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CHPR 4404 – Advanced Thermodynamics

Tutorial 4 – The Virial Equation of State

This tutorial follows through multiple aspects of one example; problems should be completed sequentially in Microsoft Excel. In this tutorial, we'll use the virial equation of state for a system with 75 mol% methane and 25 mol% propane. Each component's critical properties, molecular weight, and acentric factor will be required for future calculations; you can obtain this information from your textbook or established online references (e.g., the NIST Chemical Webbook).

1. Use the Lee-Kesler relationship (*AIChE J., 1975* - shown below) to calculate the second virial coefficients (B_{ii}, B_{ij}, B_{jj}) for the methane-propane mixture at 116 °F and 870 psia. For the mixed case, you will need to utilise the mixture critical properties. T_r is reduced temperature.

$$\frac{B_{ij}P_c}{RT_c} = 0.1181 - \frac{0.2657}{T_r} - \frac{0.1548}{T_r^2} - \frac{0.0303}{T_r^3}$$

2. Using these results, calculate the B_{mix} parameter (presented in the lectures) for the same conditions. Use the simplified relationship below to calculate the mixture density at 116 °F and 870 psia (hint: be sure to check your units carefully). You will need to solve the problem iteratively, using a numerical technique.

$$Z = 1 + B_{mix}\rho$$

3. Using the solution method in Problem 2, calculate this same mixture density at 870 psia over a range of temperatures (116 to 530 °F). Plot the resultant density as a function of reduced temperature, and compare the results to Multiflash. In what temperature region is there a better agreement between this simple model and Multiflash? Based on the lecture discussions, what physical explanation can you provide for this behaviour?

4. In seeking a better agreement with Multiflash at lower temperatures, we consider including the third virial coefficient (C_{ijk}) in our calculations. We'll use one predictive model for these calculations (shown below), from Orbey and Vera (*AIChE J., 1983*). Use this model to calculate the third virial coefficients for this mixture (C_{111}, C_{112}, C_{122}, C_{222}) at 116 °F and 870 psia. Calculate the mixture coefficient (C_{mix}) presented in the lecture.

$$f^{(0)} = 0.01407 + \frac{0.02432}{T_r^{2.8}} - \frac{0.00313}{T_r^{10.5}}$$

$$f^{(1)} = -0.02676 + \frac{0.01770}{T_r^{2.8}} + \frac{0.040}{T_r^{3.0}} - \frac{0.003}{T_r^{6.0}} - \frac{0.00228}{T_r^{10.5}}$$

$$\frac{CP_c^2}{(RT_c)^2} = f^{(0)} + \omega f^{(1)}$$

5. Using both the second and third virial coefficients, estimate the density of the mixture at 870 psia over a range of temperatures (116 to 530 °F). Compare the results with both the earlier results (using only the second virial coefficient) and Multiflash. On the reduced temperature scale, what regions yield the greatest improvement? Based on the physical meaning of the third virial coefficient, what physical insight can you draw from this result about the state of the molecules at lower temperatures?

$$Z = 1 + B_{mix}\rho + C_{mix}\rho^2$$

Helpful equations:

$$Z_i^c = 0.2905 - 0.085\omega_i$$

$$V_i^c = Z_i^c R\, T_i^c / P_i^c$$

$$\omega_{ij} = 0.5 \cdot (\omega_i + \omega_j)$$

$$V_{ij}^c = \left[(V_i^c)^{1/3} + \left(V_j^c\right)^{1/3} \right]^3 / 8$$

$$T_{ij}^c = \left(T_i^c T_j^c\right)^{0.5}$$

$$C_{ijk} = (C_{ij} C_{ik} C_{jk})^{1/3}$$