

Unit 3

AP Chemistry

Properties of Substances and Mixtures

Intermolecular forces · Phases · Gas laws · Solutions · Separation · Light and Beer's law

Unit 1
7–9%
Atomic structure

Unit 2
7–9%
Compound structure

Unit 3
18–22%
Substances and mixtures

Unit 4
7–9%
Chemical reactions

Unit 5
7–9%
Kinetics

Unit 6
7–9%
Thermochemistry

Unit 7
7–9%
Equilibrium

Unit 8
11–15%
Acids and bases

Unit 9
7–9%
Thermodynamics, electrochemistry

Unit 3 is 18–22% of the multiple-choice section. That is more than any other unit, and it turns up in several free-response questions on every recent exam, usually as parts of longer questions: explaining a boiling point or a solubility with intermolecular forces, a gas-law calculation, making or diluting a solution, or turning an absorbance into a concentration.

3.1
Intermolecular and interparticle forces

3.2
Properties of solids

3.3
Solids, liquids, gases

3.4
Ideal gas law

3.5
Kinetic molecular theory

3.6
Deviation from ideal gas law

3.7
Solutions and mixtures

3.8
Representations of solutions

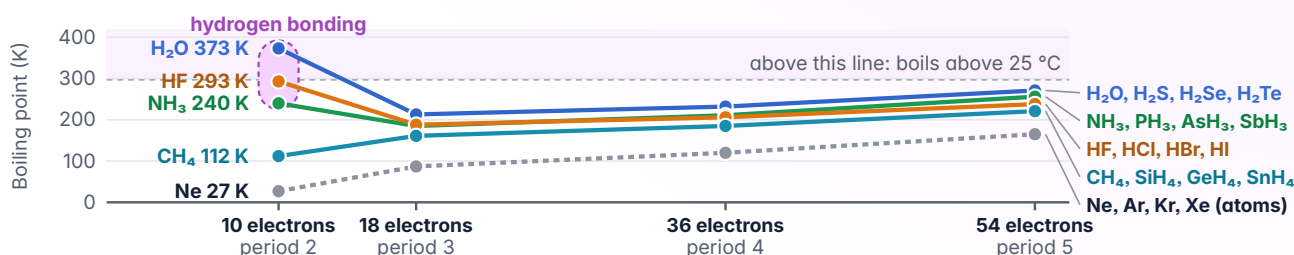
3.9
Separating mixtures

3.10
Solubility

3.11
Spectroscopy

3.12
Properties of photons

3.13
Beer–Lambert law



More electrons per molecule (or atom) mean stronger dispersion forces, so boiling points rise down each family. NH₃, H₂O and HF boil far above that trend because they hydrogen-bond. Of these twenty substances, only water is a liquid at 25 °C.

What the exam asks most

- 1 Explain a difference in boiling point or vapor pressure.** Name every intermolecular force in both substances and say which has the stronger attractions and why. Then link it to energy: stronger attractions take more energy to overcome. **3.1**
- 2 Calculate a gas's moles, pressure or volume.** Convert to kelvins, use $R = 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}$ with atmospheres and liters, and show the setup with units. **3.4**
- 3 Make or dilute a solution.** Moles = molarity $\times$ liters. After mixing two solutions, divide the moles of solute by the combined volume. To make one, dissolve the solid in some water in a volumetric flask, then add water up to the mark. **3.7**

- 4 Draw the particles.** Water's partly negative O points at cations, and its partly positive H atoms point at anions. Keep the formula's ratio: CaCl₂ gives two Cl[−] per Ca²⁺. In two drawings of the same volume, the more concentrated one has more particles. **3.8** **3.3**
- 5 Turn an absorbance into a concentration.** Use $A = \epsilon bc$ or the calibration line, then undo any dilution. For a lab error, say how it changed the absorbance, then the calculated concentration. **3.13**

On the equation sheet

$$PV = nRT \quad \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$P_A = P_{\text{total}} \times X_A \quad n = m/M$$

$$M = \frac{n_{\text{solute}}}{L_{\text{solution}}} \quad KE = \frac{1}{2}mv^2$$

$$A = \epsilon bc \quad E = h\nu, c = \lambda\nu$$

Bold M is molar mass, plain M molarity, X_A the mole fraction of A, ϵ molar absorptivity, ν (nu) frequency. Also given: both values of R , $K = ^\circ\text{C} + 273.15$, 1 atm = 760 mm Hg.

Know by heart

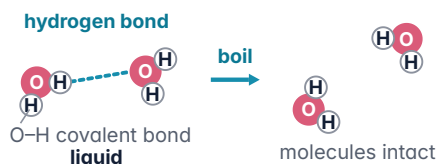
- A hydrogen bond needs an H on N, O or F, attracted to a lone pair on N, O or F in another molecule or another part of a large one.
- For a dilution, $M_1 V_1 = M_2 V_2$, where V_2 is the final total volume.
- One photon's energy is $E = hc/\lambda$, with λ in meters. Microwaves make molecules rotate, infrared makes bonds vibrate, and UV or visible light moves electrons to higher energy levels.

Not on the exam

Phase diagrams, colligative properties (such as a solute lowering water's freezing point), molality, and percent by mass or by volume of a solution.

3.1 Intermolecular and interparticle forces

A covalent bond holds the atoms of a molecule together. Intermolecular forces are the much weaker attractions between molecules. Melting or boiling a molecular substance overcomes only these, so the molecules stay whole.



Force	Acts between
London dispersion	All particles. One electron cloud shifts for an instant, and a neighbor's cloud shifts to match.
Dipole-dipole	Polar molecules: the partly positive end (δ^+) of one attracts the partly negative end (δ^-) of another.
Hydrogen bond	An H bonded to N, O or F is attracted to a lone pair on an N, O or F atom of another molecule.
Ion-dipole	An ion and a polar molecule such as water.

What makes dispersion forces stronger

- **More electrons.** A larger electron cloud is more **polarizable** (easier to distort), so the attractions are stronger.
- **More contact.** Long chains lie alongside each other; round, compact molecules touch less.
- Call them "London dispersion forces"; "van der Waals forces" also includes dipole-dipole forces.

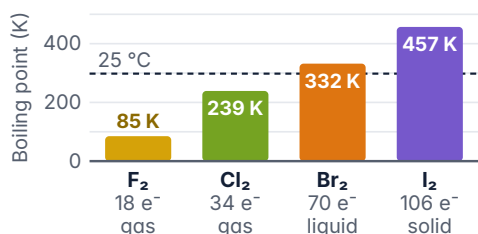
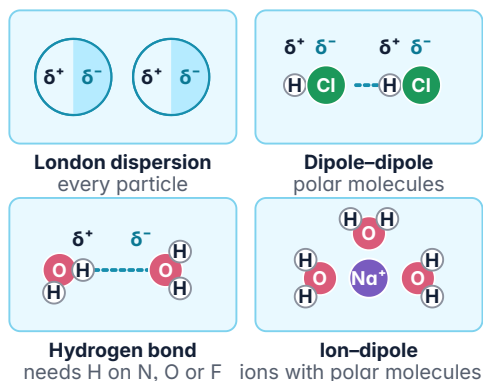
propane $\text{CH}_3\text{CH}_2\text{CH}_3$	dispersion only	231 K
dimethyl ether CH_3OCH_3	+ dipole-dipole	248 K
ethanol $\text{CH}_3\text{CH}_2\text{OH}$	+ hydrogen bonds	352 K

All three have 26 electrons, so their dispersion forces are similar. Each + adds a force to the ones above it.

