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To cite this article: A Hamersztein and N Tzabar 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **502** 012091

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A hybrid analytical method for evaluating thermodynamic properties of mixtures by the Peng-Robinson equation of state

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Abstract. A new analytical hybrid method for calculating enthalpy difference in mixtures is presented in this paper. The method is based on the Peng-Robinson cubic equation of state (PR CEOS), it is a combination of two common enthalpy calculation methods, and it does not require any experimental data. The α function of the PR CEOS for every component is selected among several models. The new hybrid method results of 8 different mixtures are compared to data from the REFPROPTM database, and a satisfying agreement is obtained.

1. Introduction

Calculating thermodynamic properties, such as enthalpy, is important in planning and characterizing thermodynamic systems. An accurate enthalpy prediction model for mixtures is desired, to be implemented in numerical models of thermodynamic systems. The Peng-Robinson cubic equation of state (PR CEOS), is a dominant model for calculating phase equilibrium and real gas properties. According to Lopez-Echeverry et al. [2], since the model was published in 1976, it took some time for the model to gain popularity, and from 1985 to 2017 there are approximately 7 researches done every year to improve its accuracy. In the current research we propose a hybrid analytical method for calculating the enthalpy of mixtures, by using the PR CEOS.

2. Method

The PR CEOS is given by:

$$p = \frac{RT}{v-b} - \frac{a_{(T)}}{v(v+b)+b(v-b)} \quad (1)$$

$$a_{(T)} = 0.45724 \frac{R^2 T_c^2}{p_c} \alpha_{(T)} \quad (2)$$



$$b = 0.07780 \frac{RT_c}{p_c} \quad (3)$$

Where p is the pressure [Pa], R is the gas constant [$J \cdot kg^{-1} \cdot K^{-1}$], T is absolute temperature [K], and v is the specific volume [$m^3 \cdot kg^{-1}$]. The subscript c denotes the critical state. To improve the accuracy of mixture property predictions, the most suitable PR modifications for each component of the mixture is desired. Table 1 summarizes several α functions for the PR CEOS.

EOSs allow calculating the enthalpy of real substances by determining the departure enthalpy, which is the difference between a real gas and an ideal gas enthalpy:

$$H = H^* + H^{dep} \quad (4)$$

where H is the enthalpy, H^* is an ideal gas enthalpy, and H^{dep} is the departure enthalpy, all in [J].

The departure enthalpy is calculated by the PR model as folloes:

$$H^{dep} = RT(z - 1) + \frac{T \left(\frac{da}{dT} \right) - a}{2\sqrt{2}b} \ln \left(\frac{Z + (1 + \sqrt{2})B}{Z + (1 - \sqrt{2})B} \right) \quad (5)$$

where $Z = \frac{pv}{RT}$ and $B = \frac{bp}{RT}$. The enthalpy of mixtures is calculated by:

$$H^M = \sum_{i=1}^n (x_i H_i) + H^E \quad (6)$$

where x_i is the molar fraction of component i and H^M is the mixture enthalpy. H^E is the excess enthalpy of mixing which represents the enthalpy difference between the linear summation of the component enthalpies and the real mixture enthalpy, and it is experimentally obtained.

Table 1. α functions.

Author(s)	Year	α function	Ref.
Peng Robinson	1976 (original)	$\alpha = \left[1 + \kappa \left(1 - \sqrt{\frac{T}{T_c}} \right) \right]^2, \kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2$	[1]
Heyen	1983	$\alpha = \exp[H_1(1 - T_r^{H_2})]$	[3]
Stryjek & Vera (SV1)	1986	$\alpha = \left[1 + \kappa \left(1 - \sqrt{\frac{T}{T_c}} \right) \right]^2, \kappa = \kappa_0 + \kappa_1(1 + T_R^{0.5})(0.7 - T_R)$ $\kappa_0 = 0.378893 + 1.4897153\omega - 0.17131848\omega^2 + 0.0196554\omega^3$	[4]
Stryjek & Vera (SV2)	1986	$\alpha = \left[1 + \kappa(1 - T_R^{0.5}) \right]^2, \kappa = \kappa_0 + \kappa_1(1 + T_R^{0.5})(0.7 - T_R)$ $\kappa = \kappa_0 + [\kappa_1 + \kappa_2(\kappa_3 - T_R)(1 - T_R^{0.5})] \times (1 + T_R^{0.5})(0.7 - T_R)$	[5]
Melhem et al.	1989	$\alpha = \exp \left[m \left[1 - \frac{T}{T_c} \right] + n \left[1 - \sqrt{\frac{T}{T_c}} \right]^2 \right]$	[6]
Twu et al.	1994	$\alpha = T_r^{N(M-1)} \exp[L(1 - T_r^{NM})]$	[7]
Gasem	2001	$\alpha = \exp \left[\left(2 + 0.836 \frac{T}{T_c} \right) \left(1 - \left(\frac{T}{T_c} \right)^{G_3} \right) \right]$ $G_3 = 0.134 + 0.508\omega - 0.0467\omega^2$	[8]
Joshiyura	2009	$\alpha = \exp \left[J \left(1 - \frac{T}{T_c} \right) \right], J = 1.252\omega + 0.4754$	[9]

