

Examining the Prediction of Vapor-Liquid Equilibria through Comparative Analysis: Deep Learning versus Classical Cubic and Associating Fluid Theory Approaches

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Abstract: Accurate vapor-liquid equilibria (VLE) calculations of carbon dioxide and hydrogen sulfide mixtures are critical to gas processing and the affordable, safe design of flow assurance technologies. Inaccurate VLE predictions can lead to inaccurate gas hydrate phase equilibria predictions and ensuing safety and economic risks. This research paper explores the potential incorporation of Deep Neural Networks (DNNs) to support conventional expert systems within the context of predicting VLE. It facilitates more flexible and data-driven approaches that are required due to the growing intricacy and dynamic character of chemical processes. Moreover, various cubic and non-cubic equation of state (EoS) models (such as SRK, PR, CPA, SAFT, and PC-SAFT) were also examined to compare predicted VLE for various mixtures of CO₂ and H₂S. Prior to the comparison of DNN-predicted VLE with EOS models, binary interaction parameters were optimized for all EOS with the available experimental phase equilibria measurements. Model accuracies were compared and analyzed for various binary systems containing CO₂/H₂S + other associative and nonassociative components. The absolute average deviation in vapor and liquid phase composition/bubble pressure was calculated and compared for all five-state EOS with DNN predictions. The DNN and equation of states with BIP gave a reliable illustration of the phase behavior of CO₂/H₂S-containing systems compared to others as indicated by the lower AADP values. By contrasting the applied DNN model with conventional techniques, we explore the promising channel for future research directions and industry applications, as well as an opportunity for innovation and field advancement for modern expert systems.

Keywords: Cubic Equation of states, Deep Neural Network, Vapor-Liquid Equilibria, PC-SAFT EOS, Process Design.

Submitted: September 07, 2024. Accepted: December 18, 2024.

Cite this: Naveed Khan, M., Warrier, P., Zaman, B., & Peters, C. J. (2025). Examining the Prediction of Vapor-Liquid Equilibria through Comparative Analysis: Deep Learning versus Classical Cubic and Associating Fluid Theory Approaches. Journal of the Turkish Chemical Society, Section B: Chemical Engineering, 8(1), 11–28. https://doi.org/10.58692/jotcsb.1545110

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1. INTRODUCTION

Vapor-liquid equilibria (VLE) calculations are of utmost importance in chemical industries, including separation, flow assurance, CO_2 sequestration, acid gas capture using amines, and gas hydrate phase equilibria prediction. While VLE of mixtures comprising of simple non-polar molecules (e.g., small hydrocarbons) can be reasonably explained using traditional estimation techniques (e.g., cubic EoS), accurate prediction of phase behavior of polar associating molecules (e.g., water, alcohols, glycols) and acid gaseous species (e.g., CO_2 , H_2S) is very difficult because of complex molecular arrangements as dictated by the nature and number of associating sites on the molecule. Errors in predicting phase behavior of these associating systems can lead to faulty design of various unit operations. Accurate prediction of VLE for CO_2 and H_2S gas mixture decides the

accuracy of the hydrate phase boundary and significant error in VLE may result in an inaccurate hydrate stability condition.

Various researchers have measured the VLE behavior of CO₂ and H₂S containing systems, as summarized in Table S1-S2. For example, a systematic study of H_2S + hydrocarbon mixtures was carried out by Stamataki and Magoulas (Stamataki & Magoulas, 2000). They employed the Jhaveri and Youngren's volume translated (J-PR) Peng-Robinson EoS to investigate the phase equilibria and volumetric behavior of H₂S containing systems (Jhaveri & Youngren, 1988). A comprehensive evaluation of H₂S containing ternary and guaternary systems (with methane, ethane, propane, and CO₂) was performed using cubic plus association EoS by Tzirakis et al. (Tzirakis et al., 2016). Additional reviews and analysis of thermophysical properties and VLE of pure and mixed systems can be obtained from the following studies (Azari et al., 2013; da Silva et al., 2018; Diamantonis et al., 2013; Espanani et al., 2016; Faúndez & Valderrama, 2013; Ghosh, 1999; Lee & Lin, 2007; Nasrifar & Tafazzol, 2010; Tzirakis et al., 2016; Young et al., 2018).

Expert systems increase the effectiveness, reliability, and safety of chemical engineering processes by utilizing state-of-the-art computational techniques and domainspecific knowledge. Expert systems have the ability to optimize chemical process operations by suggesting and implementing advanced control methods. They can be particularly useful in predicting VLE equilibrium by combining domain knowledge, thermodynamic models, and computational methods.

Recently, Deep Neural Networks (DNNs) have been applied to predict various VLE data sets over range of T, and P conditions (Azari et al., 2013; Carranza-Abaid et al., 2023; Del-Mazo-Alvarado & Bonilla-Petriciolet, 2022; Eze & Masuku, 2018; Kamari et al., 2020; Nguyen et al., 2007; Roosta et al., 2019; Sharma et al., 1999; Vaferi et al., 2018; Wu et al., 2015; Zarenezhad & Aminian, 2011). A DNN is trained on an extensive dataset obtained from chemical engineering scenarios as part of the standard technique. In order to produce more sophisticated and precise predictions, the trained model seeks to identify complex patterns and relationships within the data. The expert system's current knowledge base can be combined with DNN results, allowing rulebased reasoning and data-driven insights to work in harmony.

TensorFlow integrates the Keras library, which includes the Functional APIs for constructing complex Neural Network (NNs) in flexible and powerful ways. The Functional APIs have not been often studied or used in chemical processes like Vapor-Liquid Equilibrium (VLE) prediction. In the context of chemical processes, especially VLE prediction, we may come across situations where the input data includes a combination of several categories (e.g., molecular structures, thermodynamic

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parameters, etc.) In these circumstances, the Functional API's capacity to manage common layers and numerous inputs and outputs can be useful. In non-linear regression analysis, it is challenging to estimate the functional relationship between the multi-dimensional independent and target variables. With the availability of APIs through the modern libraries of neural networks, it is convenient to design, and train customized NNs for better prediction of target data. The models created using functional APIs are more flexible than sequential designs, especially when prediction of multiple outputs are required using multidimensional input features. Such models are guite suitable to work with shared layers, non-linear topologies, or multi-dimensional regression problems where the multiple output with different physical meanings depends on the same input dataset.