Quick check

CH_3SH has 26 electrons and CH_3OH only 18. Which boils higher?

Answer: CH_3OH , at 338 K against 279 K. Its hydrogen bonds outweigh the extra dispersion in CH_3SH .



Halogen molecules are nonpolar, so dispersion is the only force between them. Under each formula are its electrons (e^-) and its state at 25 °C.

Pentane's long chains lie side by side and touch along their length. It boils at **309 K**.

vs

Neopentane has the same formula, C_5H_{12} , but its round molecules touch less. It boils at **283 K**.

Exam trap

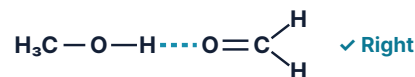
Assuming the polar substance always has the stronger attractions. Nonpolar CBr_4 boils at **463 K**, far above polar CBrClF_2 at **269 K**. CBr_4 has 146 electrons to CBrClF_2 's 76, so the dispersion forces of CBr_4 outweigh the dispersion and dipole-dipole forces of CBrClF_2 together. Compare the total strength of the attractions.

Explaining how strongly an ion attracts water

Mg^{2+} attracts water more strongly than Na^+ does. It has the **larger charge**, and because it is smaller, water's partly negative oxygen gets **closer** to its center. In Coulomb's law, $F \propto q_1q_2/r^2$ ($\propto$ means "is proportional to" and q is charge), r is the **distance from the ion to water's oxygen**, not the ion's radius.

Pair	Which boils higher, and why
HF, HCl	HF (293 K): it hydrogen-bonds and HCl can't.
HBr, HCl	HBr (206 K): 36 electrons to HCl's 18, so stronger dispersion.
ICI, Br ₂	ICI (371 K): both have 70 electrons, but only ICI is polar.

Drawing a hydrogen bond



The H on O points at the other molecule's O



An H on C is not polar enough to hydrogen-bond

What a hydrogen bond needs, and how to draw it

- 1 A **donor**: an H covalently bonded to N, O or F.
- 2 An **acceptor**: a lone pair on an N, O or F atom in another molecule, or in another part of the same large molecule, such as a protein.
- 3 Draw a dashed line from that H to the acceptor atom, **between** the molecules, never along the O-H bond.

Formaldehyde and acetone have no H on N, O or F, so their molecules can't hydrogen-bond to each other, but their O can accept one from water.

Worked example

$\Delta H_{\text{vap}}^\circ$, the heat to vaporize one mole, is 25.2 kJ/mol for HF and 17.3 kJ/mol for HBr. Explain the difference, then find the heat needed to vaporize 6.85 g of HF.

- 1 List every force. HBr has dispersion and dipole-dipole forces; HF has both of those **plus hydrogen bonding**.
- 2 HBr has more electrons (36 to 10), so stronger dispersion, but HF's hydrogen bonds more than make up for it. HF's attractions are stronger overall, so separating its molecules takes more energy.

$$3 \quad 6.85 \text{ g} \times \frac{1 \text{ mol}}{20.01 \text{ g}} \times \frac{25.2 \text{ kJ}}{1 \text{ mol}}$$

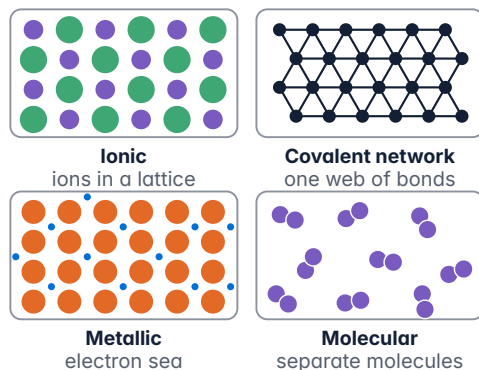
8.63 kJ (three significant figures, like 6.85 g)

Exam trap

- **Saying covalent bonds break when a liquid boils.** Boiling only overcomes the attractions between HF molecules; every H-F bond stays intact.
- **Leaving a force off the list.** HBr is polar, so it has dipole-dipole forces as well as dispersion. List both.
- **Giving mass as the reason.** Mass is not what causes the attraction. Say that HBr has more electrons, so its electron cloud is more polarizable and its dispersion forces are stronger.

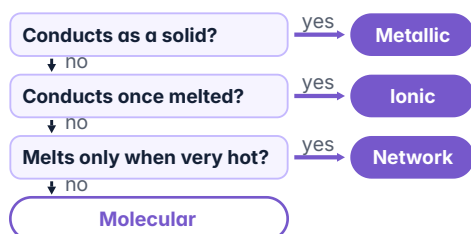
3.2 Properties of solids

What the particles are, and what holds them together, tells you how a solid melts, breaks and conducts electricity.



Solid	Melting point	Conducts	When hit
Ionic NaCl, KBr	high	only when melted or dissolved	shatters
Network diamond, SiO ₂ , SiC	very high	no (graphite does)	hard (graphite is soft)
Metallic Cu, Fe, steel	varies	yes, as a solid	bends
Molecular I ₂ , ice, sugar	low	no	soft or brittle

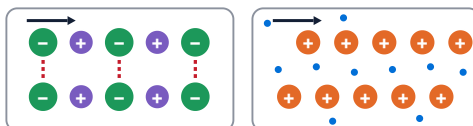
Identify a solid with three questions



Graphite is the one exception: it conducts as a solid, but it is a covalent network, not a metal.

Why each kind behaves as it does

- Ionic:** ions carry current only once they are free to move, in a melt or a solution.
- Network:** melting means breaking covalent bonds. Graphite is soft because its sheets slide over each other.
- Metallic:** mobile electrons carry the charge. Steel (iron with carbon in the gaps) is stiffer but still conducts.
- Molecular:** only weak forces hold the molecules together, and the electrons stay in their bonds.



Red dotted lines: like charges pushing apart.

What stronger attractions do

They give a liquid a higher boiling point, a larger ΔH_{vap} and a lower vapor pressure.

- Vapor pressure is the pressure of the vapor above a liquid in a closed container once evaporation and condensation balance.
- Compare vapor pressures at the **same temperature**. A liquid boils when its vapor pressure equals the pressure above it.

Pentane, C₅H₁₂ 512 mm Hg

Hexane, C₆H₁₄ 152 mm Hg

Vapor pressure at 25 °C. Hexane's extra CH₂ adds electrons and contact, so fewer molecules escape.

