Example 6.8 Estimate V, U, H, and S for 1-butene vapor at 200°C and 70 bar if H and S are set equal to zero for saturated liquid at 0°C. Assume that the only data available are

$$T_c = 420.0\ \text{K} \qquad P_c = 40.43\ \text{bar} \qquad \omega = 0.191$$

$$T_n = 266.9\ \text{K} \qquad \text{(normal boiling point)}$$

$$C_P^{ig}/R = 1.967 + 31.630 \times 10^{-3}T - 9.837 \times 10^{-6}T^2 \qquad (T/\text{K})$$

$$V = \frac{ZRT}{P}$$

$$Z = Z^0 + \omega Z^1$$

$$T_r = \frac{T}{T_c} = \frac{200 + 273.15}{420} = 1.127$$

$$P_r = \frac{70}{40.43} = 1.731$$

$$Z = 0.485 + (0.191)(0.142) = 0.512 \qquad \text{see App. E}$$

$$\Rightarrow V = \frac{(0.512)(83.14)(473.15)}{70} = 287.8\ \frac{\text{cm}^3}{\text{mol}}$$

To find H and S, we need to construct a process path as follows:

$$\Rightarrow \frac{S_1^R}{R} = -0.07745 + 0.191\,(-0.1947)$$

$$= -0.1146$$

$$\Rightarrow S_1^R = -0.9527 \ \frac{J}{mol \cdot K}$$

step (c)

$$\Delta H^{ig} = \int_{273.15}^{473.15} C_p^{ig}\, dT = 20564 \ \frac{J}{mol}$$

$$\Delta S^{ig} = \int_{273.15}^{473.15} C_p^{ig}\, \frac{dT}{T} - R \ln \frac{70}{1.2771}$$

$$= 22.18 \ \frac{J}{mol \cdot K}.$$

step (d)

$$T_r = \frac{473.15}{420} \qquad P_r = \frac{70}{40.43}$$

$$= 1.13 \qquad = 1.73$$

similar to step (b)

$$H_2^R = -8010 \ J/mol$$

$$S_2^R = -14.18 \ J/(mol \cdot K)$$

Step (6)

$$\frac{H_1^R}{RT_c} = \frac{(H_1^R)^0}{RT_c} + \omega \frac{(H_1^R)^{(1)}}{RT_c}$$

$T_r = 0.65$ & $P_r = 0.032$

$\Rightarrow$ from E.5 and E.6

$$\frac{(H_1^R)^0}{RT_c} = -0.07525$$

$$\frac{(H_1^R)^1}{RT_c} = -0.1561$$

$$\Rightarrow \frac{H_1^R}{RT_c} = -0.07526 + 0.191(-0.1561)$$

$$= -0.105$$

$$\Rightarrow H_1^R = -0.105 * 8.314 * 420 = -366.9 \, \frac{J}{mol}$$

similarly $\frac{(S_1^R)^0}{R} = -0.07745$ $\quad \frac{(S_1^R)^1}{R} =$

-0.1947

$$\Rightarrow \frac{dP^{sat}}{dT} = \frac{\Delta H}{16912.7\,T} \Rightarrow \Delta H^{lv} = 16912.7\,T\,\frac{dP}{dT}$$

$$\ln\left(P^{sat}\right) = A - \frac{B}{T}$$

$$\Rightarrow P^{sat} = A' e^{-\frac{B}{T}} \qquad \left(A' = e^{A}\right)$$

$$\frac{dP^{sat}}{dT} = A' e^{-\frac{B}{T}} \frac{B}{T^2} \qquad \left(* \; 16912.7\,T\right)$$

$$16912.7\,T \frac{dP^{sat}}{dT} = 16912.7\; A' e^{-\frac{B}{T}} \frac{B}{T}$$

$$\Rightarrow \Delta H^{lv} = 16912.7\; A' e^{-\frac{B}{T}} \frac{B}{T} \qquad \left(T = 273.15\,K\right)$$

$$= 16912.7\; e^{10.126}\; e^{\frac{-2699.11}{273.15}}\; \frac{2699.11}{273.15}$$

$$= 213426 \left(\frac{cm^3 * bar}{mol}\right) \frac{m^3}{10^6\,cm^3} \; \frac{1.033\,\frac{N}{m^2}\,10^5}{1.0133}$$

$$\Delta H^{lv} = 21342.6 \left(\frac{J}{mol}\right) \longleftarrow \text{different from value in book.}$$

$$\Delta S^{lv} = \frac{\Delta H^{lv}}{\underset{\substack{\uparrow \\ 273.15\,K}}{T}} = 78.135 \left(\frac{J}{mol\;K}\right)$$

To find ΔH^{lv}, recall:

$$\frac{dP^{sat}}{dT} = \frac{\Delta H^{lv}}{T\,\Delta V^{lv}}$$

$$\Delta V^{lv} \approx V^{v} = \frac{ZRT}{P}$$

$T = 273.15\ K$

$P = 1.2771\ bar$

$R = 83.14 \left(\frac{bar\ cm^3}{K\ mol}\right)$

$Z = Z^0 + \omega Z^1 = Z^0 + (0.191)\,Z^1$

$T_r = \frac{273.15}{420} = 0.65$

$P_r = \frac{1.2771}{40.43} = 0.032$

Interpolate $Z^0 \Rightarrow \frac{Z^0 - 0.9377}{0.9881 - 0.9377} = \boxed{\frac{0.032 - 0.05}{0.01 - 0.05}}$

