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Comparative Analysis of Thermal Properties and Equation of State Modeling for Benzene (C_6H_6) and Chloroform ($CHCl_3$) Using Van der Waals, Peng–Robinson, and Soave–Redlich–Kwong Approaches

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Abstract
This study presents a comparative investigation into the thermal properties and equation of state (EOS) performance for benzene (C_6H_6) and chloroform ($CHCl_3$) using three widely applied thermodynamic models: Van der Waals (VDW), Peng–Robinson (PR), and Soave–Redlich–Kwong (SRK). Benzene, a non-polar aromatic hydrocarbon, and chloroform, a polar halogenated solvent, exhibit distinct thermal characteristics influenced by differences in molecular geometry, polarity, and intermolecular forces. The study integrates both theoretical derivations and numerical examples to evaluate parameters such as heat capacity, thermal expansion coefficient, compressibility factor, and phase equilibrium predictions. Critical constants (Tc, Pc, and Vc) and acentric factors are employed for each EOS, with computational outputs compared against experimental datasets. Results indicate that polar–non-polar contrasts significantly impact EOS accuracy: PR and SRK demonstrate improved predictions for chloroform's polar behavior, while VDW shows higher deviation in both cases. Practical implications include solvent selection optimization in distillation, chemical separation, and refrigeration cycle design, alongside enhanced safety assessments for chemical storage.

Keywords: *Benzene, Chloroform, Thermal Properties, Van der Waals, Peng–Robinson, Soave–Redlich–Kwong, Equation of State, Polarity, Thermodynamic Modeling*

I. Introduction

Thermodynamic properties are central to the understanding of chemical processes, physical transformations, and engineering applications. Among these, *thermal properties* and *equations of state (EOS)* form the backbone of quantitative chemical engineering, physical chemistry, and process simulation. Thermal properties describe how a substance responds to heat and temperature changes, encompassing quantities such as specific heat capacity, thermal conductivity, enthalpy of phase changes, thermal expansion, and compressibility. Equations of state, on the other hand, provide mathematical relationships between pressure (P), volume (V), and temperature (T), enabling the prediction of phase behavior, density, and thermodynamic potentials under a variety of conditions. Benzene (C_6H_6) and chloroform ($CHCl_3$) are two classic organic liquids with substantial industrial, laboratory, and theoretical relevance. Benzene is a non-polar aromatic hydrocarbon with a high degree of symmetry and unique π-electron delocalization, while chloroform is a polarizable, halogenated hydrocarbon with significant dipole interactions. Although both are widely used as solvents, they differ markedly in molecular structure, polarity, mass, and intermolecular forces. These differences manifest in their thermal behavior and in the way equations of state model them, making a comparative study both scientifically and practically significant.

These differences in **molecular geometry, polarity, and bonding** influence their **thermal properties**—such as heat capacity, thermal conductivity, enthalpy of vaporization, and coefficient of thermal expansion—as well as how they respond to **Equation of State (EOS)** predictions under different thermodynamic conditions. The **EOS approach** provides a mathematical relationship between pressure, volume, and temperature (PVT) for fluids, enabling the prediction of phase behavior, density, and other thermodynamic properties. While **ideal gas law** fails to account for real-fluid interactions, models like **Van der Waals (vdW)**, **Peng–Robinson (PR)**, and **Soave–Redlich–Kwong (SRK)** incorporate corrections for **molecular size** and **intermolecular forces**, making them relevant for liquid–vapor equilibrium calculations.

In chemical process industries, accurate knowledge of thermal properties allows engineers to design heat exchangers, distillation columns, and chemical reactors with greater precision. Similarly, EOS models are indispensable for process simulation, safety analysis, and the prediction of phase equilibria, especially under conditions far from ambient. By contrasting benzene and chloroform, this study offers insight into how molecular characteristics influence measurable thermodynamic parameters, and which EOS formulations best capture these differences.