The measurement of vapor-liquid equilibria for multicomponent systems over a range of temperature and pressure conditions is a costly, time-consuming, and laborious task. Hence, the accurate estimation of VLE is of utmost importance for the accurate design of process equipment and chemical applications. Conventionally, the equation of state coupled with the flash algorithm is the most common technique to estimate phase equilibria and thermophysical properties. Over the past decades, there have been many attempts to accurately estimate the equilibrium properties of hydrocarbons with gases of acids as highlighted in the following studies (Diamantonis et al., 2013; Li, 2008; Li & Yan, 2009; Wong & Sandler, 1984). However, there is a need to compare all different EoS models to evaluate their effectiveness in predicting phase equilibria. The current study highlights the effectiveness of various EoS models such as Soave Redlich Kwong (SRK), Peng Robinson (PR), cubic plus association (CPA), Statistical Associating Fluid Theory (SAFT), and perturbed chain SAFT (PC-SAFT) for phase equilibria prediction with optimized binary interaction parameters. Moreover, a DNN model was also created by using functional APIs of Keras to predict the VLE of hydrogen sulfide and carbon dioxide-containing binary systems. The model can predict pressure and vapor phase mole fraction very close to their experimental values. Expert systems typically employ domain knowledge and rule-based procedures, but utilizing Keras' Functional API can enhance system performance, especially for applications that benefit from deep learning techniques. To compare the model accuracies EoS algorithm was implemented with a reliable multiphase flash algorithm for predicting VLE. Finally, VLE predictions utilizing DNN were compared with various EoS mentioned earlier.

2. METHODOLOGY

The significant breakthrough in the field of NN occurred with the concept of backpropagation that deal with the adjustment of weights while training a multi-layer NN for minimum prediction error (Li et al., 2012). Meanwhile, the implementation of deep learning became possible with the help of modern computing resources, like

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powerful machines, advanced algorithms, and availability of larger datasets. It served many disciplines and solved complex problems in computer vision, healthcare, stock trading, social networks, and real-world problems from numerous branches of engineering (Mahfooz et al., 2023; Mahfooz et al., 2022; Zhong et al., 2021). In chemical engineering, the use of DNN is highly valuable for solving complex problems. Some major applications of DNNs have been observed in certain areas like quality control, process modeling and control, predictive maintenance, material design, energy efficiency, flow

assurance, water treatment, etc. (Han et al., 2019; Han et al., 2023; Zhang & Zhang, 2022). While solving realworld chemical engineering problems, high-quality data, architecture of DNN, and a robust training implementation are among the crucial requirements of using a DNN. Multiple layers of interconnected nodes make up a DNN, which is often divided into three basic types: An input layer, single or numerous hidden layers, and an output layer (see Figure 1). The term "deep" refers to the availability of multiple hidden layers, which allows learning of complex data representations.



Figure 1. A generalized deep neural network structure.

Here, we have implemented a functional API for designing and training a DNN. It offers an adaptable approach to create neural network architectures by defining the connections between layers in a more evident and practical pattern. It is more flexible than its competitor i.e., the sequential approach for constructing neural networks. Functional API is useful for multi-model and multitask learning as it conveniently affords multiple input and output layers. This adaptability empowers to build intricate network structures that concurrently offers multiple predictions on diverse types of data. A mathematical representation for a simple DNN using the Functional API with one shared layer and one non-shared (specific) layer is provided below. This example considers a DNN with two branches of input data, one shared layer, and one specific layer:

Input Layers:

Input for the first branch: X_1 Input for the second branch: X_2 **Shared Layer:** Linear Transformation: $Z_s = W_s \cdot X_1 + b_s$

Activation Function: $A_s = g_s(Z_s)$ Specific Layer:

Linear Transformation: $Z_n = W_n \cdot X_2 + b_n$ Activation Function: $A_n = q_n (Z_n)$

Where, X_1 and X_2 are inputs for first and second branch, respectively. Z_s and A_s are the outputs of the shared layer after applying a linear transformation and the activation function. Similarly, Z_n and, A_n are the output of the specific layer after applying the linear transformation and the activation function. $W_{s_r} b_{s_r} W_{n_r}$ and b_n represent the weights and biases for the shared and specific layers. Here, g_s and g_n represent the activation functions applied to the shared and specific layers, respectively. The shared layer is normally used for feature extraction and the specific layer is used for task-specific processing. The input data from branches are processed separately that allows for different data types to be processed differently in the network. A simplified block flow diagram representing DNN implementation is illustrated in Figure 2.



Figure 2. A block flow diagram representing DNN implementation.

Conventionally, VLE is predicted utilizing cubic EoS and statistical associating fluids theory models (such as SAFT and PC-SAFT). Among cubic EoS, the Redlich-Kwong equation was the first reported modification to original van der Waal EoS (vd-EoS). Redlich and Kwong (RK) modified the vd-EoS with a T-dependent energy-associated term 'a(T)' to correct the PVT properties of fluids (Redlich & Kwong, 1949). The RK-EoS equation is given in by Equation 1:

$$P = \frac{RT}{v-b} - \frac{a\alpha}{v(v+b)} \tag{1}$$

Where a, b and α are described in Table S3.

To improve phase behavior calculations at higher T and P, Soave suggested the revision in the RK EoS by encompassing a more complicated T dependence term to the attraction parameter, as given in Equation 2 (Soave, 1972).

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)}$$
(2)

v is molar-volume

 $a \, \&^{b}$ are energy and volume parameters for SRK EoS

The detailed information about SRK EoS parameters is discussed in Table S3 (provided in supplementary information). Moreover, the SRK-EoS energy parameter (a) for mixture is estimated by utilizing Equation 3:

$$a = \sum_{i}^{c} \sum_{j}^{c} x_{i} x_{j} a_{ij}$$

and,

$$a_{i_j} = (1 - ki_j)(a_i a_j)^{0.5}$$
(3)

Furthermore, Peng and Robinson (1976) introduced an EoS by transforming the attractive term's denominator and developed a modified form for the EOS parameters (such as *a* and *b*), which offers additional benefits to the SRK-EOS in predicting liquids, as shown in Equation 4 (Peng & Robinson, 1976).

