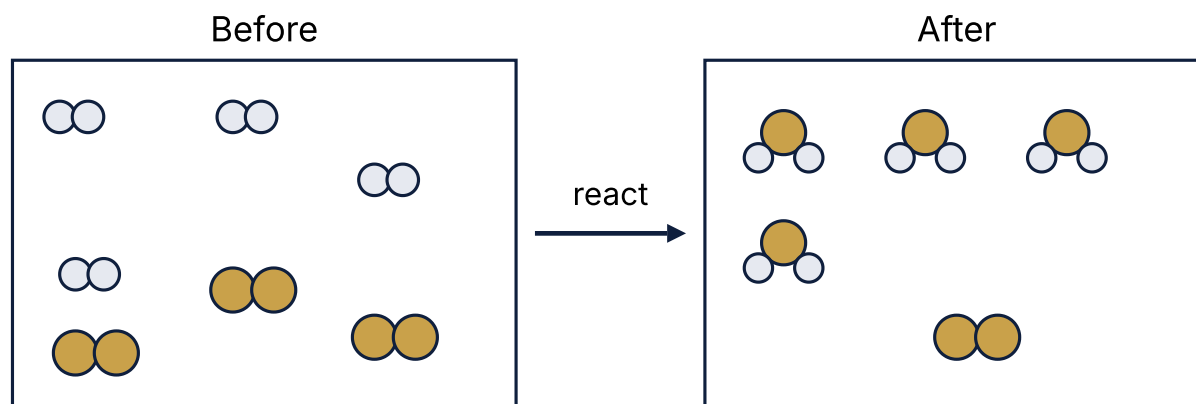
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A fixed 50.0 mL of 0.200 M KI is treated with increasing volumes of Pb(NO₃)₂. The plateau marks the point where I⁻ is used up.



Particle diagram (small circle = H, large = O): 4 H₂ + 3 O₂ gives 4 H₂O + 1 O₂. Hydrogen runs out first, so oxygen is in excess and some O₂ remains.

Stoichiometry checklist

Balance first. Convert mass to moles with the correct molar mass.

Limiting reactant: smaller value of (moles / coefficient).

Theoretical yield comes from the limiting reactant only.

Solutions: moles = molarity × volume in liters (mL/1000).

4.6 Introduction to Titration

A titration finds an unknown concentration by adding a solution of known concentration until the reaction is stoichiometrically complete (**equivalence point**). Use moles of titrant, then the mole ratio, then divide by the analyte volume only (not the total volume). For a diprotic acid with a strong base the ratio is 1 acid : 2 OH⁻.

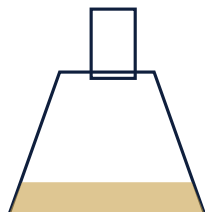
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Buret: NaOH of known molarity (titrant)
Read volume before and after



Flask: measured volume of acid (analyte)
plus indicator; swirl

Titration set-up. The equivalence point is where moles of titrant added match the stoichiometric requirement; the indicator color change (end point) approximates it.

4.7 Types of Chemical Reactions and 4.8 Introduction to Acid-Base Reactions

Type	Pattern	Quick test
Synthesis	$A + B \text{ gives } AB$	One product
Decomposition	$AB \text{ gives } A + B$	One reactant
Single replacement	$A + BC \text{ gives } AC + B$	Element + compound; redox
Double replacement	$AB + CD \text{ gives } AD + CB$	Precipitate, gas, or water forms
Combustion	$\text{fuel} + O_2 \text{ gives } CO_2 + H_2O$	Redox with oxygen

A Bronsted-Lowry acid-base reaction transfers H^+ from an acid to a base. Strong acid plus strong base gives $H^+ + OH^- \rightarrow H_2O$; a weak acid keeps its formula, for example $HC_2H_3O_2 + OH^- \rightarrow C_2H_3O_2^- + H_2O$.

4.9 Oxidation-Reduction (Redox) Reactions

Redox vocabulary

Oxidation = loss of electrons = oxidation number increases. Reduction = gain of electrons = oxidation number decreases.

The oxidizing agent is the species reduced; the reducing agent is the species oxidized.

Rules: free elements are 0; monatomic ions equal their charge; O is usually -2; H is usually +1; the sum equals the overall charge.

Balance redox equations by balancing atoms and also charge, so electrons lost equal electrons gained.

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Worked Examples

EXAMPLE 1: NET IONIC EQUATION AND PRECIPITATE MASS

50.0 mL of 0.100 M $\text{Pb}(\text{NO}_3)_2$ is added to excess KI. Write the net ionic equation and find the mass of PbI_2 (461.0 g/mol).

SOLUTION

Net ionic: $\text{Pb}^{2+}(\text{aq}) + 2\text{I}^{-}(\text{aq}) \rightarrow \text{PbI}_2(\text{s})$.

Moles $\text{Pb}^{2+} = 0.100 \text{ M} \times 0.0500 \text{ L} = 5.00\text{e-}3 \text{ mol}$; ratio 1:1, so $5.00\text{e-}3 \text{ mol PbI}_2$.

Mass = $5.00\text{e-}3 \text{ mol} \times 461.0 \text{ g/mol} = \mathbf{2.31 \text{ g}}$, which matches the plateau on the graph.

EXAMPLE 2: LIMITING REACTANT AND PERCENT YIELD

5.40 g of Al reacts with 10.0 g of Cl_2 by $2\text{Al} + 3\text{Cl}_2 \rightarrow 2\text{AlCl}_3$. The student collects 11.2 g of AlCl_3 (133.33 g/mol). Find the limiting reactant, the percent yield, and the Al left over (mass).

SOLUTION

Moles: $\text{Al} = 5.40/26.98 = 0.2002 \text{ mol}$; $\text{Cl}_2 = 10.0/70.90 = 0.1410 \text{ mol}$.

Moles/coefficient: $\text{Al } 0.2002/2 = 0.1001$; $\text{Cl}_2 \ 0.1410/3 = 0.0470$. Cl_2 is limiting.

Theoretical $\text{AlCl}_3 = 0.1410 \times (2/3) = 0.09402 \text{ mol} = 12.5 \text{ g}$.

Percent yield = $11.2/12.54 \times 100 = \mathbf{89.3\%}$.

Al used = 0.09402 mol , so $0.2001 - 0.0940 = 0.1061 \text{ mol} = \mathbf{2.86 \text{ g}}$ remains.

EXAMPLE 3: TITRATION OF A DIPROTIC ACID

A 25.00 mL sample of H_2SO_4 needs 31.42 mL of 0.1000 M NaOH to reach equivalence. Find the acid molarity.

SOLUTION

$\text{H}_2\text{SO}_4 + 2\text{NaOH} \rightarrow \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}$.

Moles NaOH = $0.1000 \times 0.03142 = 3.142\text{e-}3 \text{ mol}$.

Moles $\text{H}_2\text{SO}_4 = 3.142\text{e-}3 / 2 = 1.571\text{e-}3 \text{ mol}$ (the 1:2 ratio is the step most students skip).

Molarity = $1.571\text{e-}3 \text{ mol} / 0.02500 \text{ L} = \mathbf{0.06284 \text{ M}}$.

EXAMPLE 4: REDOX TITRATION

A 0.4000 g ore sample is dissolved and its Fe^{2+} titrated with 20.00 mL of 0.02000 M KMnO_4 : $\text{MnO}_4^{-} + 5\text{Fe}^{2+} + 8\text{H}^{+} \rightarrow \text{Mn}^{2+} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O}$. Identify the oxidizing agent and find the mass percent of iron.

SOLUTION

Mn goes from +7 to +2 (reduced), so MnO_4^{-} is the oxidizing agent; Fe goes from +2 to +3 (oxidized). Check charge: left $-1 + 10 + 8 = +17$; right $+2 + 15 = +17$.

Moles $\text{MnO}_4^{-} = 0.02000 \times 0.02000 = 4.000\text{e-}4 \text{ mol}$; moles $\text{Fe}^{2+} = 5 \times 4.000\text{e-}4 = 2.000\text{e-}3 \text{ mol}$.

Mass Fe = $2.000\text{e-}3 \times 55.85 = 0.1117 \text{ g}$; percent = $0.1117/0.4000 \times 100 = \mathbf{27.93\%}$.

Write It Like a 5

Model Response

Prompt: Aqueous Na_2CO_3 is mixed with aqueous CaCl_2 and a white solid forms. Write the net ionic equation and explain what happens to Na^{+} . Response: $\text{Ca}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \rightarrow \text{CaCO}_3(\text{s})$. The solid forms because the attraction between Ca^{2+} and CO_3^{2-} in the lattice is strong enough that these ions leave solution. Na^{+} and Cl^{-} are spectator ions: they stay dissolved, unchanged, and appear on both sides of the full ionic equation, so the amount of Na^{+} in solution does not change.

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What the grader looks for

Correct formula and charge for each species; states shown; spectators removed; atoms and charge balanced; a justification that names the ions and the solid, not just 'it precipitates'.

Coach's Playbook

- 1 Write the balanced equation before touching a calculator.
- 2 Turn every quantity into moles; keep units on each line.
- 3 Decide the limiting reactant by moles per coefficient.
- 4 For redox, write oxidation numbers under every atom that changes.
- 5 Report with correct significant figures and units.

Common traps

(1) Skipping a mole ratio such as 2 NaOH per H_2SO_4 . (2) Using total mixed volume rather than the analyte volume in titration. (3) Writing a weak acid as ions in a net ionic equation. (4) Giving a pure element such as Ag(s) an oxidation number of +1; it is 0.

Quick Check

Q1: Which species is the reducing agent in $\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}$? A: Zn (it is oxidized). Q2: Do coefficients give mass or mole ratios? A: Mole ratios. Q3: Does dissolving NaCl in water count as a chemical change? A: No, the ions are only separated.

Challenge Corner

A 1.000 g mixture of NaCl (58.44 g/mol) and NaBr (102.89 g/mol) is dissolved and treated with excess AgNO_3 ; the dried mixed precipitate of AgCl (143.32) and AgBr (187.77) has mass 2.076 g. Find the mass of NaCl. Solution: let $x = \text{g NaCl}$. Each halide gives 1 mol of silver halide per mole, so $x/58.44 \times 143.32 + (1.000 - x)/102.89 \times 187.77 = 2.076$. That is $2.4525x + 1.8250(1.000 - x) = 2.076$, so $0.6275x = 0.2510$ and $x = \mathbf{0.400 \text{ g NaCl}}$ (40.0%).

Practice**PRACTICE Unit 4 Practice**

Show your work. A calculator is allowed. Justify conclusions.

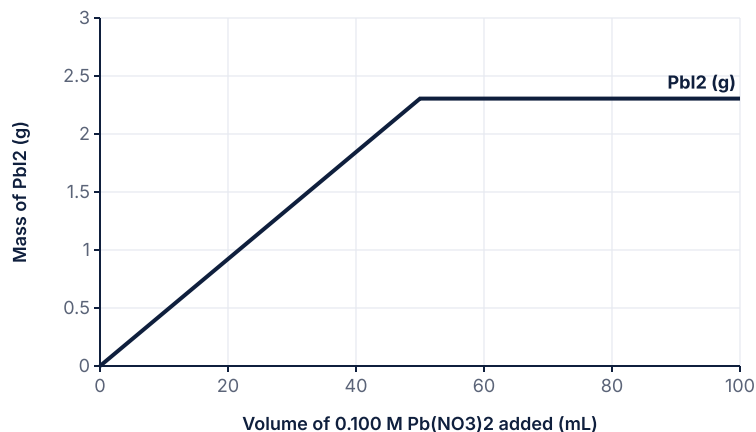
1. Aqueous acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$, is neutralized by aqueous NaOH. Which is the net ionic equation?
 (A) $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$
 (B) $\text{HC}_2\text{H}_3\text{O}_2 + \text{Na}^+ + \text{OH}^- \rightarrow \text{NaC}_2\text{H}_3\text{O}_2 + \text{H}_2\text{O}$
 (C) $\text{Na}^+ + \text{C}_2\text{H}_3\text{O}_2^- \rightarrow \text{NaC}_2\text{H}_3\text{O}_2$
 (D) $\text{HC}_2\text{H}_3\text{O}_2 + \text{OH}^- \rightarrow \text{C}_2\text{H}_3\text{O}_2^- + \text{H}_2\text{O}$
2. A reactor holds 10.0 mol of N_2 and 18.0 mol of H_2 . For $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$, what is the maximum moles of NH_3 ?
 (A) 20.0 mol (B) 28.0 mol (C) 12.0 mol (D) 36.0 mol
3. A 25.00 mL sample of HCl is neutralized by 15.00 mL of 0.0500 M $\text{Ba}(\text{OH})_2$. What is the HCl molarity?
 (A) 0.0600 M (B) 0.0300 M (C) 0.0833 M (D) 0.120 M

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4. In $\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}$, which statement is correct?
 (A) Zn is reduced because its oxidation number decreases.
 (B) Cu^{2+} is reduced and acts as the oxidizing agent.
 (C) Zn is the oxidizing agent because it loses electrons.
 (D) Zn^{2+} is the reducing agent.
5. Which observation describes a chemical change?
 (A) Mg ribbon burns in O_2 to leave a white solid.
 (B) NaCl dissolves in water, giving separated ions.
 (C) Solid I_2 sublimates to purple vapor.
 (D) Ethanol evaporates from a dish.
6. Using the graph, what mass of PbI_2 forms when 30.0 mL of 0.100 M $\text{Pb}(\text{NO}_3)_2$ is added to 50.0 mL of 0.200 M KI?



A fixed 50.0 mL of 0.200 M KI is treated with increasing volumes of $\text{Pb}(\text{NO}_3)_2$. The plateau marks the point where I^- is used up.

- (A) 2.31 g (B) 0.69 g (C) 1.50 g (D) 1.38 g
7. (a) Write the net ionic equation for mixing aqueous Na_3PO_4 with aqueous CaCl_2 , which gives solid $\text{Ca}_3(\text{PO}_4)_2$. Identify the spectator ions.
 (b) A student must prepare 250.0 mL of 0.100 M Na_2CO_3 (105.99 g/mol). Calculate the mass needed and describe, in order, how to prepare it with appropriate glassware so the concentration is accurate.
8. In $4\text{NH}_3 + 5\text{O}_2 \rightarrow 4\text{NO} + 6\text{H}_2\text{O}$, 5.00 g of NH_3 (17.03 g/mol) reacts with 10.0 g of O_2 (32.00 g/mol).
 (a) Determine the limiting reactant and justify with calculations.
 (b) Calculate the theoretical yield of NO (30.01 g/mol).
 (c) The student isolates 6.30 g of NO. Calculate the percent yield.
9. A student standardizes NaOH using 0.5105 g of solid KHP (204.22 g/mol, one acidic H per formula unit). The end point needs 24.86 mL of NaOH.
 (a) Calculate the NaOH molarity.
 (b) An air bubble in the buret tip is expelled during the titration, so the final reading includes volume that never reached the flask. Explain whether the calculated molarity is too high or too low.
 (c) Explain why the KHP is dissolved in a measured mass of solid rather than a measured volume of liquid.
10. Copper reacts with concentrated nitric acid: $\text{Cu} + 4\text{HNO}_3 \rightarrow \text{Cu}(\text{NO}_3)_2 + 2\text{NO}_2 + 2\text{H}_2\text{O}$.
 (a) Give the oxidation number of Cu and of N (in HNO_3 and in NO_2) before and after.
 (b) Identify the species oxidized, the species reduced, and the reducing agent.
 (c) How many moles of NO_2 form when 1.00 g of Cu (63.55 g/mol) reacts completely?

Answers Unit 4: Answers and Explanations

Read every explanation, including the ones for problems you answered correctly.

4 Chemical Reactions

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1. D. Acetic acid is a weak acid, so it is written as a whole molecule; Na^+ is a spectator and is removed. Choice A treats the acid as strong, and B and C keep spectators or form a soluble salt as a solid.
2. C. H_2 is limiting: $18.0 \text{ mol} \times (2/3) = 12.0 \text{ mol NH}_3$. Choice A uses N_2 (20.0 mol), which is in excess, and the other values add or triple incorrectly.
3. A. Moles of $\text{OH}^- = 0.01500 \text{ L} \times 0.0500 \text{ M} \times 2 = 1.50\text{e-}3 \text{ mol}$, so $\text{HCl} = 1.50\text{e-}3 / 0.02500 = 0.0600 \text{ M}$. Choice B forgets the two hydroxides per formula unit.
4. B. Cu goes from +2 to 0, gaining electrons, so it is reduced and is the oxidizing agent. Choice C reverses the idea: losing electrons makes Zn the reducing agent.
5. A. Burning magnesium creates a new substance, MgO. Dissolving NaCl only separates existing ions, so the tempting choice B is a physical change.
6. D. The graph rises 2.31 g over 50.0 mL, so at 30.0 mL the mass is $0.0461 \text{ g/mL} \times 30.0 = 1.38 \text{ g}$. Choice A is the plateau value, reached only at 50.0 mL.
7. (a) $3\text{Ca}^{2+}(\text{aq}) + 2\text{PO}_4^{3-}(\text{aq}) \rightarrow \text{Ca}_3(\text{PO}_4)_2(\text{s})$; spectators Na^+ and Cl^- (1 pt equation, 1 pt spectators). (b) Moles = $0.2500 \text{ L} \times 0.100 \text{ M} = 0.02500 \text{ mol}$; mass = $0.02500 \times 105.99 = \mathbf{2.65 \text{ g}}$ (1 pt). Weigh the solid, dissolve it in less than 250 mL of water in a beaker, transfer quantitatively (rinse beaker) into a 250.0 mL volumetric flask, add water to the mark, stopper and invert to mix (2 pts).
8. (a) Moles $\text{NH}_3 = 5.00/17.03 = 0.2936 \text{ mol}$; $\text{O}_2 = 10.0/32.00 = 0.3125 \text{ mol}$. NH_3 would need $0.2936 \times 5/4 = 0.3670 \text{ mol O}_2$, but only 0.3125 mol is present, so O_2 is **limiting**. (b) $0.3125 \times 4/5 = 0.2500 \text{ mol NO} = 0.2500 \times 30.01 = \mathbf{7.50 \text{ g}}$. (c) $6.30/7.50 \times 100 = \mathbf{84.0\%}$.
9. (a) Moles KHP = $0.5105/204.22 = 2.500\text{e-}3 \text{ mol} = \text{moles NaOH (1:1)}$. $M = 2.500\text{e-}3 / 0.02486 \text{ L} = \mathbf{0.1006 \text{ M}}$. (b) The reading is larger than the volume delivered, so the computed M, which divides by that volume, is **too low**. (c) A solid of known mass is a primary standard: it is pure, stable, and its moles come from a balance, whereas the NaOH concentration is the unknown being determined.
10. (a) Cu: 0 to +2. N: +5 in HNO_3 and +4 in NO_2 (two of the four N atoms stay +5 as NO_3^- in the salt). (b) Cu is oxidized; N in HNO_3 is reduced (+5 to +4); Cu is the reducing agent. (c) $1.00/63.55 = 0.01574 \text{ mol Cu}$; $\times 2 = \mathbf{0.0315 \text{ mol NO}_2}$.

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Unit 5: Kinetics

Exam weighting: about 7-9% of the multiple-choice section. Concept review, worked examples, exam-style writing, and 10 practice items, all with full explanations.

5 Kinetics

Read rates from data and graphs, write rate laws, connect mechanisms to experiment, and explain catalysis with energy profiles.

Why This Matters

Kinetics is 7 to 9 percent of the exam, and its reasoning (rate laws from data, graphs of concentration versus time, mechanisms, energy profiles) appears in both multiple-choice sets and long free-response questions. Points are lost when students say 'the rate depends on' without naming the trials compared, or confuse intermediates with catalysts.

Core Ideas

5.1 Reaction Rates

Rate is the change in concentration per unit time, always positive: for $aA \rightarrow bB$, $\text{rate} = -\frac{1}{a} \frac{\Delta[A]}{\Delta t} = \frac{1}{b} \frac{\Delta[B]}{\Delta t}$. Species with different coefficients change at different speeds, so divide by the coefficient before comparing. In $2N_2O_5 \rightarrow 4NO_2 + O_2$, NO_2 forms four times as fast as O_2 and twice as fast as N_2O_5 disappears.

5.2 Introduction to Rate Law

Rate law and the method of initial rates

Rate = $k[A]^m[B]^n$; orders m and n come only from experiment, not from coefficients.

Compare two trials where only one concentration changes: if it doubles and the rate quadruples, the order is 2.

Find k by substituting any trial; its units depend on overall order n : $M^{1-n} s^{-1}$.

