STUDY MATERIAL AND NUMERICAL PROBLEMS: DEVIATION OF GASES FROM IDEAL BEHAVIOR

1. DEVIATION OF GASES FROM IDEAL BEHAVIOR

An ideal gas is a theoretical concept where gas particles have negligible volume and no intermolecular forces. Real gases deviate from this ideal behavior primarily due to two factors:

- **Finite Molecular Volume:** Gas molecules occupy a finite volume, which becomes significant at high pressures where the volume occupied by the molecules themselves is a considerable fraction of the total volume.
- **Intermolecular Forces:** Real gas molecules exert attractive and repulsive forces on each other. These forces reduce the pressure exerted by the gas compared to an ideal gas at the same conditions.

2. COMPRESSIBILITY FACTOR (Z)

The compressibility factor, **Z**, quantifies the deviation of a real gas from ideal behavior. It is defined as:

$Z = PV / nRT$

- For an ideal gas, $Z = 1$ under all conditions.
- For real gases:
  - **$Z < 1$**: Attractive forces dominate, causing the gas to be more compressible than an ideal gas.
  - **$Z > 1$**: Repulsive forces or the finite volume of molecules dominate, causing the gas to be less compressible than an ideal gas.

3. BOYLE TEMPERATURE (T_B)

The Boyle temperature is the specific temperature at which a real gas exhibits ideal gas behavior over a wide range of pressures. At the Boyle temperature, the attractive and repulsive forces balance out, making the compressibility factor Z approximately equal to 1 over a significant pressure range.

Mathematically, it's the temperature where the second virial coefficient (B_2) is zero.

4. ANDREW'S AND AMAGAT'S PLOTS

These plots help visualize gas behavior under varying conditions.

- **Andrew's Plots:** These are isothermal plots of **PV vs. P** at different constant temperatures.
    - At high temperatures (well above T_C), the curves are nearly horizontal, indicating near-ideal behavior.
    - As temperature decreases, the curves deviate from horizontal, showing initial decrease (attraction) and then increase (repulsion/volume).
    - Below the critical temperature (T_C), the curves show a distinct liquid-gas phase transition region.
- **Amagat's Plots:** These are isochoric plots of **PV vs. P** at different constant volumes.
    - At low pressures (high volumes), the PV product is constant, indicating ideal gas behavior.
    - At higher pressures (lower volumes), deviations occur, with the nature of deviation depending on temperature.

5. VAN DER WAALS EQUATION OF STATE

The van der Waals equation corrects the ideal gas law for the finite volume of molecules and intermolecular forces:

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

Where:

- **P** is the pressure, **V** is the volume, **T** is the temperature, and **n** is the number of moles.
- **R** is the ideal gas constant.
- **a** is a constant that corrects for attractive intermolecular forces. A larger 'a' indicates stronger attractions.
- **b** is a constant that corrects for the finite volume of gas molecules. A larger 'b' indicates larger molecules.

Features and Applications:

- It qualitatively explains the deviation of real gases from ideal behavior.
- The term **$a(n/V)^2$** reduces the pressure because intermolecular attractions pull molecules away from the walls.
- The term **nb** reduces the available volume for molecules to move because of their finite size.
- It can predict the existence of a critical state and phase transitions (liquefaction).

6. EXISTENCE OF CRITICAL STATE AND CRITICAL CONSTANTS

The critical state is the unique temperature (T_C), pressure (P_C), and molar volume (V_C) at which the liquid and gas phases of a substance become indistinguishable. Above the critical temperature, a gas cannot be liquefied by pressure alone.

Critical Constants in terms of van der Waals Constants:

From the van der Waals equation, the critical constants can be expressed as:

- **$T_C = 8a / 27Rb$**
- **$P_C = a / 27b^2$**
- **$V_C = 3b$**

The compressibility factor at the critical point (Z_C) can also be derived:

$Z_C = P_C V_C / RT_C = (a/27b^2) * (3b) / (R * 8a/27Rb) = 3/8$

(Note: This calculated Z_C of 3/8 for van der Waals gas is a theoretical value. Actual gases have Z_C values closer to 0.375, highlighting the limitations of the van der Waals model.)

7. LAW OF CORRESPONDING STATES

This law states that all gases behave similarly when they are at the same reduced temperature and reduced pressure.

Reduced variables are defined relative to the critical constants:

- Reduced Temperature: **$T_r = T / T_C$**
- Reduced Pressure: **$P_r = P / P_C$**
- Reduced Volume: **$V_r = V / V_C$**

According to the law of corresponding states, if T_r and P_r are the same for two different gases, their compressibility factors (Z) will also be the same. This implies that Z can be expressed as a universal function of T_r and P_r: **$Z = f(T_r, P_r)$**.

8. VIRIAL EQUATION OF STATE

The Virial equation is an empirical or semi-empirical equation of state that expresses PV/nRT as a power series expansion in terms of molar volume (or pressure):

$$PV / nRT = 1 + B_2(T)(n/V) + B_3(T)(n/V)^2 + B_4(T)(n/V)^3 + \ldots$$

Where $B_2(T)$, $B_3(T)$, etc., are called virial coefficients, which are functions of temperature only.

The first term (1) represents the ideal gas behavior. Subsequent terms account for deviations due to intermolecular interactions.

