

Quiz 3: Thermodynamic property calculation for oxygen [Due for submission at 5 pm September 30, 2022]

The Peng-Robinson equation of state is

$$P = \frac{RT}{V - b} - \frac{a(T)}{V(V + b) + b(V - b)} \quad \text{where}$$

$$a(T) = 0.45724 \frac{R^2 T_c^2}{P_c} \left[1 + \kappa \left(1 - \sqrt{\frac{T}{T_c}} \right) \right]^2 \quad b = 0.0778 \frac{RT_c}{P_c}$$

For oxygen

$$\kappa = 0.4069$$

$$T_c = 154.6 \text{ K}$$

$$P_c = 5.046 \text{ MPa}$$

This EOS can be written in a cubic polynomial form as

$$Z^3 + \alpha Z^2 + \beta Z + \gamma = 0$$

where

$$\alpha = B - 1$$

$$A = aP/(RT)^2$$

$$\beta = A - 3B^2 - 2B$$

$$B = bP/RT$$

$$\gamma = B^3 + B^2 - AB$$

$$Z = PV/RT.$$

(a) Find the vapor pressure $P_{vap}(T)$ at temperatures $T = -125, -150$ and -175 °C.

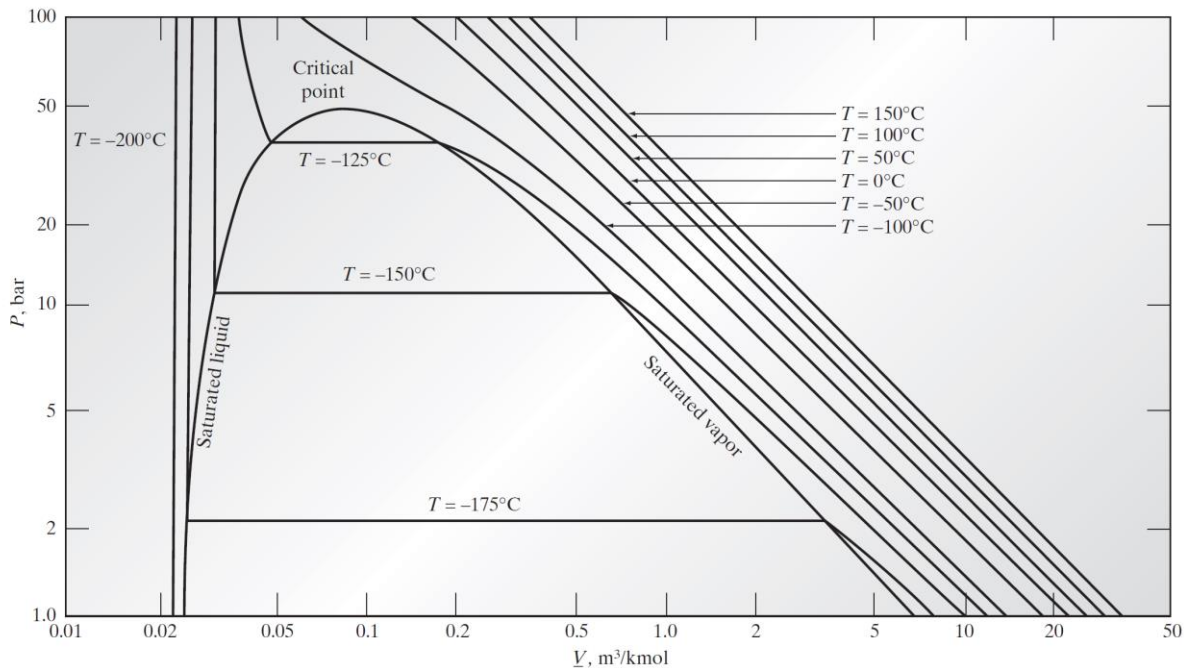


Figure 6.4-3 Pressure-volume diagram for oxygen calculated using the Peng-Robinson equation of state.

