

# NUMERICAL METHODS IN CHEMICAL ENGINEERING (CLL113)

## **Enhanced Thermodynamic Correlation: A Three-Parameter Approach**

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## Abstract

This report explores a new thermodynamic correlation using a three-parameter approach, using multivariable non-linear regression to refine  $z_0$  and  $z_1$  values. The study addresses the availability of  $z_0$  and  $z_1$  values at discrete values of reduced pressures and temperatures for real gases. Using numerical techniques, we establish a correlation for compressibility ( $z$ ) dependent on reduced temperature ( $T_r$ ) and reduced pressure ( $P_r$ ). Our model demonstrated impressive accuracy in predicting real-world ethylene data, with error percentages as low as 0.11% and 1.50% in  $z$  values .

## 1. Introduction

**Real gases** deviate from the ideal gas behavior, requiring sophisticated equations of state for accurate representation. The law of corresponding states suggests a universal reduced volume for compounds under similar conditions, forming the basis for the *compressibility factor* ( $Z$ ). This factor, crucial in chemical engineering, depends on the accurate estimation of **Pitzer factors** ( $Z_0$  and  $Z_1$ ), complicating the representation of thermodynamic properties.

The Pitzer-kind correlations, the broadly adopted one advanced by means of Lee and Kesler take the shape of tables presenting  $Z_0$  and  $Z_1$  values as features of  $T_r$  and  $P_r$ . This term paper addresses these limitations by proposing an enhanced analytical correlation based on the three-parameter corresponding states principle. This motivates us to employ **multivariable non-linear regression model** which fits the existing data helping us to create a continuous function which gives the value of  $z_0$  and  $z_1$  at any given  $T_r$  and  $P_r$ .

This work builds on the pioneering three-parameter corresponding states principle introduced by **Pitzer and co-workers(1955)** and **Lee/Kesler(1975)**. The subsequent sections delve into the background, methodology, results, and discussion, presenting a comprehensive exploration of our enhanced analytical correlation.

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### Literature cited:

1. **Byung IK Lee/ Michael G. Kesler:** A Generalized Thermodynamic Correlation Based on Three-Parameter Corresponding States

2. **Kenneth S. Pitzer, David Z. Lippmann,<sup>2</sup> R. F. Curl, Jr., Charles M. Huggins and Donald E. Petersen:** The Volumetric and Thermodynamic Properties of Fluids. II. Compressibility Factor, Vapor Pressure and Entropy of Vaporization<sup>1</sup>

This term paper is divided into the following parts:

- **Problem Discussion** – Discuss the challenges we tend to solve.
- **Theory** – The formulas and principles used.
- **Methodology and Numerical Analysis**- Discussing the numerical method used to solve the problem.
- **Results** and data plots
- **Error analysis** - comparison of estimated z values with theoretical values.
- **Future Work** - says what advancements can be done in future
- **Conclusion** - Key Findings and result impact.
- **Self-assessment**

## 2. Problem Discussion

Our study uses an enhanced analytical method based on the three-parameter corresponding states principle. The challenge lies in achieving accurate and consistent correlations using a new approach utilizing multivariable non-linear regression. There is also an absence of continuous data, which made us use the curve-fitting strategy. Using this we overcome this limitation and now can predict values between discrete data points.

## 3. Theory

The **acentric factor** is a measure of a pure chemical species' vapor pressure. This relationship can be expressed as:

$$\frac{d(\log P_r^{\text{sat}})}{d\left(\frac{1}{T_r}\right)} = S$$

where  $P_r^{\text{sat}}$  is reduced vapor pressure,  $T_r$  is reduced temperature, and S is the slope of a plot of  $\log_{10} P_r^{\text{sat}}$  vs  $1/T_r$ .

If the generally accepted two-parameter corresponding-states correlations were to

be accurate, the slope (S) would be constant for all pure fluids. However, experiments reveal that this assumption is not accurate. In a specific range, each fluid shows a different value of S, which serves as a third corresponding state parameter.

Pitzer and co-workers observed that despite this variation, the vapor-pressure data for simple fluids such as Ar, Kr, and Xe align perfectly lie on the line when represented as  $\log P_r^{\text{sat}} \text{ vs. } \frac{1}{T_r}$  and that the line passes through  $\log P_r^{\text{sat}} = 1.0$  at  $T_r = 0.7$ .