Virial form of van der Waals Equation:

Expanding the van der Waals equation and rearranging into the virial form, we get:

$$PV/nRT = 1 + (b - a/RT)(n/V) + b^2(n/V)^2 - (ab/RT)(n/V)^2 + \ldots$$

For low densities (large V), only the first few terms are significant. The second virial coefficient ($B_2(T)$) for the van der Waals equation is:

$$B_2(T) = b - a/RT$$

Significance of Second Virial Coefficient ($B_2(T)$):

- $B_2(T)$ accounts for the interaction between pairs of molecules.

- At high temperatures (large T), a/RT becomes small, and $B_2(T) \approx b$. Since 'b' is positive, $B_2(T)$ is positive, indicating that repulsive forces (due to molecular volume) dominate, and $Z > 1$.
- At low temperatures (small T), a/RT becomes large, and $B_2(T)$ can be negative if $a/RT > b$. A negative $B_2(T)$ means attractive forces dominate, and $Z < 1$.
- The Boyle temperature (T_B) is the temperature where $B_2(T) = 0$, i.e., $\mathbf{T_B = a/Rb}$.

9. INTERMOLECULAR FORCES

These are attractive or repulsive forces between molecules. They are responsible for the deviation of real gases from ideal behavior and the existence of liquid and solid states.

- **London Dispersion Forces (Induced Dipole-Induced Dipole):** Occur between all molecules, including nonpolar ones. They arise from temporary fluctuations in electron distribution, creating instantaneous dipoles that induce dipoles in neighboring molecules. They are generally weaker and become more significant for larger molecules with more electrons.
- **Dipole-Dipole Interactions (Keesom Interactions):** Occur between polar molecules that have permanent dipoles. The positive end of one molecule attracts the negative end of another. These are stronger than London forces for molecules of comparable size.
- **Dipole-Induced Dipole Interactions (Debye Interactions):** Occur between a polar molecule (with a permanent dipole) and a nonpolar molecule. The permanent dipole of the polar molecule induces a temporary dipole in the nonpolar molecule.

10. LENNARD-JONES POTENTIAL

The Lennard-Jones potential is a mathematical model used to describe the interaction energy between two non-bonded atoms or molecules. It's an empirical potential that combines attractive and repulsive forces:

$$\mathbf{U(r) = 4\varepsilon \left[(\sigma/r)^{12} - (\sigma/r)^{6} \right]}$$

Where:

- **U(r)** is the potential energy at separation distance **r**.

- **ε** (epsilon) is the depth of the potential well, representing the strength of the attraction.
- **σ** (sigma) is the finite distance at which the inter-particle potential is zero.
- The **$(\sigma/r)^{12}$** term represents the strong repulsive forces at short distances (due to electron cloud overlap).
- The **$-(\sigma/r)^6$** term represents the attractive forces at longer distances (primarily London dispersion forces).

The potential has a minimum at a certain distance, indicating the most stable separation between molecules.

NUMERICAL PROBLEMS

Problem 1: Compressibility Factor and van der Waals Equation

One mole of ammonia (NH_3) gas is contained in a 10.0 L vessel at 300 K. Calculate the pressure exerted by the gas using the van der Waals equation. Compare this with the pressure calculated using the ideal gas law. (Assume a = 4.24 L^2 atm/mol^2, b = 0.037 L/mol, R = 0.0821 L atm / (mol K)).

Solution Approach:

1. Calculate ideal gas pressure: $P_{ideal} = nRT/V$
2. Calculate van der Waals pressure: $P_{vdW} = nRT/(V-nb) - a(n/V)^2$
3. Calculate $Z = P_{vdW}V / nRT$.

Problem 2: Critical Constants from van der Waals Constants

The van der Waals constants for Helium (He) gas are a = 0.034 L^2 atm/mol^2 and b = 0.0234 L/mol. Calculate the critical temperature (T_C) and critical pressure (P_C) for Helium.

Solution Approach:

1. Use the formulas: $T_C = 8a / 27Rb$ and $P_C = a / 27b^2$.
2. Substitute the given values and R = 0.0821 L atm / (mol K).

Problem 3: Law of Corresponding States

At 100 K and 50 atm, the compressibility factor of nitrogen (N_2) is approximately 0.85. Use the law of corresponding states to estimate the compressibility factor of methane (CH_4) under the same reduced conditions (T_r = 100 K / T_{C,N_2} and P_r = 50 atm / P_{C,N_2}). (You may need critical constants for N_2 and CH_4 if they are not provided). Assume T_{C,N_2} = 126 K and P_{C,N_2} = 33.9 atm.

Solution Approach:

1. Calculate T_r and P_r for nitrogen.
2. Since methane is at the same reduced conditions, its compressibility factor will be the same as nitrogen's.

Problem 4: Second Virial Coefficient

For a certain gas, the second virial coefficient $B_2(T)$ is given by $B_2(T) = 0.05 - 600/T$ (in L/mol). Calculate the Boyle temperature (T_B) for this gas and the compressibility factor at 500 K and 1 atm pressure.

Solution Approach:

1. Set $B_2(T) = 0$ to find T_B.
2. Calculate $B_2(T)$ at 500 K.
3. Use the virial equation $Z = 1 + B_2(T)(n/V)$. For 1 mole at 1 atm and 500 K, consider V as molar volume. You might need to approximate V using the ideal gas law for the first term, or use an iterative approach if high accuracy is needed, but typically for low pressures Z is approximately $1 + B_2(T)/V_{m,ideal}$.