Hint: To find the vapor pressure you require T and a guess value of P . Figure 6.4-3 can be used to obtain a guess value. Solve for Z^L and Z^V using the cubic equation $Z^3 + \alpha Z^2 + \beta Z + \gamma = 0$. We shall employ fugacity. For vapor, calculate the vapor fugacity f^V with the help of

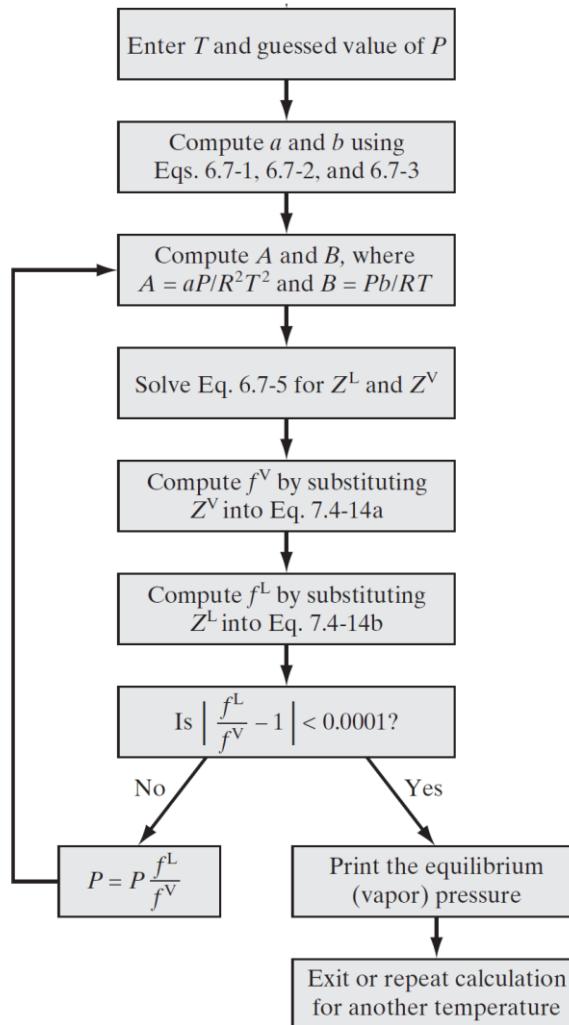
$$\ln \frac{f^V}{P} = (Z^V - 1) - \ln(Z^V - B) - \frac{A}{2\sqrt{2}B} \ln \left[\frac{Z^V + (1 + \sqrt{2})B}{Z^V + (1 - \sqrt{2})B} \right].$$

For liquid, calculate the liquid fugacity f^L with the help of

$$\ln \frac{f^L}{P} = (Z^L - 1) - \ln(Z^L - B) - \frac{A}{2\sqrt{2}B} \ln \left[\frac{Z^L + (1 + \sqrt{2})B}{Z^L + (1 - \sqrt{2})B} \right].$$

Recall that A and B depend on T and P . Therefore, they have to be calculated each time for a new value of T and P .

For vapor-liquid coexistence we require $f^V(T, P) = f^L(T, P)$. Therefore, check whether $\left| \frac{f^L}{f^V} - 1 \right| < 0.0001$. If so, then you can stop – you have a solution for P_{vap} at the selected temperature. Otherwise, set $P = P \frac{f^L}{f^V}$. The flowchart below will help:



(b) Plot the isotherm $P - \underline{V}$ curve at temperatures $T = -125, -150$ and -175 °C as shown in Figure 6.4-3 (page 1).

(c) Make a plot for P_{vap} versus T for the vapor-liquid coexistence. Choose temperatures $T = -125, -130, -140, -150, -160, -170, -175, -180$ and -183 °C.

(d) Fit a polynomial curve to P_{vap} versus T . Make sure that the polynomial curve fits your data well. Recall that according to the **Clapeyron equation**

$$\frac{dP_{vap}}{dT} = \frac{\Delta \underline{S}}{\Delta \underline{V}} = \frac{\Delta \underline{H}}{T \Delta \underline{V}}.$$

Calculate $\Delta H = H^V - H^L$, $\Delta S = S^V - S^L$ and $\Delta V = V^V - V^L$ from the information you have collected so far. For this you can also fit a curve through $\Delta V(T)$.