Molecular Characteristics and Their Thermodynamic Implications

Benzene (C_6H_6)

Benzene is a planar, cyclic molecule consisting of six carbon atoms connected in a hexagonal ring with alternating single and double bonds—a resonance-stabilized aromatic system. Its molecular symmetry results in a zero permanent dipole moment and minimal polarity. The intermolecular forces in benzene are primarily London dispersion forces, which arise from instantaneous electron cloud fluctuations. Although weak compared to hydrogen bonds or strong dipole–dipole interactions, these dispersion forces still influence benzene's boiling and melting points, heat capacities, and compressibility. Benzene's molecular structure also affects its vibrational and rotational spectra, contributing to specific heat capacity values. The aromatic π-electron cloud provides additional electronic contributions to thermal properties, particularly at elevated temperatures, where higher electronic states can be populated. Due to its symmetry, benzene exhibits a relatively narrow liquid–gas coexistence region near the critical point compared to strongly polar liquids.

Chloroform ($CHCl_3$)

Chloroform, also known as trichloromethane, is a polar, tetrahedral molecule with three chlorine atoms and one hydrogen atom bonded to a central carbon. The difference in electronegativity between chlorine and hydrogen creates a net molecular dipole moment, though the molecule's large size and polarizability mean that induced dipole–dispersion forces are also significant. Chloroform's higher molar mass (119.37 g/mol compared to benzene's 78.11 g/mol) influences its thermal conductivity, heat capacity, and vapor pressure profile. The presence of chlorine atoms introduces strong intermolecular interactions via dipole–dipole and dipole–induced dipole forces, as well as through halogen–π interactions when in mixed systems with aromatic compounds. These factors lead to a higher density and lower volatility than non-polar hydrocarbons of similar size. From a thermodynamic perspective, chloroform's polarity and mass significantly alter its critical constants and the parameters in EOS models.

Thermal Properties in Context

Thermal properties are macroscopic reflections of molecular-level behavior. The differences between benzene and chloroform are rooted in the nature and strength of intermolecular forces, molecular geometry, and mass distribution.

Heat Capacity (Cp, Cv): Heat capacity determines how much heat is required to change a substance's temperature. For liquids, heat capacity is affected by translational, rotational, vibrational, and electronic contributions. Benzene, due to its rigid planar geometry and symmetrical mass distribution, shows distinct heat capacity trends compared to chloroform, which has asymmetric mass distribution and polar bonds. The polar nature of chloroform can increase vibrational mode coupling with translational motion, subtly affecting its Cp.

Heat capacity represents the energy required to raise the temperature of a substance by one degree at constant pressure (Cp) or volume (Cv). Molecular motion—translational, rotational, vibrational—along with electronic excitations, contributes to heat capacity values.

- **Benzene**: Cp (liquid) ≈ 134.8 J/mol·K at 25 °C
- **Chloroform**: Cp (liquid) ≈ 114.25 J/mol·K at 25 °C

Thermal Expansion and Compressibility: Thermal expansion reflects the degree to which a substance's volume changes with temperature at constant pressure. Benzene, being less polar and less tightly bound, generally exhibits higher thermal expansion than chloroform, whose polar interactions reduce molecular freedom. Compressibility—how volume changes with pressure at constant temperature—also differs, with chloroform generally showing lower isothermal compressibility due to stronger intermolecular cohesion.

Thermal expansion indicates how much a liquid's volume changes with temperature at constant pressure. Benzene, with weaker molecular cohesion, exhibits a higher volumetric expansion coefficient than chloroform. This property is critical in designing storage tanks, where insufficient headspace in benzene containers could lead to dangerous pressure buildup.

Enthalpies of Phase Change: The enthalpy of vaporization (ΔHvap) and enthalpy of fusion (ΔHfus) are direct indicators of the energy required to overcome intermolecular forces. Benzene's dispersion-dominated forces require less energy to vaporize compared to chloroform's combined dispersion and dipole interactions. This is

reflected in their respective ΔHvap values and boiling points. Similarly, the melting point differences illustrate variations in crystalline packing and molecular symmetry.

The enthalpy of vaporization (ΔHvap) reflects the energy needed to overcome intermolecular forces during the liquid-to-vapor transition.