Worked example

Molecules of X and Y have the same shape, but Y has a Si atom where X has C. X boils at 82 °C and Y at 98 °C (at 1 atm). Which has the higher vapor pressure at 82 °C, and why?

- Si has one more occupied shell than C, so Y's electron cloud is larger and more polarizable, and its dispersion forces are stronger.
- At 82 °C, X is at its boiling point, so its vapor pressure is 1 atm. Y is below its boiling point, so its vapor pressure is less than 1 atm.

X, because its weaker attractions let more of its molecules escape into the vapor

Exam trap

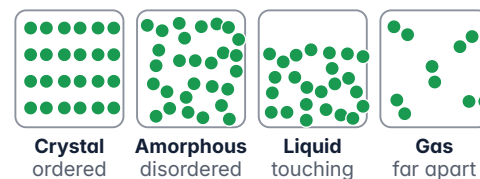
- Describing only one substance.** "X is at its boiling point" alone isn't a comparison. Say something about both: X is at its boiling point and Y is below its own, so X has the higher vapor pressure.

Melting points are harder to predict

Neopentane boils below pentane (283 K, against 309 K) but melts far higher (257 K, against 143 K): its round molecules pack neatly into a crystal.

3.3 Solids, liquids, and gases

The particles are the same in every phase. Only their spacing and their motion change.



	Spacing	Motion
Solid	touching	vibrate in place, never pass each other
Liquid	touching	slide past each other, collide constantly
Gas	far apart	fast and random, filling the whole container

The volume of one mole of water

liquid, 25 °C	18.1 mL
ice, 0 °C	19.7 mL
steam at 100 °C and 1 atm (ideal gas)	30,600 mL

The solid and the liquid are close because their particles touch. The gas takes about 1,700 times as much room. Ice is unusual: most solids sink in their own liquid, but ice floats.

Drawing particles in each phase

- Draw the particles the same size in every phase.
- In a liquid they touch but are disordered. In a gas they fill the whole container instead of piling at the bottom.
- Molecules stay whole: never split H₂O into atoms when it boils.

Worked example

CH₃OH melts at 176 K and boils at 338 K; H₂CO melts at 181 K and boils at 254 K. Give a temperature at which both are liquids.

- It must be above the higher melting point and below the lower boiling point.

181 K < T < 254 K, for example 220 K

Exam trap

- Giving only one limit.** "Below 254 K" includes 100 K, where both substances are solid. The temperature must also be above 181 K.
- Calling glass a liquid.** Glass is an amorphous solid: its particles have no regular pattern, but they stay in place.

3.4 Ideal gas law

Pressure, volume, moles and temperature (in kelvins) describe a gas, and $PV = nRT$ links all four.

On the equation sheet

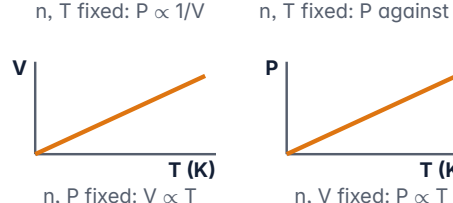
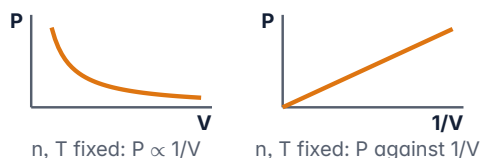
$$PV = nRT$$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \text{ for a fixed amount of gas}$$

R	0.08206 L atm mol ⁻¹ K ⁻¹ = 8.314 J mol ⁻¹ K ⁻¹
kelvins	K = °C + 273.15
pressure	1 atm = 760 mm Hg = 760 torr
STP	standard temperature and pressure, 273.15 K and 1.0 atm, where an ideal gas fills 22.4 L per mole

Your units	Use
atm and L	$R = 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}$
mm Hg or torr	divide by 760 to get atm, then use 0.08206
energy in joules, as in KE	$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

Change one quantity, hold two fixed



The symbol $\propto$ means "is proportional to." The straight lines pass through the origin only when temperature is in kelvins: on a Celsius axis, the volume line would reach zero at -273.15°C .

Worked example

A 2.50 L balloon at 25°C and 1.00 atm rises to where the pressure is 0.500 atm and the temperature is -10°C . Find its volume.

- Predict first: halving the pressure doubles the volume, and cooling from 298 K to 263 K shrinks it a little, so expect a bit under 5 L.
- $V_2 = 2.50 \text{ L} \times \frac{1.00 \text{ atm}}{0.500 \text{ atm}} \times \frac{263 \text{ K}}{298 \text{ K}}$

4.41 L

Predict before you calculate

- Double n , or halve V , and P doubles: the walls get hit twice as often.
- Raise T at fixed n and V , and P rises in proportion to the Kelvin temperature.
- Put $n = m/M$ into $PV = nRT$, and use density $D = m/V$: the molar mass is $M = \frac{DRT}{P}$.

Worked example

A 6.00 L rigid tank holds HCl gas at 7.45 atm and 296 K. Find the moles of gas, then the pressure after the tank cools to 271 K.

- $n = \frac{PV}{RT} = \frac{(7.45 \text{ atm})(6.00 \text{ L})}{(0.08206 \frac{\text{L atm}}{\text{mol K}})(296 \text{ K})}$
- $= 1.84 \text{ mol}$
- The tank is rigid and sealed, so n and V stay fixed: $P_2 = 7.45 \text{ atm} \times \frac{271 \text{ K}}{296 \text{ K}}$

1.84 mol, then 6.82 atm

Worked example

A sealed 12.5 L container holds a mixture of two gases at 198°C and 2.30 atm. Find the total moles of gas.

- Convert to kelvins first: $198 + 273.15 = 471 \text{ K}$.
- $n = \frac{(2.30 \text{ atm})(12.5 \text{ L})}{(0.08206 \frac{\text{L atm}}{\text{mol K}})(471 \text{ K})}$

0.744 mol of gas in total

What a calculation has to show

Show the equation rearranged for the unknown, every number substituted with its unit, and the answer with units and the right number of significant figures. Writing " $PV = nRT$ " alone doesn't count as work.

Exam trap

- Putting Celsius into the equation. Gas laws need kelvins. Using 198 instead of 471 K makes n 2.4 times too big.
- Using 8.314 with atmospheres. That value of R is in joules. With atm and liters, use 0.08206, or the answer is off by a factor of about 100.
- Rearranging upside down. $n = PV/RT$, not RT/PV . Check that the units cancel to leave mol.
- Using 22.4 L per mole away from STP. At 293 K and 1.25 atm, 0.0114 mol of CO_2 fills $nRT/P = 0.219 \text{ L}$, not $0.0114 \times 22.4 = 0.255 \text{ L}$.

Partial pressures in a gas mixture

Each gas in a mixture hits the walls as if it were alone. Its share of the pressure equals its share of the particles, its **mole fraction** X .