Data for other fluids define additional lines relative to simple fluids line.

$$\log P_r^{\text{sat}}(SF) - \log P_r^{\text{sat}}$$

The acentric factor is defined as this difference calculated at  $T_r = 0.7$ :

$$\omega \equiv -1.0 - \log(P_r^{\text{sat}})_{T_r=0.7}$$

The value of  $\omega$  can be calculated for any fluid based on its  $T_c$ ,  $P_c$  and a single vapour-pressure measurement made at  $T_r = 0.7$ .

The correlation for the compressibility (Z) is expressed as  $z = z_0 + \omega z_1$ , where  $z_0$  and  $z_1$  depend on reduced temperature (Tr) and reduced pressure (Pr). When  $\omega$  is 0,  $z_1$  term vanishes, and  $z_0$  equates to z.

The equation represents a linear relationship between Z and  $\omega$  at regular Tr and Pr. When Z is plotted against  $\omega$ , a linear plot is observed for nonsimple fluids (ref: Smith, J. M. - Introduction to chemical engineering thermodynamics. ). The slopes of these traces provide values for  $Z_1$ , allowing the construction of the generalized feature  $z_1 = f_1(T_r, P_r)$ .

The Lee/Kesler correlation provides correct results for nonpolar gases or slightly polar; for these, the error is typically less. In highly polar gases, larger errors can be expected. The quantum gases (e.g., hydrogen, helium, and neon) do not conform to the same corresponding state behavior as do normal fluids. Their treatment by the usual correlations is sometimes accommodated by the use of temperature-dependent effective critical parameters.

## 4. Methodology and Numerical Analysis

The correlation for z is:

$$z = z_0 + \omega z_1 \tag{1}$$

where  $z_0$  and  $z_1$  are functions of both  $T_r$  and  $P_r$ .

**Pitzer correlation for the second virial coefficient:** We use the simplest form of Virial Equation:

$$Z = 1 + \frac{BP}{RT} = 1 + \left( \frac{BPc}{RTc} \right) \left( \frac{BP}{RT} \right) = 1 + \hat{B} \left( \frac{Pr}{Tr} \right) \quad (2)$$

The reduced second Virial coefficient and the **Pitzer** correlations for it are:

$$\hat{B} = \frac{BPc}{RTc} \quad \Bigg| \quad \hat{B} = B^0 + \omega B^1 \quad (3)$$

Therefore

$$z = \left( 1 + B^0 \frac{Pr}{Tr} \right) + \omega \left( B^1 \frac{Pr}{Tr} \right)$$

which is of the form of equation (1).

$$z_0 = 1 + B^0 \frac{Pr}{Tr} \quad (4)$$

and

$$z_1 = B^1 \frac{Pr}{Tr} \quad (5)$$

Since the second Virial coefficients are function a function of Temperature only, we can unite  $B^0$  and  $B^1$  as follows:

$$B^0 = \alpha + \beta \cdot T_r^\gamma \quad (6)$$

$$B^1 = a + b \cdot T_r^c \quad (7)$$

Where  $(\alpha, \beta, \gamma)$  and  $(a, b, c)$  are constanst terms which can be evaluated using **Multivariable non-linear regression**.

We formulate  $z_0 = F_0(Tr, Pr)$  and  $z_1 = F_1(Tr, Pr)$  to be modelled as a **re-gression model**.

#### 4.1 Evaluation of $\alpha, \beta, \gamma$ :

We have:

$$z_0 = 1 + \left( \frac{Pr}{Tr} \right) (\alpha + \beta \cdot T_r^\gamma) \quad (8)$$

Let  $P_r = x$  and  $T_r = y$ . Now we have

$$f(x, y; \alpha, \beta, \gamma) = 1 + \left(\frac{x}{y}\right) (\alpha + \beta \cdot y^\gamma)$$

In short, we will write it as  $f(x, y)$ .

