

*Your lowest assignment mark will not be used to calculate your average assignment mark. So if you've handed in all the mandatory assignments (#1,2,3,5,6,7), and are happy with the results, a zero mark for #8 will not affect your course mark.

1. Standard Gibbs energies of formation are widely used to calculate equilibrium constants for chemical reactions. This question shows ΔG_f data can also be used to predict **phase equilibria**.

a) Use the data given below to calculate the vapor pressure of liquid water at 25 °C.



b) Also calculate the vapor pressure of liquid water at 60 °C. *Hint*: use the van't Hoff equation:

$$[5] \quad \ln p_{\text{H}_2\text{O}}(\text{at } T) = \ln p_{\text{H}_2\text{O}}(\text{at } 298.15 \text{ K}) - \frac{\Delta H^\circ}{R} \left(\frac{1}{T} - \frac{1}{298.15 \text{ K}} \right)$$

c) A tank contains water at 60 °C and 0.500 bar. Is the water in the tank liquid only, vapor only, or both liquid and vapor phases? Justify your answer.

Data at 25 °C:	$\Delta H_{\text{fm}}^\circ(\text{H}_2\text{O}, l) = -285,830 \text{ J mol}^{-1}$	$\Delta H_{\text{fm}}^\circ(\text{H}_2\text{O}, g) = -241,818 \text{ J mol}^{-1}$
	$\Delta G_{\text{fm}}^\circ(\text{H}_2\text{O}, l) = -237,129 \text{ J mol}^{-1}$	$\Delta G_{\text{fm}}^\circ(\text{H}_2\text{O}, g) = -228,572 \text{ J mol}^{-1}$

2. The **relative humidity** reported in weather forecasts is defined as the partial pressure of water vapor in air divided by the vapor pressure of pure liquid water at the same temperature.

For air at 25 °C and 85 % relative humidity:

a) calculate the partial pressure of water in the air

[3] b) calculate the number of grams of water in a 1.00 L sample of the air.

Data: the vapor pressure of pure liquid water at 25 °C is 0.0317 bar

3. This question refers to the **reduced van der Waals equation**:

$$p_r = \frac{8}{3} \frac{T_r}{V_r - \frac{1}{3}} - \frac{3}{V_r^2}$$

a) Explain why the reduced van der Waals equation is a universal equation of state.

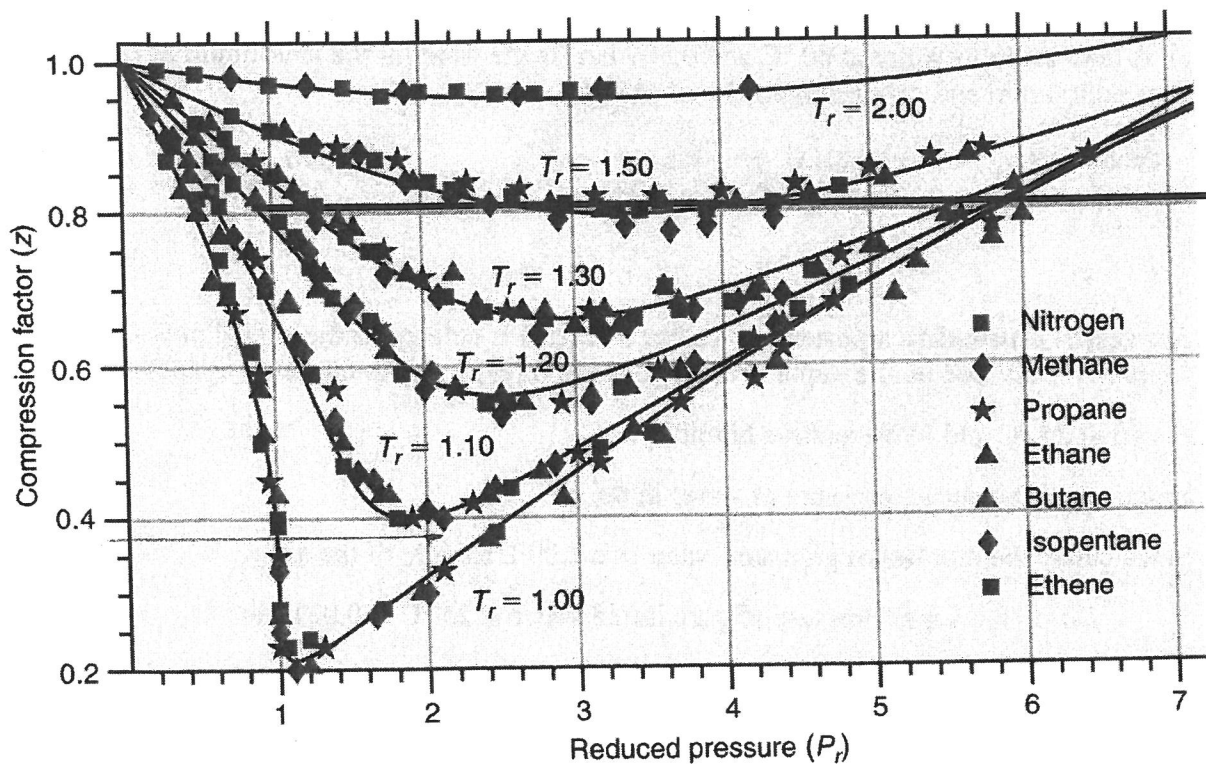
b) What does “reduced” mean in this context?