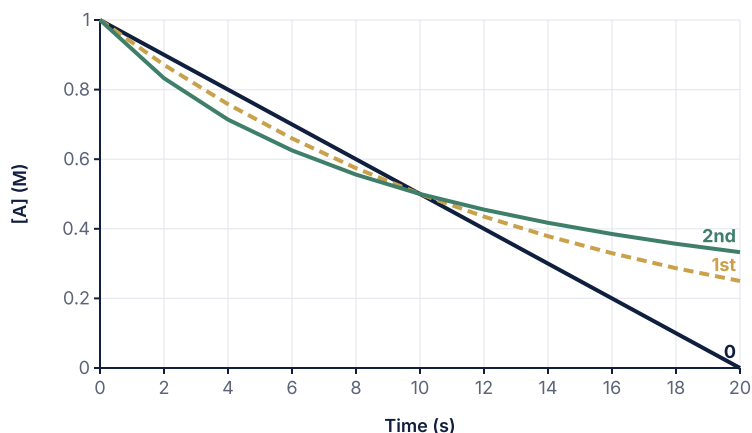
5.3 Concentration Changes Over Time

Order	Integrated law	Linear plot (slope)	Half-life
0	$[A] = [A]_0 - kt$	$[A] \text{ vs } t \text{ } (-k)$	$[A]_0 / 2k$
1	$\ln[A] = \ln[A]_0 - kt$	$\ln[A] \text{ vs } t \text{ } (-k)$	$0.693 / k$
2	$1/[A] = 1/[A]_0 + kt$	$1/[A] \text{ vs } t \text{ } (+k)$	$1 / (k[A]_0)$

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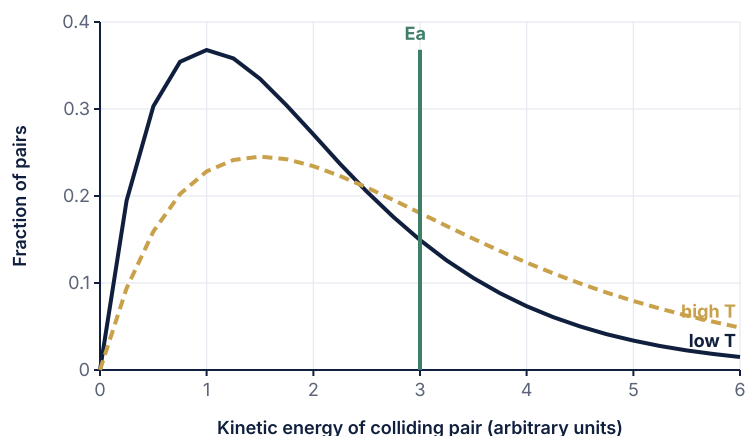


Same starting concentration. Zero order (straight line), first order (constant half-life of 10 s), second order (half-lives lengthen).

A constant half-life signals first order; a half-life that doubles each time signals second order; a constant slope in [A] versus time signals zero order. To justify an order, state which plot is linear and what its slope equals.

5.4 Elementary Reactions and 5.5 Collision Model

An **elementary step** is a single molecular event; its rate law comes directly from its coefficients (a bimolecular step $A + B \rightarrow \text{products}$ has rate $k[A][B]$). Molecularity is 1, 2 or 3. The collision model requires collisions with enough energy ($\geq E_a$) and a favorable orientation. Raising temperature raises the fraction of collisions that clear the barrier; raising concentration raises collision frequency.



The fraction of collisions with energy at least E_a (to the right of the vertical line) is larger at the higher temperature (about double here).

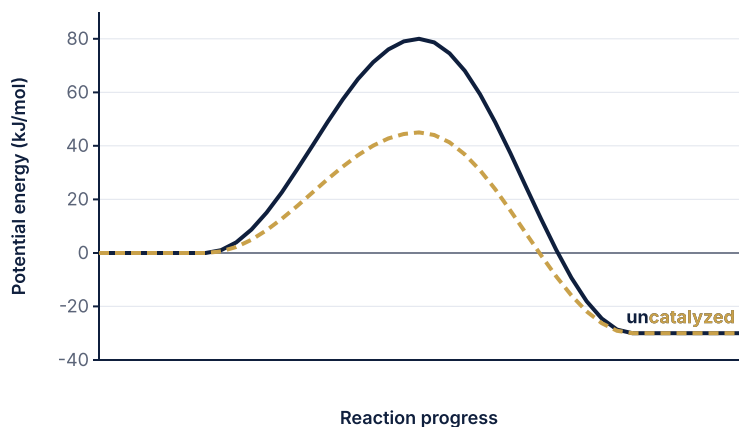
5.6 Reaction Energy Profile and 5.11 Catalysis

The peak is the transition state; the barrier from reactants is E_a (forward) and from products is E_a (reverse); ΔH is the energy difference between products and reactants. A **catalyst** provides an alternate mechanism with lower activation energy, speeds forward and reverse reactions equally, is not consumed overall, and does not change ΔH or the equilibrium position.

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A catalyst opens a path with a lower barrier. Reactant energy, product energy, and ΔH (-30 kJ/mol) are unchanged.

5.7 Mechanisms, 5.8 Mechanism and Rate Law, 5.9 Pre-Equilibrium, 5.10 Multistep Energy Profile

Reading a mechanism

The steps must add to the overall equation after canceling species.

An **intermediate** is produced in one step and consumed in a later one; a **catalyst** is consumed first and regenerated later. The slowest step (highest barrier) is rate-determining, and the observed rate law equals the rate law of that step.

If the slow step contains an intermediate, replace it using a fast equilibrium before it: forward rate = reverse rate gives $[I] = K[\text{reactants}]$.

On a multistep profile, intermediates sit in valleys between peaks, and the highest peak marks the rate-determining step.

Worked Examples

EXAMPLE 1: INITIAL RATES

Find the rate law, k , and the initial rate when $[A] = 0.15 \text{ M}$ and $[B] = 0.20 \text{ M}$.

Trial	[A] (M)	[B] (M)	Initial rate (M/s)
1	0.10	0.10	2.4×10^{-4}
2	0.20	0.10	9.6×10^{-4}
3	0.10	0.30	7.2×10^{-4}

SOLUTION

Trials 1 and 2: $[A]$ doubles, $[B]$ fixed, rate quadruples ($9.6 \times 10^{-4} / 2.4 \times 10^{-4} = 4$), so second order in A.

Trials 1 and 3: $[B]$ triples, rate triples, so first order in B. Rate = $k[A]^2[B]$.

$$k = 2.4 \times 10^{-4} / (0.10^2 \times 0.10) = \mathbf{0.24 \text{ M}^{-2}\text{s}^{-1}}.$$

$$\text{Rate} = 0.24 \times 0.15^2 \times 0.20 = \mathbf{1.1 \times 10^{-3} \text{ M/s}}.$$

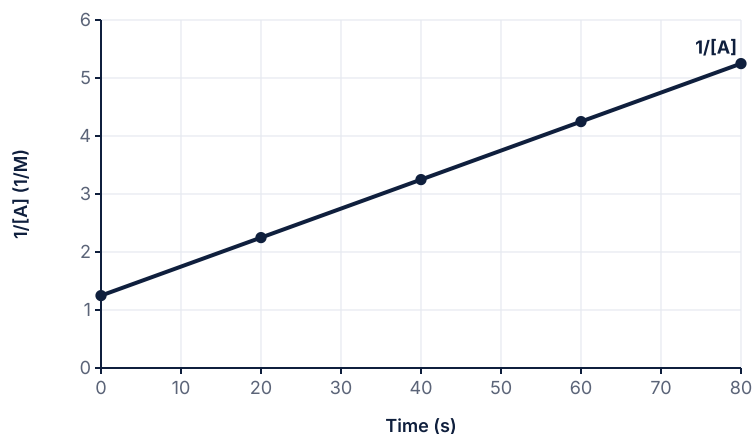
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EXAMPLE 2: ORDER FROM CONCENTRATION-TIME DATA

Use the data to decide the order of A, find k , and the first two half-lives.



A straight line of $1/[A]$ versus time is the signature of second order.

t (s)	0	20	40	60	80
[A] (M)	0.800	0.444	0.308	0.235	0.190

SOLUTION

The values of $1/[A]$ are 1.25, 2.25, 3.25, 4.25, 5.25: increasing by 1.00 every 20 s, a straight line. Second order. $\ln[A]$ is not linear (its slope changes from -0.029 to -0.018 per s).

Slope: $k = 1.00/20 = 0.0500 \text{ M}^{-1}\text{s}^{-1}$.

$t_{1/2} = 1/(k[A]_0) = 1/(0.0500 \times 0.800) = 25.0 \text{ s}$; the next, from 0.400 M, is 50.0 s: half-lives double, as expected for second order.

EXAMPLE 3: PRE-EQUILIBRIUM

For $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$ the proposed mechanism is fast equilibrium $2\text{NO} \rightleftharpoons \text{N}_2\text{O}_2$ (K), then slow $\text{N}_2\text{O}_2 + \text{O}_2 \rightarrow 2\text{NO}_2$ (k_2). Derive the rate law and predict the effect of tripling $[\text{NO}]$.

SOLUTION

The slow step controls: rate = $k_2[\text{N}_2\text{O}_2][\text{O}_2]$, but N_2O_2 is an intermediate.

Fast equilibrium: $K = [\text{N}_2\text{O}_2]/[\text{NO}]^2$, so $[\text{N}_2\text{O}_2] = K[\text{NO}]^2$.

Rate = $k_2K[\text{NO}]^2[\text{O}_2]$, third order overall, consistent with the overall reaction.

Tripling $[\text{NO}]$ multiplies the rate by $3^2 = 9$.

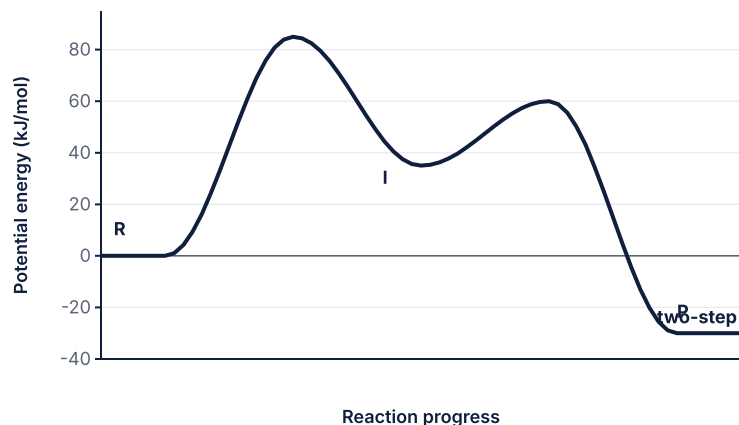
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EXAMPLE 4: MULTISTEP ENERGY PROFILE

Use the profile (kJ/mol) to identify the rate-determining step, each activation energy, the intermediate, and ΔH . The peaks are at 85 and 60; the valley is at 35.



Two peaks with an intermediate in the valley between them.

SOLUTION

Reactants 0, first peak 85, intermediate (I) 35, second peak 60, products -30.

Step 1: $E_a = 85 - 0 = 85$ kJ/mol. Step 2: $E_a = 60 - 35 = 25$ kJ/mol. The higher barrier makes **step 1 rate-determining**.

$\Delta H = -30 - 0 = -30$ kJ/mol (exothermic). Reverse barrier of step 2 = $60 - (-30) = 90$ kJ/mol.

Write It Like a 5**Model Response**

Prompt: Using the initial-rate table for $X + Y$, explain how the order in Y is found. Response: Compare trials 2 and 3, where [X] is constant at 0.40 M and [Y] doubles from 0.20 M to 0.40 M. The rate rises from 6.0×10^{-3} to 2.4×10^{-2} M/s, a factor of 4. Since doubling [Y] multiplies the rate by $4 = 2^2$, the reaction is second order in Y.

What the grader looks for

Names the two trials; states which concentration changed and which stayed constant; gives the rate ratio; links the ratio to the order with a power; includes units on k .

Coach's Playbook

- ◆ Always divide by coefficients before comparing rates of different species.
- ◆ Order from data, never from the balanced equation (unless the step is elementary).
- ◆ For a mechanism, add the steps, cancel, and compare with the overall equation.
- ◆ Catalysts and intermediates: a catalyst appears first as a reactant, an intermediate first as a product.

Common traps

(1) Using stoichiometric coefficients as orders. (2) Missing or wrong units on k . (3) Calling H_3O^+ or a regenerated species an intermediate. (4) Saying more surface area gives more product; it only increases the rate.

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Quick Check

Q1: A first-order reaction has $k = 0.0231 \text{ min}^{-1}$. Half-life? A: $0.693/0.0231 = 30.0 \text{ min}$. Q2: Does a catalyst change ΔH ? A: No. Q3: Units of k for a second-order reaction? A: $\text{M}^{-1}\text{s}^{-1}$.

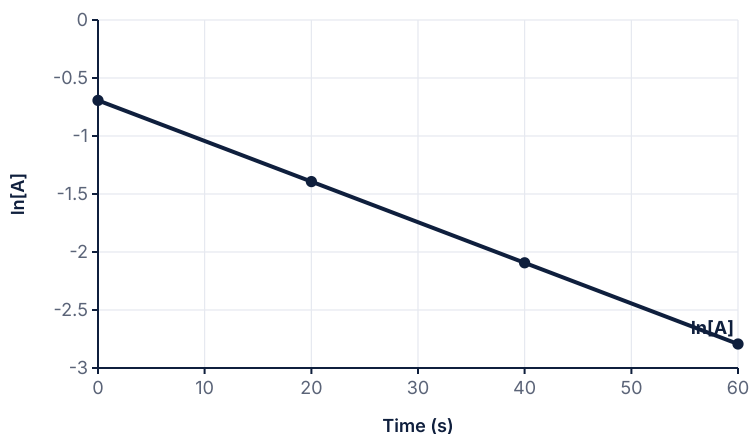
Challenge Corner

A first-order reactant at 0.800 M has $t_{1/2} = 30.0 \text{ min}$. How long until it reaches 0.100 M , and what is $[A]$ after 100 min ?
 Solution: 0.800 to 0.100 is three half-lives ($0.800, 0.400, 0.200, 0.100$), so 90.0 min . $k = 0.693/30.0 = 0.0231 \text{ min}^{-1}$; $[A] = 0.800e^{-0.0231 \times 100} = \mathbf{0.0794 \text{ M}}$.

Practice**PRACTICE Unit 5 Practice**

Show your work. A calculator is allowed. Justify conclusions.

- For $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$, N_2O_5 disappears at $6.0\text{e-}4 \text{ M/s}$. At what rate does O_2 form?
 (A) $6.0\text{e-}4 \text{ M/s}$ (B) $3.0\text{e-}4 \text{ M/s}$ (C) $1.2\text{e-}3 \text{ M/s}$
 (D) $1.5\text{e-}4 \text{ M/s}$
- A reaction has rate law $\text{Rate} = k[\text{A}][\text{B}]^2$. What are the units of k (M and s)?
 (A) s^{-1} (B) $\text{M}^{-1} \text{s}^{-1}$ (C) $\text{M}^{-2} \text{s}^{-1}$ (D) $\text{M}^{-3} \text{s}^{-1}$
- The plot of $\ln[\text{A}]$ versus time is linear with slope -0.035 s^{-1} . What is the half-life?



Linearized data for the decomposition of A.

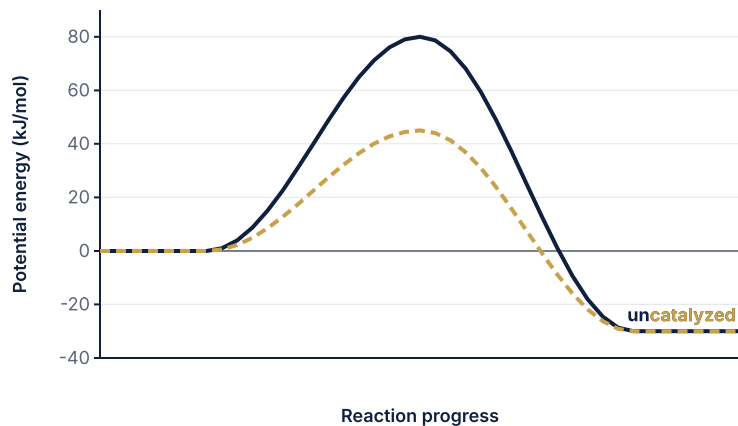
- (A) 19.8 s (B) 28.6 s (C) 39.6 s (D) 14.3 s
- A proposed mechanism: (1) slow, $\text{NO}_2 + \text{NO}_2 \rightarrow \text{NO}_3 + \text{NO}$; (2) fast, $\text{NO}_3 + \text{CO} \rightarrow \text{NO}_2 + \text{CO}_2$. Which species is an intermediate?
 (A) NO_2 (B) CO (C) NO (D) NO_3
- Which statement best explains why a reaction goes faster at higher temperature?
 (A) The activation energy becomes smaller.
 (B) A larger fraction of collisions has energy at least equal to E_a .
 (C) The reaction becomes more exothermic.
 (D) The orientation requirement is removed.

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6. The graph compares a reaction with and without a catalyst. Which statement is correct?



A catalyst opens a path with a lower barrier. Reactant energy, product energy, and ΔH (-30 kJ/mol) are unchanged.

- (A) ΔH is the same, and E_a is lower in both directions with the catalyst.
 (B) ΔH is less negative with the catalyst.
 (C) Only the forward E_a decreases with the catalyst.
 (D) The catalyst increases the equilibrium yield of products.
7. A student studies $X + 2Y \rightarrow Z$ by initial rates. Trial 1: $[X] = 0.20 \text{ M}$, $[Y] = 0.20 \text{ M}$, rate = $3.0 \times 10^{-3} \text{ M/s}$. Trial 2: $[X] = 0.40 \text{ M}$, $[Y] = 0.20 \text{ M}$, rate = $6.0 \times 10^{-3} \text{ M/s}$. Trial 3: $[X] = 0.40 \text{ M}$, $[Y] = 0.40 \text{ M}$, rate = $2.4 \times 10^{-2} \text{ M/s}$.
 (a) Determine the order in X and in Y, citing the trials compared.
 (b) Write the rate law and calculate k with units.
 (c) Predict the rate when $[X] = 0.10 \text{ M}$ and $[Y] = 0.30 \text{ M}$.
8. Reactant A decomposes. Concentrations are 0.640 M at 0 s, 0.320 M at 100 s, 0.160 M at 200 s, and 0.080 M at 300 s.
 (a) Show that the data indicate first order.
 (b) Calculate k .
 (c) Find the time for [A] to reach 0.0200 M and [A] at 250 s.
 (d) State which quantity could be plotted against time to give a straight line and the slope.
9. Iodide catalyzes decomposition of hydrogen peroxide: (1) slow, $\text{H}_2\text{O}_2 + \text{I}^- \rightarrow \text{H}_2\text{O} + \text{IO}^-$; (2) fast, $\text{H}_2\text{O}_2 + \text{IO}^- \rightarrow \text{H}_2\text{O} + \text{O}_2 + \text{I}^-$.
 (a) Write the overall equation.
 (b) Identify the catalyst and the intermediate, with reasoning.
 (c) Give the rate law and predict the effect of doubling I^- .
 (d) Describe how an energy profile of the catalyzed path compares with the uncatalyzed one.
10. For $2\text{NO} + \text{Br}_2 \rightarrow 2\text{NOBr}$, a mechanism is (1) fast equilibrium $\text{NO} + \text{Br}_2 \rightleftharpoons \text{NOBr}_2$; (2) slow $\text{NOBr}_2 + \text{NO} \rightarrow 2\text{NOBr}$.
 (a) Verify the steps add to the overall reaction and identify the intermediate.
 (b) Derive the rate law.
 (c) By what factor does the rate change if [NO] is doubled and Br_2 is halved?
 (d) Explain why an intermediate does not appear in the experimentally determined rate law.

Answers Unit 5: Answers and Explanations

Read every explanation, including the ones for problems you answered correctly.