Compare your value of ΔH to the value given in the figure below:

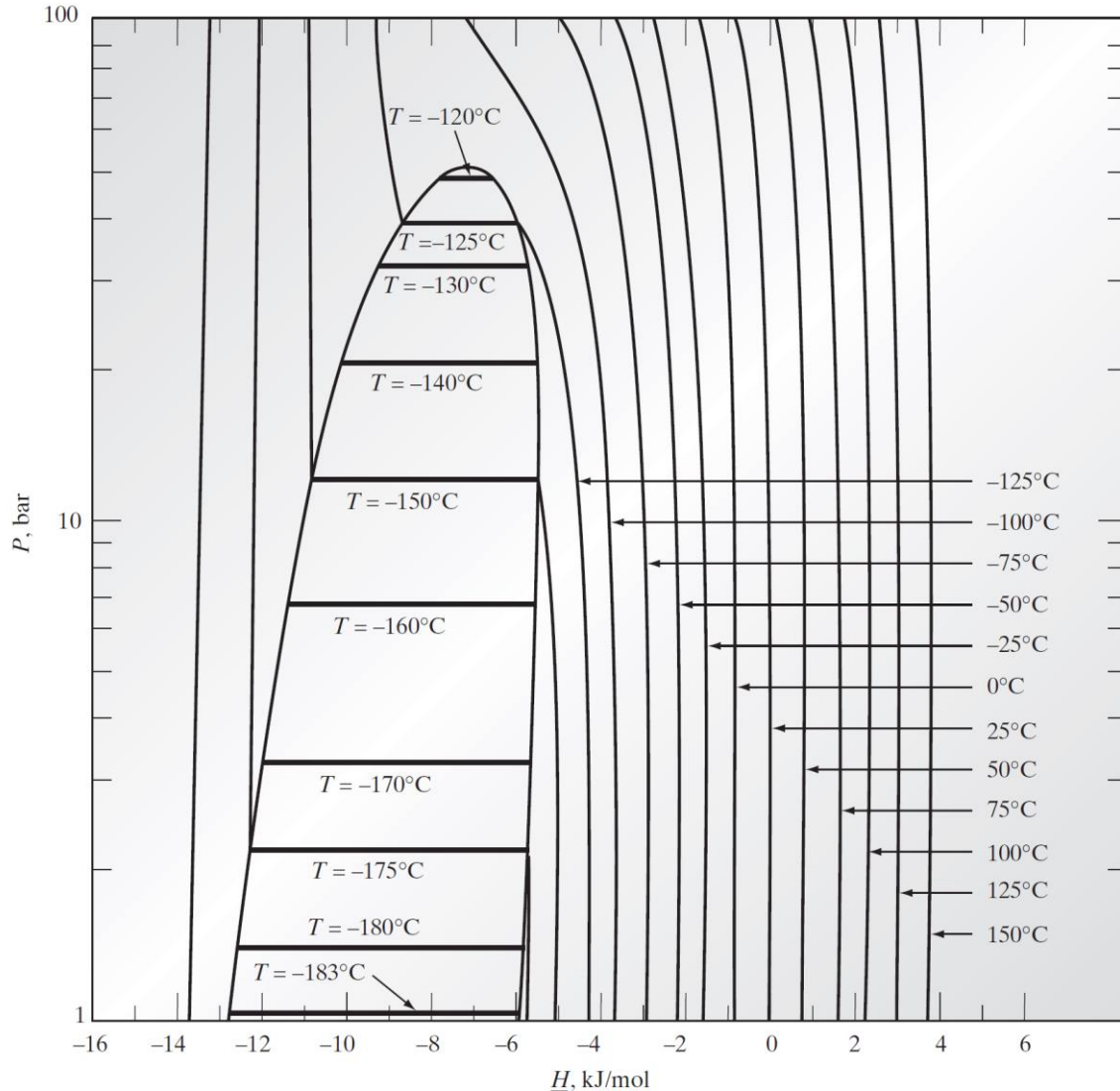


Figure 6.4-4 Pressure-enthalpy diagram for oxygen calculated using the Peng-Robinson equation of state.

