

Problems: cubic equations of state (pure substances)

You will need to use the JavaScript program on “solving cubic equations of state (pure substances)” at www.cheng.cam.ac.uk/~pjb10/thermo to do these problems.

1. Write down the Redlich-Kwong equation of state. What is the physical significance of the parameters a and b ? How are values of a and b obtained in practice? Use the program to obtain solutions to the cubic equation for the molar volumes of n -hexane at 1 bar and 298 K. Manually check that the web site program gives the correct answers.

2. Use the different cubic equations of state on the web site to predict the density for (a) liquid n -hexane, (b) liquid benzene, and (c) liquid water, at 1 bar and 298 K. Comment on the differences between your answers and the actual values (659, 885 and 998 kg/m³ respectively).

3. The fugacity coefficient, ϕ , of a pure fluid is defined by $RT \ln \phi = \underline{G} - \underline{G}^{IG}$. By recognizing that all fluids behave as ideal gases at very low pressures, show that:

$$(a) \ln \phi = \frac{1}{RT} \int_0^P \left(\underline{V} - \frac{RT}{P} \right) dP$$

$$(b) \ln \phi = \int_0^P \left(\frac{Z-1}{P} \right) dP \quad \text{where } Z \text{ is the compressibility factor, } PV/RT.$$

$$(c) \ln \phi = \int_0^\rho \frac{Z-1}{\rho} d\rho + (Z-1) - \ln Z \quad \text{where } \rho \text{ is the molar density } (=1/\underline{V}).$$

(Hint: note that $P = ZRT\rho$ implies $dP = ZRTd\rho + RT\rho dZ$)

4. Write down the Redlich-Kwong equation in the form $Z = f(\rho)$. Hence show that it predicts:

$$\ln \phi = (Z-1) - \ln(Z-B) - \frac{A}{B} \ln \left(1 + \frac{B}{Z} \right) \quad \text{where } A = \frac{aP}{R^2 T^{2.5}} \text{ and } B = \frac{bP}{RT}.$$

Use the web site program to obtain values of ϕ for n -hexane at 1 bar and 298 K. Manually check that the web site program gives the correct answers.

5. Explain why if pure liquid and pure vapour are in equilibrium with each other, then it is a requirement that $\phi^{\text{liq}} = \phi^{\text{vap}}$.
6. Use the different cubic equations of state to predict the boiling point at 1 bar of (a) oxygen, (b) *n*-hexane, (c) benzene, and (d) water. Comment on the differences between your answers and the actual values (90.1, 341.8, 353.2 and 373.1 K respectively).
7. Explain how the enthalpy departure functions can be used to predict the enthalpy of vaporization for a fluid at its boiling point. Use the Peng-Robinson equation to predict the enthalpy of vaporization for (a) oxygen, (b) *n*-hexane, (c) benzene, and (d) water, at their predicted boiling point at 1 bar. Comment on the differences between your answers and the actual values (6.82, 28.87, 30.78 and 40.68 kJ/mol respectively).
8. Which equation of state would you recommend be used for predicting thermodynamic properties in the following situations? Explain your reasoning.
 - (a) carbon dioxide at 500 K, 0.1 bar
 - (b) *n*-hexane at 300 K, 10 bar
 - (c) nitrogen at 500 K, 1000 bar
 - (d) *n*-eicosane (C₂₀H₄₂) at 500 K, 50 bar
 - (e) ethanol at 500 K, 60 bar
 - (f) ethanol at 100 K, 1 bar

(Thermodynamic data can be looked up if desired in textbooks or Perry's Chemical Engineers' Handbook)