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)+b(v-b)}$$
(4)

(-)

Concerning non-cubic equation of states, Chapman et al. (Chapman et al., 1989) proposed a SAFT EoS model to estimate accurate fluid phase equilibria, established on the Statistical Associating Fluid Theory (SAFT). The SAFT-EoS can be expressed in terms of Helmholtz free energy (A) by the generalized form as described by Equation 5:

$$A^{res} = A^{seg} + A^{chain} + A^{Assos}$$
(5)

In contrast to SAFT, the PC-SAFT EoS regard molecules as chains consist of hard spherical-segments, and the effect of chain-length is considered for both repulsive and dispersive contributions. Moreover, the PC-SAFT EoS also considers the association term is to account for, and model systems containing polar organic molecules (H_2S , CO_2), organic hydrate inhibitors (alcohols, glycols), hydrocarbons (low to medium hydrocarbon) and water. (Gross & Sadowski, 2001). The PC-SAFT EoS is implemented in the current work for various binary systems of H_2S/CO_2 + hydrocarbon and given by Equation 6.

(6)

$$A^{res} = A^{seg} + A^{chain} + A^{Assos}$$

Cubic plus association (CPA) EoS is an expansion of SRK EoS with an additional term for the association of molecules and is given by Equation 7.

 $A(T,V,n) - A^{IGM}(T,V,n) = \Delta A^{phy} + \Delta A^{Assos}$ (7) where, A^{phy} is the Helmholtz free energy (A) contribution term which considered the variation due to the presence of repulsive and attractive interactions and A^{Assos} is the Helmholtz free energy term that account for the changes in A because of association of molecules.

The A^{phy} and A^{Assos} term of the CPA equation of state is given in (Equations 8 & 9) (Soave, 1972).

$$\Delta A^{phy} = n\left(-\log\left(1 - \frac{b_m}{V}\right) - \frac{a_m}{RTb_m}\log\left(1 + \frac{b_m}{V}\right)\right)$$
(8)

$$\Delta A^{assos}(T,V,n) = nRT\sum_{S} \left(\ln X + \frac{1-X}{2}\right)$$

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Moreover, the X^A which is defined as the fraction of species not bonded at site A, and is calculated by (Equation 10) (Chapman et al., 1989; Huang & Radosz, 1991).

$$X^{A} = \left(1 + \rho \sum_{B} X^{B} \Delta^{AB}\right)^{-1}$$
(10)

The X^{A} for mixtures is calculated by utilizing Equation (11):

$$X_{A_{i}} = \frac{1}{1 + \rho \sum_{j} x_{j} \sum_{B_{j}} X_{B_{j}} \Delta^{A_{i}B_{j}}}$$
(11)

A generalized algorithm representing optimization of pure component and binary interaction parameters for numerous fluid phase models is illustrated in Figure 3. Additional details and parameters used in above mentioned EoS are provided in the supplementary materials (Equations S1-S12).



(9)

Figure 3. A generalized algorithm illustrating VLE prediction and model parameters (BIP & pure component) optimization using equation of states.

3. EXPERIMENT AND RESULTS

3.1. Data for Vapor Liquid Equilibria

Nevertheless, to achieve erroneous prediction of vaporliquid equilibria using DNN and equation of states (both cubic and non-cubic EOS), vapor-liquid equilibria experimental data was also collected over a wide range of pressure, temperature, and compositions. Tables S1 & S2 enlist the VLE experimental measurements for various binary mixtures of hydrogen sulfide and carbon dioxide in the presence of hydrocarbons. The collection of thermodynamically corrected data is essential as any

source of unreliable data sets may lead to model inaccuracies. The current data set is adapted from Khan et al. (2016)(Khan et al., 2016). The experimental dataset will ensure the accurate optimization of binary interaction parameters before the prediction of phase envelopes utilizing cubic and non-cubic equations of state. The absolute average deviation in predicting pressure and compositions is entirely dependent on the goodness of experimental data as the coupled uncertainties may result in error-based prediction.

Naveed Khan et al., (2025), 8(1), 11-28. **3.2. Deployment of DNN to Estimate Fluid Phase** Equilibria

The imprecise knowledge of VLE becomes critical for the operation and control of chemical processes. The predictions with thermodynamics models often show deviation from the experimental VLE data and some exclusively data-driven models with their parameter fitting approach may not exactly specify data-fitting function. Moreover, these models normally use iterative algorithms with significant computational cost. A neural network model trained on a dataset, can efficiently predict better results, and can be integrated with any existing software packages for data evaluations. Figure 4 shows the architecture of the designed neural network model that is constructed by utilizing TensorFlow and functional APIs of Keras (Abadi et al., 2016).



Figure 4. VLE neural network for prediction of pressure (P) and vapor phase composition (y).

As demonstrated in Figure 4, the computational model of neural network establishes a relationship between input features and outputs that are available at two different ends of the network. The first hidden layer is connected to the first output layer and second hidden layer. However, the second output layer then follows the second hidden layer. The first hidden layer is a shared layer that finds joint features advantageous to each of the two outputs. In contrast, the second hidden layer improves prediction accuracy by learning specific features for predicting the second output. The proposed architecture is quite suitable for multi-dimensional regression problems, where multiple output with different physical meanings depends on the same input dataset.



Figure 5. Comparison plot for AI trained predicted Pressure (P) and experimental pressure.