[5] c) Use the equation to calculate the reduced compression factor Z at the critical point.

d) Use the equation to show the reduced isothermal compressibility $-V_r^{-1}(\partial V_r / \partial p_r)_T$ is infinite at the critical point.

... page 2

4. A 25.0 L tank contains propane ($T_c = 369 \text{ K}$, $p_c = 42.6 \text{ bar}$) at 390 K and 85 bar.
- Is any liquid propane in the tank? Justify your answer.
- [6] b) Calculate the number of moles of propane in the tank using the ideal gas law. Why is this calculation likely to be inaccurate?
- Use the corresponding-states graph given below to calculate:
 - the compression factor Z
 - an accurate value for the number of moles of propane in the tank
- d) Do repulsive propane intermolecular forces dominate attractive forces in the tank. Explain.



5. A tank for a gas barbecue contains propane at $20 \text{ }^\circ\text{C}$ and 8.5 bar. After using the tank for several barbecues, the pressure in the tank is still 8.5 bar, indicating that the pressure in the tank does not drop as propane is removed! How is this possible? (This question explains why propane tanks are not fitted with pressure gauges to indicate the amount of propane in a tank.)
- [1]

Q1 liquid \rightleftharpoons vapor equilibrium for water



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

$$= -228,572 - (-237,129) \frac{\text{J}}{\text{mol}}$$

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

$$K = (P_{\text{H}_2\text{O}})_{\text{equil.}} = e^{(-\Delta G^\circ/RT)} = e^{-8557/(8.314)298.15}$$

$$= e^{-3.452}$$

$$K = 0.0317$$

\Rightarrow equilibrium water vapor pressure at 25 °C is 0.0317 bar

b) water vapor pressure at 60 °C?

we $T_2 = 333.15 \text{ K (60 °C)}$ $T_1 = 298.15 \text{ K (25 °C)}$

$$K_2 = P_{\text{H}_2\text{O}} \text{ at } T_2$$

$$K_1 = P_{\text{H}_2\text{O}} \text{ at } T_1$$

$$= 0.0317$$



$$\Delta H^\circ = \Delta H_{\text{fm}}^\circ(\text{H}_2\text{O}, g) - \Delta H_{\text{fm}}^\circ(\text{H}_2\text{O}, l) = -241,818 - (-285,830) = 44,012 \frac{\text{J}}{\text{mol}}$$

(Q1 b cont)

van't Hoff equation for the temperature dependence of the equilibrium constant $K = P_{H_2O}$ for water evaporation:

$$\ln K_2 = \ln K_1 - \frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

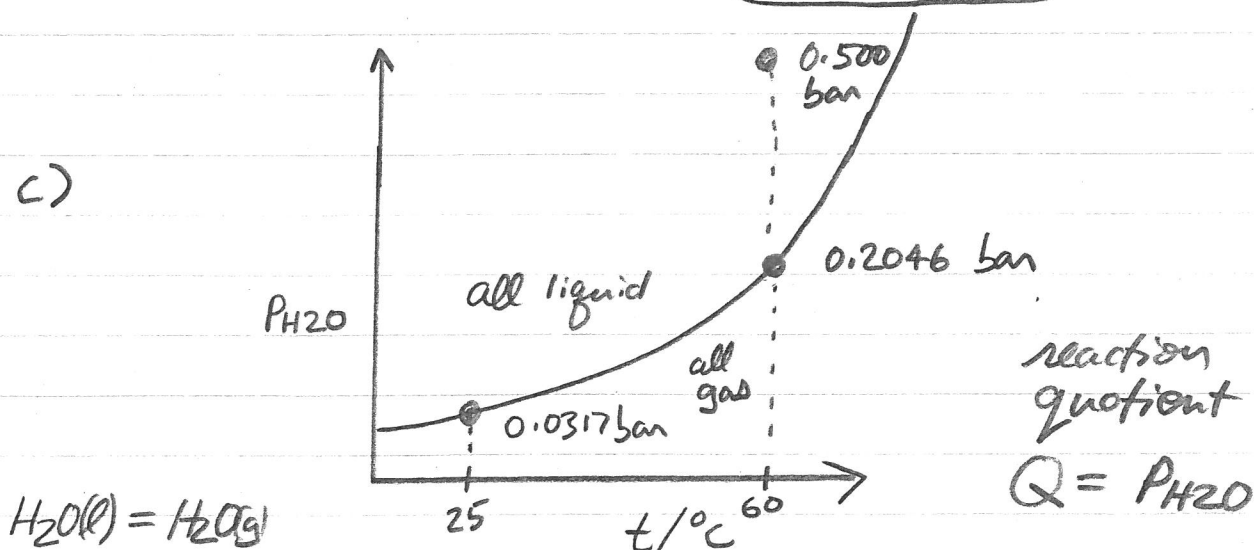
$$= \ln(0.0317) - \frac{44012}{8.314} \left(\frac{1}{333.15} - \frac{1}{298.15} \right)$$

$$= -3.452 + 1.865$$

$$\ln K_2 = -1.587$$

at 60°C : $K_2 = e^{-1.587} = \boxed{0.2046 \text{ bar}} = P_{H_2O}$

c)



at 60°C and $P_{H_2O} = 0.500 \text{ bar}$ $P_{H_2O} = Q > K = (P_{H_2O})_{\text{equi}}$

all "product" $\boxed{\text{all (liquid) } H_2O}$

Q2 a) air at 25 °C with 85% relative humidity

$$0.85 = \frac{\text{partial pressure of H}_2\text{O in air}}{\text{vapor pressure of H}_2\text{O(l) at 25}^\circ\text{C}}$$

$$0.85 = \frac{P_{\text{H}_2\text{O}}}{0.0317 \text{ bar}} \quad \leftarrow \text{from Q1}$$

$$P_{\text{H}_2\text{O}} = 0.85 (0.0317 \text{ bar}) = \boxed{0.0269 \text{ bar}}$$

b) grams of water in one liter of air with 85% relative humidity at 25 °C?

$$P_{\text{H}_2\text{O}} = \frac{n_{\text{H}_2\text{O}} RT}{V}$$

moles of H₂O
in one liter of air

$$n_{\text{H}_2\text{O}} = \frac{P_{\text{H}_2\text{O}} V}{RT}$$

$$= \frac{0.0269 (1.00)}{0.08314 (298.15)}$$

$$n_{\text{H}_2\text{O}} = 0.00109 \text{ mol}$$

$$\begin{aligned} \text{mass}_{\text{H}_2\text{O}} &= n_{\text{H}_2\text{O}} M_{\text{H}_2\text{O}} = (0.00109 \text{ mol}) \left(18.015 \frac{\text{g}}{\text{mol}} \right) \\ &= 0.0196 \text{ g} = \boxed{19.6 \text{ mg}} \end{aligned}$$

Q3 a) the reduced van der Waals equation

$$P_r = \frac{8}{3} \frac{T_r}{V_r - \frac{1}{3}} - \frac{3}{V_r^2}$$

is a "universal" equation of state because it contains no "human-defined" units

of pressure, temperature, volume

(no Pa, bar, Kelvin, L, m³ ...)

and no human-defined constants (no gas constant R)

b) "reduced" pressure means the pressure in human-defined units divided by the critical pressure (in the same human-defined units)

$$P_r = \frac{P}{P_c} \quad (\text{pressure reduced by dividing by } P_c)$$

Similarly:

$$T_r = \frac{T}{T_c}$$

$$V_{mr} = \frac{V_m}{V_{mc}}$$

P_r, T_r, V_{mr} are dimensionless pressures, temperatures, molar volumes defined in terms of natural P_c, T_c, V_{mc} units

(Q3 cont.)

c) at the critical point:

$P = P_c$, $T = T_c$, $V_m = V_{mc}$ and therefore

$$P_r = \frac{P}{P_c} = \frac{P_c}{P_c} = 1 \quad \text{and} \quad T_r = 1, \quad V_r = 1$$

