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Topic 3.6: Deviation from Ideal Gas Law

Revision Notes · AP Chemistry

UNIT 3 · PROPERTIES OF SUBSTANCES AND MIXTURES

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Two Postulates Fail, Each in Its Own Conditions

The ideal gas law, PV = nRT, rests on two simplifications: particles occupy no volume, and they exert no forces on each other. Real particles fail both, and every deviation here traces back to one or the other.

The volume failure grows as particles are forced closer together. Compress a gas and the space between particles shrinks while the particles stay the same size, so their own volume becomes a larger fraction of the container: high pressure exposes it.

The force failure grows as particles slow down and linger near each other. Cool a gas and its kinetic energy falls, so an attraction has more time to act and less energy to overcome: low temperature exposes it.

Turn both around and the ideal law recovers: at low pressure and high temperature particles are far apart, fast and barely interacting. The greatest deviation sits at the opposite corner: high pressure, low temperature.

Attractions Pull the Pressure Down

Pressure is momentum transferred to the walls. Attractions change what arrives there.

Picture a particle travelling toward the wall. The particles behind it pull it backward, so it strikes more slowly, and less often, and transfers less momentum. Multiplied over every wall collision, the measured pressure falls below the ideal prediction for the same n, V and T: $P_{real} < P_{ideal}$.

At fixed pressure the same pull draws particles closer together, so the sample occupies a smaller volume than predicted: $V_{real} < V_{ideal}$.

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Attractions strengthen on cooling toward the boiling point, because slower particles linger within reach of each other. Taken to the limit they produce condensation: cool far enough and attractions pull the gas into a liquid, which proves the attractions the ideal model sets at zero are real.

Particle Volume Pushes the Other Way

Particles are not points. Each excludes the others from the space it occupies, so the volume in which particles can actually move, the free volume, is the container volume minus the particles' own volume.

In the van der Waals picture this reads $V_{free} = V_{container} - nb$, where b is a constant for the gas, in litres per mole, that grows with particle size. In a large container nb is a tiny fraction of V; in a small one it becomes substantial.

Less free volume means particles reach the walls sooner and collide more often. At fixed V and T the measured pressure rises above the ideal prediction: $P_{real} > P_{ideal}$. At fixed P and T the sample needs a larger volume than predicted: $V_{real} > V_{ideal}$.

Note the opposition: attractions pull pressure and volume below the ideal values, particle volume pushes them above. Which error appears depends on which effect is winning.

Reading the Winner: Z = PV/nRT

The compressibility factor packages the comparison into one number: $Z = PV/nRT$, using the measured P, V and T of a real sample. For an ideal gas $Z = 1$ exactly, at every pressure and temperature.

$Z < 1$ means PV has come out smaller than nRT: the sample is more compressible than an ideal gas. Attractions are dominating, holding pressure, or volume, below the ideal value, as is usual at moderate pressures and lower temperatures.

$Z > 1$ means PV has come out larger than nRT: the sample resists compression more than an ideal gas. Finite particle volume is dominating, because at very high pressures the particles' own volume, which no pressure can squeeze away, controls the behaviour.

One caution: Z close to 1 does not prove ideal behaviour. The two errors can oppose each other at similar sizes and largely cancel, leaving Z near 1 while both are significant.

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Which Gases Deviate Most

Deviation is a property of the gas as well as the conditions: the gases that deviate most have large particles and strong attractions.

Size works through both failures at once. A large particle carries a larger b, and its large, easily distorted electron cloud is highly polarizable, so its London dispersion forces are stronger too. Xenon deviates more than neon, and both deviate more than helium, the smallest and least polarizable of all, which behaves the most ideally of any real gas.

Polarity adds attractions nonpolar particles lack, and hydrogen bonding produces the strongest deviation of all: NH_3 deviates far more than CH_4 under the same conditions, because ammonia molecules hydrogen bond while methane molecules feel only weak dispersion forces.

Boiling point is the quickest comparison: a high boiling point certifies strong attractions, since much thermal energy is needed to pull particles apart into a gas. NH_3 boils at -33 °C and deviates strongly at room temperature; N_2 boils at -196 °C, its attractions are feeble, and it sits much closer to ideal.

The van der Waals constant a ranks attractions: a larger a means stronger attractions and a bigger downward pull on pressure. The constant b ranks particle size. Both are used qualitatively: identify which effect each represents and compare gases by them, rather than calculate with the full equation.

Worked Examples

Example 1: Attractions winning, read from Z. One mole of gas at 300 K fills 0.500 L and exerts 40.0 atm. The ideal prediction is P = nRT/V = (1.00 × 0.08206 × 300) ÷ 0.500 = 49.2 atm. Then Z = PV/nRT = (40.0 × 0.500) ÷ 24.6 ≈ 0.81. Z sits well below 1, the pressure is about 19% low, and attractions dominate.

Example 2: Particle volume winning at 500 atm. One mole of gas at 300 K is held at 500 atm. The ideal volume is V = nRT/P = 24.6 ÷ 500 ≈ 0.0492 L; the measured volume is 0.0600 L. Then Z = (500 × 0.0600) ÷ 24.6 ≈ 1.22. The sample takes about 22% more room than predicted, and the particles' own incompressible volume dominates.

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Example 3: Free volume with a real b value. For N_2, b = 0.0391 L/mol. Two moles in a 1.00 L container exclude nb = 2.00 × 0.0391 = 0.0782 L, leaving free volume 1.00 - 0.0782 ≈ 0.922 L: the particles claim 7.8% of the container. Spread the same sample through 24.6 L and the excluded volume is only about 0.32% of the total, small enough to ignore.

Traps That Cost Marks in Topic 3.6

Attractions raise the pressure. They lower it: particles approaching a wall are pulled back by those behind them and strike more softly than predicted.

Particle volume makes the measured volume smaller. It makes it larger: the particles' own volume cannot be compressed away, so at fixed pressure a real sample needs more room than predicted, and Z rises above 1.

One deviation direction fits all conditions. It flips: attractions dominate at moderate pressure and low temperature, giving $Z < 1$; particle volume dominates at very high pressure, giving $Z > 1$.

Z = 1 proves ideal behaviour. It can instead mean the two corrections cancel at that point, in a gas deviating clearly at other pressures.

Big deviation means a big, heavy gas, full stop. Size is half the story: small NH_3 deviates more than larger nonpolar gases, because hydrogen bonding beats a modest size difference.

Deviation is cured by cooling. Cooling worsens it: low temperature hands attractions their influence. The fixes are heating and lowering the pressure.

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Key Relationships to Remember

- Ideal assumptions that fail: particles have finite volume, and particles attract each other; every deviation comes from one or both
- Greatest deviation at high pressure and low temperature; most ideal behaviour at low pressure and high temperature
- Attractions dominant: $P_{real} < P_{ideal}$ at fixed V and T, $V_{real} < V_{ideal}$ at fixed P and T, and $Z < 1$; they strengthen on cooling toward the boiling point, causing condensation at the limit
- Particle volume dominant: free volume = $V - nb$; $P_{real} > P_{ideal}$ at fixed V and T, $V_{real} > V_{ideal}$ at fixed P and T, and $Z > 1$; it takes over at very high pressure
- $Z = PV/nRT$: $Z = 1$ ideal; $Z < 1$ attractions winning; $Z > 1$ particle volume winning; Z near 1 can mean the two effects are cancelling
- Deviation grows with particle size and polarizability (Xe > Ne > He) and with attraction strength, ranked by the constant a; hydrogen bonding gases such as NH_3 deviate most, and a higher boiling point signals stronger attractions

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