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Our binary VLE data include molar fractions of components, temperature, pressure, and critical properties of components. The data were divided randomly into training (60%), validation (20%), and test (20%) datasets. The validation and test datasets are utilized for assessing the overall efficiency of the network. Feature scaling was also applied to preprocess the raw dataset. It confirms about the contribution of each feature is proportionately equal for the predictions and the model is trained accurately and efficiently. Our scaled features (x_i) are obtained by using standardization of input values (x) as given below by Equation 12:

$$x_{i} = \frac{x - mean(x)}{standard \, deviation(x)}$$
(12)

A neural network can approximate any function by minimizing a cost function using backpropagation or gradient descent (Hanin, 2019; Hornik, 1991; Irie & Miyake, 1988; Nasrifar & Tafazzol, 2010). The performance of neural network is measured at each learning step by observing the cost function. We used Mean Square Error (MSE) for training our model that is the most common cost function for the regression problems. It is defined as given by Equation 13:

$$MSE = \frac{1}{N} \sum_{i=1}^{N} (y_i - \hat{y}_i)^2$$
(13)

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Here, N represents the # of observations in the given input dataset. The actual and evaluated output values are represented by y_i and \hat{y}_i respectively.

Hyperparameters were optimized after very keen observations at different stages of model design. One of the objectives was to produce a model that avoids overadaption of training data and generalizes well on new data. This issue of memorization of training data by complex models is known as overfitting that always limits the generalization of any model. Early stopping is one of the techniques to overcome this issue. We applied early stopping by choosing a patience value of 20, that means training is stopped if there is no improvement over validation set for 20 consecutive epochs. To achieve better performance of optimization, we used Nadam (Nesterov-accelerated Adaptive Moment Estimation) that is an extension of the famous Adam optimizer (Tato & Nkambou, 2018). The optimizer algorithms help to achieve reduction in cost function that keep changing the weights and learning rate of the neural network. The default value of learning rate was used to initialize the training. Figures 5 & 6 compares the predicted values of P and y with their values measured experimentally. All points are close to the regressed diagonal line showing satisfactory results achieved by the model. In addition, the absolute average deviation in pressure and vapor phase (AADP/AADy %) mole fraction calculated utilizing the DNN for H_2S and CO_2 containing binary systems as represented in Figure 7 & 8 respectively. The calculated AADP/AADy using the trained model were tested for 20% of the total datasets. The model on the basis of individual critical parameters, liquid phase mole fraction, and temperature accurately output the vapor phase mole fraction and pressure.



Figure 6. Comparison plot for AI trained predicted vapor phase mole fraction and experimental vapor phase mole fraction.



Figure 7. Absolute average deviation in pressure and vapor phase mole fraction (AADP/AADy %) Using AI trained network for various CO₂ containing binary systems.



Figure 8. Absolute average deviation in pressure and vapor phase mole fraction (AADP/AADy %) Using AI trained network for various H₂S containing binary systems.

3.3. Vapor-Liquid Equilibria using Cubic Equation of States

The flash algorithm was coupled with cubic and non-cubic EoS to calculate VLE for numerous H_2S and CO2-containing binary systems. Prior to the prediction of VLE

utilizing EoS, binary interaction parameters were optimized to account for the interaction between the species. Figure 9 (a) shows predicted VLE utilizing the PR EoS for CO_2 + n- C_7 binary mixtures over a range of T & P.



Figure 9. Model predictions for (a) CO₂+ n-C₇ over a T range of 310.65 to 394.26 K (b) H₂S + cyclohexane over a T range of 323.15 to 422.60 K (c) H_2S + n-C₆ vapor-liquid equilibria over a T range of 322.9 to 422.6 K and (d) H_2S + $n-C_7$ over a temperature range of 310.92 to 477.594 K VLE using the PR EoS. Experimental measurements were taken from (Kalra et al., 1978; Laugier & Richon, 1995; Ng et al., 1980; Théveneau et al., 2006).

Figure 9 (b) represents the VLE predictions compared measurements with experimental for H₂S + cyclohexane binary mixtures over a T range of 323.15 to 422.60 K. The model estimations agree well with the experimental measurements. Nevertheless, the pressure-composition envelop predictions start deviating from experimental data within proximity of the critical point. The inaccuracy in predicting vapor-liquid equilibria near critical regions may be associated with the version of the a function. Hence, to accurately predict the phase envelop near-critical region, it is suggested here to test the PR-EOS with various correlations available for a calculation as discussed in detail by the following researchers (Dahl & Michelsen, 1990; Lopez-Echeverry et al., 2017; Mathias & Copeman, 1983; Twu et al., 2002a). The a function shows linearly dependency on temperature in the supercritical region and thus it is recommended (Twu et al., 2002b) to utilize the second function when temperature exceeds the critical point.

(Lopez-Echeverry et al., 2017). It is quite apparent from Figure 9 (c-d) that the PR EoS predictions of VLE for binary mixtures of $H_2S + n-C_7/n-C_6/cyclohexane$ over a range of temperatures and pressures show reasonably fair agreement in the dew and bubble point calculations. The calculations illustrate that the model successfully predicts binary systems VLE, and a temperaturedependent binary interaction parameter (BIP) is essential to precisely estimate the liquid part of the phase envelope. Conclusively, the PR EoS precisely predicts the phase envelope for selected self-associating systems. The predicted phase envelopes utilizing Peng Robinson EoS for all other binary systems also show reasonable accuracy with experimental measurements (see Section 3.5 for comparison and Table S6 for a summary of results without BIP).

However, the former modification may result in

implications are discussed in detail in the following study

and

the

a discontinuity in enthalpy calculation,



Figure 10. Model predictions for (a) CO_2 + n- C_7 over a T range of 310.65 to 394.26 K (b) H_2S + n-hexane over a T range of 322.9 K to 422.6 K (c) H_2S + n- C_7 vapor-liquid equilibria over a T range of 310.92 K to 477.594 K vapor-liquid equilibria utilizing the SRK EoS. Experimental measurements were taken from (Kalra et al., 1978; Laugier & Richon, 1995; Ng et al., 1980; Théveneau et al., 2006).

Similarly, to evaluate the effectiveness of SRK EoS, an algorithm was developed, and T- dependent BIP was optimized for CO₂ and H₂S binary mixtures. The SRK EoS predictions for binary systems such as CO_2+n-C_7 and H₂S + $n-C_6/n-C_7$ are also in reasonable agreement with the experimental measurements, as shown in Figure 10 (a-c). However, as evident from Figure 10 (c), the SRK predictions are accurate at low to moderate temperatures but show deviation at higher temperatures for the liquid part illustrating the importance of the SAFT-based equation of state.

