Calculate The Fugacity Of Ethanol At T = 75 C And At The Following Pressures: (a) At The Saturation Pressure:

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Understanding the concept of fugacity is fundamental in thermodynamics, especially when dealing with real gases and liquids. Fugacity provides an improved measure over pressure for describing the escaping tendency of a substance from a phase, effectively accounting for non-ideal behavior. In this article, we will explore the detailed process of calculating the fugacity of ethanol at a temperature of 75°C (which is 348.15 K) at the specific condition where the pressure equals the saturation pressure of ethanol at this temperature. We will expand on the theoretical background, the necessary thermodynamic data, and step-by-step calculation procedures.

Introduction to Fugacity and Its Significance

Fugacity is a corrected pressure that reflects the non-ideal interactions within a substance. In ideal gases, pressure directly correlates with the chemical potential, but real gases deviate due to intermolecular forces and finite molecular sizes. Fugacity corrects for these deviations, enabling more accurate thermodynamic calculations such as phase equilibria, chemical reactions, and process design.

Why is fugacity important?

- It provides a way to predict phase stability.
- It helps in designing separation processes.
- It is essential in vapor-liquid equilibrium (VLE) calculations.
- It accounts for non-idealities in real substances, especially at high pressures.

Understanding Ethanol's Thermodynamic Properties at 75°C

Before delving into calculations, it's crucial to gather the thermodynamic

data for ethanol at the specified temperature:

- Temperature (T): 75°C = 348.15 K
- Saturation Pressure (P_sat): The vapor pressure of ethanol at 75°C
- Vapor phase properties: molar volume, fugacity coefficients
- Liquid phase properties: molar volume, activity coefficients

Saturation Pressure of Ethanol at 75°C

According to Antoine equation parameters, the vapor pressure (P_sat) of ethanol at 75°C is approximately 1.49 bar (or 149 kPa). This value is obtained from empirical correlations such as Antoine's equation, which relates vapor pressure to temperature.

Step-by-Step Calculation of Ethanol's Fugacity at Saturation Pressure

Calculating the fugacity of ethanol at saturation pressure involves understanding phase equilibrium conditions and applying thermodynamic models to account for non-idealities.

Key steps include:

1. Identify the phase condition (saturated vapor at P = P_sat).
2. Calculate the fugacity coefficient (ϕ) for ethanol at T = 75°C and P = P_sat.
3. Determine the fugacity using the relation:

$$f = \phi \times P$$

where:

- f is the fugacity,
- ϕ is the fugacity coefficient,
- P is the pressure (here, P_sat).

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1. Understanding Phase Equilibrium at Saturation

At saturation pressure, the vapor and liquid phases coexist in equilibrium. The chemical potential of ethanol in the vapor phase equals that in the liquid phase:

$$
\mu_{vap} = \mu_{liq}
$$

Using the concept of fugacity, the vapor phase's chemical potential can be expressed as:

$$
\mu_{vap} = \mu^{\circ}_{vap} + RT \ln \left(\frac{f}{P^{\circ}} \right)
$$

Similarly, in the liquid phase:

$$
\mu_{liq} = \mu^{\circ}_{liq} + RT \ln \left(\frac{a}{a^{\circ}} \right)
$$

where a is the activity, which for pure substances at saturation equals 1, simplifying the relation.

At equilibrium:

$$
f_{ethanol} = P_{sat} \times \phi
$$

where ϕ is the fugacity coefficient in the vapor phase.

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2. Calculating the Fugacity Coefficient (ϕ)

The fugacity coefficient accounts for non-ideal behavior and can be calculated using different equations of state (EOS). The most common EOS used for liquids and vapors includes:

- Peng-Robinson EOS
- Soave-Redlich-Kwong EOS
- Virial equations

For ethanol at 75°C, the Peng-Robinson EOS is widely used due to its accuracy for hydrocarbons and alcohols.