The objective of the current research is to obtain an analytical method for calculating enthalpy differences of mixtures, therefore, H^E isn't eliminated ($H^E = 0$), and H^M is calculated as a linear enthalpy combination (LEC) only.

To compensate for the inaccuracy of the LEC method, the suggested hybrid model combines an additional method for calculating mixture enthalpies which is based on the basic PR CEOS in equation 1. In this method the PR parameters of the mixture, a_m and b_m , are calculated by the pure component properties and a mixing rule. In the current research, the Van der Waals mixing rule is used [1]:

$$a_m = \sum_i^n \sum_j^n x_i x_j (1 - k_{ij}) (a_{ii} a_{jj})^{1/2} \quad (7)$$

$$b_m = \sum_i^n x_i b_i \quad (8)$$

In order to use the MR method for calculating the mixture properties at multiphase states, the fluid phase equilibrium has to be determined. That means, determining which phases exist, calculating the fraction of each phase, and calculating the property of each phase. This calculation is a complicated task, especially for multi-component mixture (with four components and more). We aim to find a method to overcome this complexity.

We therefore suggest a mathematical algorithm that combines the two methods (LEC and MR) for determining mixture enthalpies, by a simple calculation procedure and avoiding any experimental data. The suggested hybrid model is a nonphysical mathematical model, which improves the LEC predictions by combining the MR model results. The algorithm is based on several rules which were found repetitive among the vast majority of the mixtures which we examined. By a comparison to the REFPROPTM database and other data from the literature [10], an optimal α function for each component is determined, both for enthalpies and saturation pressures.

3. Results and discussions

In the current research we are interested in enthalpy differences, which are calculated for a pressure change at a constant temperature. Therefore, the ideal gas enthalpy is constant and the enthalpy difference equals the departure enthalpy difference.

Eight mixtures are tested in 2 sets of pressures, 0.1-8 and 0.1-12 [MPa]. A few of the enthalpy results which are generated by the hybrid model are shown in figures 1 to 3, together with the LEC, MR and REFPROPTM results. In addition, the deviations of the hybrid method are presented in dashed lines, where the deviation is calculated as follows:

$$dev = 100 \cdot \frac{X_{ref} - X_{PR}}{X_{ref}} \quad (9)$$

where X_{ref} is the property at the reference source and X_{PR} is the property calculated by the PR CEOS.

Figure 1 refers to a ternary mixture of Ar, C₂H₆, and C₃H₈, with molar fractions of 0.3, 0.4, and 0.3, respectively, and pressures of 8 and 0.1 MPa. Figure 2 shows the results of another ternary mixture of N₂, C₂H₆, and iC₄H₁₀ with molar fractions of 0.3, 0.4, and 0.3 iC₄H₁₀, respectively, and pressures of 12 and 0.1 MPa. Figure 3 shows the results of an equal molar quadrinary mixture of N₂, CH₄, C₂H₆, and iC₄H₁₀, and pressures of 12 and 0.1 MPa. The results that are presented in the three figures shows the benefit of using the suggested hybrid method, rather than using the LEC nor the MR methods, solely.

The hybrid model is found to be most advantageous at pressures above the critical pressures of the components. In cases where the pressure of the mixture is lower than the critical pressures of the components, the method fails to determine the temperature ranges where vapor-liquid equilibria is occurred and large deviations are obtained. In addition, for binary mixtures, the advantage of using the hybrid method relative to using the LEC and MR methods is questionable.