The CPA EoS incorporates the association term in its formulation to account for the hydrogen bonding in associative molecules. Hence, it provides a significant improvement over SRK EoS for VLE prediction. Figure 11 (a-c) indicates that the CPA EoS predictions of VLE for H₂S + n-C₆/n-C₇/cyclohexane binary mixture over a T range of 310.92 to 422.6 K. It is apparent from Figure 11 (a) that the CPA EoS model is successful in capturing liquid and vapor side phase boundary for H₂S (self-association) + non-associative systems; hence illustrating the reliability of this CPA EoS.



Figure 11. CPA EoS predictions for (a) $H_2S + n-C_6$ over a T range of 322.90 to 422.6 K (b) $H_2S + n-C_7$ over a T range of 310.92 K to 422.6 K (c) $H_2S +$ cyclohexane over a T range of 323.15 K to 422.6 K. Experimental data was taken from (Laugier & Richon, 1995; Ng et al., 1980; Théveneau et al., 2006).

Figures 11 (b-c) shows the evaluation of CPA-EOS model predictions for the H_2S + n-C₇/cyclohexane binary systems VLE over a *T* range of 310.92 to 422.6 K. VLE predictions for H_2S + n-C₇/cyclohexane systems agree with the experimental measurements, except immediate to the critical point at moderately higher T. The significant errors in calculating dew and bubble point P at

higher T are credited to the range of T_r over which the CPA-EOS parameters were optimized (CPA EoS parameters were optimized up to a T_r range of 0.90). **3.4. PC-SAFT Predictions for VLE of H₂S/CO₂**

In addition, to evaluating the effectiveness of the non-cubic EoS, VLE predictions were also carried out using SAFT-EOS and its modification (PC-SAFT).





Figure 12. Model prediction for (a) H₂S + cyclohexane (b) H₂S + nC₆ and (c) H₂S + n-C₇ VLE using SAFT (statistical associating fluid) EoS. Experimental measurements were taken from (Laugier & Richon, 1995; Ng et al., 1980; Théveneau et al., 2006).

Prior to VLE calculation using SAFT EoS, binary interaction parameters were optimized utilizing carefully selected experimental data. Pure component parameters (three parameters for non-associative species (such as hydrocarbons) and 2 parameters for associating species) for SAFT were adopted from the literature (see Table S5). Figures 12 (a-c) demonstrate the dew and bubble point calculations for H_2S + n-Cyclohexane/n-C₆/n-C₇ binary mixtures. The VLE calculations are in reasonable accord with the experimental data, but the liquid part of the VLE envelope was slightly overpredicted by the SAFT-EoS. The model predictions for the selected binaries show excellent accord for the vapor part of the phase envelope, yet the VLE envelope's liquid part is slightly overpredicted. Also, it is not unusual to have wrong predictions of thermophysical properties and VLE envelopes utilizing inappropriate pure components and BIP. The uncertainties in prediction near far critical regions and the liquid part of the envelop might be associated with the poorly optimized equation of state parameters.

The higher-order SAFT EoS (Chapman et al., 1990; Wertheim, 1984) was modified to develop PC-SAFT (Gross & Sadowski, 2001; Huang & Radosz, 1990, 1991). PC-SAFT-EoS originated from SAFT, as in SAFT, the reference fluid is considered a hard sphere whereas PC-SAFT uses a hard chain. The PC-SAFT EoS contemplates molecules as chains consisting of hard spherical segments, and the effect of chain length is considered for both repulsive and dispersive contributions as discussed in Section 2. In this work, the PC-SAFT EoS algorithm was adapted from (Martín et al., 2011) and parameters used are listed in Table S4.



Figure 13. Model predictions for (a) $H_2S + n-C_6 \&$ (b) $H_2S + n-C_7$ VLE utilizing the PC SAFT EoS. Experimental measurements were taken from(Laugier & Richon, 1995; Ng et al., 1980; Théveneau et al., 2006).

The VLE predictions of CO_2 + n- C_{10} / predictions utilizing PC-SAFT with optimized binary methylcyclohexane binary mixtures reveal that model interaction parameters are in excellent accord with

experimental measurements (Figure S5 a-b). The VLE calculations were also conducted for the CO_2 + n-C₇ binary mixture as given in Figure S1. The PC-SAFT predictions are observed to be more precise for the vapor part of the VLE envelope in comparison with the liquid part; the latter was slightly under-predicted by PC-SAFT EoS in all the former binary mixtures (see Table S7 for a summary). The higher error in the liquid part of the phase envelope utilizing SRK-EOS is attributed to the inherent limitation of accurately predicting liquid densities. In contrast, Peng & Robinson's Equation of state shows reasonably better prediction because of the term b(v-b), which significantly improves the depiction of the attractive part of the equation of state, and consequently, improves the ability of the PR-EOS to predict liquid densities. Also, Figures 13 (a-b) show VLE predictions and experimental measurements for H₂S+n- $C_6/n-C_7$ binary systems over a range of T and P. It is quite evident from Figure 13 (a-b) that PC-SAFT predictions are in close accord with experimental measurements. Figure S6 compares the errors in predicting the bubble pressure for binary systems of H₂S & CO_2 using the SAFT and PC-SAFT EoS. PC-SAFT EoS was observed to provide equivalent precision to SAFT in predicting the vapor phase. However, PC-

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SAFT EoS gives overall improved prediction in estimating the bubble pressure (see Figure S6(a-b). A summary of DNN and five EoS in predicting VLE of CO_2 and H_2S containing binary mixtures is also discussed in Section 3.4.

3.5. Comparisons of DNN and EoS Models for VLE Prediction

To examine the effectiveness of DNN over cubic and noncubic EoS in the prediction of VLE of binary systems, errors in predicted P and vapor phase composition (y) are compared. Before comparing the performance of the various equations of state models, all the experimental data points were utilized in optimizing the binary interaction parameter as per the below objective functions.

$$AADP = \frac{1}{N} \sum_{i=1}^{N} \frac{P_{\exp} - P_{calc}}{P_{\exp}} * 100\%$$
(14)

As expected, the cubic equation and non-cubic EoS show drastic improvements in prediction accuracy when binary interaction parameters are carefully optimized (see also summary in Table S6 & Table S7 for comparison).