He: 8 of 12, $X = 0.667$

Ar: 4 of 12, $X = 0.333$

total pressure
1.20 atm

$$P_{\text{He}} = 0.667 \times 1.20 \text{ atm} = 0.800 \text{ atm}$$

$$P_{\text{Ar}} = 0.333 \times 1.20 \text{ atm} = 0.400 \text{ atm}$$

On the equation sheet

$$P_A = P_{\text{total}} \times X_A, \quad X_A = \frac{\text{moles A}}{\text{total moles}}$$

$$P_{\text{total}} = P_A + P_B + P_C + \dots$$

Worked example

H_2 is collected over water at 25°C in 0.250 L. The total pressure is 752 mm Hg; water's vapor pressure is 24 mm Hg. Find the moles of H_2 .

- Subtract the water vapor: $752 - 24 = 728 \text{ mm Hg}$, and $728 \div 760 = 0.958 \text{ atm}$
- $n = \frac{(0.958 \text{ atm})(0.250 \text{ L})}{(0.08206 \frac{\text{L atm}}{\text{mol K}})(298 \text{ K})}$

$9.79 \times 10^{-3} \text{ mol H}_2$

Worked example

A gas has a density of 2.60 g/L at 27.0°C and 1.00 atm. Identify it.

- $M = \frac{DRT}{P}$
- $= \frac{(2.60 \frac{\text{g}}{\text{L}})(0.08206 \frac{\text{L atm}}{\text{mol K}})(300.2 \text{ K})}{1.00 \text{ atm}}$

64.0 g/mol, which matches sulfur dioxide, SO_2

Exam trap

- Finding a mole fraction from grams. X compares moles: 4.00 g He (1.00 mol) with 4.00 g Ar (0.100 mol) gives $X_{\text{He}} = 1.00/1.10 = 0.909$, not 0.500.
- Using the total pressure for a gas collected over water. Subtract water's vapor pressure first.

Quick check

A 2.00 atm mixture holds 0.30 mol N_2 and 0.10 mol O_2 . Find the partial pressure of O_2 .

Answer: $X_{\text{O}_2} = 0.10/0.40 = 0.25$, so $P_{\text{O}_2} = 0.25 \times 2.00 = 0.50 \text{ atm}$.

3.5 Kinetic molecular theory

A gas is mostly empty space, and its particles fly in straight lines until they hit something.

What the ideal-gas model assumes

- 1 The particles move constantly and randomly, in straight lines between collisions.
- 2 Their own volume is tiny compared with the container's.
- 3 They don't attract or repel each other.
- 4 Collisions don't change the total kinetic energy.
- 5 The average kinetic energy is proportional to the Kelvin temperature.

Pressure comes from particles hitting the walls

Change	Hits per second	Force of each hit	Pressure
more gas	more	same	rises
smaller volume	more	same	rises
higher temperature	more	greater	rises

On the equation sheet

$KE = \frac{1}{2}mv^2$ for one particle, with m in kg and v in m/s

Worked example

Find the kinetic energy of one N_2 molecule moving at 500. m/s.

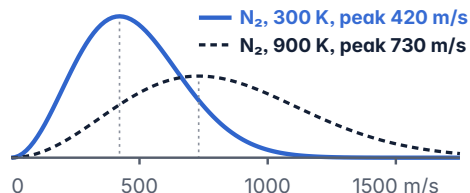
- 1 Mass of one molecule, in kg (28.02 g/mol is 0.02802 kg/mol):

$$m = \frac{0.02802 \text{ kg/mol}}{6.022 \times 10^{23} \text{ mol}^{-1}}$$
- 2 $= 4.653 \times 10^{-26} \text{ kg}$
- 3 $KE = \frac{1}{2}(4.653 \times 10^{-26} \text{ kg})(500. \text{ m/s})^2$

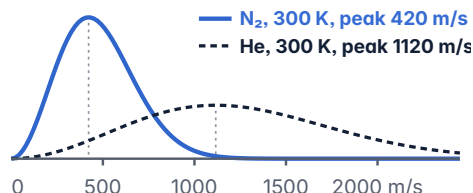
$$5.82 \times 10^{-21} \text{ J per molecule}$$

Exam trap

- Saying "same temperature, same speed." Temperature sets the average kinetic energy, $\frac{1}{2}mv^2$, not the speed. At 300 K, He and N_2 have the same average kinetic energy, so the much lighter He atoms move about 2.6 times faster.
- Using Celsius ratios. 20 °C to 40 °C does not double the kinetic energy: it is 293 K to 313 K, a rise of only 7%.



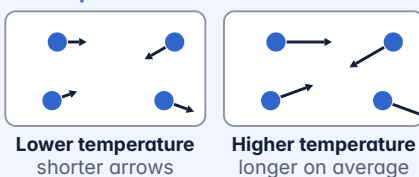
Each curve shows how many molecules move at each speed; its peak is the most common speed. At 900 K more are fast, and the area (the number of molecules) stays the same, so the peak drops.



What temperature controls

- Doubling the Kelvin temperature doubles the average kinetic energy, but the average speed rises only about 1.4 times ($\sqrt{2}$).
- At any temperature some molecules are slow and some fast, so the graph is a curve, not one speed.

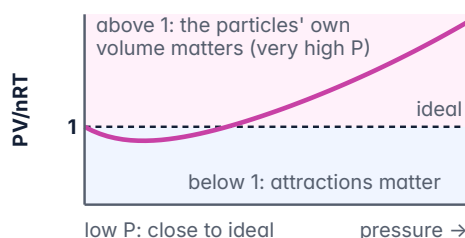
Drawing particles at a higher temperature



For a hotter sample, draw **longer arrows on average**; they needn't all be the same length. Then explain that a higher temperature means a higher average kinetic energy, so the particles move faster on average.

3.6 Deviation from ideal gas law

$PV = nRT$ assumes the particles take up no room and never attract each other. Real particles do both. For an ideal gas PV/nRT equals 1, so the ratio measures how far a real gas strays.



Condition	What matters	Real pressure
cold, near condensing	attractions	below ideal
very high pressure	the particles' own volume	above ideal
polar or large particles	stronger attractions	further below ideal

Worked example

A 2.00 L tank holds 1.00 mol of CO_2 at 300 K, and the measured pressure is 11.58 atm. What does $PV = nRT$ predict, and why is the real pressure lower?

$$1 \quad P = \frac{nRT}{V}$$

$$2 \quad = \frac{(1.00 \text{ mol})(0.08206 \frac{\text{L atm}}{\text{mol K}})(300 \text{ K})}{2.00 \text{ L}}$$

12.3 atm predicted. The real pressure is about 6% lower because CO_2 molecules attract each other.

When the particles' own volume matters

A fuel-cell car's tank stores H_2 at about 690 atm and 15 °C. Each liter holds 40.2 g, not the 58.9 g that $PV = nRT$ predicts, because the molecules' own volume fills a real share of the tank.

Which gases behave most ideally

Gases are closest to ideal at **high temperature and low pressure**, especially small nonpolar ones such as He and H_2 . They stray most at low temperature and high pressure, especially polar or large ones such as NH_3 and SO_2 .