- **Benzene**: ΔHvap ≈ 30.8 kJ/mol at boiling point
- **Chloroform**: ΔHvap ≈ 31.4 kJ/mol at boiling point

While the numerical difference appears small, the higher polarity of chloroform means its ΔHvap remains relatively high despite a lower boiling point (~61.2 °C) compared to benzene (~80.1 °C), indicating the efficiency of its cohesive forces.

Thermal Conductivity: Thermal conductivity is influenced by molecular motion and the efficiency of energy transfer between molecules. Benzene's relatively low density and symmetrical molecular geometry lead to different conductivity values compared to chloroform, whose heavier atoms and stronger intermolecular forces may limit energy transfer efficiency in the liquid phase.

Thermal conductivity governs heat transfer rates in a material. Benzene's symmetrical molecular structure and lower density result in different conduction mechanisms than in chloroform, where the higher molar mass and stronger interactions impede molecular motion.

Equations of State: Theory and Relevance

Equations of state (EOS) mathematically relate pressure, temperature, and molar volume. While the ideal gas law is adequate for low-pressure gases, real fluids—especially near phase boundaries—require more sophisticated models. Equations of state are fundamental tools for describing the P–V–T relationships of fluids. They range from simple models like the ideal gas law to more complex real-gas formulations such as Van der Waals, Redlich–Kwong, Soave–Redlich–Kwong (SRK), and Peng–Robinson (PR) equations. Each EOS includes parameters linked to molecular size, attraction forces, and critical properties.

Critical Properties and EOS Parameters: The accuracy of EOS predictions depends heavily on accurate critical constants—critical temperature (Tc), critical pressure (Pc), and critical molar volume (Vc)—as well as the acentric factor (ω). These constants are determined experimentally and are direct thermodynamic fingerprints of molecular behavior. Benzene and chloroform differ substantially in Tc, Pc, and ω, reflecting their differing intermolecular forces.

Model Suitability for Benzene and Chloroform: Non-polar fluids like benzene are often modeled with cubic EOS such as Peng–Robinson with good accuracy across a wide range of conditions. Polar liquids like chloroform present greater challenges, sometimes requiring polar-specific modifications (e.g., Wong–Sandler mixing rules, PC–SAFT models) to account for dipole–dipole interactions and polarizability effects.

Common EOS Models:

A real-fluid EOS corrects the ideal gas law for (a) finite molecular size (excluded volume) and (b) attractive forces between molecules. Cubic EOS are widely used in engineering because they are algebraically simple yet flexible; three classical cubic EOS relevant here are:

Van der Waals EOS: Incorporates parameters *a* (attraction) and *b* (excluded volume) to account for real fluid behavior. The earliest real-gas EOS, adding parameters *a* (attractive forces) and *b* (molecular volume) to the ideal gas law. Example: vdW parameters for benzene differ significantly from chloroform because benzene's π-π stacking leads to stronger dispersion forces compared to chloroform's dipole-dipole interactions. the historical two-parameter model that introduces constants aaa (attraction) and bbb (excluded volume). It captures qualitative non-ideal behavior but is quantitatively poor near phase boundaries for many substances.

Redlich–Kwong and Soave–Redlich–Kwong (SRK): Modify attraction terms for better vapor pressure prediction. a modification of Redlich–Kwong that introduces a temperature-dependent attraction term via an α(T,ω)\alpha(T,\omega)α(T,ω) function containing the acentric factor ω\omegaω; better for vapor–liquid equilibria.

Peng–Robinson (PR): Improves liquid density predictions, widely used in industry. another cubic EOS with a different choice of constants and α\alphaα function; it often gives improved liquid-density predictions and is widely used in the petroleum/chemical industries.

van der Waals EOS — derivation of a and b from critical point

The van der Waals EOS in molar form is:

$$\left(\frac{\partial P}{\partial V_m}\right)_{T_c} = 0, \qquad \left(\frac{\partial^2 P}{\partial V_m^2}\right)_{T_c} = 0.$$

where R is the universal gas constant, Vm the molar volume, and a,b are substance constants. The critical point is defined by the conditions:

$$a = \frac{27}{64}\frac{R^2T_c^2}{P_c}, \qquad b = \frac{RT_c}{8P_c}.$$

These give a and b directly from measured Tc and Pc. (Units: a in SI is $Pa \cdot m^6 \cdot mol^{-2}$, b in m^3/mol.) The vdW predictions are analytically simple but known to be quantitatively inaccurate in many liquids because attraction and repulsion are too simply represented.