Figure 14. Comparison of AADP % for H₂S containing binary mixtures.

Figure 14-15 compares the absolute average deviation in vapor phase compositions and pressures (AADy % & AADP %) prediction for DNN with cubic and SAFT-based EOS with optimized BIP. Based on the optimized binary interaction parameters for various multicomponent systems the calculated AADx/AADy and AADp enlisted in Figures 14 &15 for all equation of state (cubic and non-cubic) models. Additionally, to celebrate the impact of BIP optimization, the un-optimized VLE predictions using cubic and SAFT-based models are given in Tables S6 & S7. The hydrogen sulfide-containing systems including binary mixtures of H_2S+C_4 , H_2S+i-C_4 , H_2S+C_5 , H_2S+C_6 , H_2S+C_7 , $H_2S+cyclohexhane, and$

H₂S+Ethylcyclohexane, shows that the PC-SAFT EOS output least error (0.975% for *AAdy* and 1.420 % for *AADp* respectively). Moreover, the PC-SAFT equation of state also shows accurate predictions accuracy for CO₂-containing binary mixtures, and the binary mixture of CO₂+N₂, CO₂+C₆, CO₂+C₈, CO₂+Cyclohexane, CO₂+C₆H₆, CO₂+C₁₀, CO₂+C₇, and CO₂+Toluene shows an absolute error of 1.48 % and 2.97 % for *AAdy* and *AADp* respectively. A comparison of the CPA equation of state provides an average error in predicting y & x is to be 2.51 % & 5.96 % respectively for H₂S-containing gas mixtures and an error of 2.57 % and 17.26 % for CO₂-

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containing gas mixtures. By contrast, the trained model (DNN) predicted higher accuracy for all selected binary systems and the average error in predicting yand P is 5.20 % & 6.04 % respectively for binary CO₂ mixtures. Moreover, the trained DNN model also shows reasonable error in predicting yand P to be 4.46 % & 6.35 % respectively for H₂S-containing gas mixtures. Overall, a relative comparison of VLE prediction shows that PC SAFT EOS yielded the least deviation in comparison with other equation of state models. However, the DNN model

developed in this work is comparable to cubic and SAFTbased EoS. Designed DNN shows acceptable accuracy in predicting phase equilibria for various H_2S and CO_2 binary systems over an extended range of T and P conditions. It was also observed that the execution of flash calculation utilizing DNN does not need long computational time even if coupled with the dynamic process simulation. In contrast, non-cubic equations of states (SAFT and PC-SAFT) and CPA EoS require higher computational time when coupled with the dynamic process simulation.



Figure 15. Comparison of AADP % for CO₂ containing binary mixtures.

4. CONCLUSION AND FUTURE DIRECTIONS

The DNNs have remarkable abilities to capture complex, nonlinear correlations that are inherent in VLE systems. By using data-driven learning, the model can replace traditional methods for prediction, especially in scenarios where there are intricate interactions between multiple variables. The functional APIs have been underexplored in constructing NNs for chemical processes. They have potential to enable the expert system to integrate deep learning models and harness the power of neural networks used in chemical engineering processes. By using a DNN model through functional APIs, multiple parameters along with VLE data were included in training data sets over range of T and P conditions. Cubic, SAFT, and PC-SAFT EoS were tested to predict VLE of H2S/CO₂ containing binary mixtures. Absolute errors were estimated and compared with results obtained using the developed DNN model for various binary mixtures, including self-associating systems. The model was compared with EoS predictions utilizing optimized binary interaction parameters and provided comparable accuracy as PC-SAFT EoS (most accurate among the 5 EoS tested in this work). However, time required for flash calculation using DNN was significantly lower than SAFT, PC-SAFT, and CPA EoS. This warrants further evaluation of DNN-based approach as lower computational time along with VLE prediction accuracy comparable to PC-SAFT could be of significant interest to process simulation software developers. While, predicting the vapor part of the phase envelope, all equation of states including DNN give reasonable accuracy. However, the liquid part of the phase envelope's predictions shows significant errors using all EoS, mainly because of the poorly fitted association EoS terms for these systems.

- I. The Soave Redlich Kwong and Peng Robinson equation of states should be tested with various forms of a function to completely test the accuracy of the cubic equation of states.
- II. Over the past decades multiple formulations for $a \wedge b$ were proposed in the cubic equation of state to improve saturation pressure, liquid density, and VLE predictions. Thus, it would be recommended to thoroughly test those formulations to select optimal parameters.
- III. In addition to the testing of basic parameters in cubic equations of states, various combinations of repulsive and attractive terms should also be tested comprehensively to estimate accurate VLE and thermophysical properties.
- IV. The use of conventional and unconventional mixing rules in all equations of states should be tested extensively to locate the most suitable way to estimate a multi-component system.
- V. Generally, binary interaction parameters were optimized utilizing experimental VLE data, however, there is a need to estimate binary