5 Kinetics

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1. B. Rate of reaction = $6.0\text{e-}4 / 2 = 3.0\text{e-}4 \text{ M/s}$, and O_2 has coefficient 1. Choice A ignores the coefficient of N_2O_5 ; C is the rate of NO_2 formation.
2. C. Overall order is 3, so units are $\text{M}^{1-3}\text{s}^{-1} = \text{M}^{-2}\text{s}^{-1}$. Choice B is the second-order unit, tempting if the order of B is overlooked.
3. A. A linear $\ln[A]$ plot means first order and $k = 0.035 \text{ s}^{-1}$, so $t_{1/2} = 0.693/0.035 = 19.8 \text{ s}$. Choice B ($1/k$) is the second-order style formula and is not valid here.
4. D. NO_3 is formed in step 1 and consumed in step 2. NO_2 is a reactant in step 1 and a product of step 2, but net it is consumed (two used, one made), so it is a reactant, not an intermediate.
5. B. Higher temperature increases the fraction of collisions with energy $\geq E_a$. Choice A is wrong because E_a is a property of the pathway and does not change with temperature.
6. A. A catalyst lowers the barrier for both directions and leaves reactant and product energies, hence ΔH and K , unchanged. Choice D fails because equilibrium composition does not change.
7. (a) Trials 1 and 2: $[Y]$ constant, $[X]$ doubles, rate doubles, so first order in X . Trials 2 and 3: $[X]$ constant, $[Y]$ doubles, rate $\times 4$ ($2.4\text{e-}2 / 6.0\text{e-}3$), so second order in Y . (b) Rate = $k[X][Y]^2$; $k = 3.0 \times 10^{-3} / (0.20 \times 0.20^2) = \mathbf{0.375 \text{ M}^{-2}\text{s}^{-1}}$ (the rate law is not from coefficients: Y has coefficient 2 and order 2 here only by coincidence). (c) $0.375 \times 0.10 \times 0.30^2 = \mathbf{3.4\text{e-}3 \text{ M/s}}$.
8. (a) The concentration halves every 100 s (0.640, 0.320, 0.160, 0.080), a constant half-life, which is unique to first order. (b) $k = 0.693/100 = \mathbf{6.93\text{e-}3 \text{ s}^{-1}}$. (c) 0.640 to 0.0200 is 5 half-lives (0.640/32), so $\mathbf{500 \text{ s}}$; at 250 s, $[A] = 0.640 \times 2^{-2.5} = \mathbf{0.113 \text{ M}}$. (d) Plot $\ln[A]$ versus t : a straight line with slope $-k = -6.93 \times 10^{-3} \text{ s}^{-1}$.
9. (a) Adding: $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$. (b) I^- is the catalyst: consumed in step 1 and regenerated in step 2. IO^- is the intermediate: formed in step 1 and consumed in step 2. (c) Slow step 1 sets the rate: Rate = $k[\text{H}_2\text{O}_2][\text{I}^-]$; doubling I^- doubles the rate. (d) The catalyzed profile has a lower highest peak (smaller E_a) with the same reactant and product energies.
10. (a) Sum: $\text{NO} + \text{Br}_2 + \text{NOBr}_2 + \text{NO} \rightarrow \text{NOBr}_2 + 2\text{NOBr}$; canceling NOBr_2 gives $2\text{NO} + \text{Br}_2 \rightarrow 2\text{NOBr}$. NOBr_2 is the intermediate. (b) Slow step: rate = $k_2[\text{NOBr}_2][\text{NO}]$. Fast equilibrium: $[\text{NOBr}_2] = K[\text{NO}][\text{Br}_2]$. So rate = $k_2K[\text{NO}]^2[\text{Br}_2]$. (c) $2^2 \times 0.5 = \mathbf{2}$ times faster. (d) An intermediate is created and used up inside the mechanism and cannot be controlled or measured as a starting concentration, so the rate law is written in terms of reactants.

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Unit 6: Thermochemistry

Exam weighting: about 7-9% of the multiple-choice section. Concept review, worked examples, exam-style writing, and 10 practice items, all with full explanations.

6 Thermochemistry

Track energy in chemical and physical change: sign conventions, calorimetry, phase changes, enthalpy of formation, bond enthalpies, and Hess's law.

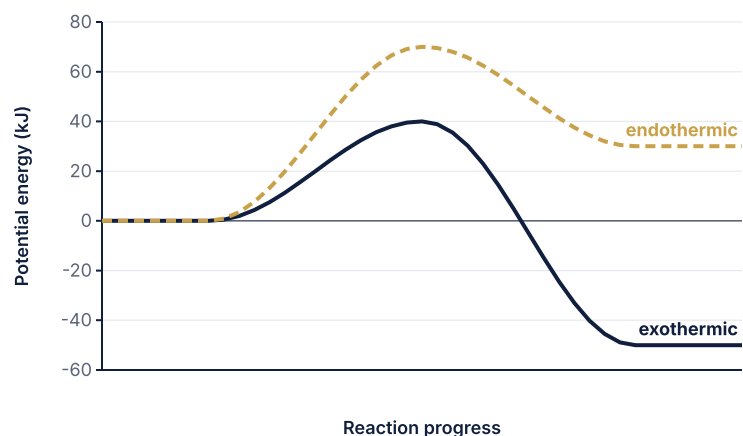
Why This Matters

Thermochemistry is 7 to 9 percent of the exam and appears in long free-response questions through calorimetry data, Hess's law, and sign conventions. Students lose points on signs, on using $mc\Delta T$ for a phase change, and on forgetting that ΔH is per mole of reaction as written.

Core Ideas

6.1 Endothermic and Exothermic Processes and 6.2 Energy Diagrams

The **system** is the reaction; everything else is the surroundings. An **exothermic** process releases energy to the surroundings ($\Delta H < 0$, the surroundings warm); an **endothermic** one absorbs energy ($\Delta H > 0$, the surroundings cool). Breaking bonds requires energy; forming bonds releases it, and the net determines the sign.



Exothermic: products lower than reactants, $\Delta H = -50$ kJ. Endothermic: products higher, $\Delta H = +30$ kJ.

6.3 Heat Transfer and Thermal Equilibrium

Heat flows spontaneously from the higher-temperature object to the lower, because temperature measures average kinetic energy of particles and collisions share energy. Heat and temperature are different: heat is energy transferred, temperature is a property. Objects reach thermal equilibrium when they share the same temperature, with $q_{\text{lost}} = q_{\text{gained}}$ in magnitude.

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6.4 Heat Capacity and Calorimetry

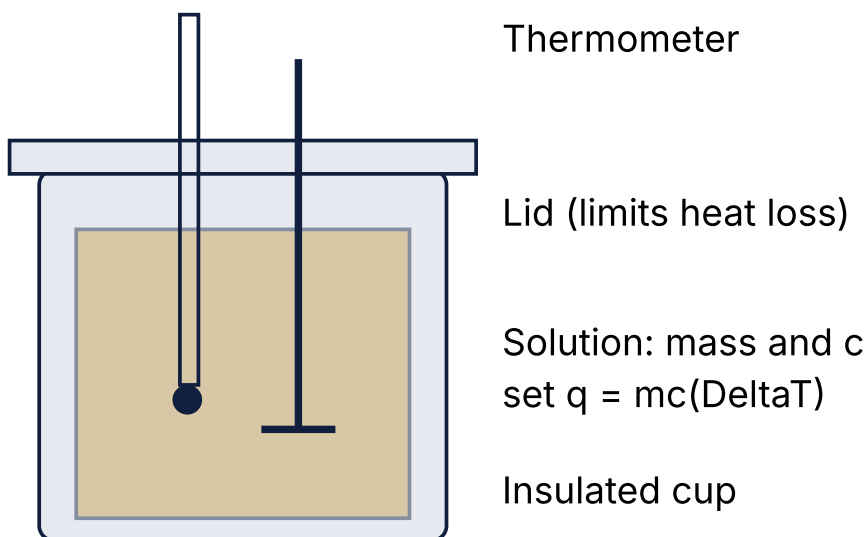
Calorimetry relations

$q = mc\Delta T$, with $\Delta T = T_{\text{final}} - T_{\text{initial}}$ (never the final temperature alone).

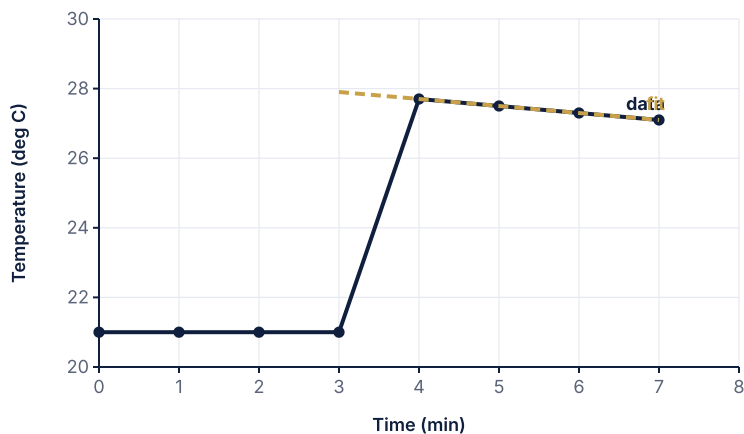
Mass is the total mass of solution, solute plus solvent; $c \approx 4.18 \text{ J}/(\text{g} \cdot ^\circ\text{C})$ for dilute water solutions.

$q_{\text{rxn}} = -q_{\text{solution}}$ (add $C_{\text{cal}}\Delta T$ if the calorimeter absorbs heat).

$\Delta H = q_{\text{rxn}}/n$, where n is moles of the limiting reactant (as written).



Coffee-cup calorimeter at constant pressure: the heat gained by the solution equals the heat lost by the reaction, so $q_{\text{rxn}} = -q_{\text{solution}}$.



Acid and base are mixed at 3.0 min. Extrapolating the cooling line back to the mixing time gives the corrected final temperature, 27.9 deg C.

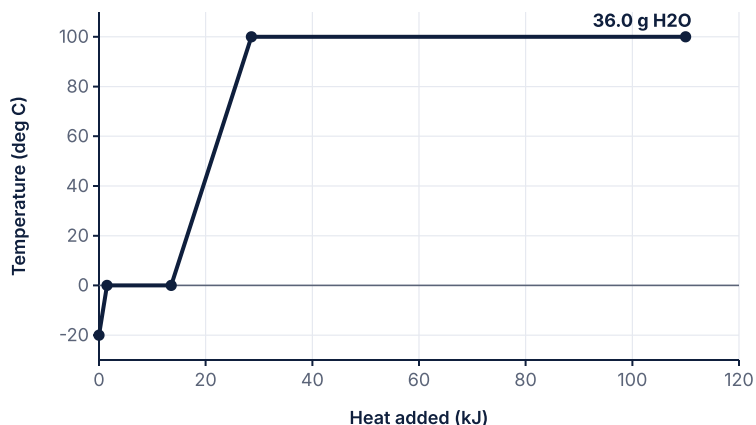
6.5 Energy of Phase Changes

During a phase change, temperature stays constant because added energy increases the potential energy of the particles as intermolecular forces are overcome, not their kinetic energy. Use $q = n\Delta H_{\text{fus}}$ or $n\Delta H_{\text{vap}}$ for these segments, and $mc\Delta T$ for the sloped ones.

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Heating curve for 36.0 g of water: slanted segments use $q = mc(\Delta T)$; flat segments use $q = n(\Delta H \text{ of the phase change})$.

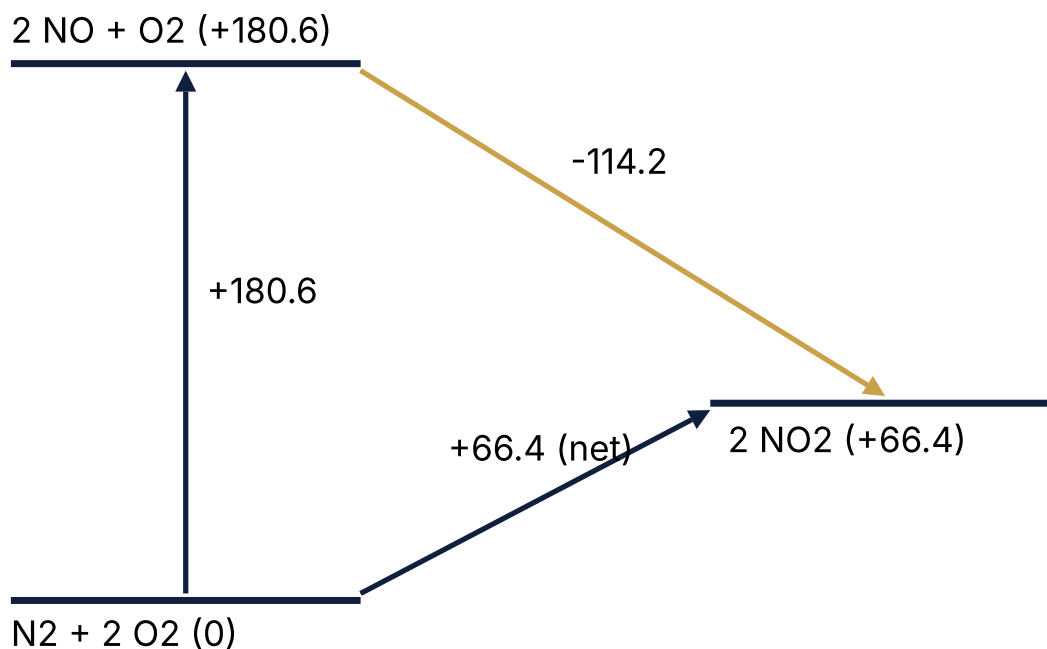
6.6 Enthalpy of Reaction, 6.8 Enthalpy of Formation, 6.9 Hess's Law

Three routes to ΔH

Formation: $\Delta H_{\text{rxn}}^{\circ} = \sum n \Delta H_f^{\circ}(\text{products}) - \sum n \Delta H_f^{\circ}(\text{reactants})$; elements in their standard state are 0.

Hess's law: ΔH is a state function, so add reaction enthalpies. Reverse a reaction: change the sign. Multiply by k : multiply ΔH by k .

ΔH is for the equation as written; heat released for a given sample is $n \times \Delta H$.



Energy ladder (kJ). The direct path and the two-step path connect the same states, so their enthalpy changes are equal: $+180.6 + (-114.2) = +66.4$.

6.7 Bond Enthalpies

Bond enthalpy estimate

$\Delta H \approx \sum (\text{bonds broken}) - \sum (\text{bonds formed})$, using gas-phase average bond enthalpies. Breaking is positive, forming is negative.

These are averages, so the result is an estimate, and it applies to gases only.

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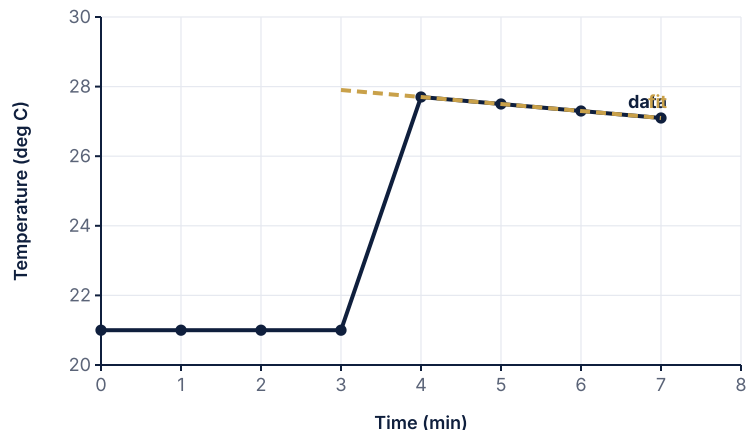
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Worked Examples

EXAMPLE 1: COFFEE-CUP CALORIMETRY

50.0 mL of 1.00 M HCl at 21.0 degrees C is mixed with 50.0 mL of 1.00 M NaOH at the same temperature. Using the corrected final temperature from the graph (27.9 degrees C), find the molar enthalpy of neutralization. Treat the solution as 100.0 g with $c = 4.18$ J/(g degrees C).



Acid and base are mixed at 3.0 min. Extrapolating the cooling line back to the mixing time gives the corrected final temperature, 27.9 deg C.

SOLUTION

$$\Delta T = 27.9 - 21.0 = 6.9\text{ }^{\circ}\text{C (not 27.9)}.$$

$$q_{\text{solution}} = 100.0 \times 4.18 \times 6.9 = 2.88 \times 10^3 \text{ J, gained by the solution.}$$

$$q_{\text{rxn}} = -2.88 \text{ kJ (exothermic). Moles of water formed} = 0.0500 \text{ mol.}$$

$$\Delta H = -2.88/0.0500 = -57.7 \text{ kJ/mol.}$$

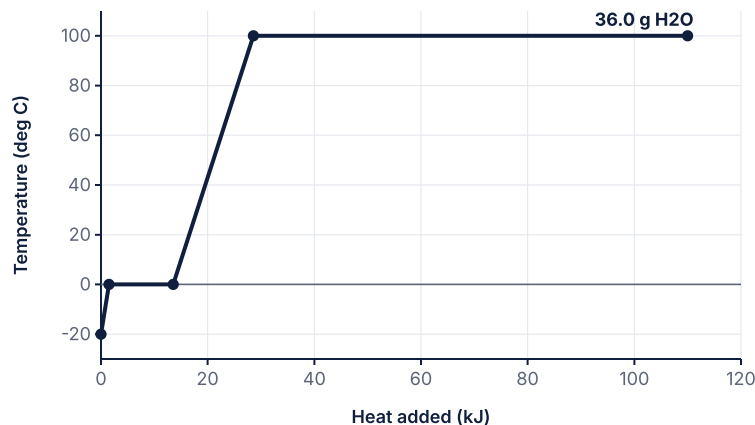
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EXAMPLE 2: HEATING CURVE

How much heat converts 36.0 g of ice at -20.0 degrees C to steam at 100.0 degrees C? Use $c_{\text{ice}} = 2.09$, $c_{\text{water}} = 4.184$ J/(g degrees C), $\Delta H_{\text{fus}} = 6.01$, $\Delta H_{\text{vap}} = 40.7$ kJ/mol.



Heating curve for 36.0 g of water: slanted segments use $q = mc(\Delta T)$; flat segments use $q = n(\Delta H \text{ of the phase change})$.

SOLUTION

Ice, -20 to 0 : $36.0 \times 2.09 \times 20.0 = 1.50$ kJ.

Melt: $2.00 \text{ mol} \times 6.01 = 12.0$ kJ (flat: not $mc\Delta T$).

Water, 0 to 100 : $36.0 \times 4.184 \times 100.0 = 15.1$ kJ.

Boil: $2.00 \text{ mol} \times 40.7 = 81.4$ kJ.

Total = **110. kJ**, the endpoint of the graph (most energy goes into vaporization).

EXAMPLE 3: HESS'S LAW

Given $\text{N}_2 + \text{O}_2 \rightarrow 2\text{NO}$ ($\Delta H = +180.6$ kJ) and $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$ ($\Delta H = -114.2$ kJ), find ΔH for $\text{N}_2 + 2\text{O}_2 \rightarrow 2\text{NO}_2$ and the enthalpy of formation of NO_2 .

SOLUTION

Add the two equations; 2NO cancels and an O_2 remains on the left: net $\text{N}_2 + 2\text{O}_2 \rightarrow 2\text{NO}_2$.

$\Delta H = +180.6 + (-114.2) = \mathbf{+66.4 \text{ kJ}}$.

Formation is per mole: $66.4 / 2 = \mathbf{+33.2 \text{ kJ/mol}}$.

EXAMPLE 4: BOND ENTHALPIES VERSUS FORMATION DATA

Estimate ΔH for $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$ from bond enthalpies, then compare with formation values (-74.8 , -393.5 , -241.8 kJ/mol) and find the heat for 8.00 g of CH_4 (16.04 g/mol).

Bond	H-H	O=O	C-H	C=O (in CO_2)	O-H
Average enthalpy (kJ/mol)	436	495	413	799	463

SOLUTION

Broken: $4(413) + 2(495) = 2642$ kJ. Formed: $2(799) + 4(463) = 3450$ kJ. $\Delta H \approx 2642 - 3450 = \mathbf{-808 \text{ kJ}}$.

Formation: $-393.5 + 2(-241.8) - (-74.8) = \mathbf{-802.3 \text{ kJ}}$; the bond estimate differs because the values are averages.

$8.00 \text{ g} = 0.4988 \text{ mol}$, so heat released = $0.4988 \times 802.3 = \mathbf{400. \text{ kJ}}$.

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Write It Like a 5

Model Response

Prompt: In a calorimetry experiment the measured temperature rise was smaller than expected. Explain. Response: The reaction released the expected amount of energy, but some energy was transferred out of the solution to the surroundings or absorbed by the cup, so the solution's temperature change ($T_{\text{final}} - T_{\text{initial}}$) was smaller than ideal. Because $q = mc\Delta T$ uses that ΔT , the calculated magnitude of ΔH is too small.

What the grader looks for

Names where the energy went; states the effect on ΔT (not just 'heat loss'); links ΔT to the calculated q and to the magnitude and sign of ΔH .

Coach's Playbook

- ◆ Label every q with its sign: heat gained by solution is positive; heat of an exothermic reaction is negative.
- ◆ Choose the formula: sloped segment, $mc\Delta T$; flat segment, $n\Delta H$.
- ◆ In Hess's law, write the target first and fix each given equation, one at a time, then cancel.
- ◆ Count bonds in a Lewis diagram for every molecule before applying bond enthalpies.

Common traps

(1) Using T_{final} as ΔT . (2) Forgetting to include solute mass in the solution mass. (3) Not changing the sign of ΔH when reversing an equation, or not scaling it when multiplying. (4) Giving a positive ΔH for an exothermic process.

Quick Check

Q1: Sign of q_{rxn} if the solution warms? A: Negative. Q2: Is ΔH_f of $\text{O}_2(\text{g})$ zero? A: Yes, a standard-state element. Q3: What happens to temperature during melting? A: It stays constant.

Challenge Corner

Burning 0.500 g of ethanol (46.07 g/mol) in a calorimeter containing 400.0 g of water with $C_{\text{cal}} = 150.0 \text{ J/degrees C}$ raises the temperature by 8.13 degrees C. Find the molar enthalpy of combustion. Solution: $q = (400.0 \times 4.184 + 150.0) \times 8.13 = 1.48 \times 10^4 \text{ J absorbed}$; moles = 0.01085 mol; $\Delta H = -14.8 \text{ kJ}/0.01085 = \mathbf{-1.37e3 \text{ kJ/mol}}$.