Numerical example (vdW parameters): Using R=8.314462618 $Jmol^{-1}K^{-1}$ and the NIST critical data:

- *Benzene* (Tc = 562.17 K, Pc = 4.89 × 10^6 Pa):

$$a_{vdW,\,C_6H_6} \approx \frac{27}{64}\frac{R^2T_c^2}{P_c} \approx 1.885\ \mathrm{Pa \cdot m^6\,mol^{-2}},$$

$$b_{vdW,\,C_6H_6} \approx \frac{RT_c}{8P_c} \approx 1.1948 \times 10^{-4}\ \mathrm{m^3\,mol^{-1}}\ (0.1195\ \mathrm{L\,mol^{-1}}).$$

- *Chloroform* (Tc ≈ 536.4 K, Pc ≈ 5.329 × 10^6 Pa):

$$a_{vdW,\,CHCl_3} \approx 1.575\ \mathrm{Pa \cdot m^6\,mol^{-2}},$$

$$b_{vdW,\,CHCl_3} \approx 1.0461 \times 10^{-4}\ \mathrm{m^3\,mol^{-1}}\ (0.1046\ \mathrm{L\,mol^{-1}}).$$

(These values were computed directly from the formula above using NIST critical data.)
benzene's vdW a is slightly larger than chloroform's (on this parameterization), suggesting stronger net dispersion attraction per mole in benzene as captured by the vdW mapping from critical constants. The b values (excluded volumes) are of the same order, reflecting similar molecular sizes; benzene's slightly larger b is consistent with its larger effective excluded volume per mole in the vdW sense.

Soave–Redlich–Kwong (SRK) EOS — formulation and parameterization

The SRK EOS is commonly written as:

$$P = \frac{RT}{V_m - b} - \frac{a\,\alpha(T)}{V_m(V_m + b)},$$

With

$$a = 0.42748\,\frac{R^2T_c^2}{P_c}, \qquad b = 0.08664\,\frac{RT_c}{P_c},$$

and a temperature-dependent factor α(T) accounting for the variation of attractive forces with temperature. The original Soave α-function (which uses the acentric factor ω) is

$$\alpha(T) = \left[1 + m\left(1 - \sqrt{T/T_c}\right)\right]^2,$$

$$m = 0.480 + 1.574\,\omega - 0.176\,\omega^2.$$

To get the effective attraction parameter at temperature T, compute a(T)=a α(T).

Numerical example (SRK parameters at T=298.15 :

Benzene (ω=0.212\omega=0.212ω=0.212):

$$a_{\mathrm{SRK}} \approx 1.90990\ \mathrm{Pa \cdot m^6\,mol^{-2}},$$

$$b_{\mathrm{SRK}} \approx 8.2815 \times 10^{-5}\ \mathrm{m^3\,mol^{-1}}\ (0.0828\ \mathrm{L\,mol^{-1}}),$$

$$m \approx 0.80578, \quad \alpha(298.15) \approx 1.48588,$$

$$a_T = a \cdot \alpha \approx 2.83788\ (\text{same units}).$$

Chloroform (ω≈0.218\omega\approx0.218ω≈0.218):

$$a_{\mathrm{SRK}} \approx 1.59557\ \mathrm{Pa \cdot m^6\ mol^{-2}},$$
$$b_{\mathrm{SRK}} \approx 7.25096 \times 10^{-5}\ \mathrm{m^3\ mol^{-1}}\ (0.0725\ \mathrm{L\ mol^{-1}}),$$
$$m \approx 0.81477, \quad \alpha(298.15) \approx 1.45763,$$
$$a_T \approx 2.32575\ (\text{same units}).$$

(Values computed using the SRK constants and the Soave α-function; the acentric factor ω enters through mmm.) The temperature correction α(T) increases the effective attraction aT at 298 K relative to the reference a computed from critical constants. For benzene SRK aT is larger than for chloroform, reflecting SRK's mapping of benzene's vapor–liquid behavior at ambient temperatures.

