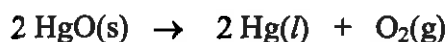


1. The decomposition of mercuric oxide



- [3] converts a bright orange-red solid to “quicksilver”, a visually striking reaction and a popular demonstration for alchemists seeking funding.

At what temperature does  $\text{HgO}(s)$  decompose when heated in air ( $p_{\text{O}_2} = 0.200$  bar)?

Data at 25 °C:  $\Delta H_{\text{fm}}^\circ(\text{HgO}, s) = -90.83 \text{ kJ mol}^{-1}$ ,  $\Delta G_{\text{fm}}^\circ(\text{HgO}, s) = -58.54 \text{ kJ mol}^{-1}$ .

2. Use the following data for water at 25 °C to answer this question.

$$\begin{array}{ll} \Delta H_{\text{fm}}^\circ(\text{H}_2\text{O}, l) = -285.830 \text{ kJ mol}^{-1} & \Delta G_{\text{fm}}^\circ(\text{H}_2\text{O}, l) = -237.129 \text{ kJ mol}^{-1} \\ \Delta H_{\text{fm}}^\circ(\text{H}_2\text{O}, g) = -241.818 \text{ kJ mol}^{-1} & \Delta G_{\text{fm}}^\circ(\text{H}_2\text{O}, g) = -228.572 \text{ kJ mol}^{-1} \end{array}$$

a) Calculate the vapor pressure of water at 25 °C. [Hint: Calculate the equilibrium constant for the “reaction”  $\text{H}_2\text{O}(l) = \text{H}_2\text{O}(g)$ .]

[5]

b) Calculate the normal boiling point of water ( $p_{\text{H}_2\text{O}} = 1$  atm).

c) Why does the answer to part b differ from 100.00 °C (373.15 K), the correct normal boiling point of water?

3. Use the density data for liquid chlorine and chlorine vapor below to estimate the critical temperature and the critical density of chlorine. [Suggestion: Try plotting  $\rho_{\text{liquid}} - \rho_{\text{vapor}}$  against  $t$  and  $(\rho_{\text{liquid}} + \rho_{\text{vapor}})/2$  against  $t$ , respectively.]

[3]

$t / ^\circ\text{C}$	$\rho_{\text{liquid}} / \text{g cm}^{-3}$	$\rho_{\text{vapor}} / \text{g cm}^{-3}$
98.9	1.115	0.124
104.4	1.087	0.139
110.0	1.057	0.156
115.6	1.025	0.179
121.1	0.989	0.203
126.7	0.949	0.231
132.2	0.894	0.268
137.8	0.814	0.321
141.6	0.706	0.422
143.3	0.599	0.523

4. Use the critical temperature (289.7 K) and critical pressure (58.8 bar) of xenon to estimate the van der Waals  $a$  and  $b$  coefficients of the gas.

[2]

... page 2

5. Xenon, the first “noble” gas discovered to form a chemical compound (xenon hexafluoroplatinate), has many other fascinating properties. It’s expensive too!

[4]

Suppose you have a 50.0 L tank filled with xenon at 300 K and 250 bar. Using \$5 per gram for the price of xenon, estimate the dollar value of xenon in the tank using:

a) the ideal gas law

b) the law of corresponding states and the diagram below

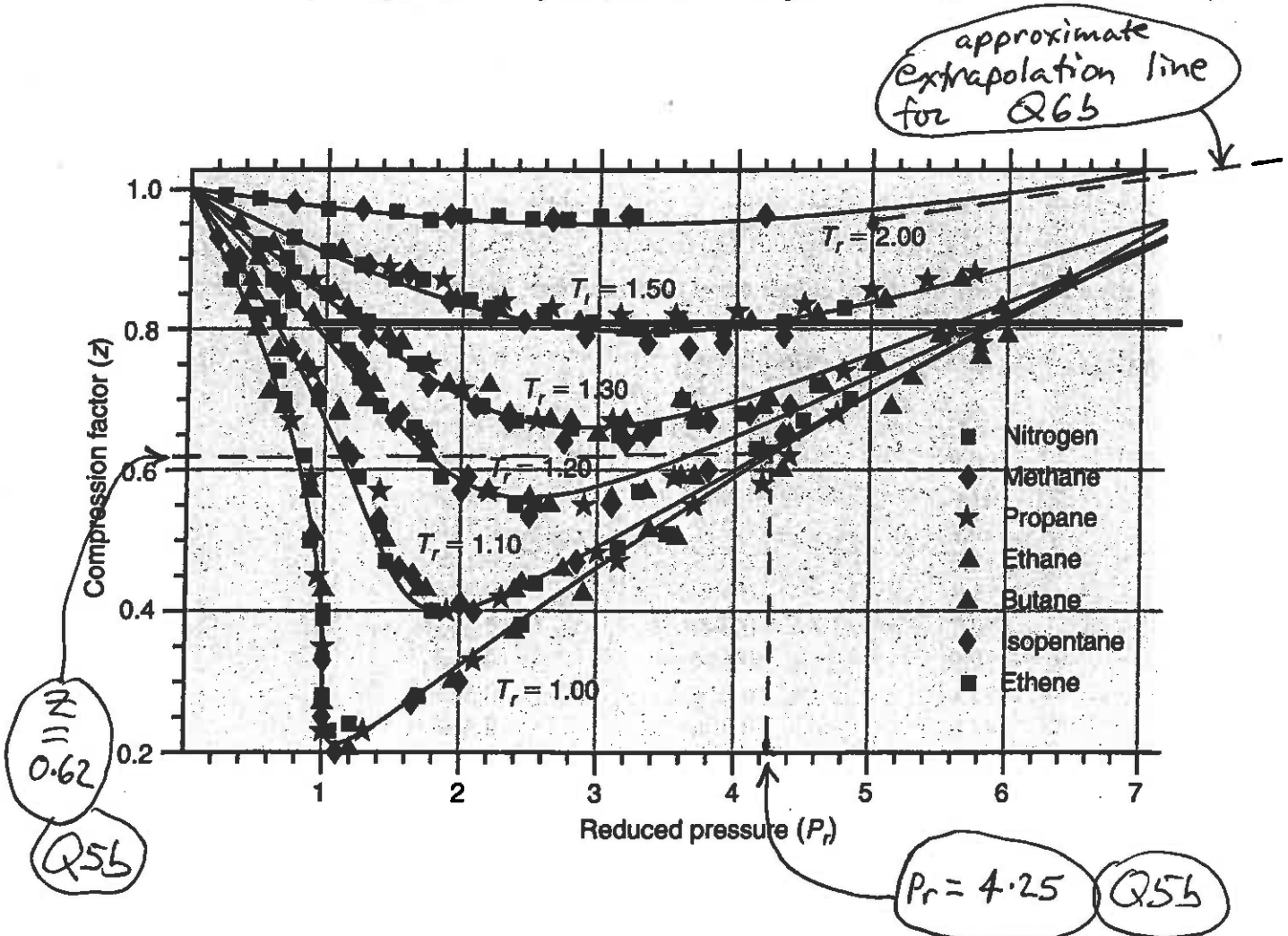
c) Which estimate, a or b, is more reliable? Explain.

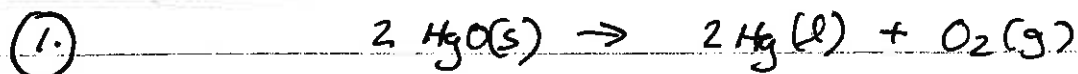
6. A thin-wall low-pressure tank filled with liquid oxygen (density  $1.141 \text{ g cm}^{-3}$ ) at 90 K and 1 bar is accidentally allowed to warm up to room temperature (300 K) at constant volume, producing a dangerously high pressure. Data for  $\text{O}_2$ :  $T_C = 154.6 \text{ K}$ ,  $p_C = 50.43 \text{ bar}$ .

[3]

a) Is there any liquid oxygen in the tank at 300 K? Justify your answer.

b) Use the corresponding-states diagram below to estimate the pressure in the tank at 300 K. (Hint: A long extrapolation is required, but even a rough estimate is better than no estimate!)





equilibrium constant  $K = P_{\text{O}_2}/P^\circ$      $P^\circ = 1 \text{ bar}$   
 $= P_{\text{O}_2}$  (numerically)

at  $25^\circ\text{C}$ :

$$\Delta G^\circ = 2 \Delta G_{\text{fm}}^\circ(\text{Hg}, l) + \Delta G_{\text{fm}}^\circ(\text{O}_2, g) - 2 \Delta G_{\text{fm}}^\circ(\text{HgO}, s)$$

$$= 2(0) + (0) - 2(-58.57) = -2\Delta G_{\text{fm}}^\circ(\text{HgO}, s)$$

$$\Delta G^\circ = +117.08 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ = -2\Delta H_{\text{fm}}^\circ(\text{HgO}, s) = 181.66 \text{ kJ mol}^{-1}$$