Explaining a pressure below the ideal value

The measured pressure is **lower** than predicted because **attractions between the particles** pull them back as they approach the walls, so they strike the walls with less force. The effect is largest near condensation.

Exam trap

- Saying real gases are always below ideal. Attractions lower the pressure, but at very high pressure the particles' own volume raises it above ideal, as in the hydrogen tank.
- Blaming particle size near 1 atm. Size matters only when particles are squeezed together.

3.7 Solutions and mixtures

A solution is a mixture that is the same all the way through. It can be a liquid (salt water), a gas (air) or a solid (brass). A heterogeneous mixture changes from place to place.

On the equation sheet

$$M = \frac{n_{\text{solute}}}{L_{\text{solution}}} \quad \text{so } n = MV$$

What molarity means

- It counts moles per liter of **solution**, not per liter of water.
- Pour out half and the molarity stays the same. Add water and it drops.
- Count the ions: 0.100 M CaCl_2 is 0.100 M Ca^{2+} and 0.200 M Cl^- .

Worked example

4.00 g of NaOH (40.00 g/mol) is dissolved to make 250.0 mL of solution. Find the molarity.

- 4.00 g $\div$ 40.00 g/mol = 0.100 mol, and 0.100 mol $\div$ 0.2500 L

0.400 M NaOH

Making 100.0 mL of 0.340 M NaCl



Worked example

What mass of NaCl is needed?

$$1 \quad 0.1000 \text{ L} \times \frac{0.340 \text{ mol}}{1 \text{ L}} \times \frac{58.44 \text{ g}}{1 \text{ mol}}$$

1.99 g NaCl

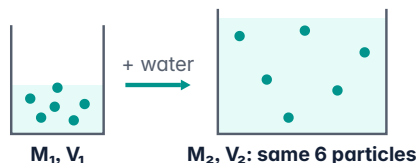
Describing how to make the solution

Weigh the solid, transfer it to a **100.0 mL volumetric flask**, add some distilled water and swirl to dissolve it, then add water **up to the calibration mark**. If you dissolve it in a beaker first, rinse the beaker into the flask.

Quick check

Find the concentration of each ion in 0.150 M $\text{Al}_2(\text{SO}_4)_3$.

Answer: $[\text{Al}^{3+}] = 2 \times 0.150 = 0.300 \text{ M}$ and $[\text{SO}_4^{2-}] = 3 \times 0.150 = 0.450 \text{ M}$.



Diluting adds only water, so the moles of solute stay the same. They spread through a larger volume.

Dilution (not on the equation sheet)

$$M_1 V_1 = M_2 V_2$$

It works because the moles of solute before and after are equal. V_2 is the final **total** volume.

Worked example

What volume of 2.00 M HCl is needed to make 250.0 mL of 0.150 M HCl?

$$1 \quad V_1 = \frac{M_2 V_2}{M_1} = \frac{(0.150 \text{ M})(250.0 \text{ mL})}{2.00 \text{ M}}$$

18.8 mL, then add water up to the 250.0 mL mark

Worked example

35.00 mL of $1.85 \times 10^{-3} \text{ M Mg}(\text{NO}_3)_2$ is mixed with 50.00 mL of NaOH solution (any concentration). Find $[\text{Mg}^{2+}]$, the concentration of Mg^{2+} , before any reaction.

- Moles: $0.03500 \text{ L} \times 1.85 \times 10^{-3} \text{ M} = 6.48 \times 10^{-5} \text{ mol}$
- Divide by the **total** volume, 35.00 + 50.00 mL = 0.08500 L.

$7.62 \times 10^{-4} \text{ M Mg}^{2+}$

Exam trap

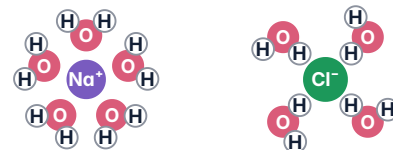
- Dissolving the solid "in 100.0 mL of water."** The solid adds volume, so the solution would no longer be exactly 100.0 mL. Dissolve it in some water in the flask, then fill to the mark.
- Dividing molarity by volume.** Moles = $M \times V$: 0.250 L of 0.400 M solution holds 0.100 mol ($\text{mol/L} \times \text{L} = \text{mol}$).
- Dividing by one volume after mixing.** Each ion spreads through both solutions, so in the example above divide by 85.00 mL, not 35.00 mL.

Making standards by serial dilution

Standards are solutions of known concentration. Dilute 10.00 mL of 0.100 M solution to 100.0 mL to get 0.0100 M. Dilute 10.00 mL of that to 100.0 mL to get 0.00100 M. Each step uses a pipet and a volumetric flask.

3.8 Representations of solutions

A particle drawing of a solution shows one of two things: **which particles attract which**, or **how much of each** is there.



$\delta^- \text{ O toward Na}^+$

$\delta^+ \text{ H toward Cl}^-$



0.10 M CaCl_2

1 : 2 ratio

0.10 M sugar

whole molecules

0.05 M CaCl_2

half as many

Equal volumes with the water left out (sizes not to scale). Circles marked 2+ are Ca^{2+} , green dots are Cl^- and ovals are sugar molecules.

Drawing a dissolved ionic compound

- Draw the ions apart, never as NaCl "pairs," and make the charges balance.
- Keep the formula's ratio: $\text{Sr}(\text{OH})_2$ gives two OH^- for each Sr^{2+} .
- In equal volumes, more particles means a higher concentration. If the volumes differ, divide each particle count by its volume first.

Worked example

A drawing of a vanadium (V^{2+}) solution with absorbance 0.32 shows eight ions. How many should a same-volume drawing show for absorbance 0.08?

- Absorbance is proportional to concentration, and 0.08 is a quarter of 0.32.

2 ions

Drawing strong and weak acids

A soluble ionic compound or a strong acid is drawn as separate **ions only**. A weak acid such as HNO_2 is drawn as mostly **whole HNO_2 molecules**, with only a few H_3O^+ and NO_2^- ions.

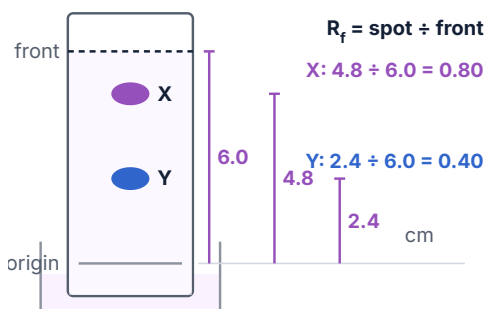
Exam trap

- Pointing water's oxygen at Cl^- .** The oxygen end of water is partly negative, so it is pushed away from a negative ion. Point the partly positive hydrogen atoms at anions like Cl^- , and the oxygen at cations like Na^+ .