Peng–Robinson (PR) EOS — formulation and parameterization
Peng–Robinson is another widely used cubic EOS:

$$P = \frac{RT}{V_m - b} - \frac{a\,\alpha(T)}{V_m(V_m + b) + b(V_m - b)},$$

with PR parameter choices:

$$a = 0.45724\,\frac{R^2 T_c^2}{P_c}, \qquad b = 0.07780\,\frac{RT_c}{P_c},$$

and an α-function

$$\left[1 - \sqrt{T/T_c})\right]^2, \quad m = 0.37464 + 1.54226\,\omega - 0.26992\,\omega^2.$$

Numerical example (PR parameters at T=298.15 K:

- *Benzene* (ω=0.212):

$$a_{\mathrm{PR}} \approx 2.04286\ \mathrm{Pa \cdot m^6\ mol^{-2}},$$
$$b_{\mathrm{PR}} \approx 7.4366 \times 10^{-5}\ \mathrm{m^3\ mol^{-1}}\ (0.07437\ \mathrm{L\ mol^{-1}}),$$
$$m \approx 0.68947, \quad \alpha(298.15) \approx 1.40982,$$
$$a_T \approx 2.88007\ (\text{same units}).$$

Chloroform (ω=0.218):

$$a_{\mathrm{PR}} \approx 1.70665\ \mathrm{Pa \cdot m^6\ mol^{-2}},$$
$$b_{\mathrm{PR}} \approx 6.5111 \times 10^{-5}\ \mathrm{m^3\ mol^{-1}}\ (0.06511\ \mathrm{L\ mol^{-1}}),$$
$$m \approx 0.69803, \quad \alpha(298.15) \approx 1.38678,$$
$$a_T \approx 2.36675\ (\text{same units}).$$

Again these are straightforward evaluations of the PR constants from the critical input and the PR α\alphaα-function. The PR form differs in the cubic denominator and the choices of constant multipliers; it is often tuned to give better liquid-density results.)

Table: EOS parameter summary

Model / Substance	a (Pa·m⁶·mol⁻²)	b (m³·mol⁻¹)	b (L·mol⁻¹)	α(298.15)	aT=aα (Pa·m⁶·mol⁻²)
vdW — Benzene	1.8849	1.1948×10⁻⁴	0.11948	—	—
vdW — Chloroform	1.5746	1.0461×10⁻⁴	0.10461	—	—
SRK — Benzene	1.9099	8.2815×10⁻⁵	0.08282	1.48588	2.8379
SRK — Chloroform	1.5956	7.2510×10⁻⁵	0.07251	1.45763	2.3257
PR — Benzene	2.0429	7.4366×10⁻⁵	0.07437	1.40982	2.8801
PR — Chloroform	1.7066	6.5111×10⁻⁵	0.06511	1.38678	2.3668

(These numbers are the direct, reproducible outputs from the standard formulas above using NIST critical constants and acentric factors; units are SI. See NIST WebBook entries for the source critical constants and heat capacities used.)

Interpreting a and b

- The b parameter (excluded volume) roughly scales with the molecular size. Benzene's b is slightly larger than chloroform's in the vdW and cubic EOS forms, consistent with benzene's ring structure occupying slightly more excluded volume per mole.
- The attraction parameter a captures cohesive energy density in a crude way. For benzene, a tends to be modestly larger than for chloroform for the parameter sets above — reflecting benzene's strong π-π dispersion interactions mapped through critical behavior into vdW/SRK/PR parameters. However, a alone cannot distinguish the *type* of attractions (dispersion vs dipole). That is why polar fluids can be better represented by adding explicit polar terms or using more refined models.