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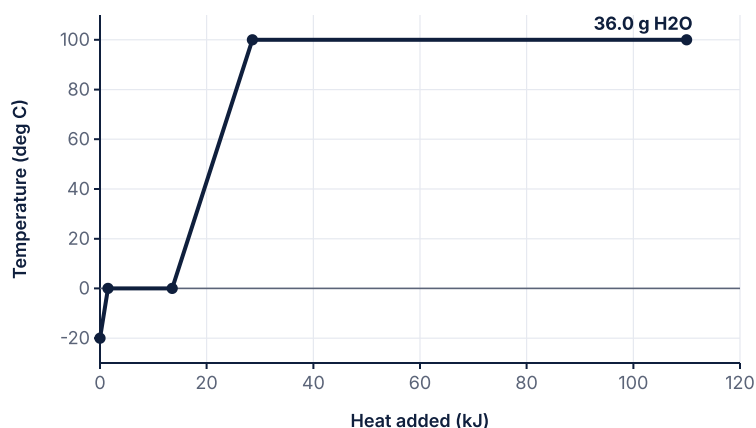
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Practice

PRACTICE Unit 6 Practice

Show your work. A calculator is allowed. Justify conclusions.

- A reaction mixture in a flask warms from 21 degrees C to 27 degrees C. Which statement is correct?
 - The reaction is exothermic, and $\Delta H < 0$.
 - The reaction is endothermic, because energy was absorbed.
 - The reaction is exothermic, and $\Delta H > 0$.
 - The reaction has $\Delta H = 0$ because temperature changed only slightly.
- 2.50 g of a salt dissolves in 50.0 g of water, and the temperature falls from 25.0 to 22.4 degrees C. Taking $c = 4.18 \text{ J/(g degrees C)}$ and the whole solution mass, what is q for the dissolving process?
 - 571 J
 - +543 J
 - +571 J
 - +27 J
- Using bond enthalpies H-H 436, Cl-Cl 243, H-Cl 431 (kJ/mol), what is ΔH for $\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl}$?
 - +183 kJ
 - 183 kJ
 - 246 kJ
 - +431 kJ
- Given $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$, $\Delta H = -393.5 \text{ kJ}$, and $\text{CO} + 1/2\text{O}_2 \rightarrow \text{CO}_2$, $\Delta H = -283.0 \text{ kJ}$, what is ΔH for $\text{C} + 1/2\text{O}_2 \rightarrow \text{CO}$?
 - 676.5 kJ
 - +110.5 kJ
 - 283.0 kJ
 - 110.5 kJ
- Based on the heating curve, what is happening to water at the flat segment at 100 degrees C?



Heating curve for 36.0 g of water: slanted segments use $q = mc(\Delta T)$; flat segments use $q = n(\Delta H \text{ of the phase change})$.

- The temperature is constant because no energy is being added.
 - The average kinetic energy of the molecules is increasing.
 - The added energy increases potential energy as intermolecular attractions are overcome.
 - Covalent O-H bonds in the molecules are breaking.
- For $2\text{Al} + \text{Fe}_2\text{O}_3 \rightarrow \text{Al}_2\text{O}_3 + 2\text{Fe}$, using ΔH_f of $\text{Al}_2\text{O}_3 = -1675.7$ and $\text{Fe}_2\text{O}_3 = -824.2 \text{ kJ/mol}$, what is ΔH ?
 - 851.5 kJ
 - +851.5 kJ
 - 2499.9 kJ
 - 1675.7 kJ
 - A student dissolves 4.00 g of NH_4NO_3 (80.04 g/mol) in 100.0 g of water in a coffee-cup calorimeter. The temperature falls from 22.0 to 18.9 degrees C. Assume $c = 4.18 \text{ J/(g degrees C)}$.
 - Calculate the heat transferred to the solution, with sign.
 - Calculate the molar enthalpy of dissolution, with sign.
 - Explain whether heat leaking in from the room would make the calculated ΔH too large or too small in magnitude.
 - Describe two procedure improvements.
 - Calculate the heat needed to convert 54.0 g of ice at 0.0 degrees C to water at 25.0 degrees C ($\Delta H_{\text{fus}} = 6.01 \text{ kJ/mol}$, $c = 4.184 \text{ J/(g degrees C)}$).
 - Explain, in terms of particles, why the temperature of an ice-water mixture stays at 0 degrees C while it is heated.
 - 50.0 g of water at 80.0 degrees C is mixed with 100.0 g of water at 20.0 degrees C. Calculate the final temperature, assuming no loss.

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9. Standard enthalpies of formation (kJ/mol): $\text{C}_2\text{H}_5\text{OH}(\text{l})$ -277.7, $\text{CO}_2(\text{g})$ -393.5, $\text{H}_2\text{O}(\text{l})$ -285.8, $\text{H}_2\text{O}(\text{g})$ -241.8.
 (a) Write the balanced combustion equation for one mole of ethanol and calculate ΔH° using liquid water.
 (b) Calculate the heat released by 5.00 g of ethanol (46.07 g/mol).
 (c) Would ΔH be more or less negative if water vapor formed? Justify.
10. For $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$, bond enthalpies (kJ/mol) are N-N triple 945, H-H 436, N-H 391.
 (a) Estimate ΔH for the reaction as written.
 (b) Sketch and label an energy diagram showing reactants, products, and ΔH .
 (c) Explain why the sign is predicted by comparing energy released in forming bonds with energy absorbed in breaking them.
 (d) Calculate the heat for 2.80 g of N_2 (28.02 g/mol) reacting.

Answers Unit 6: Answers and Explanations

Read every explanation, including the ones for problems you answered correctly.

6 Thermochemistry

PRACTICE · UNIT 6 PRACTICE

1. A. The solution warms because energy is released to the surroundings, so the process is exothermic and $\Delta H < 0$. Choice B confuses the warming of the mixture (the surroundings) with energy absorbed by the system.
2. C. The dissolving process absorbs the energy the solution lost: $q = 52.5 \times 4.18 \times 2.6 = +571 \text{ J}$. Choice B uses only the water mass, and A has the wrong sign.
3. B. Broken: $436 + 243 = 679 \text{ kJ}$; formed: $2(431) = 862 \text{ kJ}$; $\Delta H = 679 - 862 = -183 \text{ kJ}$. Choice A reverses broken and formed bonds.
4. D. Reaction 1 minus reaction 2: $-393.5 - (-283.0) = -110.5 \text{ kJ}$. Choice A adds the two values instead of reversing the second equation.
5. C. Heat added at 100 degrees C goes into potential energy as molecules separate into the gas phase; kinetic energy (temperature) stays constant. Choice A is false: energy is being added. Covalent bonds stay intact.
6. A. $\Delta H = \Delta H_f(\text{products}) - \Delta H_f(\text{reactants}) = -1675.7 - (-824.2) = -851.5 \text{ kJ}$; Al and Fe are elements with $\Delta H_f = 0$. Choice C adds instead of subtracting.
7. (a) Total mass = 104.0 g; $\Delta T = 18.9 - 22.0 = -3.1$ degrees C. Solution $q = 104.0 \times 4.18 \times (-3.1) = -1.3 \times 10^3 \text{ J}$ (lost); the dissolving process gains $+1.3 \times 10^3 \text{ J}$. (b) $4.00 \text{ g} = 0.04998 \text{ mol}$; $\Delta H = +1.35 \text{ kJ} / 0.04998 = +27 \text{ kJ/mol}$ (endothermic). (c) Heat gained from the room warms the solution, so the observed ΔT is smaller than it should be and the calculated magnitude is **too small**. (d) Use an insulated, lidded cup; stir; extrapolate the temperature to mixing time; use a calibrated thermometer.
8. (a) Moles = 3.00. Melting: $3.00 \times 6.01 = 18.03 \text{ kJ}$; warming: $54.0 \times 4.184 \times 25.0 = 5648 \text{ J} = 5.65 \text{ kJ}$; total **23.7 kJ**. (b) Added energy overcomes attractions between water molecules in the solid, increasing potential energy; the average kinetic energy (temperature) of the particles does not change until all the ice has melted. (c) Lost = gained: $50.0(80.0 - T) = 100.0(T - 20.0)$, so $T = \mathbf{40.0 \text{ degrees C}}$.
9. (a) $\text{C}_2\text{H}_5\text{OH}(\text{l}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l})$. $\Delta H^\circ = 2(-393.5) + 3(-285.8) - (-277.7) = -787.0 - 857.4 + 277.7 = \mathbf{-1366.7 \text{ kJ}}$. (b) $5.00 \text{ g} = 0.1085 \text{ mol}$; $q = 0.1085 \times (-1366.7) = \mathbf{-148 \text{ kJ}}$ (148 kJ released). (c) **Less negative** (-1234.7 kJ): vapor has more energy than liquid, and converting to vapor requires $3(44.0) = 132 \text{ kJ}$.
10. (a) Broken: $945 + 3(436) = 2253 \text{ kJ}$. Formed: $6(391) = 2346 \text{ kJ}$. $\Delta H = 2253 - 2346 = \mathbf{-93 \text{ kJ}}$. (b) Reactants at higher energy on the left, a single hill, products at a lower plateau on the right; a downward arrow labeled $\Delta H = -93 \text{ kJ}$. (c) More energy is released making six N-H bonds than is required to break one N-N triple and three H-H bonds, so the net is exothermic. (d) $2.80 \text{ g} = 0.09993 \text{ mol}$; heat = $0.09993 \times (-93) = \mathbf{-9.3 \text{ kJ}}$.

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Unit 7: Equilibrium

Exam weighting: about 7-9% of the multiple-choice section. Concept review, worked examples, exam-style writing, and 10 practice items, all with full explanations.

7 Equilibrium

Dynamic equilibrium, reaction quotients, ICE tables, Le Chatelier's principle and solubility equilibria: the quantitative toolkit reused in acids, bases and electrochemistry.

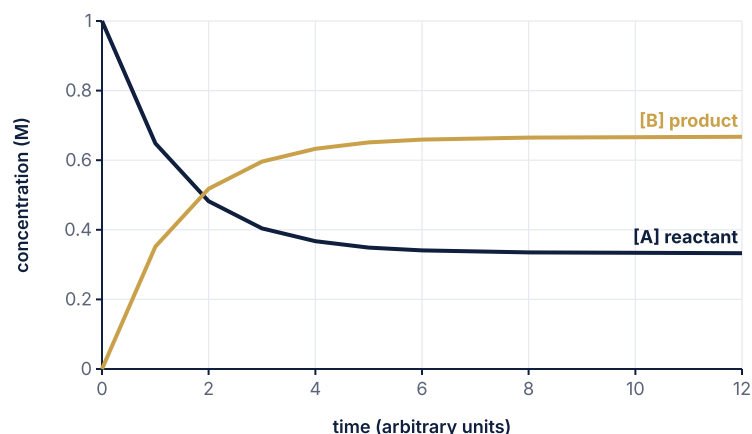
Why This Matters

Equilibrium is the first of the big quantitative ideas that carry into acids, bases, buffers, solubility and electrochemistry, so Unit 7 skills are used again in about a quarter of the exam. Students lose points by writing K with solids included, by comparing Q and K in the wrong direction, by claiming a catalyst shifts equilibrium, and by justifying a prediction with a slogan instead of with Q versus K .

Core Ideas

7.1 Introduction to Equilibrium

A reversible reaction reaches **dynamic equilibrium** when the forward and reverse rates are equal. Concentrations stop changing, but both reactions keep running. Equilibrium is never a halt, and it does not mean the concentrations are equal.



A converts to B until the curves level off. Here $K = 0.667/0.333 = 2.0$.

7.2 Direction of Reversible Reactions and 7.3 Reaction Quotient and Equilibrium Constant

Q and K

For $aA + bB \rightleftharpoons cC + dD$:

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

using the concentrations at any moment. K is the same expression evaluated at equilibrium.

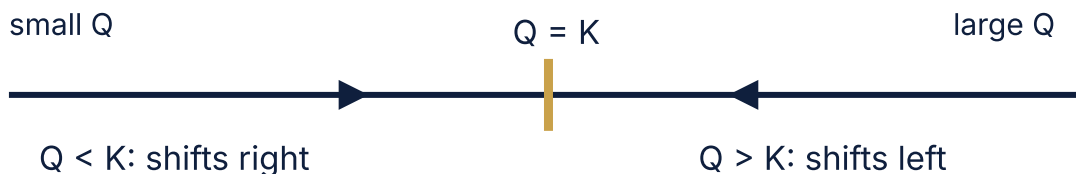
Pure solids and pure liquids are left out. Use brackets (molarity) for K_c and partial pressures for K_p .

$Q < K$: net forward. $Q > K$: net reverse. $Q = K$: at equilibrium.

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Q moves toward K . The system always changes in the direction that brings Q to K .

Reading K as a ratio of rates is a useful mental model: at equilibrium the forward and reverse rates match, so a reaction with a fast forward step and a slow reverse step ends up with a large K . But the size of K never tells you how quickly equilibrium arrives. A reaction with a huge K can still take years if its activation energy is high.

7.4 Calculating the Equilibrium Constant and 7.5 Magnitude of the Equilibrium Constant

Substitute equilibrium concentrations into the expression, keeping units out of K . A very large K ($\gg 1$) means products dominate; a very small K ($\ll 1$) means reactants dominate. K says where equilibrium lies, not how fast it is reached.

Size of K	Meaning at equilibrium
$K > 10^3$	Reaction essentially complete; products dominate
$10^{-3} < K < 10^3$	Significant amounts of both reactants and products
$K < 10^{-3}$	Hardly any reaction; reactants dominate

7.6 Properties of the Equilibrium Constant

Change to the equation	New K
Reverse the reaction	$1/K$
Multiply coefficients by n	K^n
Add two reactions	$K_1 \times K_2$
Change temperature	K changes (the only thing that changes it)
Change concentrations, pressure, add catalyst	K unchanged

For gases, $K_p = K_c(RT)^{\Delta n}$, where Δn is moles of gaseous products minus moles of gaseous reactants.

Worked idea for gases: for $2\text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g)$, $\Delta n = 1 - 2 = -1$, so $K_p = K_c(RT)^{-1}$. Use $R = 0.08206 \text{ L atm/(mol K)}$ with pressures in atm and T in kelvin. Pure solids and liquids contribute nothing to Δn .

7.7 Calculating Equilibrium Concentrations and 7.8 Representations of Equilibrium

ICE method

1. Write the balanced equation and the K expression. 2. Build an Initial, Change, Equilibrium table, with Change in the ratio of coefficients (+x, -x, +2x). 3. Substitute the E row into K . 4. Solve. If K is small and x looks less than 5% of the initial value, you may state and test the approximation; otherwise use the quadratic. 5. Check by recalculating K .

Equilibrium also appears as particle diagrams (the ratio of particles stays constant over time), as concentration-time graphs (curves flatten, but not necessarily to equal heights) and as tables of equilibrium data.

7.9 Introduction to Le Chatelier's Principle and 7.10 Reaction Quotient and Le Chatelier's Principle

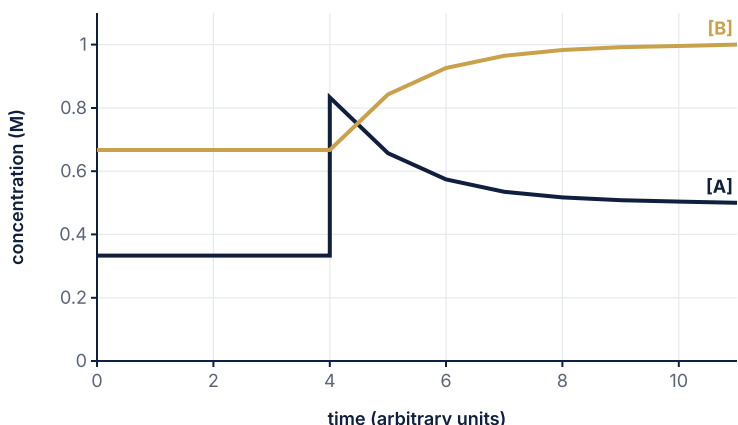
When an equilibrium is disturbed, the system shifts to partly offset the change. The exam wants the reasoning through Q : a stress changes Q (or, for temperature, changes K), and the system moves until $Q = K$ again.

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Stress	Effect on Q or K	Shift
Add reactant	Q falls below K	Forward
Remove product	Q falls below K	Forward
Decrease volume (gas)	Q rises or falls depending on moles of gas	Toward fewer gas moles
Raise T, endothermic forward	K increases	Forward
Raise T, exothermic forward	K decreases	Reverse
Add catalyst or inert gas at constant V	No change	None



A is added at $t = 4$. [A] jumps up, then falls as B forms. The new equilibrium has $K = 1.00/0.50 = 2.0$, the same K .

Two special cases appear often. Adding an inert gas at constant volume leaves every partial pressure unchanged, so Q still equals K and nothing shifts. Adding a catalyst lowers the activation energy of both directions equally, so the time to reach equilibrium shortens but the equilibrium mixture is identical. Temperature is the one stress that changes K itself: treat heat as a product of an exothermic reaction and a reactant of an endothermic one.

7.11 Introduction to Solubility Equilibria and 7.12 Common-Ion Effect

K_{sp} and the common-ion effect

For $M_aX_b(s) \rightleftharpoons aM^{b+} + bX^{a-}$: $K_{sp} = [M^{b+}]^a[X^{a-}]^b$. The solid is not in the expression.

Precipitation occurs when $Q > K_{sp}$. Adding an ion already in the equilibrium lowers solubility because Q rises above K_{sp} and the system shifts toward the solid.

Comparing solubilities: only compare K_{sp} values directly when salts have the same formula type (both 1:1, for instance). A salt with a smaller K_{sp} but a 1:2 or 2:1 ratio can be more soluble in mol/L than a 1:1 salt, so convert to molar solubility first. Dissolving a slightly soluble salt is also affected by acid: if the anion is basic (such as F^- , OH^- or CO_3^{2-}), added H^+ removes it, pulling the equilibrium toward more dissolving (Unit 8 develops this).

Worked Examples

EXAMPLE 1: CALCULATING K

At a fixed temperature an equilibrium mixture of $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ contains 0.060 M SO_2 , 0.030 M O_2 and 0.14 M SO_3 . Find K_c and state what it means.

SOLUTION

$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{(0.14)^2}{(0.060)^2(0.030)} = 1.8 \times 10^2.$$

Square the coefficients: the 2 on SO_2 and SO_3 are exponents.

$K > 1$, so products are favored at equilibrium.

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EXAMPLE 2: Q VERSUS K AND AN ICE TABLE

For $\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$, $K_c = 0.36$. (a) A mixture has 0.30 M NO_2 and 0.50 M N_2O_4 . Which way does it shift? (b) Pure N_2O_4 starts at 0.100 M. Find the equilibrium concentrations.

	N_2O_4	NO_2
Initial (M)	0.100	0
Change (M)	-x	+2x
Equilibrium (M)	0.100 - x	2x

SOLUTION

(a) $Q = \frac{(0.30)^2}{0.50} = 0.18 < 0.36$, so the net reaction goes forward (toward NO_2).

(b) $K = \frac{(2x)^2}{0.100 - x} = 0.36$ gives $4x^2 + 0.36x - 0.036 = 0$, so $x = 0.060$ M.

Check the shortcut: $x = 0.060$ is 60% of 0.100, far above 5%, so the quadratic was required.

$[\text{NO}_2] = 2x = 0.12$ M and $[\text{N}_2\text{O}_4] = 0.040$ M. Check: $0.12^2/0.040 = 0.36$.

EXAMPLE 3: MANIPULATING K

Given $\text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}(g)$, $K_1 = 4.5 \times 10^{-31}$, and $2\text{NO}(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}_2(g)$, $K_2 = 6.0 \times 10^{12}$, find K for $\text{N}_2(g) + 2\text{O}_2(g) \rightleftharpoons 2\text{NO}_2(g)$ and for the reverse reaction.

SOLUTION

Adding the two equations cancels 2 NO and gives the target, so the constants multiply.

$K = K_1 K_2 = (4.5 \times 10^{-31})(6.0 \times 10^{12}) = 2.7 \times 10^{-18}$.

The reverse reaction has $1/K = 3.7 \times 10^{17}$.

EXAMPLE 4: KSP AND THE COMMON-ION EFFECT

For CaF_2 , $K_{sp} = 3.5 \times 10^{-11}$. Find the molar solubility in (a) pure water and (b) 0.010 M NaF.

SOLUTION

(a) Let s mol/L dissolve: $[\text{Ca}^{2+}] = s$, $[\text{F}^-] = 2s$. $K_{sp} = s(2s)^2 = 4s^3$, so $s = \left(\frac{3.5 \times 10^{-11}}{4}\right)^{1/3} = 2.1 \times 10^{-4}$ M.

(b) Initial $[\text{F}^-] = 0.010$ M. $K_{sp} = s(0.010 + 2s)^2 \approx s(0.010)^2$, so $s = 3.5 \times 10^{-11}/1.0 \times 10^{-4} = 3.5 \times 10^{-7}$ M.

The approximation holds because $2s \ll 0.010$. Solubility dropped by a factor of about 600 because added F^- pushes Q above K_{sp} .