**Pseudo code:**

$\alpha = 1, \quad \beta = 1, \quad \gamma = 1 \quad (\text{initial guess})$

while (error  $\geq 10^{-5}$ ) {

$$D = \begin{bmatrix} z_0^{(1)} - f(x^{(1)}, y^{(1)}) \\ z_0^{(2)} - f(x^{(2)}, y^{(2)}) \\ \vdots \\ z_0^{(m)} - f(x^{(m)}, y^{(m)}) \end{bmatrix} \quad Z = \begin{bmatrix} \frac{\partial f}{\partial \alpha} \Big|_{(x_1, y_1)} & \frac{\partial f}{\partial \beta} \Big|_{(x_1, y_1)} & \frac{\partial f}{\partial \gamma} \Big|_{(x_1, y_1)} \\ \frac{\partial f}{\partial \alpha} \Big|_{(x_2, y_2)} & \frac{\partial f}{\partial \beta} \Big|_{(x_2, y_2)} & \frac{\partial f}{\partial \gamma} \Big|_{(x_2, y_2)} \\ \vdots & \vdots & \ddots \\ \frac{\partial f}{\partial \alpha} \Big|_{(x_m, y_m)} & \frac{\partial f}{\partial \beta} \Big|_{(x_m, y_m)} & \frac{\partial f}{\partial \gamma} \Big|_{(x_m, y_m)} \end{bmatrix}$$

$$\Delta A = (Z^T Z)^{-1} [Z^T D] = \begin{bmatrix} \Delta \alpha \\ \Delta \beta \\ \Delta \gamma \end{bmatrix}$$

$$\text{error} = \max \left( \frac{\Delta \alpha}{\alpha}, \frac{\Delta \beta}{\beta}, \frac{\Delta \gamma}{\gamma} \right)$$

$$\alpha = \alpha + \Delta \alpha, \quad \beta = \beta + \Delta \beta, \quad \gamma = \gamma + \Delta \gamma$$

}

A similar methodology is applied to estimate a, b and c. We omit the repetition here.

## 5. Results

Through the C++ code that we developed to model the values of  $z_0$  and  $z_1$  to fit in the regression model, we arrive at the following results:

For  $z_0$ :

$$\alpha = 0.0911593$$

$$\beta = -0.516497$$

$$\gamma = -1.92508$$

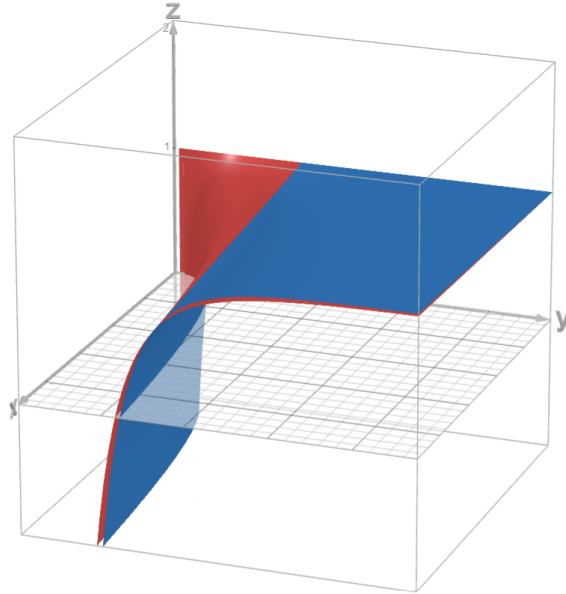
For  $z_1$ :

$$\begin{aligned} a &= 0.498346 \\ b &= -0.435466 \\ c &= -3.20078 \end{aligned}$$

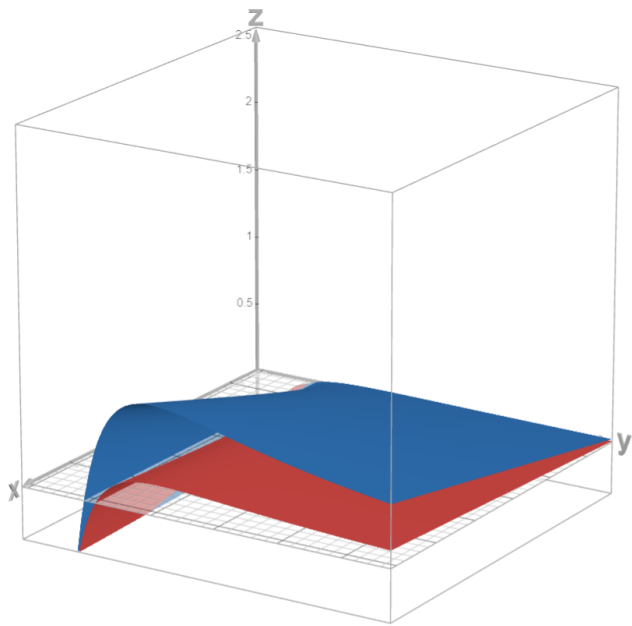
Thus,

$$Z = 1 + \frac{P_r}{T_r} \left( 0.0911593 - \frac{0.516497}{T_r^{1.92508}} \right) + \frac{P_r}{T_r} \left( 0.498346 - \frac{0.435466}{T_r^{3.20078}} \right)$$