$$K(T_1) = e^{-\Delta G^\circ/RT} = e^{-117080/(8.314 \times 298.15)}$$

$$= e^{-47.23}$$

$$K(298.15\text{K}) = 3.071 \times 10^{-21}$$

in air at  $298.15 \text{ K}$ ,  
 $Q = P_{\text{O}_2} = 0.200 \text{ bar}$   
 $Q \gg K$  no decomposition

at  $T_2 = ?$ :

$$K(T_2) = P_{\text{O}_2}(\text{in air}) = 0.200 \text{ bar} = Q$$

for decomposition

we want van't Hoff's equation:  $\frac{d \ln K}{d \frac{1}{T}} = -\frac{\Delta H^\circ}{R} \approx \frac{\Delta \ln K}{\Delta \frac{1}{T}}$

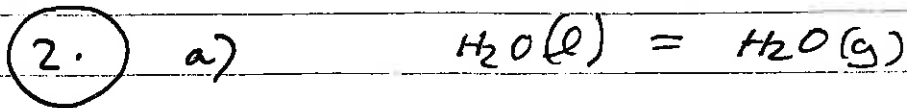
$$\frac{\ln K(T_2) - \ln K(T_1)}{\frac{1}{T_2} - \frac{1}{T_1}} = -\frac{\Delta H^\circ}{R} = \frac{\ln(0.200) - (-47.23)}{\frac{1}{T_2} - \frac{1}{T_1}} = \frac{45.62}{\frac{1}{T_2} - \frac{1}{T_1}}$$

$$\frac{1}{T_2} - \frac{1}{T_1} = -\frac{R}{\Delta H^\circ} (45.62) \quad \frac{1}{T_2} = \frac{1}{T_1} - 0.002088 \text{ K}^{-1}$$

$$\frac{1}{T_2} = 0.001266 \text{ K}^{-1}$$

$$T_2 = 790 \text{ K}$$

$$(-517^\circ\text{C})$$



$$K = P_{\text{H}_2\text{O}}/p^\circ = P_{\text{H}_2\text{O}} \text{ numerically}$$

at 25°C:  $\Delta G^\circ = \Delta G_{\text{fm}}^\circ(\text{H}_2\text{O}, g) - \Delta G_{\text{fm}}^\circ(\text{H}_2\text{O}, l)$

$$= -228572 - (-237129)$$

$$= 8557 \text{ J mol}^{-1}$$

$$K = e^{-\Delta G^\circ/RT} = e^{-8557/(8.314 \times 298.15)} = e^{-3.452}$$

$K = 0.03168 \Rightarrow P_{\text{H}_2\text{O}} = 0.03168 \text{ bar}$  for  
water vapor in equilibrium with  
liquid water at 25°C

b) at  $T_1 = 298.15 \text{ K}$ ,  $K_1$  for the reaction  
 $\text{H}_2\text{O}(l) = \text{H}_2\text{O}(g)$  is  $0.03168 = P_{\text{H}_2\text{O}}$

at  $T_2$ ,  $K_2$  for the reaction  $\text{H}_2\text{O}(l) = \text{H}_2\text{O}(g)$   
is  $K = P_{\text{H}_2\text{O}} = 1 \text{ atm} = 1.013 \text{ bar}$

$$\frac{d \ln K}{d(1/T)} = -\frac{\Delta H^\circ}{R} \Leftrightarrow \frac{\ln K_2 - \ln K_1}{\frac{1}{T_2} - \frac{1}{T_1}} = \frac{-\Delta H^\circ}{R}$$

$$\frac{1}{T_2} = \frac{1}{T_1} - \frac{R}{\Delta H^\circ} \ln \left( \frac{K_2}{K_1} \right) = \frac{1}{298.15} - \frac{8.314}{(241818 + 285830)} \ln \frac{1.01325}{0.03168}$$

$$\frac{1}{T_2} = 0.002699 \text{ K}^{-1} \quad T_2 = 370.45 \text{ K} \quad (97.30^\circ\text{C})$$

c) Why not 100.0°C in b?  $\Delta H^\circ$  not constant from 25°C to 100°C  
Also, water vapor is not an ideal gas.