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5. REFERENCES

- Abadi, M., Agarwal, A., Barham, P., Brevdo, E., Chen, Z., Citro, C.,...Devin, M. (2016). Tensorflow: Large-scale machine learning on heterogeneous distributed systems. *arXiv preprint arXiv:1603.04467*.
- Azari, A., Atashrouz, S., & Mirshekar, H. (2013). Prediction the vapor-liquid equilibria of CO2containing binary refrigerant mixtures using artificial neural networks. *International Scholarly Research Notices*, 2013.
- Carranza-Abaid, A., Svendsen, H. F., & Jakobsen, J. P. (2023). Thermodynamically consistent vaporliquid equilibrium modelling with artificial neural networks. *Fluid Phase Equilibria*, *564*, 113597.
- Chapman, W. G., Gubbins, K. E., Jackson, G., & Radosz, M. (1989). SAFT: equation-of-state solution model for associating fluids. *Fluid Phase Equilibria*, *52*, 31-38.
- Chapman, W. G., Gubbins, K. E., Jackson, G., & Radosz, M. (1990). New reference equation of state for associating liquids. *Industrial & Engineering Chemistry Research*, 29(8), 1709-1721.
- da Silva, V. M., do Carmo, R. P., Fleming, F. P., Daridon, J.-L., Pauly, J., & Tavares, F. (2018). High pressure phase equilibria of carbon dioxide+ n-alkanes mixtures: Experimental data and modeling. *Fluid Phase Equilibria*, *463*, 114-120.
- Dahl, S., & Michelsen, M. L. (1990). High-pressure vapor-liquid equilibrium with a UNIFAC-based equation of state. *AIChE journal*, *36*(12), 1829-1836.
- Del-Mazo-Alvarado, O., & Bonilla-Petriciolet, A. (2022). Assessment of the simultaneous regression of liquid-liquid and vapor-liquid equilibria data of binary systems using NRTL and artificial neural networks. *Fluid Phase Equilibria*, 561, 113537.
- Diamantonis, N. I., Boulougouris, G. C., Mansoor, E., Tsangaris, D. M., & Economou, I. G. (2013). Evaluation of cubic, SAFT, and PC-SAFT equations of state for the vapor-liquid equilibrium modeling of CO2 mixtures with other gases. *Industrial & Engineering Chemistry Research*, *52*(10), 3933-3942.
- Espanani, R., Miller, A., & Jacoby, W. (2016). Prediction of vapor-liquid equilibria for mixtures of low boiling point compounds using Wong-Sandler mixing rule and EOS/GE model. *Chemical Engineering Science*, *152*, 343-350.
- Eze, P. C., & Masuku, C. M. (2018). Vapour–liquid equilibrium prediction for synthesis gas conversion using artificial neural networks. *South African journal of chemical engineering*, 26(1), 80-85.
- Faúndez, C. A., & Valderrama, J. O. (2013). Modeling associating hydrocarbon+ alcohol mixtures using the Peng-Robinson equation of state and

the Wong-Sandler mixing rules. *Comptes Rendus Chimie*, *16*(2), 135-143.

- Ghosh, P. (1999). Prediction of vapor-liquid equilibria using peng-robinson and soave-redlich-kwong equations of state. *Chemical Engineering & Technology: Industrial Chemistry-Plant Equipment-Process Engineering-Biotechnology*, 22(5), 379-399.
- Gross, J., & Sadowski, G. (2001). Perturbed-chain SAFT: An equation of state based on a perturbation theory for chain molecules. *Industrial & Engineering Chemistry Research*, 40(4), 1244-1260.
- Han, X., Zhang, L., Zhou, K., & Wang, X. (2019). ProGAN: Protein solubility generative adversarial nets for data augmentation in DNN framework. *Computers & chemical engineering*, 131, 106533.
- Han, Y., Du, Z., Geng, Z., Fan, J., & Wang, Y. (2023). Novel long short-term memory neural network considering virtual data generation for production prediction and energy structure optimization of ethylene production processes. *Chemical Engineering Science*, *267*, 118372.
- Hanin, B. (2019). Universal function approximation by deep neural nets with bounded width and relu activations. *Mathematics*, *7*(10), 992.
- Hornik, K. (1991). Approximation capabilities of multilayer feedforward networks. *Neural networks*, 4(2), 251-257.
- Huang, S. H., & Radosz, M. (1990). Equation of state for small, large, polydisperse, and associating molecules. *Industrial & Engineering Chemistry Research*, *29*(11), 2284-2294.
- Huang, S. H., & Radosz, M. (1991). Equation of state for small, large, polydisperse, and associating molecules: extension to fluid mixtures. *Industrial & Engineering Chemistry Research*, 30(8), 1994-2005.
- Irie, & Miyake. (1988). Capabilities of three-layered perceptrons. IEEE 1988 international conference on neural networks,
- Jhaveri, B. S., & Youngren, G. K. (1988). Threeparameter modification of the Peng-Robinson equation of state to improve volumetric predictions. *SPE reservoir engineering*, *3*(03), 1033-1040.
- Kalra, H., Kubota, H., Robinson, D. B., & Ng, H.-J. (1978). Equilibrium phase properties of the carbon dioxide-n-heptane system. *Journal of chemical and Engineering Data*, 23(4), 317-321.
- Kamari, E., Hajizadeh, A. A., & Kamali, M. R. (2020). Experimental investigation and estimation of light hydrocarbons gas-liquid equilibrium ratio in gas condensate reservoirs through artificial neural networks. *Iranian Journal of Chemistry* and Chemical Engineering (IJCCE), 39(6), 163-172.
- Khan, M. N., Warrier, P., Peters, C. J., & Koh, C. A. (2016). Review of vapor-liquid equilibria of gas hydrate formers and phase equilibria of

Naveed Khan et al., (2025), 8(1), 11-28. hydrates. *Journal of Natural Gas Science and Engineering*, *35*, 1388-1404.