Write It Like a 5**Model Response**

Prompt: $2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g)$ is exothermic. At equilibrium $K_c = 1.8 \times 10^2$. (a) Write K_c . (b) The temperature is raised. Predict the change in K_c and the shift. (c) The volume is halved at constant temperature. Justify the shift using Q . \ (a) $K_c = [\text{SO}_3]^2/([\text{SO}_2]^2[\text{O}_2])$. \ (b) The forward reaction releases heat, so heat acts like a product. Raising the temperature favors the endothermic reverse reaction, so K_c decreases and the equilibrium shifts toward SO_2 and O_2 . \ (c) Halving the volume doubles every concentration. The numerator of Q increases by $2^2 = 4$ and the denominator by $2^3 = 8$, so $Q = K_c/2$. Since $Q < K_c$, the reaction proceeds forward, toward the side with fewer gas moles (2 versus 3), until $Q = K_c$ again. K_c itself is unchanged.

What the grader looks for

A correct expression with brackets, products on top, exponents from coefficients and no pure solids. A temperature argument that names the sign of the enthalpy change and says K changes. A volume argument that compares Q with K (or counts gas moles) and states that K does not change. A direction for every shift.

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Coach's Playbook

- 1 Write the balanced equation first, then the K expression, then decide whether the question asks for K , Q or an equilibrium amount.
- 2 Convert everything to concentration (or pressure) before substituting. Moles must be divided by volume.
- 3 For a prediction, compute or reason about Q and say whether $Q < K$, $Q > K$ or $Q = K$.
- 4 Test any x -is-small shortcut by checking that x is under 5% of the starting value; say so in the answer.
- 5 After solving an ICE table, plug the values back into K as a check.

Common traps

(1) Including solids or liquids in K . (2) Saying a catalyst shifts equilibrium; it speeds both directions equally and leaves K and the equilibrium amounts unchanged. (3) Describing equilibrium as static or as equal concentrations. (4) Writing that H^+ reacts with solid $Mg(OH)_2$; it reacts with dissolved OH^- , which pulls the dissolution equilibrium forward.

Quick Check

Q1. What is the unit of K for $H_2 + I_2 \rightleftharpoons 2HI$? A: None; the exponents cancel here and K is treated as unitless. Q2. K is 2.0×10^{-3} for a reaction. Which species dominate? A: Reactants. Q3. What is the only factor that changes K ? A: Temperature.

Challenge Corner

Equal volumes of $2.0 \times 10^{-3} \text{ M AgNO}_3$ and $1.0 \times 10^{-3} \text{ M NaCl}$ are mixed (K_{sp} of $AgCl = 1.8 \times 10^{-10}$). Does $AgCl$ precipitate? Solution: mixing halves each concentration, so $[Ag^+] = 1.0 \times 10^{-3}$ and $[Cl^-] = 5.0 \times 10^{-4}$. $Q = (1.0 \times 10^{-3})(5.0 \times 10^{-4}) = 5.0 \times 10^{-7}$, which exceeds 1.8×10^{-10} , so a precipitate forms. Forgetting to halve gives the wrong Q but the same conclusion here, so always show the dilution step.

Practice

PRACTICE Unit 7 Practice

Show your work. A calculator is allowed. Justify conclusions.

1. For $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$, which is the correct equilibrium expression?
 (A) $K = \frac{[CaO][CO_2]}{[CaCO_3]}$ (B) $K = [CO_2]$ (C) $K = \frac{1}{[CO_2]}$
 (D) $K = \frac{[CaCO_3]}{[CaO][CO_2]}$
2. For $A(g) + B(g) \rightleftharpoons C(g)$, $K_c = 50$. A mixture has $[A] = 0.20 \text{ M}$, $[B] = 0.10 \text{ M}$ and $[C] = 0.50 \text{ M}$. Which statement is correct?
 (A) $Q = 0.04$, so the reaction shifts left. (B) $Q = 25$, so the reaction shifts left.
 (C) $Q = 25$, so the reaction shifts right. (D) $Q = 50$, so the mixture is at equilibrium.
3. For $N_2 + 3H_2 \rightleftharpoons 2NH_3$, $K_c = 3.6 \times 10^2$ at some temperature. What is K_c for $\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightleftharpoons NH_3$ at that temperature?
 (A) 19 (B) 1.3×10^5 (C) 1.8×10^2 (D) 2.8×10^{-3}
4. $A(g) + B(g) \rightleftharpoons 2C(g)$ has $\Delta H = -40 \text{ kJ}$. The temperature of an equilibrium mixture is raised at constant volume. Which is true?
 (A) K is unchanged because the number of gas moles is equal on both sides.
 (B) K increases and the equilibrium shifts toward C.
 (C) K is unchanged but the rate of the reverse reaction exceeds the forward rate permanently.
 (D) K decreases and the equilibrium shifts toward A and B.

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5. The K_{sp} of Ag_2CrO_4 is 1.1×10^{-12} . What is its molar solubility in pure water?
 (A) 1.0×10^{-6} M (B) 1.0×10^{-4} M (C) 6.5×10^{-5} M
 (D) 1.3×10^{-4} M
6. In which solution is AgCl ($K_{sp} = 1.8 \times 10^{-10}$) least soluble?
 (A) Pure water (B) 0.10 M KNO_3 (C) 0.10 M NH_3
 (D) 0.10 M NaCl
7. At a certain temperature $K_c = 50.0$ for $\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g)$. A 1.00 L flask is filled with 0.400 mol each of H_2 and I_2 (no HI).
 (a) Write the expression for K_c .
 (b) Calculate the equilibrium concentration of each species.
 (c) Explain why the approximation that x is small cannot be used.
8. Equilibrium data were collected for $\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g)$ in three trials at one temperature.
 Trial 1: $[\text{H}_2] = 0.050$, $[\text{I}_2] = 0.20$, $[\text{HI}] = 0.224$ M.
 Trial 2: $[\text{H}_2] = 0.30$, $[\text{I}_2] = 0.10$, $[\text{HI}] = 0.39$ M.
 Trial 3: $[\text{H}_2] = 0.10$, $[\text{I}_2] = 0.40$, $[\text{HI}] = 0.45$ M.
 (a) Calculate K_c for each trial. (b) Do the data support one value of K_c ? Justify. (c) Describe an observation that shows a system has reached equilibrium and explain why the reactions have not stopped.
9. K_{sp} of PbI_2 is 9.8×10^{-9} .
 (a) Calculate its molar solubility in pure water.
 (b) Calculate its molar solubility in 0.050 M NaI .
 (c) Explain, using Q , why the answers to (a) and (b) differ.
10. At 25 degrees C, $\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$ has $K_c = 0.36$. An equilibrium mixture has $[\text{N}_2\text{O}_4] = 0.040$ M and $[\text{NO}_2] = 0.12$ M. The volume is suddenly cut in half at constant temperature.
 (a) Calculate Q immediately afterward.
 (b) Predict the direction of shift and justify it.
 (c) Calculate the new equilibrium concentrations.

Answers Unit 7: Answers and Explanations

Read every explanation, including the ones for problems you answered correctly.

7 Equilibrium

PRACTICE · UNIT 7 PRACTICE

- B. Pure solids do not appear in K , so only $[\text{CO}_2]$ remains. Choice A is the tempting error of including solids; choices C and D invert or include them.
- C. $Q = 0.50 / (0.20 \times 0.10) = 25$. Since $25 < 50$, products must form (shift right). Choice B has the right number but the wrong direction, a common Q versus K reversal.
- A. Halving the coefficients takes the square root: $\sqrt{360} = 19$. Squaring (B) would apply to doubling; dividing by 2 (C) is not how exponents work; D reverses the reaction as well.
- D. An exothermic forward reaction releases heat, so raising T favors the reverse reaction and lowers K . Equal gas moles matter for pressure changes, not temperature (choice A).
- C. $K_{sp} = 4s^3$, so $s = (1.1 \times 10^{-12} / 4)^{1/3} = 6.5 \times 10^{-5}$ M. Taking a square root (A) or cube root without the 4 (B) ignores the stoichiometry.
- D. Adding Cl^- raises Q above K_{sp} , the common-ion effect. NH_3 forms a complex with Ag^+ and increases solubility (C); KNO_3 has no common ion (B).
- (a) $K_c = [\text{HI}]^2 / ([\text{H}_2][\text{I}_2])$. [1 point]
 (b) ICE: $[\text{H}_2] = [\text{I}_2] = 0.400 - x$, $[\text{HI}] = 2x$. $(2x)^2 / (0.400 - x)^2 = 50.0$ so $2x / (0.400 - x) = \sqrt{50.0} = 7.07$; $x = 0.312$. $[\text{HI}] = 0.624$ M, $[\text{H}_2] = [\text{I}_2] = 0.088$ M. Check: $0.624^2 / 0.088^2 = 50$. [3 points]
 (c) $x = 0.312$ is 78% of 0.400, far above 5%, so $0.400 - x$ cannot be treated as 0.400 (K is large, so the reaction goes nearly to completion). [1 point]
- (a) $K = (0.224)^2 / (0.050 \times 0.20) = 5.0$; Trial 2: $(0.39)^2 / (0.30 \times 0.10) = 5.1$; Trial 3: $(0.45)^2 / (0.10 \times 0.40) = 5.1$.
 (b) Yes: the three values agree within rounding (about 5.1) even though the concentrations differ, as expected because K depends only on temperature.
 (c) Constant, unchanging concentrations (or a constant color or pressure) over time. The forward and reverse reactions continue at equal rates, so there is no net change: equilibrium is dynamic.

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9. (a) $K_{sp} = 4s^3$, $s = (9.8 \times 10^{-9}/4)^{1/3} = 1.3 \times 10^{-3} \text{ M}$.
(b) $K_{sp} = s(0.050 + 2s)^2 \approx s(0.050)^2$; $s = 9.8 \times 10^{-9}/2.5 \times 10^{-3} = 3.9 \times 10^{-6} \text{ M}$ ($2s$ is negligible against 0.050).
(c) Extra I^- from NaI makes $Q = [\text{Pb}^{2+}][\text{I}^-]^2$ larger than K_{sp} in a saturated solution, so the dissolution equilibrium shifts toward the solid and less PbI_2 dissolves.
10. (a) Halving the volume doubles both concentrations: $[\text{NO}_2] = 0.24$, $[\text{N}_2\text{O}_4] = 0.080$. $Q = (0.24)^2/0.080 = 0.72$.
(b) $Q = 0.72 > K_c = 0.36$, so the reaction shifts in reverse, toward N_2O_4 (1 gas mole instead of 2), until $Q = K_c$.
(c) Let y mol/L of NO_2 pairs react: $(0.24 - 2y)^2/(0.080 + y) = 0.36$. Solving gives $y = 0.0235$. $[\text{NO}_2] = 0.19 \text{ M}$ and $[\text{N}_2\text{O}_4] = 0.10 \text{ M}$. Check: $0.193^2/0.1035 = 0.36$.

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Unit 8: Acids and Bases

Exam weighting: about 11-15% of the multiple-choice section. Concept review, worked examples, exam-style writing, and 10 practice items, all with full explanations.

8 Acids and Bases

From pH and weak-acid equilibria to buffers and titration curves: the Henderson-Hasselbalch toolkit and the reasoning behind acid strength and solubility.

Why This Matters

Acids and bases carry the largest unit weighting after Unit 3 (11 to 15% of the multiple-choice section), and the ideas return in solubility, buffers and electrochemistry. Points are lost by treating a weak acid as strong, reading pK_a at the equivalence point instead of the half-equivalence point, flipping the base-to-acid ratio in Henderson-Hasselbalch, and forgetting to do the stoichiometry before the equilibrium step.

Core Ideas

8.1 Introduction to Acids and Bases

A Bronsted-Lowry acid donates H^+ ; a base accepts it. Each acid has a conjugate base one proton lighter, and water is amphiprotic. At 25 degrees C, $K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$, so $pH + pOH = 14.00$. For a conjugate pair, $K_a \times K_b = K_w$, which means a stronger acid has a weaker conjugate base.

8.2 pH and pOH of Strong Acids and Bases

Strong acid and base pH

$$pH = -\log[H^+] \text{ and } pOH = -\log[OH^-].$$

Strong acids (HCl, HBr, HI, HNO_3 , $HClO_4$, H_2SO_4 first proton) and strong bases (group 1 hydroxides, $Ca(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$) ionize or dissociate completely, so $[H^+]$ or $[OH^-]$ comes straight from stoichiometry. Count hydroxides: 0.015 M $Ba(OH)_2$ gives 0.030 M OH^- .

In logs, the number of decimal places in the pH equals the number of significant figures in the concentration.

8.3 Weak Acid and Base Equilibria

A weak acid ionizes only slightly, $HA + H_2O \rightleftharpoons H_3O^+ + A^-$, with $K_a = \frac{[H^+][A^-]}{[HA]}$. Use an ICE table with $[H^+] = [A^-] = x$ and, when x is under 5% of the initial concentration, $K_a \approx x^2/C$. Percent ionization is $\frac{x}{C} \times 100$ and rises on dilution. Weak bases work the same way with K_b and $[OH^-]$.

8.4 Acid-Base Reactions and Buffers

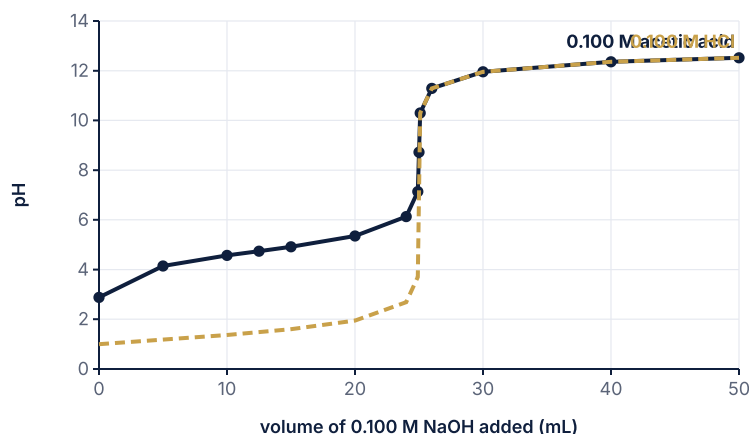
A strong acid or strong base reacts with a weak partner essentially to completion, so do the mole stoichiometry first, then treat what is left as an equilibrium problem. A **buffer** contains a weak acid and its conjugate base (or a weak base and its conjugate acid) in comparable amounts. Added acid is consumed by the base component, added base by the acid component, so the pH barely moves.

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8.5 Acid-Base Titrations



25.0 mL of each acid titrated with 0.100 M NaOH. Equivalence is at 25.0 mL for both; the weak acid starts higher, has a buffer region, passes through $\text{pH} = \text{pK}_a = 4.74$ at 12.5 mL, and reaches equivalence above pH 7.

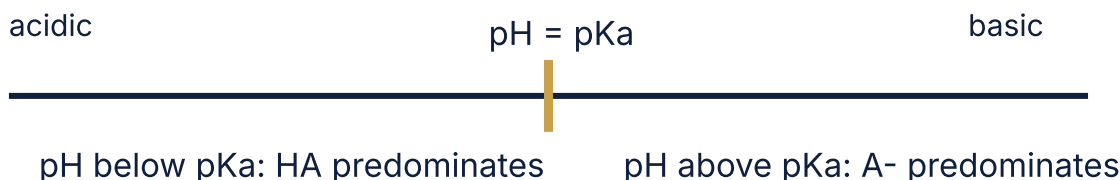
Reading a weak acid titration curve

Initial point: weak-acid equilibrium. Buffer region: Henderson-Hasselbalch. **Half-equivalence** (half the acid neutralized): $[\text{HA}] = [\text{A}^-]$, so $\text{pH} = \text{pK}_a$. **Equivalence**: moles base equal moles acid; the solution holds only A^- , so pH is above 7. Beyond equivalence: excess strong base sets the pH.

8.6 Molecular Structure of Acids and Bases

Acid strength depends on how easily H^+ leaves and how stable the conjugate base is. Down a group (HF to HI) the H-X bond lengthens and weakens, so acidity increases even though electronegativity falls. Across a period, a more electronegative atom makes the bond more polar and the anion more stable. In oxyacids, more oxygen atoms on the central atom pull electron density away and stabilize the anion: $\text{HClO} < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}_4$. Carboxylic acids are stronger than alcohols because resonance delocalizes the negative charge in the carboxylate.

8.7 pH and pKa



The pK_a marks the pH at which an acid is half converted to its conjugate base.

8.8 Properties of Buffers, 8.9 Henderson-Hasselbalch Equation and 8.10 Buffer Capacity

Henderson-Hasselbalch

$$\text{pH} = \text{pK}_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

Base on top, acid on the bottom, base-10 log. Because both species share one volume, you may use moles instead of concentrations.

Buffer capacity depends on the amounts of both components. A buffer works best within about one pH unit of pK_a (ratio between 1:10 and 10:1). Diluting both components equally keeps the pH but lowers capacity.

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8.11 pH and Solubility

Adding acid dissolves salts whose anion is basic (F^- , OH^- , CO_3^{2-} , PO_4^{3-}) because H^+ reacts with the dissolved anion and pulls the dissolution equilibrium forward. Salts of anions that are negligibly basic (Cl^- , Br^- , I^-) do not change. The acid reacts with the dissolved anion, not with the solid.

Worked Examples

EXAMPLE 1: STRONG ACID AND BASE

Find the pH of (a) 0.0025 M HCl and (b) 0.015 M $Ba(OH)_2$.

SOLUTION

(a) $[H^+] = 0.0025\text{ M}$, $pH = -\log(0.0025) = 2.60$.

(b) $[OH^-] = 2(0.015) = 0.030\text{ M}$, $pOH = 1.52$, so $pH = 14.00 - 1.52 = 12.48$.

EXAMPLE 2: K_a FROM A MEASURED PH

A 0.200 M solution of a weak monoprotic acid HX has pH 2.85. Find K_a and the percent ionization.

	HX	H^+	X^-
Initial (M)	0.200	0	0
Change (M)	-x	+x	+x
Equilibrium (M)	$0.200 - x$	x	x

SOLUTION

$[H^+] = 10^{-2.85} = 1.4 \times 10^{-3}\text{ M} = x$.

$$K_a = \frac{x^2}{0.200 - x} = \frac{(1.4 \times 10^{-3})^2}{0.199} = 1.0 \times 10^{-5}.$$

Percent ionization = $1.4 \times 10^{-3} / 0.200 \times 100 = 0.71\%$, under 5%, so the approximation is valid.

EXAMPLE 3: A BUFFER AFTER ADDING STRONG ACID

A buffer holds 0.0100 mol CH_3COOH and 0.0150 mol CH_3COO^- ($K_a = 1.8 \times 10^{-5}$). Find the pH before and after adding 0.0020 mol HCl.

SOLUTION

$pK_a = 4.74$. Before: $pH = 4.74 + \log(0.0150/0.0100) = 4.92$.

HCl reacts with the base: CH_3COO^- falls to 0.0130 mol and CH_3COOH rises to 0.0120 mol.

After: $pH = 4.74 + \log(0.0130/0.0120) = 4.78$. The pH fell by only 0.14.

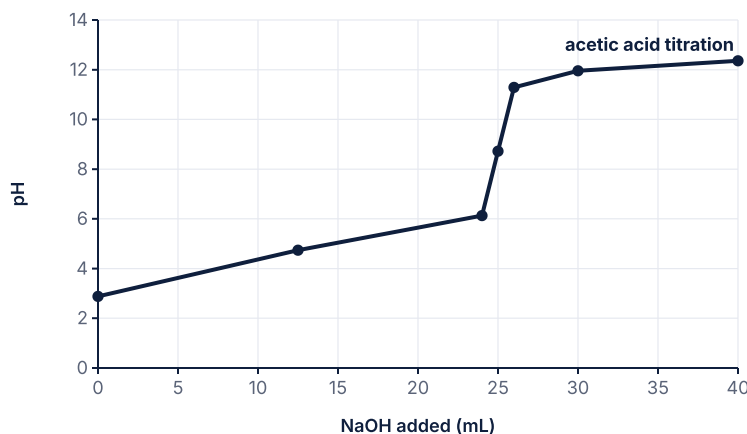
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EXAMPLE 4: POINTS ON A TITRATION CURVE

25.0 mL of 0.100 M acetic acid is titrated with 0.100 M NaOH. Find the pH at 12.5 mL, 25.0 mL and 30.0 mL.



Selected points from Example 4.

SOLUTION

12.5 mL: half-equivalence, $[HA] = [A^-]$, $pH = pK_a = 4.74$.

25.0 mL: 2.50 mmol of A^- in 50.0 mL gives 0.0500 M. $K_b = 1.0 \times 10^{-14} / 1.8 \times 10^{-5} = 5.6 \times 10^{-10}$, $[OH^-] = \sqrt{(5.6 \times 10^{-10})(0.0500)} = 5.3 \times 10^{-6}$ M, $pOH = 5.28$, $pH = 8.72$.