3.9 Separation of solutions and mixtures

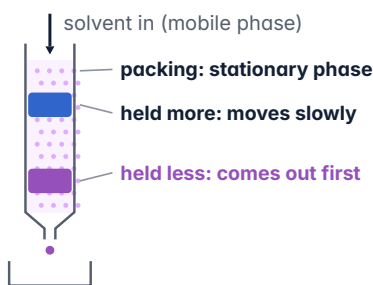
A filter catches solid pieces, not dissolved particles. Solutions are separated by differences in intermolecular forces.

In **chromatography**, a **mobile phase** (the solvent) flows past a **stationary phase** (paper, silica or a packed column). Each component is attracted to both. The one held more strongly by the stationary phase travels less far.



Reading a chromatogram

- R_f , the retention factor, = the distance the spot moved $\div$ the distance the solvent front moved, both measured from the origin, the line where the spots started. It has no units and is never more than 1.
- With a polar stationary phase (paper or silica), the **more polar** component sticks more, moves less and has the smaller R_f . A spot at $R_f = 0.20$ is more polar than one at 0.75.



Column chromatography works the same way in a tube.

Explaining why one spot traveled farther

X traveled farther than Y because X is attracted **more to the mobile phase** and **less to the stationary phase**, so it spends more time moving with the solvent.

Distillation

Heating a liquid mixture boils off more of the component with the **weaker** intermolecular forces, which has the higher vapor pressure and the lower boiling point. The first liquid collected is **richer** in that component, but not pure. Distilling a mixture of hexane (boils at 69 °C) and heptane (98 °C) gives a first liquid rich in hexane, which has weaker dispersion forces. With salt water, the water boils off and the salt stays behind.

Mixture	Separate it by
sand in salt water	filtration (removes the sand), then distillation
salt water	distillation or evaporation
two liquids with different boiling points	distillation
dyes or pigments in a solution	chromatography

Worked example

A paper chromatogram of dyes X and Y runs for 30 minutes. A second run is stopped after 15 minutes. How does the distance between the two spots change?

- In half the time neither spot travels as far, so they have less time to pull apart.

The spots end closer together, though each R_f stays about the same

Exam trap

- Filtering to remove dissolved salt.** Dissolved ions are far smaller than the holes in filter paper, so they pass through with the water. Use distillation or evaporation.
- Saying the more polar dye always moves farther.** How far a dye travels depends on its attraction to **both** phases. On polar paper with a nonpolar solvent, the more polar dye is held back and moves less.
- Measuring from the edge of the paper.** Measure both distances from the origin, the line where the spots started.

Leaf pigments

Spinach extract on paper with a nonpolar solvent separates clearly. Orange β -carotene, which is made only of carbon and hydrogen, travels almost as far as the solvent. The chlorophylls, which carry polar groups, trail behind.

3.10 Solubility

Dissolving breaks solute–solute and solvent–solvent attractions and forms solute–solvent ones. A substance dissolves well when the new attractions are about as strong as the ones they replace.

Alcohols with longer nonpolar tails dissolve less

	g per 100 mL of water, 20 °C
methanol	mixes in any amount
ethanol	mixes in any amount
1-propanol	mixes in any amount
1-butanol	7.7 g
1-pentanol	2.2 g
1-hexanol	0.59 g

Each extra CH_2 group adds nonpolar surface, which can attract water only through dispersion forces.

Like dissolves like

- Polar and hydrogen-bonding solutes dissolve in water; nonpolar solutes dissolve in nonpolar solvents. I_2 dissolves far better in hexane than in water.
- For an ionic solid, water's attraction to the ions competes with the ions' attraction to each other, so not every ionic solid dissolves.
- All sodium, potassium, ammonium and nitrate salts dissolve in water. This is the only solubility rule the exam expects you to know.

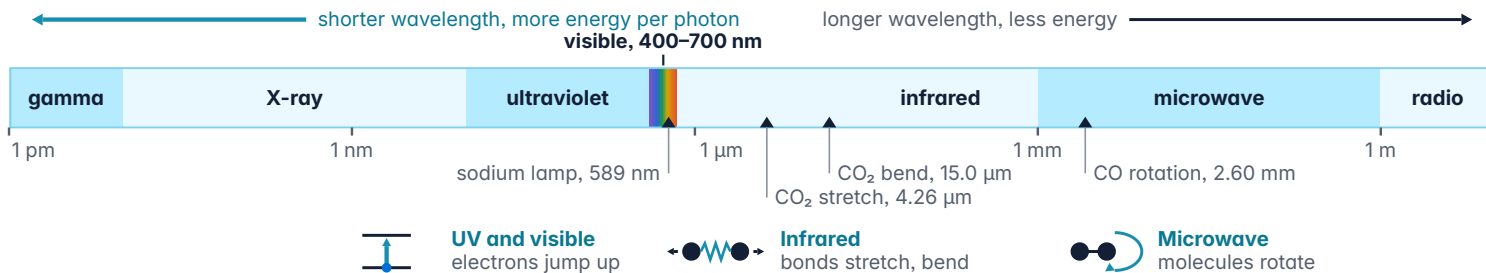
Explaining why one liquid mixes with water

Ethanol mixes with water because ethanol–water **hydrogen bonds** replace the water–water and ethanol–ethanol hydrogen bonds that break. Hexane doesn't: it can attract water only through **dispersion** forces, which are too weak to replace water's hydrogen bonds.

Exam trap

- Describing only the solute.** "Ethanol is polar" is not an explanation. Compare the attractions that form with the ones that break.
- Assuming any –OH makes a compound dissolve.** A long nonpolar tail outweighs one –OH group: 1-hexanol dissolves only 0.59 g per 100 mL of water, while ethanol mixes in any amount.

3.11 Spectroscopy and the electromagnetic spectrum

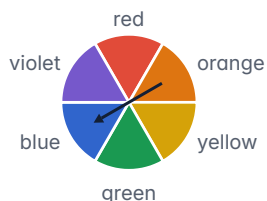


A molecule absorbs a photon only when the photon's energy matches one of its own energy gaps.

Light	What it changes	Energy
Microwave	rotation of the whole molecule	lowest
Infrared	vibration: bonds stretch and bend	middle
UV, visible	electrons move to higher levels	highest

Absorbing, emitting and color

- Absorbing a photon **raises** a molecule's energy by exactly the photon's energy; emitting one **lowers** it by that amount.
- A colored solution shows you the light it **lets through**. A blue dye absorbs red-orange light near 630 nm.



You see the color opposite the one it absorbs:

absorbs orange, looks blue
absorbs violet, looks yellow

Exam trap

- Saying infrared light breaks bonds.** An infrared photon has only enough energy to make a bond stretch or bend. Breaking it takes far more.
- Saying microwaves excite electrons.** Microwave photons have the least energy of these three, enough only to make molecules rotate.
- Saying you see the color that is absorbed.** You see the light that gets through.

Quick check

CO₂ absorbs 15.0 μm light. Which region is that, and what does it do to the molecule?

Answer: Infrared (700 nm to 1 mm), so it makes CO₂ vibrate by bending.

3.12 Properties of photons

Every photon of one frequency has the same energy; brighter light just has **more** photons.

