

Problem #1: (5 points each) Answer or describe each of the following as briefly as possible

- How are the forms and numerical values of the "a" and "b" parameters determined for a cubic equation of state?
- What is a supercritical fluid?
- What is the Clausius-Clapeyron equation and how can it be used with a vapor pressure equation to find the heat of vaporization?
- What does the area beneath a path curve between two states on a pressure versus volume plot describe?
- What is the 3<sup>rd</sup> law of thermodynamics? /85

Problem #2: (35 points) Calculate both the vapor and liquid molar volume of SO<sub>2</sub> at 100° C and where  $P^{\text{sat}} = 28.74$  bar. Consider SO<sub>2</sub> to be a real gas with the following properties:  $T_c = 430.8$  K,  $P_c = 78.8$  bar,  $V_c = 1.22 \times 10^{-4}$  m<sup>3</sup>/gmol,  $\omega = 0.251$ . Use an appropriate method of your own choice, but show all of your work!

Problem #3 (40 points) A tank of 0.1 m<sup>3</sup> volume contains air at 25°C and 101.33 kPa. The tank is connected to a compressed air line at 45°C and 1500 kPa. The valve is opened a little to allow the compressed air to flow slowly into the tank until the final pressure is equal to the compressed air line. If the process is to occur isothermally (i.e. the tank remains at 25°C) how much heat must be added to or removed from the tank? Assume air to be an ideal gas for this problem.

## Problem 1

a)  $a, b$  parameters are determined for a cubic equation of state by using:

$$\left(\frac{\partial^2 p}{\partial v^2}\right)_{T_c} = 0 \text{ at inflection points and}$$

$$\left(\frac{\partial p}{\partial v}\right)_{T_c} = 0 \text{ at max. \& min. and}$$

finding  $a, b$  in the resulting equation when  $T=T_c, P=P_c, \& V=V_c$

b) Supercritical fluid: fluid that has higher pressure, temperature and volume than the critical  $p$  values for that substance. The fluid is no longer solid, liquid or gas.

c) Clausius-Clapeyron Equation

$$\Delta H_{\text{vap}} = T \Delta V \frac{dp^{\text{sat}}}{dT}$$

Derivative of vapor pressure equation with respect to temperature to find the heat of vaporization.

d) Work for that path.

e) entropy for a perfect crystal at absolute zero is zero.

## Problem 2

Given =  $\text{SO}_2$  real gas  $T = 100^\circ\text{C} = 373.5 \text{ K}$

$$p^{\text{sat}} = 28.74 \text{ bar}$$

$$T_c = 430.8 \text{ K} \quad p_c = 78.8 \text{ bar} \quad V_c = 1.22 \times 10^{-4} \frac{\text{m}^3}{\text{gmol}}$$

$$W = 0.251 \quad R = 83.14 \text{ cm}^3 \text{ bar} / \text{mol K}$$

Required =  $V^L, V^G$

Solution = Using Rackett Equation

$$V^L = \frac{RT_c}{p_c} Z_R [1 + (1 - T_R)^{2/7}]$$

$$Z_R = 0.29056 - 0.08775 W$$

$$= 0.29056 - 0.08775 (0.251) = 0.268535$$

$$T_R = \frac{T}{T_c} = \frac{373.5 \text{ K}}{430.8 \text{ K}} = 0.866992$$

$$V^L = \frac{(83.14 \frac{\text{cm}^3 \text{ bar}}{\text{mol K}})(430.8 \text{ K})}{78.8 \text{ bar}} (0.268535) [1 + (1 - 0.866992)^{2/7}]$$

$$V^L = 58.3 \frac{\text{cm}^3}{\text{mol}}$$

## Problem 2 cont.

Pitzer Equation

$$T_r = \frac{100 + 273}{430.8} = 0.87$$

$$P_r = \frac{28.74}{78.8} = 0.365$$

$$B^{\circ} = 0.083 - \frac{0.422}{T_r^{1.6}} = -0.444$$

$$B' = 0.139 - \frac{0.172}{T_r^{4.2}} = -0.174$$

$$\frac{B P_c}{R T_c} = B^{\circ} + \omega B' = 0.444 + (0.251)(-0.174) \\ = -0.487$$

$$Z = 1 + (-0.487) \frac{P_r}{T_r} \\ = 1 + (-0.487) \frac{0.365}{0.87} \\ = 0.796$$