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

reduced compression factor $z_r = \frac{z}{z_c}$

$$= \frac{\frac{P V_m}{RT}}{\frac{P_c V_{mc}}{RT_c}} = \frac{\frac{P}{P_c} \frac{V_m}{V_{mc}}}{\frac{T}{T_c}}$$

$$= \frac{P_r V_r}{T_r}$$

at the critical point: $P_r = \frac{P}{P_c} = \frac{P_c}{P_c} = 1$
($P = P_c$ $T = T_c$ $V_m = V_{mc}$)

also $T_r = 1$, $V_r = 1$ at the critical point

$$z_{rc} = \frac{P_{rc} V_{rc}}{T_{rc}} = \frac{(1)(1)}{1} = 1$$

(Q3 cont.)

d) Calculate the reduced isothermal compressibility:

$$\kappa_r = -\frac{1}{v_r} \left(\frac{\partial v_r}{\partial p_r} \right)_{T_r}$$

$$\left(\frac{\partial p_r}{\partial v_r} \right)_{T_r} = \frac{1}{\left(\frac{\partial v_r}{\partial p_r} \right)_{T_r}} = \left[\frac{\partial}{\partial v_r} \left(\frac{8}{3} \frac{T_r}{v_r^{-1/3}} - \frac{3}{v_r^2} \right) \right]_{T_r}$$

$$= \frac{8}{3} T_r \left(\frac{\partial}{\partial v_r} (v_r^{-1/3})^{-1} \right)_{T_r} - 3 \left(\frac{\partial}{\partial v_r} v_r^{-2} \right)_{T_r}$$

$$= \frac{8}{3} T_r (-1) (v_r^{-1/3})^{-2} - 3(-2) v_r^{-3}$$

$$\left(\frac{\partial p_r}{\partial v_r} \right)_{T_r} = -\frac{8}{3} T_r \frac{1}{(v_r^{-1/3})^2} + \frac{6}{v_r^3}$$

$$\kappa_r = -\frac{1}{v_r} \frac{1}{\left(\frac{\partial p_r}{\partial v_r} \right)_{T_r}} = -\frac{1}{v_r} \frac{1}{-\frac{8}{3} \frac{T_r}{(v_r^{-1/3})^2} + \frac{6}{v_r^3}}$$

at the critical point ($T_r = v_r = 1$):

$$\kappa_r = -\frac{1}{1} \frac{1}{-\frac{8}{3} \frac{1}{(1/3)^2} + \frac{6}{1^3}} = -\frac{1}{-6+6} = \frac{-1}{0} = \infty$$

Q4

A 25.0-L tank contains propane
($T_c = 369 \text{ K}$, $p_c = 42.6 \text{ bar}$) at
390 K and 85 bar.

a) Any liquid propane in the tank?

No! 390 K is above the critical temperature
(the maximum temperature where the liquid exists)
at 369 K.

b) moles of propane using the ideal gas law

$$n = \frac{pV}{RT} = \frac{85.0 \text{ bar} \cdot 25.0 \text{ L}}{(0.08314 \frac{\text{L bar}}{\text{K mol}}) 390 \text{ K}} = \boxed{65.5 \text{ mol}}$$

This value of n is unlikely to be accurate:
the propane is near the critical point where
nonideal gas behavior is significant.

$$\begin{aligned} \text{c) i) } T_r = T/T_c &= (390 \text{ K})/(369 \text{ K}) = 1.057 \\ p_r = p/p_c &= (85 \text{ bar})/(42.6 \text{ bar}) = 1.995 \end{aligned} \left. \begin{array}{l} \text{read} \\ z = 0.37 \\ \text{from} \\ \text{graph} \end{array} \right\}$$

$$\text{ii) } z = \frac{pV}{nRT} \quad n = \frac{1}{z} \frac{pV}{RT}$$

$$n = \frac{1}{0.37} (65.5 \text{ mol}) = \boxed{177 \text{ mol}}$$

$$\text{) } z = \frac{p}{p_{\text{ideal}}} = 0.37 < 1$$

attractive forces
dominate

Q5

A tank for a gas barbecue contains propane at 20°C , 8.5 bar.

As propane is removed from the tank, the pressure stays at 8.5 bar.

Why?

The tank contains liquid propane in equilibrium with propane vapor.

As propane is removed from the tank, some liquid propane evaporates, maintaining the pressure at 8.5 bar.