30.0 mL: excess OH^- is 0.500 mmol in 55.0 mL = 9.09×10^{-3} M, $pOH = 2.04$, $pH = 11.96$.

Write It Like a 5**Model Response**

Prompt: A weak acid HA is titrated with NaOH. Explain why the pH at the half-equivalence point equals pK_a and why the pH at the equivalence point is greater than 7. At half-equivalence half of the HA has been converted to A^- by the added OH^- , so $[A^-] = [HA]$. In $pH = pK_a + \log([A^-]/[HA])$ the log of 1 is zero, so $pH = pK_a$. At equivalence all HA has been converted to A^- , the conjugate base of a weak acid. A^- reacts with water, $A^- + H_2O \rightleftharpoons HA + OH^-$, producing OH^- , so the solution is basic and the pH is above 7.

What the grader looks for

The two points are named separately. The ratio $[A^-]/[HA] = 1$ is stated and tied to the log term for the half-equivalence point. The equivalence argument identifies the species present (only the conjugate base) and writes or describes its reaction with water that produces OH^- . Vague statements such as 'it becomes basic' earn nothing.

Coach's Playbook

- 1 Classify first: strong acid or base (stoichiometry only), weak acid or base (ICE), buffer (H-H after stoichiometry), or titration point (identify which region).
- 2 In any mixing problem convert to moles, react the strong species to completion, then use the leftover moles or the new total volume.
- 3 Estimate before calculating: a weak-acid pH should be well above the strong-acid pH of the same concentration; a pH of 1.00 for 0.10 M of a weak acid signals a mistake.
- 4 For H-H, write 'base over acid' on your paper, and compute the ratio before taking the log.
- 5 Match answer precision to the concentration: two significant figures gives two decimals in pH.

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Common traps

(1) Reading pK_a at the equivalence point; it belongs to the half-equivalence point. (2) Inverting the ratio or using $\ln$ in Henderson-Hasselbalch. (3) Writing that $K_a \times K_b = K_w$ as $K_a = K_w - K_b$ or $K_a = 1/K_b$. (4) Giving pOH when the question asks for pH , or treating a weak acid as fully ionized.

Quick Check

Q1. What is the pH of 0.020 M NaOH? A: 12.30. Q2. A buffer has $pH = pK_a$. What is $[A^-]/[HA]$? A: 1. Q3. Does the solubility of AgCl change much in acid? A: No, because Cl^- is a negligible base.

Challenge Corner

K_{sp} of $Mg(OH)_2$ is 5.6×10^{-12} . Compare its molar solubility in pure water with that in a solution buffered at pH 9.00. Solution: pure water: $4s^3 = 5.6 \times 10^{-12}$, $s = 1.1 \times 10^{-4}$ M. At pH 9.00, $[OH^-] = 1.0 \times 10^{-5}$ M, so $s = K_{sp}/[OH^-]^2 = 5.6 \times 10^{-12}/1.0 \times 10^{-10} = 5.6 \times 10^{-2}$ M, about 500 times larger. The buffer keeps OH^- low by removing it with H^+ , so more solid dissolves.

Practice**PRACTICE Unit 8 Practice**

Show your work. A calculator is allowed. Justify conclusions.

- What is the pH of 0.020 M NaOH at 25 degrees C?
(A) 1.70 (B) 12.00 (C) 12.30 (D) 13.30
- A 0.10 M solution of a weak acid HX has $K_a = 4.0 \times 10^{-6}$. What is the pH , using the usual approximation?
(A) 1.00 (B) 3.20 (C) 5.40 (D) 6.40
- During the titration of a weak monoprotic acid with NaOH, the pH at the half-equivalence point is 4.20. What is K_a of the acid?
(A) 6.3×10^{-5} (B) 4.2×10^0 (C) 1.6×10^{-10} (D) 6.3×10^{-10}
- A buffer contains 0.10 M $HCOOH$ ($K_a = 1.8 \times 10^{-4}$) and 0.20 M $HCOO^-$. What is its pH ?
(A) 3.44 (B) 3.74 (C) 7.00 (D) 4.05
- Which statement best explains why HI is a stronger acid than HF in water?
(A) Fluorine is more electronegative, so the H-F bond is more polar and breaks more easily.
(B) The H-I bond is longer and weaker than the H-F bond, so H^+ is released more easily.
(C) Iodine has a larger molar mass, which increases ionization.
(D) HF forms hydrogen bonds with itself, which makes it a stronger acid.
- A saturated solution of each salt is acidified. For which salt does the solubility increase the most?
(A) CaF_2 (B) AgCl (C) AgI (D) AgBr
- (a) Calculate the pH of 0.0040 M $Ba(OH)_2$.
(b) Calculate the pH of 0.250 M methylamine, CH_3NH_2 ($K_b = 4.4 \times 10^{-4}$).
(c) Show that the approximation used in (b) is valid.
- A buffer is made in 0.500 L of solution with 0.20 M acetic acid and 0.30 M sodium acetate ($K_a = 1.8 \times 10^{-5}$).
(a) Calculate the pH .
(b) Calculate the pH after 0.0100 mol HCl is added (no volume change).
(c) Explain, with a net ionic equation, why the pH changes so little.

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9. A student titrates 20.0 mL of an unknown monoprotic weak acid with 0.100 M NaOH. The steepest part of the pH curve is at 30.0 mL, and the pH at 15.0 mL is 4.20.
- Calculate the concentration of the acid.
 - Determine K_a and justify your method.
 - Calculate the pH at the equivalence point.
 - The student has indicators that change color near pH 3, pH 6 and pH 9. Which should be used? Justify.
10. (a) Rank HClO , HClO_2 and HClO_3 by acid strength and explain using structure.
- An acid has $pK_a = 4.8$. At pH 6.0, which form predominates and what is the ratio $[\text{A}^-]/[\text{HA}]$?
 - A buffer is 1.0 M/1.0 M in acid and base; another is 0.10 M/0.10 M. Both have the same pH. Which has more capacity? Explain.

Answers Unit 8: Answers and Explanations

Read every explanation, including the ones for problems you answered correctly.

8 Acids and Bases

PRACTICE · UNIT 8 PRACTICE

- C. $pOH = -\log(0.020) = 1.70$, so $pH = 14.00 - 1.70 = 12.30$. Choice A reports the pOH, the classic wrong-quantity error.
- B. $x = \sqrt{(4.0 \times 10^{-6})(0.10)} = 6.3 \times 10^{-4}$, $pH = 3.20$. Choice C is $-\log K_a$ and choice A treats the acid as strong.
- A. At half-equivalence $pH = pK_a$, so $K_a = 10^{-4.20} = 6.3 \times 10^{-5}$. Choice C is K_b of the conjugate base (K_w/K_a), a different quantity.
- D. $pK_a = 3.74$ and $\log(0.20/0.10) = 0.30$, so $pH = 4.05$. Choice A inverts the ratio, and choice B forgets the ratio entirely.
- B. Acidity in the hydrogen halides is controlled by bond strength: the long H-I bond is much weaker. Choice A cites bond polarity, which is real but is outweighed by bond strength, which is why HF is the weakest.
- A. F^- is the conjugate base of a weak acid, so H^+ removes dissolved F^- and pulls CaF_2 into solution. The halides of silver have anions that are negligible bases.
- (a) $[\text{OH}^-] = 2(0.0040) = 0.0080 \text{ M}$, $pOH = 2.10$, $pH = 11.90$. [1 point]
 (b) $x = \sqrt{(4.4 \times 10^{-4})(0.250)} = 0.0105 \text{ M} = [\text{OH}^-]$, $pOH = 1.98$, $pH = 12.02$. [2 points]
 (c) $0.0105/0.250 = 4.2\%$, under 5%, so $0.250 - x \approx 0.250$ is acceptable. [1 point]
- (a) $pH = 4.74 + \log(0.30/0.20) = 4.92$. [1 point]
 (b) Moles: $\text{HAc } 0.100$, $\text{Ac}^- 0.150$. After HCl : $\text{HAc } 0.110$, $\text{Ac}^- 0.140$. $pH = 4.74 + \log(0.140/0.110) = 4.85$. [2 points]
 (c) $\text{CH}_3\text{COO}^- + \text{H}^+ \rightarrow \text{CH}_3\text{COOH}$. The added acid is consumed by the large reservoir of acetate, so the ratio of base to acid changes only slightly and the log term barely moves. [1 point]
- (a) Equivalence at 30.0 mL: $n = 0.100 \times 0.0300 = 3.00 \times 10^{-3} \text{ mol}$, so $C = 3.00 \times 10^{-3}/0.0200 = 0.150 \text{ M}$. [1 point]
 (b) 15.0 mL is half of 30.0 mL, so $pH = pK_a = 4.20$ and $K_a = 10^{-4.20} = 6.3 \times 10^{-5}$. At half-equivalence $[\text{HA}] = [\text{A}^-]$. [2 points]
 (c) $[\text{A}^-] = 3.00 \text{ mmol}/50.0 \text{ mL} = 0.0600 \text{ M}$. $K_b = 1.0 \times 10^{-14}/6.3 \times 10^{-5} = 1.6 \times 10^{-10}$. $[\text{OH}^-] = \sqrt{(1.6 \times 10^{-10})(0.0600)} = 3.1 \times 10^{-6}$, $pOH = 5.51$, $pH = 8.49$. [2 points]
 (d) The pH-9 indicator, because its color change range lies on the steep part around pH 8.5; the others change color well before equivalence. [1 point]
- (a) $\text{HClO}_3 > \text{HClO}_2 > \text{HClO}$. More oxygen atoms on chlorine withdraw electron density from the O-H bond and stabilize the anion by spreading its charge, so the H leaves more easily. [2 points]
 (b) $pH > pK_a$, so A^- predominates. $[\text{A}^-]/[\text{HA}] = 10^{6.0-4.8} = 16$. [2 points]
 (c) The 1.0 M/1.0 M buffer has more capacity because it contains more moles of both components to neutralize added acid or base; the pH is the same because the ratio is the same. [1 point]

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Unit 9: Thermodynamics and Electrochemistry

Exam weighting: about 7-9% of the multiple-choice section. Concept review, worked examples, exam-style writing, and 10 practice items, all with full explanations.

9 Thermodynamics and Electrochemistry

Entropy, Gibbs free energy, and how ΔG links to K and cell potential, followed by galvanic and electrolytic cells, the Nernst equation and Faraday's law.

Why This Matters

This unit joins thermodynamics to equilibrium and to electricity: the same quantity, ΔG° , links favorability, K and cell potential. It is a smaller share of the exam (7 to 9%), but it is heavy on reasoning. Points are lost by arguing favorability from ΔH alone, by explaining entropy with the word 'disorder' instead of a particle-level change, by multiplying E° by coefficients, and by skipping the electron-to-metal mole ratio in electrolysis.

Core Ideas

9.1 Introduction to Entropy and 9.2 Absolute Entropy and Entropy Change

Entropy (S) measures how many ways energy can be distributed among the particles of a system, so it increases when particles gain freedom of motion or when the number of particles in the gas phase goes up. Absolute entropies are always positive, $S^\circ(\text{gas}) \gg S^\circ(\text{liquid}) > S^\circ(\text{solid})$, and larger or more complex molecules have more. For a reaction, $\Delta S^\circ = \sum S^\circ(\text{products}) - \sum S^\circ(\text{reactants})$.

- ◆ Positive ΔS : a gas forms from a solid or liquid, more gas moles, a solid dissolves into free ions, temperature rises.
- ◆ Negative ΔS : gas moles decrease, ions precipitate, a gas condenses.
- ◆ Write the particle-level cause: 'two moles of gas form from one mole of a solid', not 'more disorder'.

9.3 Gibbs Free Energy and Thermodynamic Favorability

Gibbs free energy

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

with T in kelvin and ΔH and ΔS in matching energy units (kJ with kJ/K, or J with J/K).

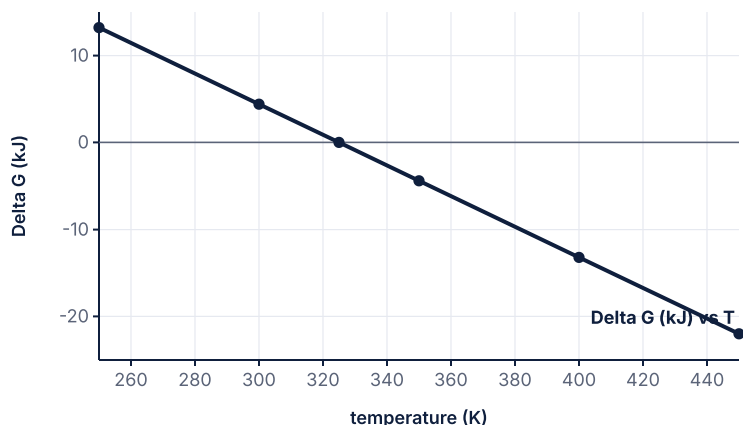
$\Delta G < 0$ means thermodynamically favorable; $\Delta G > 0$ unfavorable. Favorable says nothing about speed.

Delta H	Delta S	Favorable?
negative	positive	At all temperatures
positive	negative	At no temperature
negative	negative	Only at low T
positive	positive	Only at high T

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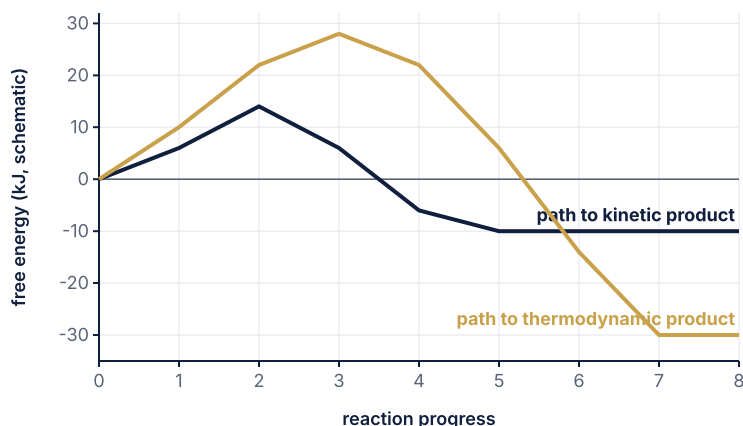
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For $\text{N}_2\text{O}_4(\text{g})$ going to $2 \text{NO}_2(\text{g})$: $\Delta H = +57.2 \text{ kJ}$, $\Delta S = +176 \text{ J/K}$. The line has slope $-\Delta S$ and crosses zero at $T = \Delta H/\Delta S = 325 \text{ K}$.

9.4 Thermodynamic and Kinetic Control

Thermodynamics tells you whether a change is favorable; kinetics, through the activation energy, tells you whether it is fast. Diamond is slightly less stable than graphite, yet it persists for ages because the activation barrier is enormous. When two products can form, the faster path gives the kinetic product and the more stable one the thermodynamic product.



Lower barrier: formed faster. Lower final energy: more stable.

9.5 Free Energy and Equilibrium

Delta G and K

$$\Delta G^\circ = -RT \ln K \quad R = 8.314 \text{ J/(mol K)}$$

$K > 1$ when $\Delta G^\circ < 0$; $K < 1$ when $\Delta G^\circ > 0$; $K = 1$ when $\Delta G^\circ = 0$.

Away from standard conditions, $\Delta G = \Delta G^\circ + RT \ln Q$, so $\Delta G < 0$ whenever $Q < K$.

9.6 Free Energy of Dissolution and 9.7 Coupled Reactions

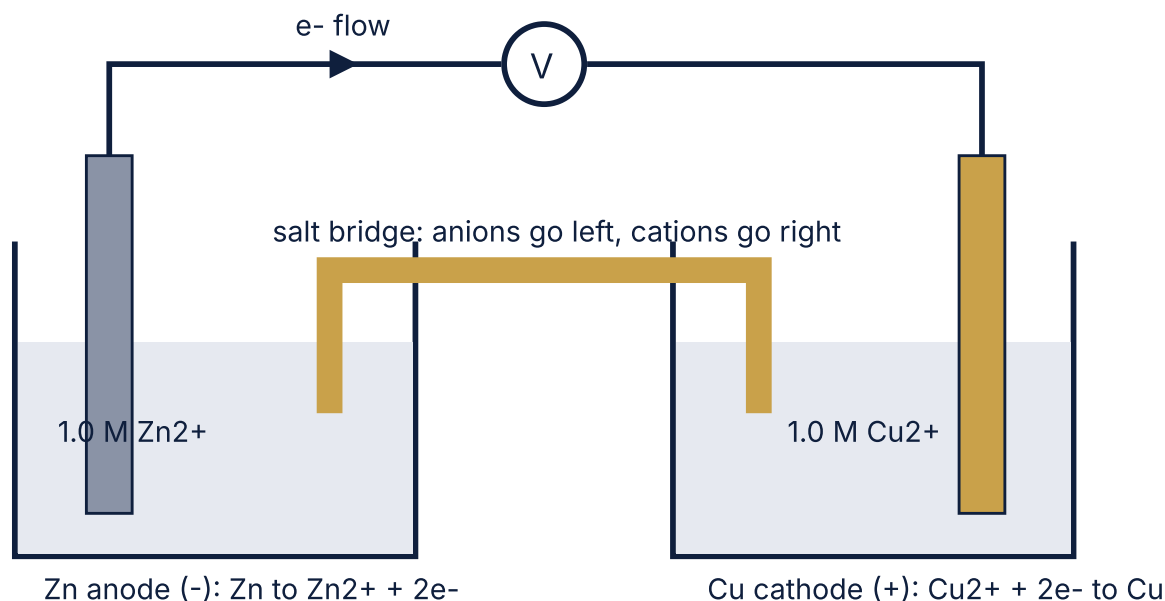
For dissolving, $\Delta G_{\text{diss}}^\circ = -RT \ln K_{\text{sp}}$. A small K_{sp} gives a positive ΔG° . A salt can dissolve even if $\Delta H > 0$ when the entropy gain of freed ions makes $-T\Delta S$ large enough. An unfavorable reaction can be driven by coupling it to a favorable one that shares an intermediate: free energies add, so $\Delta G_{\text{total}} = \Delta G_1 + \Delta G_2$. For example $+31 \text{ kJ}$ and -48 kJ combine to -17 kJ .

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9.8 Galvanic (Voltaic) and Electrolytic Cells



A zinc-copper galvanic cell. Oxidation at the anode, reduction at the cathode; electrons flow through the wire from anode to cathode.

Cell facts

Oxidation occurs at the **anode**; reduction at the **cathode** (in every cell). Electrons travel through the wire from anode to cathode; ions carry charge through the salt bridge.

Galvanic cell: spontaneous, $E_{\text{cell}}^{\circ} > 0$, anode is negative. Electrolytic cell: driven by an external source because $E_{\text{cell}}^{\circ} < 0$, anode is positive.

$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$ using reduction potentials. Never multiply E° by coefficients.

9.9 Cell Potential and Free Energy and 9.10 Cell Potential Under Nonstandard Conditions

Electrochemical relationships

$\Delta G^{\circ} = -nFE^{\circ}$ with $F = 96,485 \text{ C/mol e}^{-}$ and n the moles of electrons transferred. Also $nFE^{\circ} = RT \ln K$.

Nernst: $E = E^{\circ} - \frac{RT}{nF} \ln Q$, which at 25 degrees C is $E = E^{\circ} - \frac{0.0592}{n} \log Q$. $E = 0$ at equilibrium (a dead cell).

9.11 Electrolysis and Faraday's Law

Charge passed is $q = It$ (coulombs from amperes times seconds). Moles of electrons = q/F . Convert to moles of metal using the half-reaction ratio (Cu²⁺ needs 2 e⁻, Ag⁺ needs 1, Al³⁺ needs 3), then multiply by molar mass.

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Worked Examples

EXAMPLE 1: ENTROPY, ENTHALPY AND TEMPERATURE

For $\text{N}_2\text{O}_4(g) \rightarrow 2\text{NO}_2(g)$, $\Delta H^\circ = +57.2 \text{ kJ}$. Use the data to find ΔS° , ΔG° at 298 K and the temperature above which the reaction is favorable.

Species	S (J/(mol K))
$\text{N}_2\text{O}_4(g)$	304.2
$\text{NO}_2(g)$	240.1

SOLUTION

$\Delta S^\circ = 2(240.1) - 304.2 = +176.0 \text{ J/K}$. Positive: one mole of gas becomes two.

$\Delta G^\circ = 57.2 - 298(0.1760) = +4.8 \text{ kJ}$, unfavorable at 298 K.

$\Delta G = 0$ at $T = \Delta H / \Delta S = 57,200 / 176.0 = 325 \text{ K}$. Above 325 K, $-T\Delta S$ outweighs ΔH and the reaction is favorable.

EXAMPLE 2: DELTA G AND K

(a) For the reaction in Example 1, find K at 298 K. (b) Use $K_{sp}(\text{AgCl}) = 1.8 \times 10^{-10}$ to find ΔG° for dissolving AgCl and interpret it.

SOLUTION

(a) $K = e^{-\Delta G^\circ / RT} = \exp[-4752 / (8.314 \times 298)] = 0.15$. $K < 1$ matches $\Delta G^\circ > 0$.