Note that in general the pressure where the transition happens from one phase to another is also called **saturation pressure** $P^{sat}(T)$. For vapor-liquid equilibrium (VLE) $P^{sat}(T) \equiv P^{vap}(T)$.

(e) Plot ΔH and ΔS as a function of temperature.

(f) Enthalpy calculations:

Choose $H^{IG}(T = 25^\circ\text{C}, P = 1 \text{ bar}) = 0$. **IG implies ideal gas.** This sets our reference state. Now calculate enthalpy as

$$H(T, P) - H^{IG}(T = 25^\circ\text{C}, P = 1 \text{ bar}) = \{H(T, P) - H^{IG}(T, P)\} + \{H^{IG}(T, P) - H^{IG}(T = 25^\circ\text{C}, P = 1 \text{ bar})\}$$

Here $H^{IG}(T = 25^\circ\text{C}, P = 1 \text{ bar})$ has a value zero therefore it has been struck through.

For Peng-Robinson equation, the departure function for enthalpy or residual enthalpy

$$\underline{H}(T, P) - \underline{H}^{IG}(T, P) = RT(Z - 1) + \frac{T \left(\frac{da}{dT} \right) - a}{2\sqrt{2}b} \ln \left[\frac{Z + (1 + \sqrt{2})B}{Z + (1 - \sqrt{2})B} \right].$$

Also

$$\underline{H}^{IG}(T, P) - \underline{H}^{IG}(T = 25^\circ\text{C}, P = 1 \text{ bar}) = \int_{T=298.15 \text{ K}}^T C_p^* dT$$

where

$$C_p^* = 25.46 + 1.519 \times 10^{-2}T - 0.7151 \times 10^{-5}T^2 + 1.311 \times 10^{-9}T^3 \left(\frac{\text{J}}{\text{mol} \cdot \text{K}} \right)$$

for oxygen and T is in K.

Obtain the pressure-enthalpy along the isotherm as shown in Figure 6.4-4 in page 3.

(g) Entropy calculations:

Choose $\underline{S}^{IG}(T = 25^\circ\text{C}, P = 1 \text{ bar}) = 0$. **IG implies ideal gas.** This sets our reference state. Now calculate entropy as

$$\underline{S}(T, P) - \underline{S}^{IG}(T = 25^\circ\text{C}, P = 1 \text{ bar}) = \{ \underline{S}(T, P) - \underline{S}^{IG}(T, P) \} + \{ \underline{S}^{IG}(T, P) - \underline{S}^{IG}(T = 25^\circ\text{C}, P = 1 \text{ bar}) \}$$

Here $\underline{S}^{IG}(T = 25^\circ\text{C}, P = 1 \text{ bar})$ has a value zero therefore it has been struck through.

For Peng-Robinson equation, the departure function for entropy or the residual entropy

$$\underline{S}(T, P) - \underline{S}^{IG}(T, P) = R \ln(Z - B) + \frac{\frac{da}{dT}}{2\sqrt{2}b} \ln \left[\frac{Z + (1 + \sqrt{2})B}{Z + (1 - \sqrt{2})B} \right].$$

Also

$$\underline{S}^{IG}(T, P) - \underline{S}^{IG}(T = 25^\circ\text{C}, P = 1 \text{ bar}) = \int_{T=298.15 \text{ K}}^T \frac{C_p^*}{T} dT - R \ln \left(\frac{P}{1 \text{ bar}} \right).$$

Obtain the pressure-entropy along the isotherm.

