Chapter 8

Phase Equilibrium in a Pure Fluid
Example. Pressure in a Variable Volume Cylinder

A piston-cylinder contains some propane liquid and some vapor at -12°C. The piston is forced down a specified distance and the pressure is increased. The vessel is allowed to cool back to its original temperature. What is the final pressure in this vessel?

Solution This is a trick question. If there is still vapor left, then the pressure will go back to where it started. If not, then we are compressing a liquid and the pressure could become quite high. We would need to compute how high based on an equation of state. First, let’s examine the case of no change in pressure. Since the temperature and pressure from beginning to end are constant, the change in Gibbs energy of the system from beginning to end must be zero.

For the whole system \( G = M_L G_L + M_V G_V \) \( \Rightarrow dG = M_L dG_L + M_V dG_V + G_L dM_L + G_V dM_V \)

Since \( T \) and \( p \) are constant, \( dG_L = dG_V = 0 \). But \( dM_L = -dM_V \Rightarrow 0 = G_L - G_V \) or \( G_L = G_V \). This is a very significant result! If the pressure comes back to the original pressure then \( G_L = G_V \).

If \( G_L \neq G_V \), then the pressure does not come back to the original pressure. But we know that when the pressure does not come back it must be because there is only liquid. In other words, \( G_L = G_V \) is a constraint for phase equilibrium. If we specify one more constraint (eg. \( T \)), then all of our other state properties can be calculated.
The Clausius-Clapeyron Equation:

If starting from VLE, and maintaining VLE while changing $T$, $dG^V = dG^L$

Fundamental property relation $\Rightarrow V^V dP_{sat}^{sat} - S^V dT = V^L dP_{sat}^{sat} - S^L dT$

By definition of $G$: $G^V = H^V - TS^V = H^L - TS^L = G^L$

$\Rightarrow S^V - S^L = (H^V - H^L)/T$

\[
\frac{dP_{vap}^{vap}}{p_{vap}^{vap}} = \frac{(H^V - H^L) dT}{T(p_{vap}^{vap} V^V - p_{vap}^{vap} V^L)(1/RT)} = \frac{(H^V - H^L) dT}{RT^2(Z^V - Z^L)}
\]

Clausius-Clapeyron Equation

Dividing by $P_{sat}^{sat}$ $\Rightarrow$

\[
\frac{dP_{sat}}{P_{sat}^{sat}} = \frac{(H^V - H^L) dT}{T(P_{sat}^{sat} V^V - P_{sat}^{sat} V^L)(1/RT)} = \frac{(H^V - H^L) dT}{RT^2(Z^V - Z^L)}
\]

\[
\frac{dP_{sat}}{P_{sat}^{sat}} = d\ln P_{sat}^{sat}; d\left(\frac{1}{T}\right) = -\frac{dT}{T^2} \Rightarrow d\ln P_{sat}^{sat} = -\frac{(H^V - H^L)}{R(Z^V - Z^L)} d\left(1/T\right)
\]
Example. Clausius-Clapeyron near or below the boiling point

What is the value of the pressure in a piston-cylinder at -12°C with vapor and liquid propane present? Recall that $Z^V \approx 1$ and $Z^L \approx 0$ and $(H^V - H^L) \approx$ constant. Integrate

$$
\ln \left( \frac{P_{\text{sat}}}{1 \text{ atm}} \right) = - \frac{(H^V - H^L)}{R} \left[ \frac{1}{T} - \frac{1}{T_b} \right]
$$

For propane, $\omega = 0.152 \Rightarrow \left( P_{\text{sat}} \bigg|_{T_r=0.7} \right) = P_c \times 10^{[-(1+0.152) \times 10]} = 3.034 \text{ atm.}$

at $T_r=0.7 \Rightarrow T = 259 \text{ K}$ The CRC lists the boiling temperature of propane as -42°C=231K.