(b) $\Delta G^\circ = -RT \ln K_{sp} = -(8.314)(298) \ln(1.8 \times 10^{-10}) = +5.6 \times 10^4 \text{ J} = +56 \text{ kJ/mol}$.

The large positive value means that dissolving is unfavorable at standard state, so very little AgCl dissolves.

EXAMPLE 3: A GALVANIC CELL

A cell has Zn in 1.0 M Zn^{2+} and Cu in Cu^{2+} . Standard reduction potentials: Zn^{2+}/Zn is -0.76 V and Cu^{2+}/Cu is $+0.34 \text{ V}$. Find E° , ΔG° and K , then E when $[\text{Cu}^{2+}] = 0.010 \text{ M}$.

SOLUTION

Cathode Cu, anode Zn: $E^\circ = 0.34 - (-0.76) = 1.10 \text{ V}$, with $n = 2$.

$\Delta G^\circ = -2(96,485)(1.10) = -2.12 \times 10^5 \text{ J} = -212 \text{ kJ}$.

$K = \exp[nFE^\circ / RT] = \exp(85.7) \approx 1.6 \times 10^{37}$.

$Q = [\text{Zn}^{2+}] / [\text{Cu}^{2+}] = 1.0 / 0.010 = 100$. $E = 1.10 - \frac{0.0592}{2} \log 100 = 1.10 - 0.059 = 1.04 \text{ V}$. Less reactant gives a smaller voltage.

EXAMPLE 4: FARADAY'S LAW

A current of 2.50 A flows for 30.0 minutes through $\text{Cu}^{2+}(aq)$. (a) What mass of copper plates out? (b) How long does 1.00 g of silver take to plate from Ag^+ at 0.800 A?

SOLUTION

(a) $q = 2.50 \times 1800 = 4500 \text{ C}$; $n_{e^-} = 4500 / 96,485 = 0.04664 \text{ mol}$. $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$: $0.02332 \text{ mol Cu} \times 63.55 = 1.48 \text{ g}$.

(b) $n_{\text{Ag}} = 1.00 / 107.87 = 9.27 \times 10^{-3} \text{ mol} = n_{e^-}$ (1 e^- per Ag). $q = (9.27 \times 10^{-3})(96,485) = 894 \text{ C}$; $t = 894 / 0.800 = 1.12 \times 10^3 \text{ s}$, about 18.6 min.

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Write It Like a 5

Model Response

Prompt: Dissolving salt MX has $\Delta H^\circ = +26 \text{ kJ/mol}$ and $\Delta S^\circ = +108 \text{ J/(mol K)}$. Calculate ΔG° at 298 K and explain, in terms of particles, why the salt can dissolve although the process is endothermic. $\Delta G^\circ = 26 - 298(0.108) = 26 - 32.2 = -6.2 \text{ kJ/mol}$, so dissolving is thermodynamically favorable at 298 K. The process absorbs heat ($\Delta H > 0$, unfavorable), but $\Delta S > 0$ because ions leave the ordered crystal and move freely in solution, so the energy of the system can be distributed in many more ways. At 298 K the term $-T\Delta S = -32.2 \text{ kJ}$ is larger in magnitude than ΔH , so $\Delta G < 0$. The reaction is favorable above $T = \Delta H/\Delta S = 241 \text{ K}$.

What the grader looks for

A correct substitution with consistent units (kJ with kJ) and the answer with sign. A particle-level reason for the sign of delta S. A statement that delta G less than zero means favorable, with both delta H and delta S used. Vague phrases such as 'more disorder' without naming the particles lose the explanation point.

Coach's Playbook

- 1 For favorability, write the sign of delta H and delta S first, then use the table before touching numbers.
- 2 Convert units early: delta S is usually in J/K, delta H in kJ.
- 3 For electrochemistry, write both half-reactions as reductions, pick the larger E as the cathode, then flip the other. Do not scale E.
- 4 Count the electrons for n by balancing the overall equation, not by guessing.
- 5 For Faraday problems, run the chain: I and t, to q, to moles of electrons, to moles of metal, to grams.

Common traps

(1) Arguing that a reaction is favorable because it is exothermic, ignoring entropy and temperature. (2) Explaining delta S as 'disorder' with no particles. (3) Doubling E when a half-reaction is multiplied. (4) Skipping the mole ratio between electrons and metal in an electrolysis problem.

Quick Check

Q1. Sign of ΔS for $2\text{H}_2\text{O}_2(l) \rightarrow 2\text{H}_2\text{O}(l) + \text{O}_2(g)$? A: Positive (a gas forms). Q2. Which electrode is the anode in a galvanic cell, and what is its sign? A: Where oxidation occurs; negative. Q3. What is E at equilibrium? A: 0 V.

Challenge Corner

A cell has $\text{Cu}(s)$ in 1.0 M Cu^{2+} and $\text{Ag}(s)$ in 0.010 M Ag^+ (E° : $\text{Ag}^+/\text{Ag} +0.80 \text{ V}$, $\text{Cu}^{2+}/\text{Cu} +0.34 \text{ V}$). Find E . Solution: $\text{Cu} + 2\text{Ag}^+ \rightarrow \text{Cu}^{2+} + 2\text{Ag}$; $E^\circ = 0.80 - 0.34 = 0.46 \text{ V}$ (not 0.80 doubled), $n = 2$. $Q = [\text{Cu}^{2+}]/[\text{Ag}^+]^2 = 1.0/(0.010)^2 = 1.0 \times 10^4$. $E = 0.46 - \frac{0.0592}{2} \log(10^4) = 0.46 - 0.118 = 0.34 \text{ V}$.

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Practice

PRACTICE Unit 9 Practice

Show your work. A calculator is allowed. Justify conclusions.

- Which process has the largest positive change in entropy?
 (A) $\text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g)$
 (B) $\text{CaCO}_3(s) \rightarrow \text{CaO}(s) + \text{CO}_2(g)$
 (C) $\text{H}_2\text{O}(g) \rightarrow \text{H}_2\text{O}(l)$
 (D) $\text{Ag}^+(aq) + \text{Cl}^-(aq) \rightarrow \text{AgCl}(s)$
- A reaction has $\Delta H = +40 \text{ kJ}$ and $\Delta S = -50 \text{ J/K}$. Which statement is correct?
 (A) It is favorable only at high temperatures.
 (B) It is favorable only at low temperatures.
 (C) It is unfavorable at every temperature.
 (D) It is favorable at every temperature.
- A reaction has $K = 1.0 \times 10^{-3}$ at 298 K. What is ΔG° ?
 (A) +7.4 kJ/mol
 (B) -17 kJ/mol
 (C) 0 kJ/mol
 (D) +17 kJ/mol
- A cell is built from Zn^{2+}/Zn (-0.76 V) and Ag^+/Ag ($+0.80 \text{ V}$). What is E°_{cell} for the spontaneous reaction?
 (A) 1.56 V
 (B) 0.04 V
 (C) 2.36 V
 (D) -1.56 V
- In the standard Zn-Cu cell, $[\text{Cu}^{2+}]$ is lowered to 0.010 M with $[\text{Zn}^{2+}] = 1.0 \text{ M}$. How does the cell potential compare with E° ?
 (A) E equals E° because E° depends only on the half-cells.
 (B) E is zero because the cell is at equilibrium.
 (C) E is greater than E° .
 (D) E is less than E° because Q is greater than 1.
- A current of 2.00 A runs for 1.00 h through molten MgCl_2 . What mass of Mg forms ($M = 24.31 \text{ g/mol}$)?
 (A) 0.0373 g
 (B) 1.81 g
 (C) 0.907 g
 (D) 0.453 g
- For $\text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g)$, $\Delta H^\circ = -92 \text{ kJ}$ and $\Delta S^\circ = -199 \text{ J/K}$.
 (a) Explain the sign of ΔS° in terms of particles.
 (b) Calculate ΔG° at 298 K.
 (c) Calculate the temperature above which the reaction is unfavorable.
 (d) Calculate K at 298 K.
- A galvanic cell uses Ag^+/Ag ($E^\circ = +0.80 \text{ V}$) and Cu^{2+}/Cu ($E^\circ = +0.34 \text{ V}$).
 (a) Write the anode half-reaction, the cathode half-reaction and the overall equation.
 (b) Calculate E°_{cell} and ΔG° .
 (c) State the direction of electron flow in the wire and of anion flow in the salt bridge.
 (d) Calculate E when $[\text{Cu}^{2+}] = 1.0 \text{ M}$ and $[\text{Ag}^+] = 0.010 \text{ M}$.
- A student plates nickel from 1.0 M Ni^{2+} using a 3.00 A current for 45.0 min.
 (a) Calculate the mass of Ni deposited ($M = 58.69 \text{ g/mol}$).
 (b) How long would it take to deposit 1.00 g at 3.00 A?
 (c) The student's measured mass is lower than predicted. Give one reason and one way to test it.
 (d) For $\text{Ni}^{2+} + 2\text{Cl}^- \rightarrow \text{Ni} + \text{Cl}_2$, $E^\circ = -0.25 - 1.36 = -1.61 \text{ V}$. Explain what this value means for building the cell.
- (a) Graphite is more stable than diamond ($\Delta G^\circ = -2.9 \text{ kJ/mol}$ for diamond to graphite), yet diamond does not convert. Explain.
 (b) Reaction X has $\Delta G^\circ = +31 \text{ kJ}$ and reaction Y has $\Delta G^\circ = -48 \text{ kJ}$. Can they be coupled to drive X? Calculate and describe what the coupling requires.
 (c) Use $K_{\text{sp}}(\text{AgCl}) = 1.8 \times 10^{-10}$ to calculate ΔG° for dissolution at 298 K and interpret the sign.

Answers Unit 9: Answers and Explanations

Read every explanation, including the ones for problems you answered correctly.

9 Thermodynamics and Electrochemistry

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- B. Solid reactant becomes a solid plus a gas, so gas particles appear and entropy rises sharply. A and D lose particles' freedom (fewer gas moles, ions precipitate) and C is a condensation, all negative.
- C. Positive ΔH and negative ΔS give $\Delta G = \Delta H - T\Delta S > 0$ at all T. Choice B treats it like an exothermic reaction; the table decides, not the magnitudes.
- D. $\Delta G^\circ = -RT \ln K = -(8.314)(298) \ln(10^{-3}) = +17 \text{ kJ/mol}$. Choice B has the wrong sign (small K means unfavorable). Choice A uses log10 instead of ln.
- A. $E^\circ = E_{\text{cathode}} - E_{\text{anode}} = 0.80 - (-0.76) = 1.56 \text{ V}$. Choice C wrongly doubles the Ag potential; potential is intensive. Choice B subtracts the wrong way.
- D. With the reactant concentration reduced, $Q = [\text{Zn}^{2+}]/[\text{Cu}^{2+}] = 100 > 1$, so the Nernst term is subtracted and $E < E^\circ$ (1.04 V). Choice A forgets that E depends on concentrations.
- C. $q = 7200 \text{ C}$, $n_{e^-} = 0.07462 \text{ mol}$, $n_{\text{Mg}} = 0.03731 \text{ mol}$ (2 e⁻ per Mg), mass 0.907 g. Choice B skips the 2:1 ratio and choice A stops at moles.
- (a) Four moles of gas become two moles of gas, so fewer free particles and fewer ways to distribute energy. [1 point]
 (b) $\Delta G^\circ = -92 - 298(-0.199) = -92 + 59.3 = -32.7 \text{ kJ}$. [1 point]
 (c) $\Delta G = 0$ at $T = \Delta H/\Delta S = -92,000/-199 = 462 \text{ K}$; above 462 K, $-T\Delta S$ outweighs ΔH and $\Delta G > 0$. [1 point]
 (d) $K = \exp(32,700/(8.314 \times 298)) = 5 \times 10^5$ (5.4e5). [1 point]
- (a) Anode: $\text{Cu} \rightarrow \text{Cu}^{2+} + 2e^-$. Cathode: $\text{Ag}^+ + e^- \rightarrow \text{Ag}$. Overall: $\text{Cu} + 2\text{Ag}^+ \rightarrow \text{Cu}^{2+} + 2\text{Ag}$. [3 points]
 (b) $E^\circ = 0.80 - 0.34 = 0.46 \text{ V}$; $\Delta G^\circ = -2(96,485)(0.46) = -89 \text{ kJ}$. [2 points]
 (c) Electrons flow from Cu to Ag through the wire; anions move through the bridge toward the Cu (anode) half-cell. [2 points]
 (d) $Q = 1.0/(0.010)^2 = 1.0 \times 10^4$; $E = 0.46 - (0.0592/2)(4) = 0.34 \text{ V}$. [3 points]
- (a) $q = 3.00 \times 2700 = 8100 \text{ C}$; $n_{e^-} = 0.08395$; $n_{\text{Ni}} = 0.04198$; mass 2.46 g. [3 points]
 (b) $n_{\text{Ni}} = 1.00/58.69 = 0.01704$; $n_{e^-} = 0.03408$; $q = 3288 \text{ C}$; $t = 1096 \text{ s}$, 18.3 min. [2 points]
 (c) Some current drives a side reaction (such as reduction of water) or the deposit flaked; test by weighing the dried electrode, or by measuring the gas collected. [1 point]
 (d) The negative E° means the reaction is not spontaneous, so an external source above 1.61 V is needed; this is an electrolytic cell with Ni at the cathode and Cl⁻ oxidized at the anode. [2 points]
- (a) A negative ΔG means favorable, not fast. The conversion needs a very large activation energy because C-C bonds must break, so the rate is negligible: diamond is kinetically stable. [1 point]
 (b) $\Delta G_{\text{total}} = +31 + (-48) = -17 \text{ kJ}$, so the coupled process is favorable. The reactions must share an intermediate (energy is transferred through a common species), otherwise energy cannot pass from Y to X. [2 points]
 (c) $\Delta G^\circ = -(8.314)(298) \ln(1.8 \times 10^{-10}) = +5.6 \times 10^4 \text{ J} = +56 \text{ kJ}$. Positive: dissolving is unfavorable and the solid is only slightly soluble ($K < 1$). [1 point]

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Mixed Practice Test

A mixed set of multiple-choice and free-response questions across all units, with answers, explanations, and scoring guidance.

T Mixed Practice Test

A cumulative practice test covering all nine AP Chemistry units, with point-by-point scoring guides for the free-response questions.

Instructions and timing (about 50 minutes): Part A is 12 multiple-choice questions, weighted across the nine units roughly in proportion to their exam share. Part B is one long free-response question (10 points) and two short ones (4 points each). A calculator is allowed. Score with the guide that follows: one point per multiple-choice answer and the listed points for each free-response part.

PRACTICE TEST Mixed Practice Test

Part A: choose the best answer for items 1 to 12. Part B: items 13 to 15 are free response; show all work and justify your answers.

- A sample of an element contains two isotopes: 75.0% of atoms have mass 35 u and 25.0% have mass 37 u. What is the average atomic mass?
(A) 35.0 u (B) 36.0 u (C) 35.5 u (D) 36.5 u
- What are the molecular geometry and the central-atom hybridization of the chlorate ion, ClO_3^- ?
(A) trigonal planar, sp^2 (B) trigonal pyramidal, sp^3 (C) tetrahedral, sp^3
(D) bent, sp^3
- A 1.50 L rigid container holds 0.0500 mol of an ideal gas at 27 degrees C. What is the pressure? ($R = 0.08206 \text{ L atm/(mol K)}$)
(A) 0.0739 atm (B) 0.747 atm (C) 1.64 atm
(D) 0.821 atm
- Ethanol, $\text{CH}_3\text{CH}_2\text{OH}$ (boiling point 78 degrees C), boils at a much higher temperature than dimethyl ether, CH_3OCH_3 (-24 degrees C), which has the same molar mass. Which is the best explanation?
(A) Ethanol molecules form hydrogen bonds with one another; dimethyl ether molecules cannot.
(B) Ethanol has stronger covalent bonds, which must be broken during boiling.
(C) Ethanol has a larger molar mass and therefore stronger London dispersion forces.
(D) Dimethyl ether is nonpolar, so it has no intermolecular forces.
- A calibration standard of a colored ion, 0.0200 M, gives absorbance 0.640 in a 1.00 cm cell. An unknown gives absorbance 0.320 in a 2.00 cm cell. What is the unknown's concentration?
(A) 0.0100 M (B) 0.00500 M (C) 0.0200 M (D) 0.0400 M
- 4.00 g of Al reacts with 0.300 mol of Cl_2 : $2\text{Al} + 3\text{Cl}_2 \rightarrow 2\text{AlCl}_3$ (M of Al = 26.98, AlCl_3 = 133.3 g/mol). What is the maximum mass of AlCl_3 ?
(A) 19.8 g (B) 26.7 g (C) 13.2 g (D) 25.3 g
- Which rate law and rate constant fit the initial-rate data?

Experiment	[A] (M)	[B] (M)	Initial rate (M/s)
1	0.10	0.10	2.0×10^{-3}
2	0.20	0.10	8.0×10^{-3}
3	0.10	0.30	2.0×10^{-3}

(A) rate = $k[\text{A}]$, $k = 2.0 \times 10^{-2} \text{ s}^{-1}$

(C) rate = $k[\text{A}]^2$, $k = 0.20 \text{ M}^{-1} \text{ s}^{-1}$

(B) rate = $k[\text{A}]^2 [\text{B}]$, $k = 2.0 \text{ M}^{-2} \text{ s}^{-1}$

(D) rate = $k[\text{A}]^2$, $k = 2.0 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$

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8. When 0.0250 mol of a salt dissolves in 100.0 g of water, the temperature falls by 3.0 degrees C. Taking $c = 4.18 \text{ J/(g degrees C)}$ for the solution and ignoring the salt's mass, what is the molar enthalpy of dissolution?
- (A) -50 kJ/mol (B) +50 kJ/mol (C) +1.3 kJ/mol
(D) +0.050 kJ/mol
9. Equal volumes of $2.0 \times 10^{-5} \text{ M AgNO}_3$ and $2.0 \times 10^{-5} \text{ M NaCl}$ are mixed (K_{sp} of $\text{AgCl} = 1.8 \times 10^{-10}$). What happens?
- (A) A precipitate forms because $Q = 4.0 \times 10^{-10} > K_{sp}$.
(B) A precipitate forms because $Q = 1.0 \times 10^{-10} > K_{sp}$.
(C) No precipitate forms because $Q = 2.0 \times 10^{-5} < K_{sp}$.
(D) No precipitate forms because $Q = 1.0 \times 10^{-10} < K_{sp}$.
10. A buffer contains 0.10 M NH_3 and 0.20 M NH_4Cl . The K_a of NH_4^+ is 5.6×10^{-10} . What is the pH?
- (A) 9.25 (B) 8.95 (C) 9.55 (D) 4.75
11. 25.0 mL of 0.100 M HCl and 25.0 mL of 0.100 M acetic acid are each titrated with 0.100 M NaOH. Which statement is true?
- (A) Acetic acid needs more NaOH because it is weaker.
(B) Both need 25.0 mL of NaOH and both reach pH 7.00 at equivalence.
(C) Both need 25.0 mL of NaOH, but the equivalence point pH is 7 for HCl and above 7 for acetic acid.
(D) HCl needs more NaOH because it is a stronger acid.
12. A galvanic cell has $E^\circ_{\text{cell}} = +0.50 \text{ V}$ for a reaction transferring 2 mol of electrons. What is ΔG° ? ($F = 96,485 \text{ C/mol}$)
- (A) -96 kJ/mol (B) +96 kJ/mol (C) -48 kJ/mol
(D) -193 kJ/mol
13. A 25.00 mL sample of a monoprotic weak acid HA is titrated with 0.1000 M NaOH. The equivalence point is reached after 20.00 mL of NaOH, and the pH after 10.00 mL of NaOH is 4.60. [10 points]
- (a) Calculate the molarity of HA. [1 point]
(b) Determine the pKa and the Ka of HA, and justify your method. [2 points]
(c) Calculate the pH of the HA solution before any NaOH is added, and show that your approximation is valid. [2 points]
(d) Calculate the pH at the equivalence point. [2 points]
(e) An indicator that changes color near pH 4 and another that changes color near pH 9 are available. Which should be used? Justify. [1 point]
(f) A second acid, HB, has pH 3.60 at its half-equivalence point. Which acid is stronger? Justify. [2 points]
14. A 0.250 g sample of a volatile liquid is completely vaporized in a 125 mL flask at 100 degrees C and 0.980 atm. [4 points]
- (a) Calculate the molar mass of the liquid. [2 points]
(b) The liquid is ethanethiol, $\text{C}_2\text{H}_5\text{SH}$ (boiling point 35 degrees C). Ethanol, $\text{C}_2\text{H}_5\text{OH}$, has nearly the same molar mass but boils at 78 degrees C. Explain this difference in terms of intermolecular forces. [2 points]
15. The decomposition of A is monitored at constant temperature. The concentration falls from 0.800 M to 0.400 M in 23.1 s and to 0.200 M at 46.2 s. [4 points]
- (a) Show that the reaction is first order. [2 points]
(b) Calculate the rate constant, including units. [1 point]
(c) How long does it take for [A] to fall from 0.800 M to 0.100 M? [1 point]

Key Mixed Practice Test: Answers, Explanations, and Scoring

T Mixed Practice Test

PRACTICE TEST · MIXED PRACTICE TEST

- C. Weighted average: $0.750(35) + 0.250(37) = 35.5 \text{ u}$. The simple mean of 35 and 37, 36.0 u, ignores the abundances. Unit 1.
- B. ClO_3^- has four electron domains on Cl (three bonds and one lone pair), so sp^3 and a trigonal pyramidal shape. Tetrahedral would be the electron-domain geometry, not the molecular geometry. Unit 2.
- D. $P = nRT/V = (0.0500)(0.08206)(300.)/1.50 = 0.821 \text{ atm}$. Using 27 instead of 300 K gives 0.0739 atm, and using 22.4 L/mol gives 0.747 atm, which is valid only at STP. Unit 3.
- A. Ethanol has an O-H bond, so it hydrogen-bonds; the ether has no H on oxygen. Boiling overcomes intermolecular forces, not covalent bonds, and the molar masses are equal. Unit 3.
- B. $A = abc$: $a = 0.640/(0.0200 \times 1.00) = 32.0 \text{ M}^{-1}\text{cm}^{-1}$, so $c = 0.320/(32.0 \times 2.00) = 0.00500 \text{ M}$. Ignoring the longer path length gives 0.0100 M. Unit 3.
- A. Al is 0.148 mol and needs 0.222 mol Cl_2 , so Al is limiting; $0.148 \text{ mol AlCl}_3 \times 133.3 = 19.8 \text{ g}$. Using Cl_2 as limiting gives 26.7 g. Unit 4.

