Why Gases Show Non-ideal Behavior

1. Intermolecular forces of attraction exist.

$$\Rightarrow V_{\text{real}} < V_{\text{ideal}}$$

If P is applied pressure, then

$$PV/RT < n$$

☞ The stronger the forces of attraction between molecules, the greater will be the deviation from ideal behavior.

2. Molecular volumes are not negligible under some conditions.

$$\Rightarrow V_{\text{real}} > V_{\text{ideal}}$$

If P is applied pressure, then

$$PV/RT > n$$

☞ The larger the molecules, the greater will be the deviation from ideal behavior.

When Are Real Gases Most Likely to Deviate from Ideal Gas Behavior?

1. Low Temperature, T:

   Kinetic energy is lower and sample volume is smaller, fostering intermolecular attractions.

   $$\Rightarrow V_{\text{real}} < V_{\text{ideal}}$$

2. High Pressure, P:

   Molecules crowd together, making their volumes a more significant part of the sample volume.

   $$\Rightarrow V_{\text{real}} > V_{\text{ideal}}$$

The van der Waals Equation

Johannes van der Waals (1873)

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

- The constants *a* and *b* are empirically determined for the specific gas.

- P and V are the *measured* values of the real gas, not the ideal gas values.

- The term n^2a/V^2 is added to the measured P to correct for intermolecular attractive forces. (P would be greater if these attractions did not restrain the molecules in their collisions, so $P + n^2a/V^2 = P_{\text{ideal}}$.)

$$P_{\text{real}} < P_{\text{ideal}}$$

- The term nb is subtracted from the measure V to correct for the portion of the sample that is not compressible due to the molecules' individual volumes. (Molecular volume is part of the measured V, so $V - nb = V_{\text{ideal}}$.)

$$V_{\text{real}} > V_{\text{ideal}}$$