OPTIONAL

(h) Obtain the T-S diagram for oxygen at the pressures shown

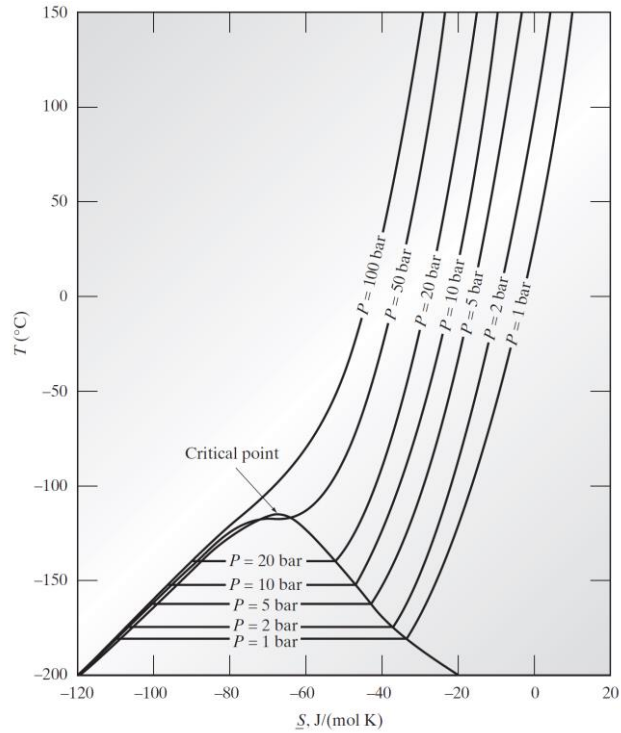


Figure 6.4-5 Temperature-entropy diagram for oxygen calculated using the Peng-Robinson equation of state.

(i) For conditions that do not involve the two-phase region obtain the following plot for Z versus P_r .

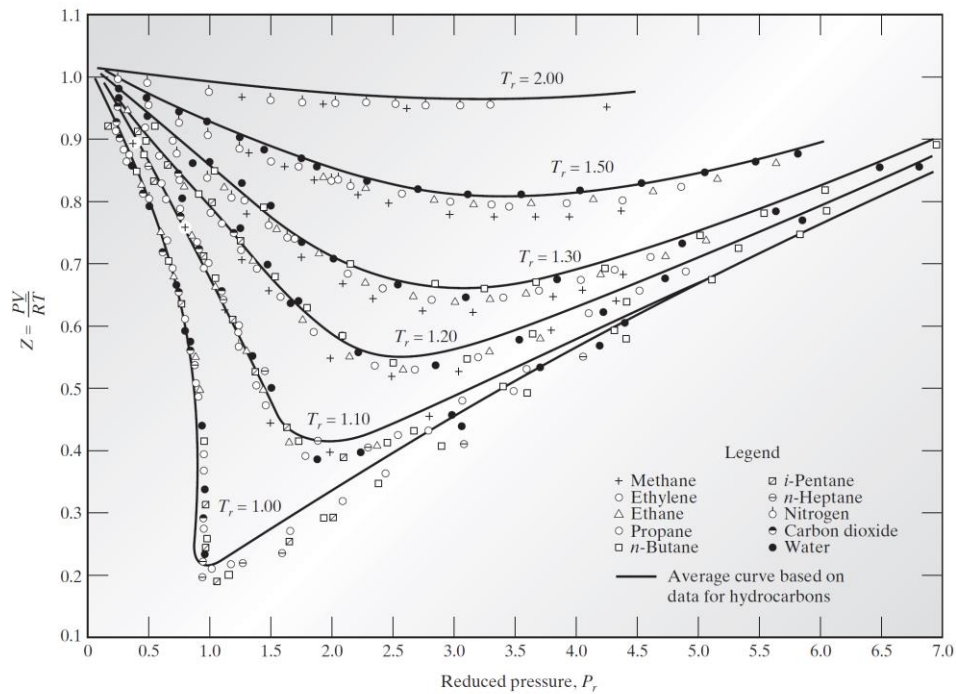


Figure 6.6-2 Compressibility factors for different fluids as a function of the reduced temperature and pressure. [Reprinted with permission from G.-J. Su, *Ind. Eng. Chem.* **38**, 803 (1946). Copyright American Chemical Society.]