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7. C. Doubling [A] quadruples the rate (second order); tripling [B] changes nothing (zero order). $k = 2.0 \times 10^{-3} / (0.10)^2 = 0.20 \text{ M}^{-1}\text{s}^{-1}$. Using a wrong k comes from not squaring [A]. Unit 5.
8. B. $q_{\text{water}} = (100.0)(4.18)(3.0) = 1.25 \text{ kJ}$ lost by the water, so the dissolving absorbed it: $\Delta H = +1.25/0.0250 = +50 \text{ kJ/mol}$. A temperature drop means endothermic (positive); dividing by moles is required. Unit 6.
9. D. Mixing halves each concentration to $1.0 \times 10^{-5} \text{ M}$, so $Q = 1.0 \times 10^{-10}$, which is less than K_{sp} . Forgetting the dilution gives 4.0×10^{-10} and the wrong conclusion. Unit 7.
10. B. $pK_a = 9.25$; $pH = 9.25 + \log(0.10/0.20) = 8.95$. Inverting the ratio gives 9.55. Unit 8.
11. C. Equivalence depends on moles of acid, which are equal. Acetate at equivalence is a weak base, so the pH is above 7; chloride is neutral. Unit 8.
12. A. $\Delta G^\circ = -nFE^\circ = -(2)(96,485)(0.50) = -96 \text{ kJ/mol}$. A positive potential means a negative ΔG ; forgetting n gives -48 kJ. Unit 9.
13. Scoring guide (10 points)
- (a) 1 point: $n_{\text{NaOH}} = 0.1000 \times 0.02000 = 2.000 \times 10^{-3} \text{ mol}$, so $[\text{HA}] = 2.000 \text{ mmol}/25.00 \text{ mL} = 0.08000 \text{ M}$.
- (b) 1 point for recognizing that 10.00 mL is half of the 20.00 mL equivalence volume so $[\text{HA}] = [\text{A}^-]$ and $pH = pK_a$; 1 point for $pK_a = 4.60$, $K_a = 10^{-4.60} = 2.5 \times 10^{-5}$.
- (c) 1 point for $x = \sqrt{(2.5 \times 10^{-5})(0.0800)} = 1.4 \times 10^{-3} \text{ M}$ and $pH = 2.85$; 1 point for $x/0.0800 = 1.8\% < 5\%$ so the approximation is valid.
- (d) 1 point for $[\text{A}^-] = 2.000 \text{ mmol}/45.00 \text{ mL} = 0.04444 \text{ M}$ and $K_b = 1.0 \times 10^{-14}/2.5 \times 10^{-5} = 4.0 \times 10^{-10}$; 1 point for $[\text{OH}^-] = \sqrt{(4.0 \times 10^{-10})(0.04444)} = 4.2 \times 10^{-6} \text{ M}$, $pOH = 5.38$, $pH = 8.62$.
- (e) 1 point: the indicator that changes near pH 9, because the equivalence point (pH 8.6) lies within its range and the steep rise includes it; the pH 4 indicator would change during the buffer region.
- (f) 1 point: HB is stronger (it has the lower pK_a , 3.60 versus 4.60); 1 point: K_a of HB is $10^{-3.60} = 2.5 \times 10^{-4}$, ten times larger, so it ionizes more.
- Model response: HA is 0.0800 M; its pK_a is 4.60 because at half-equivalence $[\text{HA}] = [\text{A}^-]$; pH before NaOH is 2.85 (1.8% ionized); the equivalence pH is 8.62 because A^- hydrolyzes; use the indicator near pH 9; HB is stronger because its pK_a is lower.
14. Scoring guide (4 points)
- (a) 1 point: $T = 373 \text{ K}$ and $V = 0.125 \text{ L}$ converted; 1 point: $M = mRT/(PV) = (0.250)(0.08206)(373)/((0.980)(0.125)) = 62.5 \text{ g/mol}$.
- (b) 1 point: ethanol molecules form hydrogen bonds (O-H bonded to the lone pair on another O), which are much stronger than the forces in ethanethiol, where S-H does not hydrogen bond effectively; 1 point: boiling overcomes intermolecular forces, so ethanol needs more energy, despite similar molar mass and London dispersion forces.
- Model response: $M = 62.5 \text{ g/mol}$. Ethanol has an O-H group and hydrogen bonds; ethanethiol has only dipole-dipole and dispersion forces, so its intermolecular forces are weaker and it boils lower.
15. Scoring guide (4 points)
- (a) 1 point: the time to halve is 23.1 s from 0.800 to 0.400 and 23.1 s from 0.400 to 0.200; 1 point: the half-life is constant regardless of concentration, which is the signature of first order.
- (b) 1 point: $k = \ln 2/t_{1/2} = 0.693/23.1 \text{ s} = 0.0300 \text{ s}^{-1}$.
- (c) 1 point: 0.800 to 0.100 is three half-lives, $3 \times 23.1 = 69.3 \text{ s}$.
- Model response: Constant half-life (23.1 s) shows first order; $k = 0.0300$ per second; 69.3 s.

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Reference: Formulas, Skills Checklist, and Glossary

Quick-reference pages to review the night before the exam.

R1 Constants, Equations, and Solubility/Acid Data

A compact reference of constants, equations and typical acid, base and solubility data used throughout the book.

How to Use This Reference

This page collects the constants, equations and data used most often in the book, written in our own wording and grouped by topic. The exam supplies its own reference information, and which items it provides can change from year to year. Check the current official materials before test day, and practice recalling the items you would otherwise have to remember. Reduction potentials, K_a and K_{sp} values are normally given in a problem when needed.

Constants and Conversions

Quantity	Value
Gas constant R	$8.314 \text{ J/(mol K)} = 0.08206 \text{ L atm/(mol K)}$
Avogadro's number	6.022×10^{23} per mol
Faraday constant F	96,485 C per mol of electrons
Planck's constant h	$6.626 \times 10^{-34} \text{ J s}$
Speed of light c	$2.998 \times 10^8 \text{ m/s}$
Ion-product of water K_w	1.0×10^{-14} at 25 degrees C
Pressure	$1 \text{ atm} = 760 \text{ torr} = 760 \text{ mm Hg} = 101.325 \text{ kPa}$
Temperature	$T(\text{K}) = T(^{\circ}\text{C}) + 273.15$
Specific heat of liquid water	$4.18 \text{ J/(g degrees C)}$
Molar volume of ideal gas at STP (0 degrees C, 1 atm)	22.4 L/mol (use only at STP)

Equations by Topic

Atoms, light and solutions

$E = h\nu$, $c = \lambda\nu$; photon energy rises with frequency.

Molarity $M = n/V$ (liters); dilution $M_1V_1 = M_2V_2$; mass percent = mass of part/mass of whole $\times 100$.

Beer-Lambert: $A = \epsilon bc$ (absorbance is proportional to concentration at fixed path length).

Gases

$PV = nRT$ (kelvin); $P_{\text{total}} = \sum P_i$ and $P_i = \chi_i P_{\text{total}}$; $M = \frac{mRT}{PV}$.

Average kinetic energy is proportional to T alone; at equal T , lighter gas molecules move faster.

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Thermochemistry

$q = mc\Delta T$ with $\Delta T = T_{\text{final}} - T_{\text{initial}}$; phase change $q = n\Delta H_{\text{fus or vap}}$.

$\Delta H_{\text{rxn}}^{\circ} = \sum \Delta H_f^{\circ}(\text{products}) - \sum \Delta H_f^{\circ}(\text{reactants})$; with bond enthalpies, $\Delta H \approx \sum(\text{bonds broken}) - \sum(\text{bonds formed})$. Reversing a reaction changes the sign of ΔH ; multiplying scales it.

Kinetics

Zero order: $[A] = [A]_0 - kt$. First order: $\ln[A] = \ln[A]_0 - kt$, $t_{1/2} = 0.693/k$. Second order: $1/[A] = 1/[A]_0 + kt$, $t_{1/2} = 1/(k[A]_0)$.

The linear plot identifies the order: $[A]$ vs t (zero), $\ln[A]$ vs t (first), $1/[A]$ vs t (second). Rate constants have units that depend on the overall order.

Equilibrium and acid-base

K_c from concentrations, K_p from partial pressures; $K_p = K_c(RT)^{\Delta n}$; Q has the same form as K .

$pH = -\log[H^+]$; $pH + pOH = 14.00$ at 25 degrees C; $K_a K_b = K_w$; $pH = pK_a + \log([A^-]/[HA])$.

Thermodynamics and electrochemistry

$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$; $\Delta G^{\circ} = -RT \ln K$; $\Delta G^{\circ} = -nFE^{\circ}$; $\Delta G = \Delta G^{\circ} + RT \ln Q$.

$E = E^{\circ} - \frac{RT}{nF} \ln Q = E^{\circ} - \frac{0.0592}{n} \log Q$ at 25 degrees C. Charge $q = It$; moles of electrons = q/F .

Typical Acid and Base Constants (25 degrees C)

These are typical textbook values at 25 degrees C. Published tables differ slightly in the second digit, so use the number given in a problem when there is one.

Acid	Ka	Conjugate base	Kb of conjugate base
Formic, HCOOH	1.8×10^{-4}	HCOO ⁻	5.6×10^{-11}
Acetic, CH ₃ COOH	1.8×10^{-5}	CH ₃ COO ⁻	5.6×10^{-10}
Benzoic, C ₆ H ₅ COOH	6.3×10^{-5}	C ₆ H ₅ COO ⁻	1.6×10^{-10}
Hydrofluoric, HF	6.8×10^{-4}	F ⁻	1.5×10^{-11}
Nitrous, HNO ₂	4.5×10^{-4}	NO ₂ ⁻	2.2×10^{-11}
Hypochlorous, HClO	3.0×10^{-8}	ClO ⁻	3.3×10^{-7}
Hydrocyanic, HCN	6.2×10^{-10}	CN ⁻	1.6×10^{-5}
Carbonic, H ₂ CO ₃ (Ka1)	4.3×10^{-7}	HCO ₃ ⁻	2.3×10^{-8}
Bicarbonate, HCO ₃ ⁻ (Ka2)	4.7×10^{-11}	CO ₃ ²⁻	2.1×10^{-4}
Phosphoric, H ₃ PO ₄ (Ka1)	7.5×10^{-3}	H ₂ PO ₄ ⁻	1.3×10^{-12}
Dihydrogen phosphate (Ka2)	6.2×10^{-8}	HPO ₄ ²⁻	1.6×10^{-7}
Hydrogen phosphate (Ka3)	4.2×10^{-13}	PO ₄ ³⁻	2.4×10^{-2}
Hydrogen sulfate, HSO ₄ ⁻ (Ka2)	1.2×10^{-2}	SO ₄ ²⁻	8.3×10^{-13}
Ammonium, NH ₄ ⁺	5.6×10^{-10}	NH ₃ (Kb)	1.8×10^{-5}
Methylammonium, CH ₃ NH ₃ ⁺	2.3×10^{-11}	CH ₃ NH ₂ (Kb)	4.4×10^{-4}

Weak bases for quick reference: ammonia, $K_b = 1.8 \times 10^{-5}$; methylamine, 4.4×10^{-4} ; pyridine, 1.7×10^{-9} ; aniline, 4.3×10^{-10} .

Typical Solubility Product Constants (25 degrees C)

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Compound	K _{sp}	Compound	K _{sp}
AgCl	1.8×10^{-10}	Mg(OH) ₂	5.6×10^{-12}
AgBr	5.0×10^{-13}	Ca(OH) ₂	5.0×10^{-6}
AgI	8.5×10^{-17}	Cu(OH) ₂	2.2×10^{-20}
Ag ₂ CrO ₄	1.1×10^{-12}	Fe(OH) ₃	2.8×10^{-39}
BaSO ₄	1.1×10^{-10}	Al(OH) ₃	1.9×10^{-33}
CaCO ₃	3.4×10^{-9}	PbCl ₂	1.7×10^{-5}
CaF ₂	3.5×10^{-11}	PbI ₂	9.8×10^{-9}
CaSO ₄	4.9×10^{-5}	PbSO ₄	2.5×10^{-8}

Selected Standard Reduction Potentials (25 degrees C)

Half-reaction	E degree (V)
Li ⁺ + e ⁻ to Li	-3.04
Zn ²⁺ + 2e ⁻ to Zn	-0.76
Fe ²⁺ + 2e ⁻ to Fe	-0.44
Ni ²⁺ + 2e ⁻ to Ni	-0.25
2H ⁺ + 2e ⁻ to H ₂	0.00
Cu ²⁺ + 2e ⁻ to Cu	+0.34
Ag ⁺ + e ⁻ to Ag	+0.80
Cl ₂ + 2e ⁻ to 2Cl ⁻	+1.36
F ₂ + 2e ⁻ to 2F ⁻	+2.87

Reminders

These values are typical textbook values and may differ slightly from those in other tables or on an exam; always use the data supplied in a question. Potentials are not multiplied by coefficients. Larger (more positive) E degree means a stronger tendency to be reduced.

R2 Skills Checklist and Glossary

A practice-by-practice checklist and a glossary of the key terms from the nine units.

Skills Checklist

Tick each skill when you can do it from a blank page. The six science practices below are the thinking habits the exam rewards in both multiple-choice and free-response questions.

Models and Representations

- ◆ [] Draw particle diagrams in which relative numbers, spacing and motion are accurate.
- ◆ [] Draw Lewis diagrams with correct electron counts, formal charges and resonance.
- ◆ [] Sketch energy profiles with reactants, products, activation energy and intermediates labeled.

Question and Method

- ◆ [] Choose volumetric glassware when precise concentration is needed, and describe dissolving first, then diluting to the mark.
- ◆ [] Identify the variable measured, the variable controlled and the source of likely error.
- ◆ [] Propose a control or a repeat trial to test a claim.

Representing Data and Phenomena

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- ◆ [] Read and draw titration curves, linearized kinetics plots, PES and mass spectra.
- ◆ [] Label axes with quantities and units; mark equivalence and half-equivalence points.
- ◆ [] Convert between tables, graphs and equations.

Model Analysis

- ◆ [] Compare Q with K and predict the shift in words.
- ◆ [] Use VSEPR, collision theory or intermolecular forces to predict and explain a property.
- ◆ [] State when a model fails (for example, a gas deviating from ideal behavior).

Mathematical Routines

- ◆ [] Carry units through every step and report the right significant figures.
- ◆ [] Use ICE tables, state the x -is-small approximation and check it.
- ◆ [] Set up stoichiometry in moles first, then convert to concentration or mass.

Argumentation

- ◆ [] Write claim, evidence, reasoning: state the claim, cite the specific quantity, link it to a principle.
- ◆ [] Use particle-level language for entropy and intermolecular forces.
- ◆ [] Avoid vague words such as 'disorder' or 'heat was lost' without naming the particles or the quantity.

Last-week checklist

Re-do one past practice test under time. For each missed item, name the practice it tested (for example, Mathematical Routines) and write one sentence on what you will do differently. Review the Common traps boxes in Units 7, 8 and 9.

Glossary

Term	Meaning
Absorbance	Measure of how much light a sample absorbs at a given wavelength.
Acid dissociation constant (K_a)	Equilibrium constant for the ionization of a weak acid in water.
Activation energy	Minimum energy needed for a collision to lead to reaction.
Amphiprotic	Able to act as both an acid and a base, like water.
Anode	Electrode where oxidation occurs.
Buffer	Solution of a weak acid and its conjugate base that resists pH change.
Buffer capacity	Amount of added acid or base a buffer can absorb before its pH changes sharply.
Cathode	Electrode where reduction occurs.
Catalyst	Substance that speeds a reaction by providing a lower-energy path without being consumed.
Common-ion effect	Decrease in solubility or ionization caused by adding an ion already present.
Conjugate pair	Acid and base that differ by one proton.
Dynamic equilibrium	State in which forward and reverse rates are equal and concentrations stay constant.
E degree cell	Standard cell potential, cathode minus anode reduction potentials.
Electrolysis	Use of external electrical energy to drive a nonspontaneous redox reaction.
Electrolytic cell	Cell in which an external source forces a nonspontaneous reaction.
Endothermic	Process that absorbs heat from the surroundings.
Enthalpy (H)	Heat content at constant pressure; its change equals heat at constant pressure.
Entropy (S)	Measure of the number of ways energy can be distributed among particles.
Equivalence point	Point in a titration where moles of titrant equal moles of analyte (by stoichiometry).

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Term	Meaning
Exothermic	Process that releases heat to the surroundings.
Faraday constant	Charge of one mole of electrons, 96,485 C.
Galvanic cell	Cell in which a spontaneous redox reaction produces electrical energy.
Gibbs free energy (G)	H minus TS; negative change means a favorable process.
Half-equivalence point	Point at which half of a weak acid is neutralized; pH equals pKa.
Half-life	Time for a reactant concentration to fall to half its value.
Henderson-Hasselbalch equation	$\text{pH} = \text{pKa} + \log$ of the base-to-acid ratio, for buffers.
Hess's law	Enthalpy change of a reaction equals the sum of the changes of its steps.
Hydrogen bond	Strong dipole attraction between H bonded to N, O or F and a lone pair on another N, O or F.
Indicator	Weak acid or base whose color changes over a narrow pH range.
Intermolecular force	Attraction between separate molecules or particles.
Ion-product constant (K_w)	Product of $[\text{H}^+]$ and $[\text{OH}^-]$ in water, 1.0×10^{-14} at 25 degrees C.
Kinetic control	Product distribution set by the fastest pathway rather than the most stable product.
Law of mass action	Equilibrium ratio of concentrations raised to coefficients is constant at a given temperature.
Le Chatelier's principle	A system at equilibrium shifts to partly offset an imposed change.
Limiting reagent	Reactant that runs out first and sets the maximum product.
London dispersion force	Attraction from temporary dipoles, present in all particles and growing with size.
Molar solubility	Moles of solute that dissolve per liter of saturated solution.
Molarity	Moles of solute per liter of solution.
Nernst equation	Relates cell potential to standard potential and the reaction quotient.
Net ionic equation	Equation showing only species that change, leaving out spectator ions.
Oxidation	Loss of electrons; increase in oxidation number.
pH	Negative base-10 logarithm of hydrogen-ion concentration.
pKa	Negative log of K_a ; the pH at which an acid is half ionized.
Q (reaction quotient)	Ratio with the form of K evaluated at any moment.
Rate constant (k)	Proportionality constant in a rate law; depends on temperature.
Rate law	Equation relating reaction rate to reactant concentrations.
Reduction	Gain of electrons; decrease in oxidation number.
Salt bridge	Connection that lets ions move to keep the half-cells electrically neutral.
Solubility product (K_{sp})	Equilibrium constant for dissolving a sparingly soluble salt.
Specific heat capacity	Heat needed to raise 1 g of a substance by 1 degree C.
Spectator ion	Ion present but unchanged by a reaction.
Standard state	Reference conditions for thermodynamic data: 1 M solutions, 1 atm gases.
Stoichiometry	Quantitative relationships between amounts of reactants and products.
Strong acid	Acid that ionizes essentially completely in water.
Thermodynamic control	Product distribution set by relative stability when paths can equilibrate.
Titrant	Solution of known concentration added from a buret.
Titration	Procedure to find an unknown concentration by reacting it with a measured volume of titrant.
VSEPR	Model predicting molecular shape from electron-domain repulsion.

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Term	Meaning
Weak acid	Acid that ionizes only partially, so K_a is small.
Coupled reactions	Pairing of an unfavorable reaction with a favorable one so the total free energy change is negative.

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