$\ln(3.034/1) = - \Delta H/R (1/259 - 1/231) \Rightarrow -\Delta H/R = -2372$

Therefore, $P_{\text{sat}}^{\text{sat}} (261 \text{ K}) = \exp[-2372(1/261 - 1/231)] = 3.277 \text{ atm.}$
Short-cut Estimation of Saturation Properties

If \( \Delta H_{vap}/\Delta Z_{vap} \) was constant, then we could recover the simple low-\( P \) form. To find out, plot \( \ln(P_{sat}) \) vs. \( 1/T \). A straight line means the slope is constant.

\[
\ln \left( \frac{P_{vap}}{P_{ref}} \right) = -\frac{\Delta H}{R\Delta Z} \left( \frac{1}{T} - \frac{1}{T_{ref}} \right)
\]

Setting \( P_{ref} = P_c \) and \( T_{ref} = T_c \),

\[
\ln P_r^{sat} = -\frac{\Delta H}{R\Delta Z T_c} \left( \frac{T_c}{T} - \frac{T_c}{T_c} \right) = \frac{\Delta H}{2.303 R\Delta Z T_c} \left( 1 - \frac{1}{Tr} \right) \Rightarrow \log(P_r^{sat}) = \frac{1}{2.303} \frac{\Delta H}{R\Delta Z} \left( 1 - \frac{1}{Tr} \right) = A \left( 1 - \frac{1}{Tr} \right)
\]

@ \( T_r = 0.7 \) \( \log_{10} P_r^{sat} \equiv -(\omega + 1) = A \left( \frac{1}{.7} - 1 \right) = A(-3/7) \Rightarrow A = \frac{7}{3}(1+\omega)
\]

\[
\therefore \log_{10}(P_r^{sat}) = \frac{7}{3}(1+\omega)\left(1 - \frac{1}{Tr} \right) \quad \text{SHORT-CUT VAPOR PRESSURE EQUATION}
\]

e.g. For propane \( P^{sat} (-12^\circ C) = P_c \times 10^{** \frac{7}{3}(1+\omega)\left(1 - \frac{1}{0.7057} \right)} = 3.26 \text{ atm} \)
Example. General Application of the Clausius-Clapeyron equation.

Liquid butane is pumped to a vaporizer as a saturated liquid under a pressure of 1.88 MPa. The butane leaves the exchanger as a wet vapor of 90 percent quality and at practically the same pressure as it entered. From the following information, estimate the heat load on the vaporizer per gram of butane entering.

\( T_c = 425.2 \, \text{K}; \quad P_c = 3.797 \, \text{MPa}; \quad \omega = 0.193; \)

Solution: Use VP eqn. to find the \( T \) at which this takes place \( \Rightarrow T_{sat} = 383 \, \text{K} \)

\[
\text{PREOS} \Rightarrow \left( \frac{H^v - H^g}{nRT} \right) = -0.9952; \quad \left( \frac{H^L - H^g}{nRT} \right) = -5.2567;
\]

Therefore, \( H_v = (-0.9952 + 5.2567) \times 8.314 \times 383 = 13568 \, \text{J/mol} \)

90% quality \( \Rightarrow Q = 0.9 \times 13568 = 12211 \, \text{J/mol} \times \frac{1 \, \text{mol}}{58 \, \text{g}} = 211 \, \text{J/g} \)

Note:

Alternatively, we could have used the short-cut Clausius-Clapeyron another way

\[
\text{Clausius-Clapeyron} \Rightarrow \ln(P_{sat}) = -\Delta H_{vap}/RT(Z_V - Z_L) + B
\]

\[
\frac{\Delta H_{vap}}{R \Delta Z} = 2.3025 \times \frac{7}{3} (1 + \omega) T_c = 2726
\]

\[
\Delta H_{vap} = 2726 \times R \times (Z_V - Z_L) = 2726 \times 8.314 \times (0.67434 - 0.07854) = 13503 \, \text{J/mol}
\]
II. Generalized Fluid Properties

Overview of UNIT II.

1. Calculus of State Functions
   a) FPR
   b) Maxwell’s Relations
   c) \( P = P(T,V) \Rightarrow dU(T,V), dS(T,V) \Rightarrow dH(T,P), dS(T,P) \)

2. Equations of state: e.g. \( P = RT/(V-b) - a/V^2RT \)

3. Departure Functions: e.g. \( (U-U^{\text{ig}})/RT = \int -T(\partial Z/\partial T)d\rho/\rho \)
   e.g. \( (U-U^{\text{ig}})/RT = -a\rho/RT = -aP/ZR^2T^2 \)

4. Phase Equilibrium in a Pure Fluid:
   e.g. VLE \( \Rightarrow \log (P^{\text{sat}}/P) = 7/3(1+\omega)(1-1/T_r) \)