# CAPE Laboratory
# Assignment 1: Numerical Solution of Molar Volume for Ammonia

Spring Semester 2025-2026

## 1 Objective

The goal of this study is to determine the molar volume ($v$) of ammonia ($NH_3$) at a temperature $T = 250°C$ and pressure $P = 10$ atm. The analysis is conducted using two primary Equations of State (EOS):

1. **Van der Waals (VdW) Equation:** $(P + \frac{a}{v^2})(v - b) = RT$
2. **Redlich-Kwong (RK) Equation:** $P = \frac{RT}{v-b} - \frac{a}{\sqrt{T}v(v+b)}$

## 2 Numerical Methodologies

### 2.1 Fixed-Point Iteration (Direct Substitution)

This approach transforms the nonlinear equation into a recursive form $v = g(v)$.

- **Rearrangement:** For the VdW model, a stable iterative form is $v_{i+1} = \frac{RT}{P+a/v_i^2} + b$.
- **Initialization:** The starting value $v_0$ is set using the Ideal Gas Law $v_0 = \frac{RT}{P}$.
- **Procedure:** Compute $v_{i+1} = g(v_i)$ repeatedly until $|v_{i+1} - v_i| < 10^{-6}$.

### 2.2 Bisection Method

A bracketing technique that halves the search interval in each step.

- **Setup:** Define $f(v) = 0$ and choose an initial range $[v_{low}, v_{high}]$ where $f(v_{low}) \cdot f(v_{high}) < 0$.
- **Iteration:** Calculate the midpoint $v_{mid} = \frac{v_{low}+v_{high}}{2}$.
- **Refinement:** If $f(v_{low}) \cdot f(v_{mid}) < 0$, the root lies in the lower half; otherwise, it is in the upper half.
- **Tolerance:** Repeat the process until the interval radius $(v_{high} - v_{low})/2 < 10^{-6}$.

### 2.3 Newton's Method

The Newton-Raphson method utilizes the function's derivative for rapid, quadratic convergence.

- **Iteration Formula:** $v_{i+1} = v_i - \frac{f(v_i)}{f'(v_i)}$.
- **Derivatives:**
  - For VdW: $f'(v) = P - \frac{a}{v^2} + \frac{2ab}{v^3}$.
  - For RK: $f'(v) = \frac{RT}{(v-b)^2} - \frac{a(2v+b)}{\sqrt{T}(v^2+vb)^2}$.
- **Termination:** Iterate starting from $v_0$ until the change $|v_{i+1} - v_i| < 10^{-6}$.

### 2.4 Built-in Numerical Solvers

Modern computational tools like MATLAB's `fzero` employ hybrid algorithms, such as Brent's Method, to solve nonlinear equations efficiently. These solvers combine the reliability of bracketing techniques with the rapid convergence of open methods like Secant or Inverse Quadratic Interpolation. They automatically switch strategies to ensure fast convergence without requiring the manual calculation of derivatives. In practice, a residual function $f(v)$ is defined and solved starting from an Ideal Gas initial guess. This approach serves as a high-precision benchmark for evaluating the accuracy and speed of the other implemented numerical methods.

## 3 Numerical Outputs (Terminal Results)

The following results were obtained from the execution of the developed C++ scripts:

### 3.1 Fixed Point Iteration Results

```
Final RK Molar Volume: 4.23049729 L/mol
Total Iterations: 5
Execution Time: 0.00000024 seconds

Final VdW Molar Volume: 4.23124326 L/mol
Total Iterations: 5
Execution Time: 0.00000109 seconds
```

### 3.2 Bisection Method Results

```
Final RK Molar Volume: 4.23049704 L/mol
Total Iterations: 23
Execution Time: 0.00000198 seconds

Final VdW Molar Volume: 4.23124309 L/mol
Total Iterations: 23
Execution Time: 0.00000375 seconds
```

### 3.3 Newton's Method Results

```
Final RK Molar Volume: 4.23049729 L/mol
Total Iterations: 3
Execution Time: 0.00000200 seconds

Final VdW Molar Volume: 4.23124325 L/mol
Total Iterations: 3
Execution Time: 0.00000127 seconds
```

### 3.4 MATLAB fzero Results

| EOS Method | Volume (v) | Time (sec) | Function evals |
|---|---|---|---|
| Van der Waals | 4.23124 | 0.0024 | 8 |
| Redlich-Kwong | 4.23050 | 0.0010 | 11 |

## 4 Comparison Table of Results

*Conditions: $T = 523.15$ K, $P = 10$ atm, $R = 0.08206$ L·atm/(mol·K)*

| Equation | Numerical Method | Volume ($v$) [L/mol] | Iterations | Time (s) |
|---|---|---|---|---|
| Van der Waals | Fixed-Point | 4.23124326 | 5 | 0.00000109 |
| Van der Waals | Bisection | 4.23124309 | 23 | 0.00000375 |
| Van der Waals | Newton's | 4.23124325 | 3 | 0.00000127 |
| Van der Waals | fzero (Built-in) | 4.23124 | 8 | 0.0024 |
| Redlich-Kwong | Fixed-Point | 4.23049729 | 5 | 0.00000024 |
| Redlich-Kwong | Bisection | 4.23049704 | 23 | 0.00000198 |
| Redlich-Kwong | Newton's | 4.23049729 | 3 | 0.00000200 |
| Redlich-Kwong | fzero (Built-in) | 4.23050 | 11 | 0.0010 |

Table 1: Efficiency comparison based on experimental outputs.

## 5 Discussion of Results

### 5.1 Accuracy and Model Comparison

The molar volumes calculated for ammonia using both the Van der Waals (4.23124326 L/mol) and Redlich-Kwong (4.23049729 L/mol) equations are consistently lower than the Ideal Gas volume ($v = RT/P \approx 4.293$ L/mol). This deviation effectively quantifies the influence of intermolecular forces and the finite volume of gas molecules at $250°C$ and 10 atm. It is noteworthy that all four numerical methodologies converged to identical values for their respective thermodynamic models, validating the mathematical integrity of the C++ implementations.

## 5.2 Efficiency Analysis

- **Newton's Method:** This approach demonstrated the highest efficiency, achieving convergence in just 3 iterations. This confirms the quadratic convergence behavior inherent to derivative-based solvers when initiated with a reasonable guess.
- **Bisection Method:** As expected, this was the most computationally intensive method, requiring 23 iterations. Its linear reduction of the error interval makes it highly robust but significantly slower than open methods.
- **Fixed-Point Iteration:** This method was remarkably effective for the Van der Waals model, converging in only 5 iterations. Its high efficiency in this context is attributed to the initial Ideal Gas guess being geographically close to the actual root.
- **MATLAB fzero:** The built-in solver showed significantly higher execution times (approx. 0.23 s) compared to the raw C++ iterations. This overhead is due to the initialization of the MATLAB environment and the more complex robust-checking logic inherent in multi-strategy hybrid solvers.