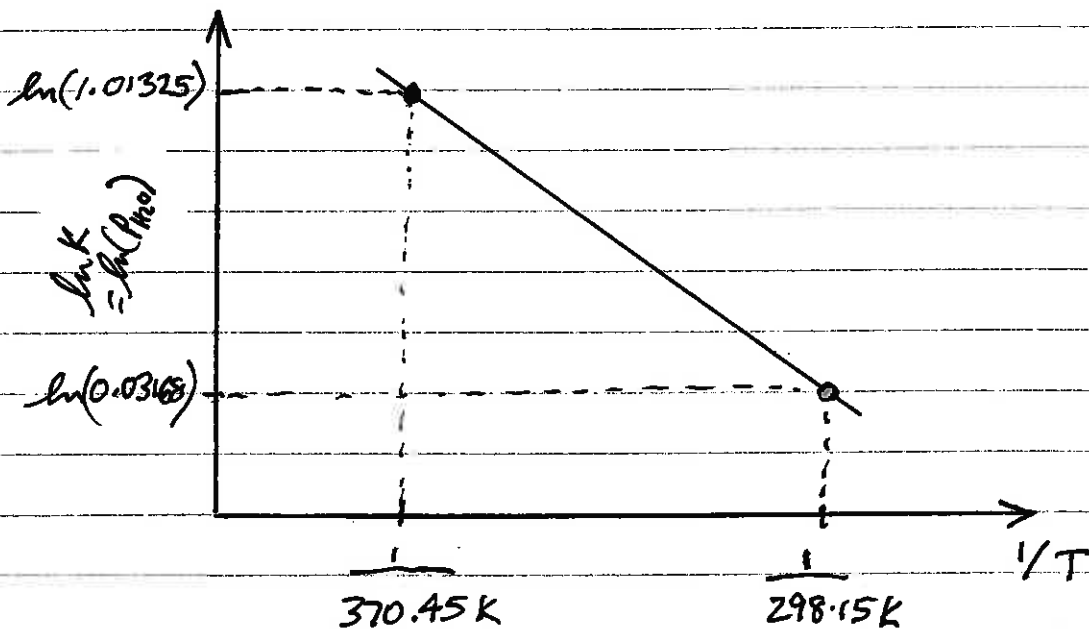
vant' Hoff Prof for  $\text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{O}(g)$

$$K = P_{\text{H}_2\text{O}}$$

plot  $\ln K$  against  $1/T$

$$\begin{aligned} \text{slope} &= -\frac{\Delta H^\circ}{R} = -\frac{\Delta H_{\text{vap,m}}^\circ}{R} \\ &= -\frac{\Delta H_{\text{f,m}}^\circ(\text{H}_2\text{O},g) - \Delta H_{\text{f,m}}^\circ(\text{H}_2\text{O},l)}{R} \\ &= -\frac{-241818 - (-285830)}{R} \end{aligned}$$