Steps to compute ϕ using Peng-Robinson EOS:

a. Determine the EOS parameters (a, b):

$$
a = \frac{0.45724 R^2 T^2}{P_c} \left[1 + k (\sqrt{T_r} - 1) \right]^2
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$$
$$

$$
b = \frac{0.07780 R T_c}{P_c}
$$

where:

- R = 8.314 J/(mol·K),
- T_c and P_c are critical temperature and pressure for ethanol,
- k is an alpha function parameter depending on acentric factor.

b. Calculate the compressibility factor Z.

c. Determine ϕ using the relation:

$$
\ln \phi = Z - 1 - \ln(Z - B) - \frac{A}{2 \sqrt{2} B} \ln \left(\frac{Z + (1 + \sqrt{2}) B}{Z + (1 - \sqrt{2}) B} \right)
$$

where A and B are reduced EOS parameters.

Note: For pure substances at saturation, the vapor phase fugacity coefficient is calculated at the vapor pressure.

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3. Final Calculation of Fugacity

Once the fugacity coefficient ϕ is determined:

$$
f_{ethanol} = \phi \times P_{sat}
$$

Given that at saturation and the vapor phase, the pressure equals the vapor pressure, the fugacity of ethanol at this point is essentially:

$$
f_{ethanol} \approx P_{sat} \times \phi
$$

If the vapor behaves ideally ($\phi \approx 1$), then:

$$
f_{ethanol} \approx P_{sat}
$$

However, for real gases and liquids, ϕ typically deviates slightly from 1, especially at higher pressures.

Practical Example: Calculating Ethanol Fugacity at Saturation Pressure

Let's approximate the calculation with typical data:

- Vapor pressure of ethanol at 75°C: 1.49 bar (149 kPa)
- Fugacity coefficient (ϕ) in vapor phase: approximately 0.95 to 1.05 (depends on EOS calculations)

Assuming $\phi \approx 1$ for simplicity:

$$
f_{ethanol} \approx 1.49\, \text{bar} \times 1 = 1.49\, \text{bar}
$$

Thus, the fugacity of ethanol at 75°C at saturation pressure is approximately 1.49 bar.

In more precise calculations, EOS methods could refine this value further, considering specific interactions.

Factors Influencing Fugacity of Ethanol

Several factors influence the fugacity calculation:

- Temperature: As temperature increases, vapor pressure increases, affecting the fugacity.
- Pressure: Higher pressures elevate fugacity, but deviations from ideality become more significant.
- Composition: Mixtures involving ethanol require activity coefficients and mixing rules.
- Interactions: Hydrogen bonding and polarity of ethanol affect non-ideal behavior.

Applications of Fugacity Calculations for Ethanol

Understanding and calculating ethanol’s fugacity has several practical applications:

- Distillation and Separation: Accurate fugacity data help optimize separation processes.
- Phase Equilibria Modeling: Essential for designing processes involving ethanol-water mixtures.
- Chemical Reaction Engineering: Fugacity informs about the chemical potential, guiding reaction conditions.
- Environmental Impact Assessments: Knowing fugacity helps predict ethanol’s environmental fate.

Conclusion

Calculating the fugacity of ethanol at a specific temperature and pressure, especially at saturation, involves a combination of thermodynamic principles, empirical data, and equations of state. While simplified calculations assume ideal behavior, real-world scenarios often require detailed EOS computations to account for non-ideality. At 75°C, with a vapor pressure of approximately 1.49 bar, the fugacity of ethanol at saturation closely approximates this pressure, adjusted by the fugacity coefficient derived from models like Peng-Robinson EOS. Accurate fugacity determination is crucial across chemical engineering applications, ensuring efficient process design, safety, and environmental compliance.

References:

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- Antoine Equation Parameters for Ethanol: NIST Chemistry WebBook.
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Frequently Asked Questions

How do you calculate the fugacity of ethanol at its

saturation pressure at 75°C?

To calculate the fugacity of ethanol at saturation pressure, you first determine the saturation pressure at 75°C using vapor pressure equations (such as Antoine's equation). Then, you use the fugacity coefficient (from an appropriate equation of state like Peng-Robinson or Soave-Redlich-Kwong) to find the fugacity: fugacity = saturation pressure × fugacity coefficient.

What is the significance of calculating the fugacity of ethanol at saturation pressure?

Calculating the fugacity at saturation pressure helps in understanding phase equilibrium, designing separation processes, and predicting the behavior of ethanol in various industrial applications, especially in distillation and vapor-liquid equilibrium studies.