On the equation sheet

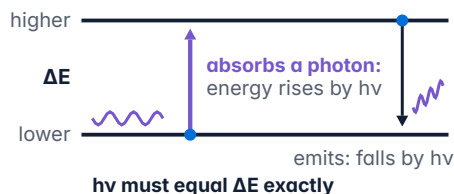
$$E = h\nu \quad c = \lambda\nu$$

ν (nu) is the frequency and λ (lambda) the wavelength; $h = 6.626 \times 10^{-34}$ J s and $c = 2.998 \times 10^8$ m s⁻¹.

Know by heart

$$E = \frac{hc}{\lambda}$$

Substitute $\nu = c/\lambda$ into $E = h\nu$, with λ in meters (1 nm = 10^{-9} m, 1 μm = 10^{-6} m).



Why CO₂ traps heat

Earth gives off heat as infrared light, strongest near 10 μm. CO₂'s bending vibration absorbs strongly near 15.0 μm, in that range, which makes it a greenhouse gas.

Quick check

CO₂ absorbs infrared light at 4.26 μm. Find the energy of one of these photons.

Answer: $\frac{(6.626 \times 10^{-34})(2.998 \times 10^8)}{4.26 \times 10^{-6}} = 4.66 \times 10^{-20}$ J, about a seventh of a 589 nm photon's energy: vibrations need less energy than electron jumps.

Quick check

Find the energy of one photon of 250. nm ultraviolet light.

Answer: $hc/\lambda = 7.95 \times 10^{-19}$ J, more than twice the energy of a 589 nm photon.

Worked example

A sodium lamp emits orange-yellow light at 589 nm. Find the frequency, the energy of one photon, and the energy of a mole of photons.

- $589 \text{ nm} = 5.89 \times 10^{-7} \text{ m}$
- $\nu = \frac{c}{\lambda} = \frac{2.998 \times 10^8 \text{ m s}^{-1}}{5.89 \times 10^{-7} \text{ m}} = 5.09 \times 10^{14} \text{ s}^{-1}$
- $E = h\nu = (6.626 \times 10^{-34})(5.09 \times 10^{14}) = 3.37 \times 10^{-19} \text{ J}$
- Times Avogadro's number: $2.03 \times 10^5 \text{ J/mol} = 203 \text{ kJ/mol}$

$5.09 \times 10^{14} \text{ s}^{-1}$; $3.37 \times 10^{-19} \text{ J}$; 203 kJ/mol

Enter powers of ten

TI-84 Plus CE. Type 6.626, then $\boxed{\text{2nd}} \boxed{\text{E}}$ (EE, "times ten to the"), then $\boxed{(-)} \boxed{34}$. The screen shows 6.626E-34. Use $\boxed{(-)}$ for a negative sign, never the subtraction key.

TI-Nspire CX. Type 6.626 $\boxed{\times 10^{\wedge}} \boxed{(-)} \boxed{34}$.

Desmos. Type 6.626*10^-34.

Exam trap

- Leaving the wavelength in nanometers.** Use meters: 589 nm is 5.89×10^{-7} m. Putting in 589 makes the energy 10^9 times too small.
- Mixing up one photon and a mole of photons.** $E = h\nu$ is for one photon; multiply by Avogadro's number only for a mole.
- Dividing by a power of ten without parentheses.** Typing $\div 5.89 \times 10^{-7}$ divides by 5.89, then multiplies by 10^{-7} . Use EE or parentheses.

Linking a photon to an energy change

The photon's energy, $E = hc/\lambda$, equals the energy gap between the two levels, so absorbing it raises the molecule from the lower level to the higher one.

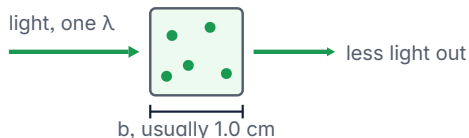
3.13 Beer-Lambert law

The more absorbing particles the light meets on its way through a sample, the less light gets out.

On the equation sheet

$$A = \epsilon bc$$

- A absorbance, which has no units
 ϵ molar absorptivity, in $\text{M}^{-1} \text{cm}^{-1}$; it depends on the substance and the wavelength
 b path length, in cm: the width of the cuvette (the sample holder)
 c concentration, in M



Worked example

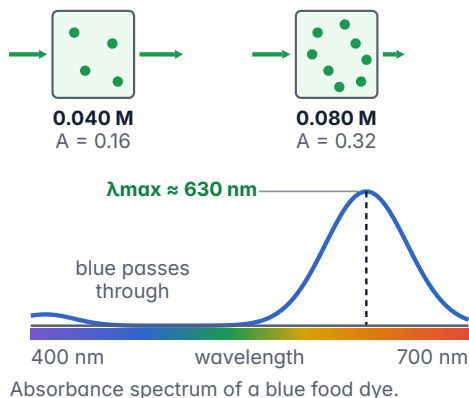
A 0.050 M standard solution of V^{2+} , in a 1.0 cm cuvette, reads $A = 0.20$. Find ϵ .

$$1 \quad \epsilon = \frac{A}{bc} = \frac{0.20}{(1.0 \text{ cm})(0.050 \text{ M})}$$

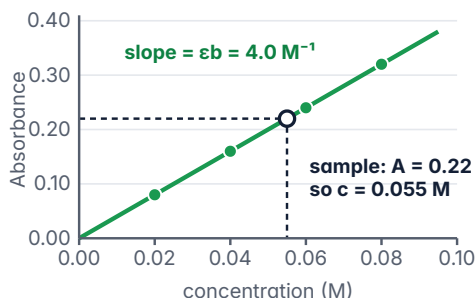
$$4.0 \text{ M}^{-1} \text{cm}^{-1}$$

Running the experiment, in order

- 1 Pick λ_{max} , the wavelength the substance absorbs most: where A changes the most when c changes.
- 2 Zero the instrument with a **blank**, the solvent alone in the same cuvette.
- 3 Measure the standards, rinsing the cuvette with each new solution first. Keep b and λ fixed so that A is proportional to c.
- 4 Plot A against c and fit the best line.
- 5 Measure the unknown, and dilute it if it reads above the top standard.



From a calibration line to a concentration



Worked example

A vanadium (V^{2+}) solution reads above the top standard, so 3.00 mL is diluted to 25.0 mL. That reads $A = 0.22$; the calibration slope, ϵb , is 4.0 M^{-1} . Find the original molarity.

- 1 $c = \frac{A}{\epsilon b} = \frac{0.22}{4.0 \text{ M}^{-1}} = 0.055 \text{ M}$ in the diluted solution
- 2 Undo the dilution: $M_1 = \frac{M_2 V_2}{V_1}$
- 3 $= \frac{(0.055 \text{ M})(25.0 \text{ mL})}{3.00 \text{ mL}}$

0.46 M (two significant figures, like 0.22)

Answering an error question

A student overfills the 25.0 mL flask. Agree or disagree: the calculated original molarity is too low.