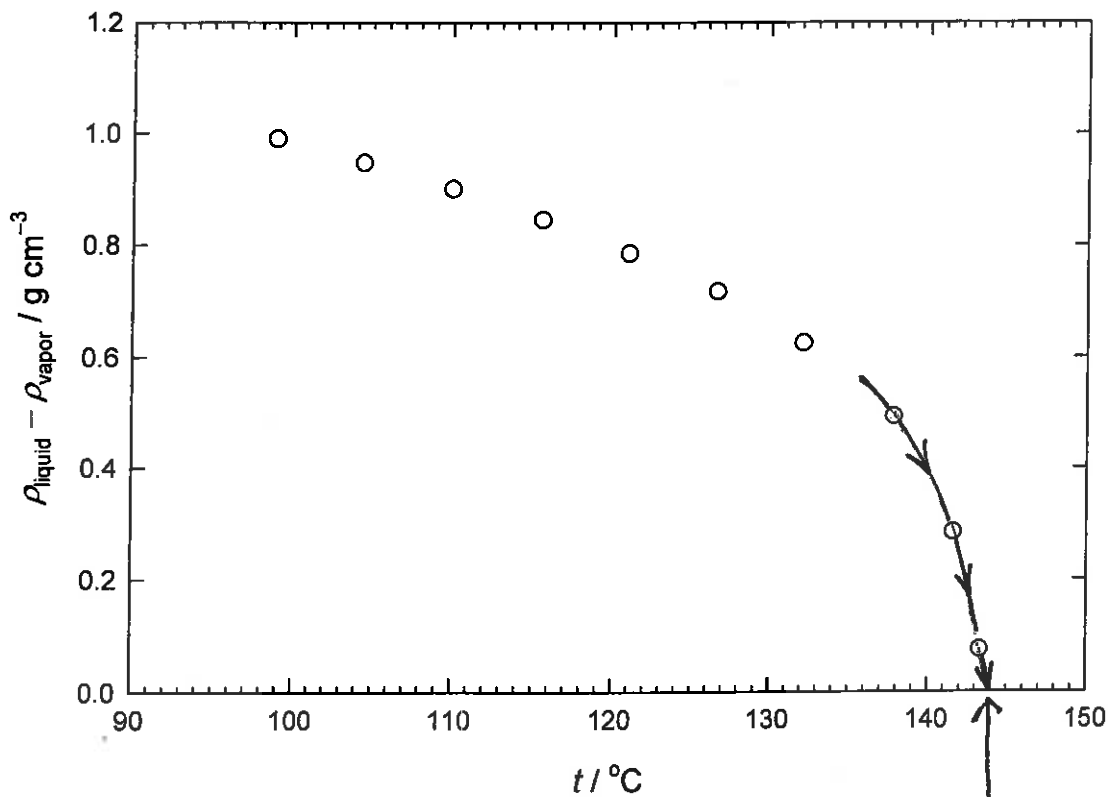
$$\text{slope} = -5294 \text{ K}$$



Q3

The difference between the liquid  $\text{Cl}_2$  density and the vapor chlorine density drops to zero at the critical point.

Plot  $\rho_{\text{liquid}} - \rho_{\text{vapor}}$  against temperature.  
The intercept at  $\rho_{\text{liquid}} - \rho_{\text{vapor}} = 0$  is the critical temperature.



estimate

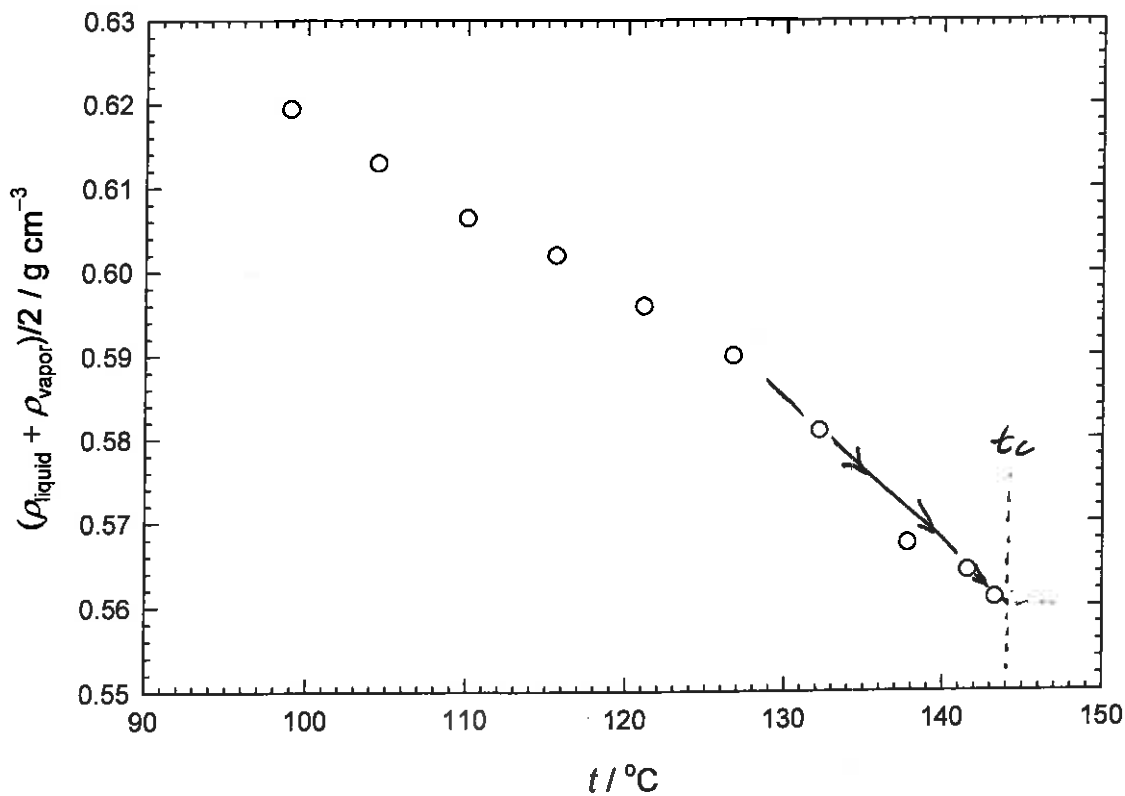
$$t_c = 144^\circ\text{C}$$

(Q3 cont.)