Which equations or models are typically used to determine the fugacity coefficient of ethanol at 75°C?

Common models include the Peng-Robinson and Soave-Redlich-Kwong equations of state, which provide the fugacity coefficient based on critical properties, temperature, pressure, and acentric factor of ethanol.

How does temperature affect the calculation of ethanol's fugacity at saturation pressure?

Temperature influences the vapor pressure of ethanol, which is essential for calculating saturation pressure. As temperature increases, vapor pressure rises, affecting the fugacity, and the corresponding fugacity coefficient depends on temperature-dependent properties modeled by equations of state.

Why is it important to consider the fugacity of ethanol at different pressures, including saturation pressure?

Considering the fugacity at various pressures allows for accurate modeling of ethanol's phase behavior under different conditions, facilitating process design, safety assessments, and understanding of mixture interactions in chemical engineering applications.

Additional Resources

Calculate The Fugacity Of Ethanol At T = 75°C And At The Following Pressures: (a) At The Saturation Pressure

Understanding the behavior of liquids and vapors under varying conditions is fundamental in chemical engineering and thermodynamics. Among the key properties that describe the real behavior of a substance in phase equilibrium is fugacity—a corrected pressure that accounts for deviations from ideality. Ethanol, a widely used solvent in industries ranging from pharmaceuticals to biofuels, exhibits complex phase behavior that necessitates precise calculations of fugacity, especially at elevated temperatures like 75°C.

In this article, we delve into the methodology for calculating the fugacity of ethanol at a temperature of 75°C, focusing initially on the scenario where the pressure equals the saturation pressure. This involves understanding the thermodynamic principles, employing equations of state, and interpreting experimental data. Whether you're a student, researcher, or practitioner, this comprehensive guide aims to clarify the process with clarity and depth.

Understanding Fugacity: A Thermodynamic Perspective

Before embarking on the calculation, it's essential to grasp what fugacity represents and why it matters in thermodynamics.

What Is Fugacity?

Fugacity is a thermodynamic property that extends the concept of pressure to real (non-ideal) systems. In an ideal gas, the pressure directly correlates with the tendency of molecules to escape or expand. However, real gases and liquids experience interactions that cause deviations from ideality. Fugacity corrects for these effects, representing an effective pressure that accounts for intermolecular forces and molecular sizes.

Mathematically, for a component in a mixture, the fugacity f relates to the chemical potential μ via:

$$
\mu = \mu^\circ + RT \ln \left(\frac{f}{f^\circ}\right)
$$

where:
- μ° is the standard chemical potential,
- R is the universal gas constant,
- T is temperature,
- f° is the standard fugacity, often taken as the fugacity at the standard state.

In pure substances, the fugacity equals the partial pressure at ideal conditions but diverges at high pressures or in the liquid phase, necessitating calculation.

Why Is Fugacity Important?

- Phase Equilibria: Determining vapor-liquid equilibria (VLE) requires knowledge of fugacity in both phases.
- Design and Optimization: Processes like distillation, absorption, and extraction depend on accurate fugacity data.
- Thermodynamic Modeling: It enables the use of equations of state (EoS) to predict real behavior.

Fundamentals for Calculating Ethanol Fugacity at 75°C

Calculating the fugacity of ethanol at a specified temperature and pressure involves several key steps:

1. Identify the thermodynamic state parameters: Temperature (75°C) and pressure (saturation pressure or other specified values).
2. Determine the phase of ethanol: Is it in vapor, liquid, or at equilibrium?
3. Select an appropriate equation of state: To model the non-ideal behavior of ethanol.
4. Calculate the fugacity coefficient (ϕ): Which relates fugacity to pressure.
5. Compute fugacity: Using $f = \phi P$.

Let's examine each step in detail.

Step 1: Determining the Saturation Pressure of Ethanol at 75°C

The initial step involves establishing the saturation pressure at 75°C (which is 348.15 K). Saturation pressure is the equilibrium vapor pressure of ethanol at this temperature and can be obtained from empirical correlations or vapor pressure tables.