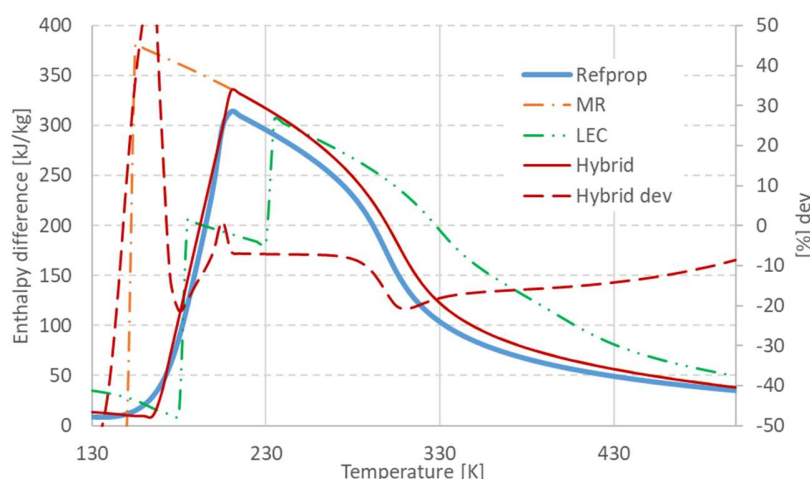


Figure 1. Enthalpy difference of 0.3Ar+0.4C₂H₆+0.3C₃H₈, between pressures of 0.1 and 8 [MPa].

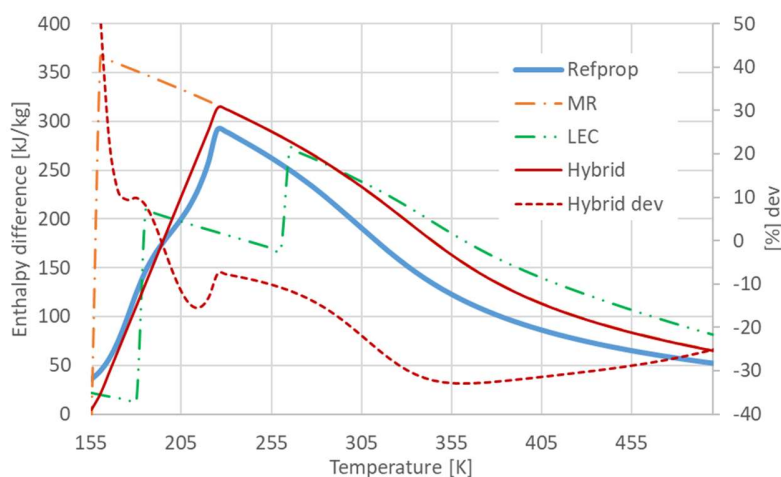


Figure 2. Enthalpy difference of 0.3N₂+0.4C₂H₆+0.3iC₄H₁₀, between pressures of 0.1 and 12 [MPa].

4. Conclusions

A new hybrid model, based on a nonphysical mathematical algorithm, for calculating departure enthalpies of gas mixtures is suggested. The hybrid model doesn't require any experimental data, therefore it is suitable for investigating a variety of mixtures and can be easily incorporated in numerical codes and thermodynamic

simulations. This model shows a significant increase in the accuracy of enthalpy calculations relative to the MR and LEC methods, especially at pressures above the critical pressures of the pure components.

In this research, 6 components are used to define 8 ternary and quaternary mixtures, and more compounds can be added to the model. In future work, the new hybrid models shall be improved in different manners, by incorporating different mixing rules, using different fitting parameters, and more.

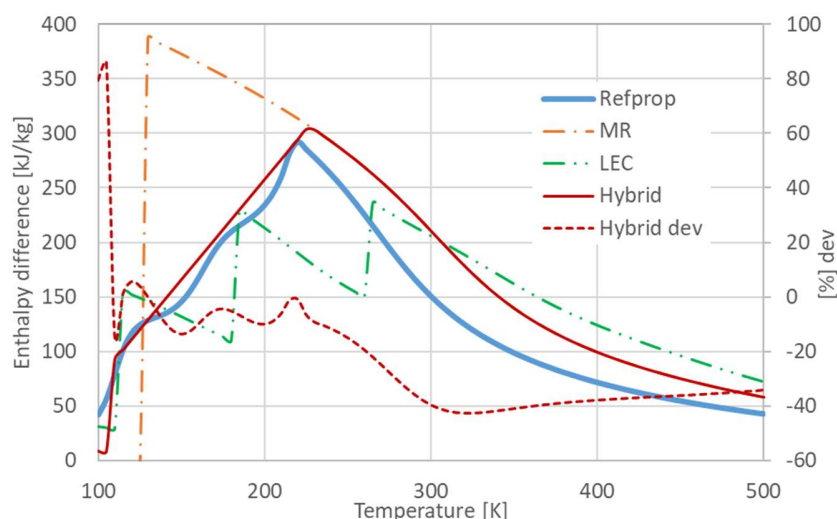


Figure 3. Enthalpy difference of $0.25\text{N}_2+0.25\text{CH}_4+0.25\text{C}_2\text{H}_6+0.25\text{iC}_4\text{H}_{10}$, between pressures of 0.1 and 12 [MPa].

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