Agree. Too much water makes the diluted solution **less concentrated**, so its absorbance is **lower**. A lower absorbance gives a lower diluted molarity, and so a **lower** calculated original molarity.

Exam trap

- **Forgetting to undo the dilution.** The line gives the concentration of the diluted solution you measured, so multiply by 25.0/3.00 as in steps 2 and 3.
- **Wrong units on ϵ .** They are $\text{M}^{-1} \text{cm}^{-1}$, so that $\epsilon \times b \times c$ has no units, like A.
- **Forcing the line through zero.** If the best-fit line has an intercept, keep it; forcing the line through the origin shifts every concentration.

Quick check

The same solution is moved from a 1.00 cm cuvette to a 2.00 cm one. What happens to A?

Answer: It doubles: the light meets twice as many absorbing particles.

Lab errors and what they do to the result

What went wrong	What it does to the result
Water drops left in the cuvette	They dilute the sample, so A reads low and the concentration comes out too low .
Fingerprints or scratches on the cuvette	Less light gets through, so A reads high and the concentration comes out too high .
The sample's dilution flask filled past the mark	The sample is too dilute, so A is low and the original concentration comes out too low .
Solid left in the beaker, not rinsed into the flask	Fewer moles reach the flask, so the real molarity is lower than the value calculated from the mass.
Water vapor not subtracted for a gas collected over water	The gas pressure used is too high, so the moles of gas come out too high .

Writing the error chain

Because the cuvette held water, the measured absorbance was lower than it should be, so the calculated concentration is lower than the true value.

Name the measured quantity and which way it changed, then which way the result changed. "Human error" earns no credit, and neither does "no effect" without a reason.

Glassware for measuring volume

- **Volumetric flask:** one exact volume, such as 100.0 mL, for making a solution.
- **Pipet or buret:** a measured volume to transfer.
- **Graduated cylinder:** a volume good to about 1%. **Beaker:** only a rough volume.
- Read any scale to **one digit past** its smallest marking: a buret marked every 0.1 mL reads to 0.01 mL, such as 12.35 mL.

Quick check

Why not measure the blue dye at 450 nm?

Answer: It barely absorbs blue light, so A stays small and changes little with concentration. The measurement would be much less sensitive.

Free-response questions on Unit 3

When the question asks you to	What earns the point	Topic
Identify all the intermolecular forces in a liquid	List dispersion forces for every substance, dipole–dipole forces if the molecule is polar, and hydrogen bonding only if an H is bonded to N, O or F.	3.1
Explain a higher boiling point or a larger ΔH_{vap}	Name the force that differs and say why it is stronger, then say that more energy is needed to separate those molecules.	3.1
Agree or disagree that one substance has stronger dispersion forces	Compare electrons or occupied shells: more electrons make a larger, more polarizable electron cloud. Molar mass on its own is not a reason.	3.1
Draw a hydrogen bond between two molecules	Draw one dashed line from an H on N, O or F in one molecule to a lone pair on N, O or F in the other.	3.1
Say which has the higher vapor pressure	It is the substance with the weaker attractions. At a given temperature, the liquid closer to its boiling point has the higher vapor pressure. Say something about both substances.	3.2
Calculate the moles, pressure or volume of a gas	Convert to kelvins, use $R = 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}$ with atm and liters, and show the setup with every unit.	3.4
Draw particles at a higher temperature or another concentration	Draw longer motion arrows on average. For a new concentration in the same volume, change the number of particles in proportion.	3.5 3.8
Explain why a measured pressure differs from the ideal value	Below ideal: attractions between the particles, strongest near condensing. Above ideal: the particles' own volume, at very high pressure.	3.6
Calculate the mass needed for a solution, then describe how to make it	Use $n = MV$ with V in liters, then multiply by the molar mass. Dissolve the solid in some water in a volumetric flask and add water up to the mark.	3.7
Find a concentration after mixing or diluting	Divide the moles of that ion or molecule by the final total volume.	3.7
Draw water molecules around an ion	Draw several water molecules, with oxygen pointing at a cation and hydrogens pointing at an anion.	3.8
Explain a chromatogram or predict a change in the run	Name both phases and say which one each component is more attracted to. A shorter run leaves the spots closer together.	3.9
Explain why one substance dissolves in another	Compare the attractions that form between solute and solvent with the ones that break. If the new attractions are about as strong as the ones broken, it dissolves.	3.10
Name the region of light, or calculate a photon's energy	Microwaves rotate molecules, infrared makes bonds vibrate, and UV or visible light moves electrons. Use $E = hc/\lambda$ with λ in meters.	3.11 3.12
Find a concentration from a calibration line	Use $c = A/\epsilon b$ or read the line, then undo any dilution.	3.13
Agree or disagree about an effect of a lab error	Say what the mistake changed, which way the measured value moved, and then which way the result moved.	3.13

 A full explanation, one sentence at a time

1-Propanol, $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$, boils at 370 K and butane, C_4H_{10} , at 273 K. Both have 34 electrons. Explain the difference.

- Both molecules have 34 electrons, so their London dispersion forces are about equally strong.
- 1-Propanol is polar and has an H bonded to O, so its molecules also form dipole–dipole forces and hydrogen bonds. Butane is nonpolar, with only C–H bonds, so it has neither.
- The extra attractions mean more energy is needed to separate 1-propanol molecules, so 1-propanol boils at the higher temperature.

 Worked example

8.59 g of CH_3OH vapor (32.04 g/mol) condenses at constant temperature. With $\Delta H_{\text{vap}} = 37.6 \text{ kJ/mol}$, how much heat, q , is released?

$$1 \quad 8.59 \text{ g} \times \frac{1 \text{ mol}}{32.04 \text{ g}} \times \frac{37.6 \text{ kJ}}{1 \text{ mol}}$$

10.1 kJ. The temperature doesn't change while it condenses, so use $q = n\Delta H_{\text{vap}}$ rather than $q = mc\Delta T$.

 Store a value to keep every digit

TI-84 Plus CE. After a result, press **(sto→)** **[alpha]** **[math]** (the letter A) and **[enter]**.

Use A later with **[alpha]** **[math]**.

TI-Nspire CX. After a result, press **[ctrl]** **[var]** (sto→), type a name such as a, and press **[enter]**. Type the name to use it later.

Desmos. Type $a = 8.59/32.04$, then use a later, as in $a \cdot 37.6$.

 Where Unit 3 comes back

- Unit 4** uses the rule that every sodium, potassium, ammonium and nitrate salt dissolves, and it uses molarity in titrations.
- Unit 5** brings back the speed curve: only collisions with at least the activation energy react.
- Unit 6** finds the heat for a phase change with $q = n\Delta H_{\text{vap}}$; stronger forces mean a larger ΔH_{vap} .
- Unit 7** puts partial pressures into K_p , the pressure equilibrium constant, and treats solubility as an equilibrium.
- Unit 8** asks for particle drawings of strong and weak acids, and uses dilution in pH problems.
- Unit 9** explains that entropy rises from solid to liquid to gas, and that dissolving spreads particles out.