as  $t \rightarrow t_c$ ,  $\rho_{\text{liquid}} \rightarrow \rho_c$   
 $\rho_{\text{vapor}} \rightarrow \rho_c$

$$\frac{\rho_{\text{liquid}} + \rho_{\text{vapor}}}{2} \rightarrow \rho_c$$

why?  
liquid and vapor  
indistinguishable  
at the  
critical point



$$t_c = 144^\circ\text{C}$$

$$\text{estimate } \rho_c = 0.560 \frac{\text{g}}{\text{cm}^3}$$

4. Estimate  $a$  and  $b$  for xenon using  $T_c = 289.7 \text{ K}$   
 $P_c = 58.8 \text{ bar}$

$$a = \frac{27R^2T_c^2}{64P_c} = \frac{27(0.08314 \text{ L bar K}^{-1} \text{ mol}^{-1})^2(289.7 \text{ K})^2}{64(58.8 \text{ bar})}$$

$$a = 4.16 \text{ L}^2 \text{ bar mol}^{-2}$$

$$b = \frac{RT_c}{8P_c} = \frac{(0.08314 \text{ L bar K}^{-1} \text{ mol}^{-1})(289.7 \text{ K})}{8(58.8 \text{ bar})}$$

$$b = 0.0512 \text{ L mol}^{-1}$$

Table 7.4 gives:

$$a = 4.192 \text{ L}^2 \text{ bar mol}^{-2}$$

$$b = 0.0516 \text{ L mol}^{-1}$$

(good agreement)

5. a)  $V = 50.0 \text{ L}$      $T = 300 \text{ K}$      $p = 250 \text{ bar}$

ideal gas law  $n = \frac{pV}{RT} = \frac{250(50.0)}{0.08314(300)} = 501.2 \text{ mol}$

$$\text{grams of Xe} = (501.2 \text{ mol}) \left( \frac{131.3 \text{ g}}{\text{mol}} \right) = 65800 \text{ g}$$

$$\text{value} = 5 \frac{\$}{\text{g}} (65800 \text{ g}) = \$329,000.$$

b) corresponding states     $T_c = 289.7 \text{ K}$      $P_c = 58.8 \text{ bar}$

$$\left. \begin{aligned} T_r = T/T_c = 300/289.7 = 1.035 \\ P_r = P/P_c = 250/58.8 = 4.25 \end{aligned} \right\} \begin{array}{l} \text{estimate } z = 0.62 \\ \text{from} \\ \text{corresponding principle} \\ \text{graph} \end{array}$$

$$z = \frac{pV_m}{RT} \quad V_m = \frac{RT}{P} z = \frac{0.08314(300)}{250} 0.62 = 0.06186 \text{ L mol}^{-1}$$

$$n = V/V_m = 50.0/0.06186 = 808.3 \text{ mol} \quad (106,130 \text{ g})$$

value  $\$530,700.$  ← c) more reliable estimate, Xe not ideal



6. a)  $O_2$  at 300K no liquid

300 K is above the critical temperature of  $O_2$   
(154.6 K)

$$b) T_r = \frac{300 \text{ K}}{154.6 \text{ K}} = \frac{T}{T_c} = 1.94$$

$$V_m = \frac{M}{\rho} = \frac{32.00 \text{ g mol}^{-1}}{1.141 \text{ g cm}^{-3}}$$

$$V_m = 28.04 \frac{\text{cm}^3}{\text{mol}} = 0.02804 \frac{\text{L}}{\text{mol}}$$

compression factor  $z = \frac{PV_m}{RT} \Rightarrow z = \frac{P}{P_c} \frac{P_c V_m}{RT}$

on the  $T_r = 1.94$  reduced isotherm:

$$z = \frac{P}{P_c} \frac{50.43 \text{ bar} (0.02804 \text{ L mol}^{-1})}{(0.08314 \text{ L bar K}^{-1} \text{ mol}^{-1}) 300 \text{ K}}$$

solve  $z = P_r \cdot 0.0567$  or  $P_r = 17.6 z$  on  $T_r = 1.94$  isotherm

(see graph)

Estimate  $z \approx 0.95 + (P_r - 5.0) \cdot 0.05$  for the 1.94 isotherm

very crude  
long extrop.

[very long (unreliable!) extrapolation]

solve  $0.0567 P_r = 0.95 + (P_r - 5.0) \cdot 0.05$  ← slope  $\frac{dz}{dP_r}$

$P_r = 104$   $P = 104 P_c \approx 5300 \text{ bar}$