$$V_g = \frac{ZRT}{P} = \frac{(0.796)(83.14)(373)}{28.74}$$

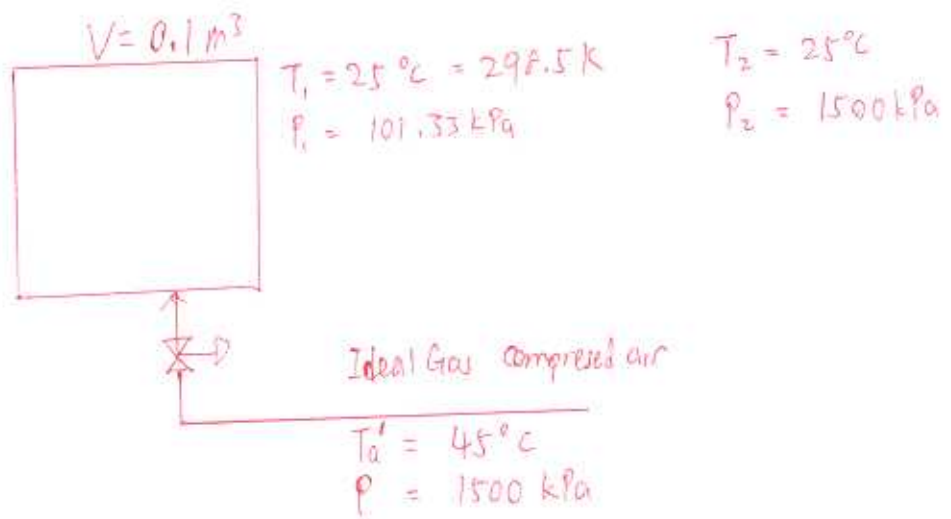
$$V_g = 858.9 \frac{\text{cm}^3}{\text{mol}}$$

Using R-K equation

$$V_L = 70.8 \frac{\text{cm}^3}{\text{mol}}$$

$$V_g = 835.6 \frac{\text{cm}^3}{\text{mol}}$$

### Problem 3



$$dU - H dN = dQ + dW \quad \text{(no volume change, no work)}$$

$$d(NU) - \underset{\substack{\uparrow \\ \text{constant}}}{H'} dN = dQ$$

$$N_2 U_2 - N_1 U_1 - H' (N_2 - N_1) = Q$$

$$N_2 (U_2 - H') - N_1 (U_1 - H') = Q$$

Since  $H' = U' + P'V' = U' + RT'$

$$N_2 (U_2 - U' - RT') - N_1 (U_1 - U' - RT') = Q$$

Since  $\Delta U = C_v \Delta T$  and  $R = C_p - C_v$

$$N_2 (C_v T_2 - C_p T') - N_1 (C_v T_1 - C_p T') = Q$$

$$N_1 = \frac{P_1 V_1}{R T_1} = \frac{(101,330 \text{ Pa})(0.1 \text{ m}^3)}{\left(8.314 \frac{\text{m}^2 \text{Pa}}{\text{mol K}}\right)(298.5 \text{ K})} = 4.083 \text{ mol}$$

$$N_2 = \frac{P_2 V_2}{R T_2} = \frac{(1500000 \text{ Pa})(0.1 \text{ m}^3)}{\left(8.314 \frac{\text{m}^2 \text{Pa}}{\text{mol K}}\right)(298.5 \text{ K})} = 60.44 \text{ mol}$$

Problem 3 cont

$$C_p = \frac{7}{2} R = \frac{7}{2} (8.314) = 29.099$$

$$C_v = \frac{5}{2} R = \frac{5}{2} (8.314) = 20.785$$

$$T_2 = T_1 = 298.5 \text{ K}$$

$$T' = 45 + 273 = 318.5 \text{ K}$$

$$Q = 60.44 \text{ mol} \left[ (20.785)(298.5 \text{ K}) - (29.099)(318.5 \text{ K}) \right]$$

$$- 4.083 \text{ mol} \left[ (20.785)(298.5) - (29.099)(318.5) \right]$$

$$= 60.44 \text{ mol} [-3063.709] - 4.083 [-3063.709]$$

$$= -185170.572 + 12509.12385$$

$$= -172661.4482 \text{ J}$$

$$= \boxed{-172.66 \text{ kJ}} \quad \text{heat removed.}$$