The plot(s) for  $z_0$  as a function of  $P_r(x-axis)$  and  $T_r(y-axis)$  with the predicted model shown in **blue** and equation present in text by Smith, J. M. shown in **red**.



Similarly, the plot(s) for the function  $z_1$  are:





## 6. Errors

The model was evaluated using real-world data for **Ethylene** ( $\omega = 0.089$ ,  $T_c = 282.8\text{K}$  and  $P_c = 50.5\text{ atm}$ ) at two different temperature and pressure conditions. The experimental conditions are summarised in the table below:

| P/T   | 300K  | 350K  |
|-------|-------|-------|
| 30atm | 0.812 | -     |
| 5atm  | -     | 0.983 |

Table 1: experimental values of  $z$  for ethylene at different temperatures and pressures

On substituting the  $z_0$  and  $z_1$  values predicted from the model into the equation of  $z$  and using  $\omega = 0.089$ , we get the following output values:

| P/T   | 300K     | 350K     |
|-------|----------|----------|
| 30atm | 0.799758 | 0.89118  |
| 5atm  | 0.966626 | 0.981863 |

Table 2: predicted values of  $z$  for ethylene at different temperatures and pressures

The C++ code for the verification of the  $z$  data for Ethylene (*verify.cpp*) reports error percentages as 0.11% and 1.50% for the aforementioned physical experimental conditions. A snippet of the output is also attached.

```
For condition 1 (P = 5atm, T = 350K):
z0 = 0.979882, z1 = 0.0222606 z = 0.981863
Error 1 = 0.115624 %

For condition 2 (P = 30atm, T = 300K):
z0 = 0.792887, z1 = 0.0772054 z = 0.799758
Error 2 = 1.50764 %
```

## 7. Future Work

The code currently focuses on simple gases, which can be expanded to accommodate complex mixtures, enabling a more comprehensive representation of real-world scenarios. We can also find new machine learning algorithms to enhance predictive accuracy and accommodate different and new thermodynamic behaviours.

## 8. Conclusion

We have created a multivariable nonlinear regression model that provides more accurate  $z_0$  and  $z_1$  values. The correlation accurately represents volumetric and thermodynamic properties over a wide range of temperatures and pressures. Therefore, these values aid in calculating the compressibility factor  $z$ , which helps us to apply the gas law to real gases.

The regression model we developed produced values very close to those in the reference paper, demonstrating its accuracy. Further research can explore potential applications and address the remaining challenges.

Our model has a few limitations with regard to the predictions it can make. The training data had a few flaws, so we had to truncate some data points. The error may be less when compared to the experimental data but due to bizarre changes in  $z_0$  data at low reduced temperature regions, the predictions are highly off track. The model could not handle such changes in data frame because it was limited to only two terms from the Virial equation of state.

## 9. Self-assessment

We have tried our best to achieve level 2 and succeeded in the same. The report showcases our findings through the self-code development and utilisation of a **multivariable nonlinear regression model**. Through this successful implementation of the Pitzer correlation for the second virial coefficient, we have thoroughly explained the methods and numerical analysis approach that we have used. Our report not only reproduced the results, it also deeply focused on the underlying concepts. Using graphs, equations, and personally developed code demonstrates a newer approach towards calculating the constants which makes our term paper worthy enough to get published in any International journal. In conclusion, the report stands as a testament to our commitment towards the term paper and the originality of our work.

## 10. References

Smith, J. M. (Joseph M., van Ness, H. C. (Hendrick C. ), Abbott, M. M., Swihart, M. T. (Mark T. (n.d.). Introduction to chemical engineering thermodynamics.

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Lee, B. I., Kesler, M. G. (1975). A generalized thermodynamic correlation based on three-parameter corresponding states. *AIChE Journal*, 21(3), 510–527. <https://doi.org/10.1002/aic.690210313>

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