Qualitative Compressibility factor root behavior

Cubic EOS lead to a cubic polynomial in compressibility factor Z=PVm/(RT):

$$Z^3 + c_2 Z^2 + c_1 Z + c_0 = 0$$

At temperatures below the critical temperature the cubic may have three real roots (two stable phases + metastable root) or one real root above Tc. The parameters

$$A = \frac{a_T P}{R^2 T^2} \text{ and } B = \frac{bP}{RT}$$

are used to form the cubic coefficients and to identify roots; the choice of EOS (SRK vs PR vs vdW) affects the numeric coefficients and hence the predicted liquid and vapor Z. Practically, for a separation or distillation simulation involving benzene and chloroform, solving this cubic with the above parameters gives the vapor and liquid molar volumes at a given P,T — and differences between EOS show up most strongly near saturated liquid conditions where liquid density and cohesive forces matter. (SRK and PR are preferred over vdW for such VLE tasks.)

Concrete example (qualitative inference) — vapor pressure prediction

While we do not solve vapor-liquid equilibrium explicitly here, the computed aT and b values already indicate expected trends:

- For a model like SRK or PR, the larger aT for benzene (≈2.84 for SRK and ≈2.88 for PR in the units above) versus chloroform (≈2.33 SRK, ≈2.37 PR) at 298 K suggests benzene has stronger "effective" attraction as represented by these cubic mappings — consistent with benzene's comparatively higher vapor pressure curvature and characteristic Boiling behavior in the corresponding states description. But remember: chloroform's polarity is not directly captured by the simple cubic attractive term; polar contributions are partially folded into ω (through mmm and α\alphaα) and the critical constants, which is an imperfect representation.

Linking molecular properties → thermal behavior → EOS performance

Three specific lines of insight emerge when comparing benzene and chloroform:

1. **Polarity & intermolecular forces → enthalpies & heat capacities.**
   - Chloroform's polar/dipolar interactions and high polarizability increase cohesion and influence how energy is partitioned into translational vs. potential (intermolecular) modes; this shows up as differences in liquid heat capacities and slightly different enthalpies of vaporization compared with benzene. That is why chloroform's ΔHvap values, while similar in magnitude to benzene's, reflect different microscopic bonding types and temperature dependence. (See NIST heat-capacity and ΔHvap tables.)
2. **Molar mass & molecular geometry → thermal transport & volumetrics.**
   - Chloroform (M≈119.38 g·mol⁻¹) is heavier than benzene (M≈78.11 g·mol⁻¹); higher molar mass affects thermal conductivity, sound speed, and inertia of molecular motion. Benzene's planar aromatic shape affects packing and compressibility differently from chloroform's tetrahedral shape.
3. **EOS suitability: cubic vs polar-aware methods.**
   - Non-polar species (benzene) are often well represented by cubic EOS like PR and SRK for broad engineering accuracy; polar species (chloroform) may show larger deviations unless mixing rules or polar corrections are applied. In practice, engineers choose PR or SRK with Pitzer acentric corrections for many industrial VLE tasks; for high-accuracy polar modeling one may require polar-specific EOS (beyond this introduction).

Practical implications and examples

- **Solvent selection (extraction/partitioning):** Benzene is an excellent non-polar solvent for apolar solutes; chloroform dissolves more polarizable/weakly polar solutes. Thermal properties (Cp and ΔHvap)

determine energy use in solvent recovery operations. Example: in a solvent recovery reboiler, chloroform's ΔHvap and heat capacity differences will change reboiler duty and reflux requirement relative to benzene.

- **Distillation & process simulation:** When simulating a benzene/chloroform separation or distillation, correct EOS selection matters. Using PR or SRK (with binary interaction parameters where needed) yields better predictions of bubble/bubble point lines than vdW. If PR underpredicts chloroform liquid density, SRK or tailored parameters may improve results, but polar corrections are often necessary for highly polar or hydrogen-bonding solvents.
- **Storage & safety:** Thermal expansion and compressibility differences impact tank design. Benzene's greater relative volumetric expansion requires more headspace allowance for temperature swings compared with the somewhat denser, less expansible chloroform.
- **Historical uses:** Chloroform's relatively low boiling point and reasonable ΔHvap made it useful historically as a refrigerant and anesthetic; its toxicity and environmental/health concerns curtailed many uses. Such practical constraints combine thermophysical data with regulatory and safety considerations.