- Laugier, S., & Richon, D. (1995). Vapor-liquid equilibria for hydrogen sulfide+ hexane,+ cyclohexane,+ benzene,+ pentadecane, and+(hexane+ pentadecane). *Journal of chemical and Engineering Data*, 40(1), 153-159.
- Lee, M.-T., & Lin, S.-T. (2007). Prediction of mixture vapor–liquid equilibrium from the combined use of Peng–Robinson equation of state and COSMO-SAC activity coefficient model through the Wong–Sandler mixing rule. *Fluid Phase Equilibria*, 254(1-2), 28-34.
- Li, H. (2008). Thermodynamic properties of CO2 mixtures and their applications in advanced power cycles with CO2 capture processes KTH].
- Li, H., & Yan, J. (2009). Evaluating cubic equations of state for calculation of vapor–liquid equilibrium of CO2 and CO2-mixtures for CO2 capture and storage processes. *Applied Energy*, *86*(6), 826-836.
- Li, J., Cheng, J.-h., Shi, J.-y., & Huang, F. (2012). Brief introduction of back propagation (BP) neural network algorithm and its improvement. Advances in Computer Science and Information Engineering: Volume 2,
- Lopez-Echeverry, J. S., Reif-Acherman, S., & Araujo-Lopez, E. (2017). Peng-Robinson equation of state: 40 years through cubics. *Fluid phase equilibria*, 447, 39-71.
- Mahfooz, S., Alhasani, A., & Hassan, A. (2023). SDG-11.6. 2 Indicator and Predictions of PM2. 5 using LSTM Neural Network. 2023 1st International Conference on Advanced Innovations in Smart Cities (ICAISC),
- Mahfooz, S., Ali, I., & Khan, M. N. (2022). Improving stock trend prediction using LSTM neural network trained on a complex trading strategy. *International Journal for Research in Applied Science and Engineering Technology*, 10(7), 4361-4371.
- Martín, Á., Bermejo, M. D., Mato, F. A., & Cocero, M. J. (2011). Teaching advanced equations of state in applied thermodynamics courses using open source programs. *Education for Chemical Engineers*, 6(4), e114-e121.
- Mathias, P. M., & Copeman, T. W. (1983). Extension of the Peng-Robinson equation of state to complex mixtures: Evaluation of the various forms of the local composition concept. *Fluid phase equilibria*, *13*, 91-108.
- Nasrifar, K., & Tafazzol, A. H. (2010). Vapor– liquid equilibria of acid gas– aqueous ethanolamine solutions using the PC-SAFT equation of state. *Industrial & Engineering Chemistry Research*, 49(16), 7620-7630.
- Ng, H.-J., Kalra, H., Robinson, D. B., & Kubota, H. (1980). Equilibrium phase properties of the toluene-hydrogen sulfide and heptane-hydrogen sulfide binary systems. *Journal of chemical and Engineering Data*, *25*(1), 51-55.

RESEARCH ARTICLE

- Nguyen, V. D., Tan, R. R., Brondial, Y., & Fuchino, T. (2007). Prediction of vapor–liquid equilibrium data for ternary systems using artificial neural networks. *Fluid Phase Equilibria*, 254(1-2), 188-197.
- Peng, D.-Y., & Robinson, D. B. (1976). A new twoconstant equation of state. *Industrial & Engineering Chemistry Fundamentals*, 15(1), 59-64.
- Redlich, O., & Kwong, J. (1949). On the thermodynamics of solutions. V. An equation of state. Fugacities of gaseous solutions. *Chemical Reviews*, 44(1), 233-244.
- Roosta, A., Hekayati, J., & Javanmardi, J. (2019). Application of artificial neural networks and genetic programming in vapor–liquid equilibrium of C 1 to C 7 alkane binary mixtures. *Neural Computing and Applications*, *31*, 1165-1172.
- Sharma, R., Singhal, D., Ghosh, R., & Dwivedi, A. (1999). Potential applications of artificial neural networks to thermodynamics: vapor–liquid equilibrium predictions. *Computers & chemical engineering*, 23(3), 385-390.
- Soave, G. (1972). Equilibrium constants from a modified Redlich-Kwong equation of state. *Chemical Engineering Science*, *27*(6), 1197-1203.
- Stamataki, S., & Magoulas, K. (2000). Prediction of phase equilibria and volumetric behavior of fluids with high concentration of hydrogen sulfide. *Oil & Gas Science and Technology*, *55*(5), 511-522.
- Tato, A., & Nkambou, R. (2018). Improving adam optimizer.
- Théveneau, P., Coquelet, C., & Richon, D. (2006). Vapour–liquid equilibrium data for the hydrogen sulphide+ n-heptane system at temperatures from 293.25 to 373.22 K and pressures up to about 6.9 MPa. *Fluid phase equilibria*, 249(1-2), 179-186.
- Twu, C. H., Sim, W. D., & Tassone, V. (2002a). An extension of CEOS/AE zero-pressure mixing rules for an optimum two-parameter cubic equation of state. *Industrial & Engineering Chemistry Research*, 41(5), 931-937.
- Twu, C. H., Sim, W. D., & Tassone, V. (2002b). Getting a handle on advanced cubic equations of state. *Chemical engineering progress*, 98(11), 58-65.
- Tzirakis, F., Karakatsani, E., & Kontogeorgis, G. M. (2016). Evaluation of the cubic-plus-association equation of state for ternary, quaternary, and multicomponent systems in the presence of monoethylene glycol. *Industrial & Engineering Chemistry Research*, 55(43), 11371-11382.
- Vaferi, B., Lashkarbolooki, M., Esmaeili, H., & Shariati, A. (2018). Toward artificial intelligence-based modeling of vapor liquid equilibria of carbon dioxide and refrigerant binary systems. *Journal* of the Serbian Chemical Society, 83(2), 199-211.

- Wertheim, M. S. (1984). Fluids with highly directional attractive forces. I. Statistical thermodynamics. *Journal of statistical physics*, *35*(1-2), 19-34.
- Wong, D. S., & Sandler, S. I. (1984). Calculation of vapor-liquid-liquid equilibrium with cubic equations of state and a corresponding states principle. *Industrial & engineering chemistry fundamentals*, 23(3), 348-354.
- Wu, Y., Kowitz, C., Sun, S., & Salama, A. (2015). Speeding up the flash calculations in two-phase compositional flow simulations–The application of sparse grids. *Journal of Computational Physics*, 285, 88-99.
- Young, A. F., Magalhães, G. D., Pessoa, F. L., & Ahón, V. R. (2018). Vapor-liquid equilibrium of binary systems with EoS/GE models at low pressure: Revisiting the Heidemann-Kokal Mixing Rule. *Fluid Phase Equilibria*, 466, 89-102.
- Zarenezhad, B., & Aminian, A. (2011). Predicting the vapor-liquid equilibrium of carbon dioxide+ alkanol systems by using an artificial neural network. *Korean Journal of Chemical Engineering*, 28, 1286-1292.
- Zhang, K., & Zhang, H. (2022). Predicting solute descriptors for organic chemicals by a deep neural network (DNN) using basic chemical structures and a surrogate metric. *Environmental Science & Technology*, *56*(3), 2054-2064.
- Zhong, S., Zhang, K., Wang, D., & Zhang, H. (2021). Shedding light on "Black Box" machine learning models for predicting the reactivity of HO radicals toward organic compounds. *Chemical Engineering Journal*, 405, 126627.