$\Rightarrow Z^0 = 0.9604$

similarly $\Rightarrow \frac{Z^1 - (-0.0772)}{-0.0137 - (-0.0772)} =$

$\Rightarrow Z^1 = -0.0486$

$\Rightarrow \quad Z = 0.9511 \quad \Rightarrow V^{v} = 16912.7\ \frac{cm^3}{mol}$

$= 0.0169\ \frac{m^3}{mol}$

step (a) First we need to find the vapor pressure of butene at 0°C. The following equation is applicable:

$$\ln(P^{sat}) = A - \frac{B}{T}$$

Constants A & B are unknowns, however, we have two data points to evaluate them:

1. at normal boiling point $\boxed{T_n}$, $P^{sat} = P_{atm}$

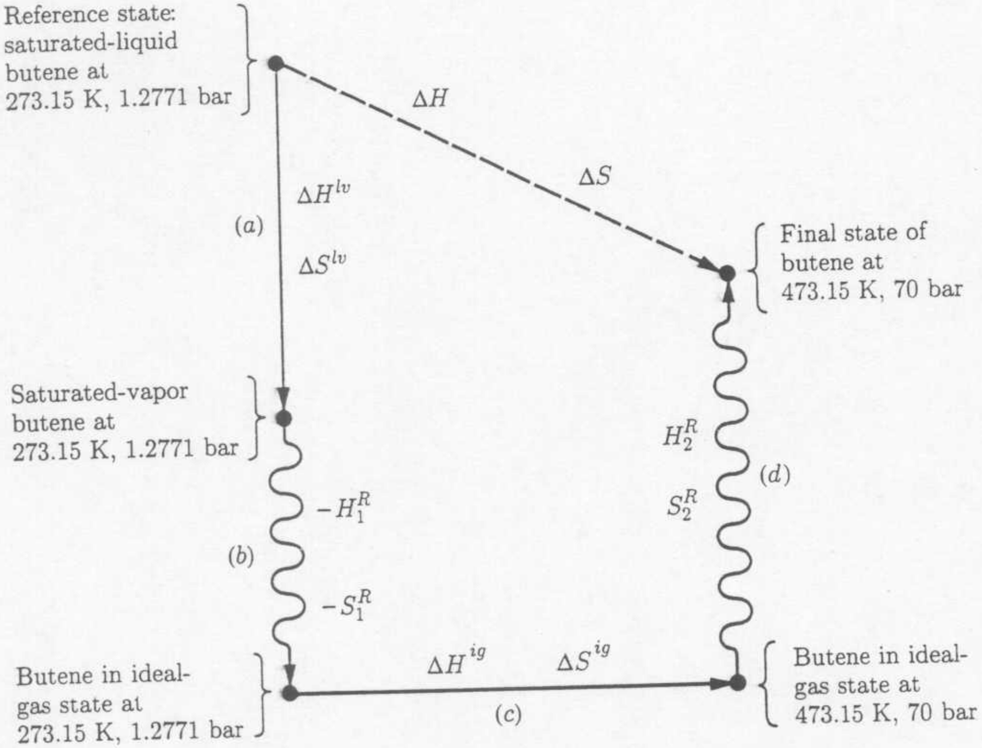
2. at T_c, $P^{sat} = P_c$

$$\Rightarrow \left.\begin{aligned} \ln(1.0133) &= A - \frac{B}{266.9} \\ \ln(40.43) &= A - \frac{B}{420} \end{aligned}\right\} \Rightarrow \begin{aligned} A &= 10.126 \\ B &= 2699.11 \end{aligned}$$

$$\Rightarrow \boxed{\ln(P^{sat}) = 10.126 - \frac{2699.11}{T}}$$

$\Rightarrow$ @ $T = 273.15\ K$ $\quad P^{sat} = 1.2771$ bar

step (a) involves evaporation at constant T & P. we need to evaluate ΔH^{lv} & ΔS^{lv} to find ΔH & ΔS for this step.



(a) Vaporization at T_1 and $P_1 = P^{\text{sat}}$.

(b) Transition to the ideal-gas state at (T_1, P_1).

(c) Change to (T_2, P_2) in the ideal-gas state.

(d) Transition to the actual final state at (T_2, P_2).

$$H = \Delta H^{lv} + \left(-H_1^{R}\right) + \Delta H^{ig} + H_2^{R}$$

$$= 21342.6 + \left(-\left(\underset{-366}{-0.105}\right)^{\times RT_c}\right) + 20564 + (-8010)$$

$$= 33896.7 \text{ J/mol}$$

$$S = \Delta S^{lv} + \left(-S_1^{R}\right) + \Delta S^{ig} + S_2^{R}$$

$$= 78.135 + \left(-(-0.9527)\right) + 22.18 + (-14.18)$$

$$= 87.09 \ \frac{\text{J}}{\text{mol.K}}$$

$$U = H - PV = 33896.7 - \frac{(70)(287)}{10 \text{ cm}^3 \text{ bar J}^{-1}}$$

$$= 31887.7 \ \frac{\text{J}}{\text{mol}}$$