Vapor Pressure Data for Ethanol

Vapor pressures are often fitted using Antoine equations—a widely adopted empirical correlation:

$$
\log_{10} P_{sat} = A - \frac{B}{C + T}
$$

where:
- P_{sat} is in mmHg or bar,
- T is in °C,
- A, B, and C are Antoine constants.

For ethanol, typical Antoine constants valid over a certain temperature range are:

Parameter	Value
A	8.20417
B	1642.89
C	11.76

These constants are valid approximately between 0°C and 78°C. Since 75°C is within this range, we can use them to estimate the vapor pressure.

Calculating:

$$
\log_{10} P_{sat} = 8.20417 - \frac{1642.89}{11.76 + 75} = 8.20417 - \frac{1642.89}{86.76}
$$

$$
\frac{1642.89}{86.76} \approx 18.92
$$

$$
\log_{10} P_{sat} = 8.20417 - 18.92 = -10.71583
$$

Converting back to pressure:

$$
P_{sat} = 10^{-10.71583} \text{ atm}
$$

which is extremely low and indicates the constants may not be suitable at high temperatures. Alternatively, using more precise data from vapor pressure tables:

- The vapor pressure of ethanol at 75°C is approximately 1.12 atm (from literature data).

Hence, for the purpose of calculations, we'll take:

$$
P_{sat} \approx 1.12\, \text{atm}
$$

Step 2: Choosing the Equation of State (EoS)

Modeling the non-ideal behavior of ethanol requires selecting an appropriate EoS. Common choices include:

- Peng-Robinson (PR) EoS
- Soave-Redlich-Kwong (SRK) EoS
- Van der Waals EoS

Given ethanol's molecular complexity and the need for accuracy near vapor-liquid equilibrium, the Peng-Robinson equation is often preferred.

Peng-Robinson Equation:

$$
P = \frac{RT}{V - b} - \frac{a(T)}{V(V + b) + b(V - b)}
$$

where:
- P is pressure,
- V is molar volume,
- $a(T)$ and b are substance-specific parameters.

Parameters for Ethanol:

- Critical temperature, T_c: 516.2 K
- Critical pressure, P_c: 6.14 MPa
- Acentric factor, ω: 0.635

Using these, the parameters $a(T)$ and b are computed as:

$$
a(T) = 0.45724 \frac{R^2 T_c^2}{P_c} \left[1 + k \left(1 - \sqrt{\frac{T}{T_c}}\right)\right]^2
$$
$$
b = 0.0778 \frac{RT_c}{P_c}
$$

where $k = 0.37464 + 1.54226 \omega - 0.26992 \omega^2$.

Step 3: Calculating the Fugacity Coefficient (ϕ)

The fugacity coefficient quantifies deviation from ideality. For the Peng-Robinson EoS, ϕ is derived from the residual Helmholtz free energy or directly via thermodynamic relations.

The expression for $\ln \phi$ in PR EoS is:

$$
\ln \phi = Z - 1 - \ln(Z - B) - \frac{A}{2 \sqrt{2} B} \left[\frac{2}{A} \sum_{i} \left(\frac{a_i}{a} \right) - \frac{B}{Z} \right]
$$

where:
- Z is the compressibility factor, solution of the cubic PR equation,
- A and B are dimensionless parameters:

$$
A = \frac{a(T) P}{R^2 T^2}
$$
$$
B = \frac{b P}{RT}
$$

- a_i are component-specific.

The steps involve:

1. Calculating $a(T)$ and b,
2. Computing A and B,
3. Solving the cubic for Z,
4. Computing ϕ from Z.

Step 4: Calculating Ethanol Fugacity at Saturation Pressure

Once the fugacity coefficient ϕ is determined, the fugacity f at saturation pressure P_{sat} is:

$$
f = \phi P_{sat}
$$

Given that at saturation, the vapor phase is in equilibrium with the liquid, the fugacity of ethanol in the vapor phase equals that in the liquid phase. Often, for vapor phase calculations:

- $f_{vapor} \approx \phi_{gas} P_{sat}$

Since the vapor phase behaves approximately as a real gas, the fugacity in the vapor phase is computed using the above relation.

Practical Calculation Example