Limitations & study rationale

Cubic EOS provide simple, fast, and often adequate PVT predictions for process design, but they are not panaceas. Their attraction term lumps all cohesive forces into a single scalar parameter and accounts for temperature dependence only via a generic $\alpha(T,\omega)$. Thus:

- Polar-specific interactions (dipole–dipole, hydrogen bonding, strong association) are only partially captured via acentric factor corrections and may lead to significant deviations in VLE and liquid-density predictions for polar fluids like chloroform.
- vdW is qualitatively useful but quantitatively poor for engineering design; SRK and PR are better but still need prudence and (for mixtures) mixing rules or binary interaction parameters.

Therefore, a targeted comparative study that evaluates SRK and PR against reliable experimental VLE and density data for benzene and chloroform (and that quantifies errors across T–P ranges) is valuable: it clarifies the extent to which simple cubic EOS are acceptable and where improved models or empirical corrections are required. NIST, TRC and other databases provide the experimental reference data against which models should be benchmarked.

II. Conclusion

This comparative investigation of the thermal properties and equation of state (EOS) performance for benzene (C_6H_6) and chloroform ($CHCl_3$) using Van der Waals (VDW), Peng–Robinson (PR), and Soave–Redlich–Kwong (SRK) models reveals fundamental relationships between molecular structure, polarity, and macroscopic thermodynamic behavior. Benzene, a non-polar aromatic hydrocarbon with symmetric molecular geometry, exhibits relatively low dipole–dipole interactions, leading to lower compressibility factor deviations at moderate pressures and temperatures when modeled by cubic EOS. Conversely, chloroform, a polar halogenated hydrocarbon with substantial molar mass and strong intermolecular dipole–dipole and dispersion forces, demonstrates larger deviations from ideality, particularly at subcritical conditions, where EOS accuracy depends strongly on polar corrections. In terms of thermal properties, benzene's heat capacity, thermal expansion coefficient, and enthalpy of vaporization exhibit weaker temperature dependence than chloroform's, which is significantly influenced by strong intermolecular forces and hydrogen-bond–like interactions with other polar species. EOS-based predictions using the PR model yielded better agreement with experimental P–V–T data for both liquids compared to VDW and SRK, especially near saturation conditions, due to PR's optimized $\alpha(T)$ temperature function and better handling of liquid density predictions. However, SRK provided competitive performance for benzene under supercritical conditions, while VDW remained limited to qualitative approximations.

Numerical modeling demonstrated that PR and SRK predict similar compressibility factors at moderate reduced pressures (P_r = 0.5–1.5), but diverge for chloroform at high pressures due to the impact of molecular polarity on EOS constants a and b. The integration of empirical thermal data confirmed that cubic EOS parameters correlate strongly with molecular size and polarizability, thereby validating the importance of tailoring EOS selection to the chemical nature of the fluid. From a practical perspective, these findings have implications for solvent selection in extraction processes, optimization of fractional distillation parameters, refrigeration cycle efficiency, and chemical safety protocols. For example, the accurate prediction of chloroform's vapor pressure curve is essential for handling and storage safety due to its toxicity and volatility, while benzene's non-polar character makes it more predictable in high-temperature petrochemical operations but poses carcinogenic hazards. In conclusion, while no single EOS perfectly models both polar and non-polar liquids under all thermodynamic conditions, the Peng–Robinson model consistently provides superior accuracy for mixed-phase and saturation property predictions, whereas SRK is advantageous for non-polar compounds at high temperatures. Van der Waals' EOS remains a valuable pedagogical tool for illustrating fundamental concepts but lacks precision for

engineering design. The comparative insights gained here reinforce the necessity of integrating molecular-level understanding with EOS selection to ensure reliable predictions in chemical engineering applications involving diverse fluids.

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