

\*This assignment is optional. (You lose no marks if you don't hand it in.) *Happy Thanksgiving.*

1. The molar volume of chloroform is  $80.21 \text{ cm}^3 \text{ mol}^{-1}$  at  $20 \text{ }^\circ\text{C}$  and 1 bar. Estimate the molar volume of chloroform at  $50 \text{ }^\circ\text{C}$  and 1 bar. (Data:  $\alpha = 0.001273 \text{ K}^{-1}$ .) Why can't the ideal gas equation  $pV_m = RT$  be used to calculate the chloroform molar volume?  
[3]

2. a) Calculate  $(\partial p / \partial T)_V$  for liquid mercury at 298 K and 1 bar using data from Tables 3.1 and 3.2 in the course notes and in the textbook.  
[3]

b) Use the result from part a) to explain why mercury-in-glass thermometers break if heated beyond their temperature range. Also, explain why mercury thermometers are banned in many countries.

3. a) Calculate the work  $w$  for the irreversible isothermal expansion of one mole of **ideal gas** from 50 bar to 1.00 bar at  $25 \text{ }^\circ\text{C}$  with  $p_{\text{external}} = 1.00 \text{ bar}$ .  
[4]

b) Calculate the work  $w$  for the reversible isothermal expansion of one mole of **liquid water** ( $V_m = 18.07 \text{ cm}^3 \text{ mol}^{-1}$  and  $\kappa = 0.000046 \text{ bar}^{-1}$  at 1.00 bar) from 50 bar to 1.00 bar at  $25 \text{ }^\circ\text{C}$  with  $p_{\text{external}} = 1.00 \text{ bar}$ .

c) Use the results from parts a) and b) to suggest why a leak from a tank of compressed gas can be much more dangerous (even lethal) than a leak from a tank of compressed liquid.

4. Use the result  $(\partial H / \partial p)_T = V(1 - \beta T)$  derived in class to prove the enthalpy of an isothermal ideal gas is constant and independent of the pressure.  
[2]

5. As pointed out in class, the cyclic rule for partial derivatives contains a *mysterious* minus that doesn't seem to make sense at first glance. For an ideal gas ( $pV_m = RT$ ), prove the cyclic rule  
[3]

$$\left(\frac{\partial p}{\partial T}\right)_{V_m} = -\left(\frac{\partial p}{\partial V_m}\right)_T \left(\frac{\partial V_m}{\partial T}\right)_p$$

is correct only if the minus sign is included.

6. a) The volumetric thermal expansion coefficient is defined as  $\beta = V^{-1}(\partial V/\partial T)_p$ . In terms of the density ( $\rho = \text{mass} / \text{volume}$  is the density), prove

[2] 
$$\beta = -\frac{1}{\rho} \left( \frac{\partial \rho}{\partial T} \right)_p$$

7. a) Use density data for liquid water at 1.00 bar (tabulated at right) to calculate\*\*:

| $t / ^\circ\text{C}$ | $\rho / (\text{kg m}^{-3})$ |
|----------------------|-----------------------------|
| -30.                 | 983.8541                    |
| -20.                 | 993.5471                    |
| -10.                 | 998.1173                    |
| 0.                   | 999.8395                    |
| 10.                  | 999.7026                    |
| 20.                  | 998.2071                    |
| 25.                  | 997.0479                    |
| 30.                  | 995.6502                    |

- [3] i)  $\beta$  for liquid water at 0 °C

- ii)  $\beta$  for liquid water at 25 °C

- b) Why is the thermal expansion of liquid water unusual?

\*\*For data at equally-spaced temperature intervals  $\Delta T$ , the derivative  $\partial\rho/\partial T$  at  $T_1$  can be estimated as  $[\rho(T_1 + \Delta T) - \rho(T_1 - \Delta T)]/(2 \Delta T)$ . Alternatively, a suitable equation can be fitted to the data and differentiated. For example, if the equation  $C_{pm}(T) = a_0 + a_1T + a_2T^2 + a_3T^3$  provides a good fit, the derivative at  $T = T_1$  is  $\partial\rho/\partial T = a_1 + 2a_2T_1 + 3a_3T_1^2$ .

$$1. \quad \alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p = \frac{1}{V_m} \left( \frac{\partial V_m}{\partial T} \right)_p$$

$$\frac{dV_m}{V_m} = \alpha dT$$

assume  $\alpha$  is constant  
(no other information)

$$\int_{V_m(T_1)}^{V_m(T_2)} \frac{dV_m}{V_m} = \alpha \int_{T_1}^{T_2} dT$$

$$\ln \left[ \frac{V_m(T_2)}{V_m(T_1)} \right] = \alpha (T_2 - T_1)$$

$$\frac{V_m(T_2)}{V_m(T_1)} = e^{\alpha(T_2 - T_1)}$$

$$T_1 = 293.15 \text{ K}$$

$$T_2 = 323.15 \text{ K}$$

$$V_m(T_1) = 80.21 \text{ cm}^3 \text{ mol}^{-1}$$

$$\alpha = 0.001273 \text{ K}^{-1}$$

$$\begin{aligned} V_m(T_2) &= V_m(T_1) e^{\alpha(T_2 - T_1)} \\ &= (80.21 \text{ cm}^3 \text{ mol}^{-1}) e^{(0.001273 \text{ K}^{-1})(30 \text{ K})} \\ &= (80.21 \text{ cm}^3 \text{ mol}^{-1}) 1.0389 \\ &= \boxed{83.33 \text{ cm}^3 \text{ mol}^{-1}} \end{aligned}$$

Can't use  
 $pV_m = RT$ . Chloroform  
is a liquid.

can also use:

$$\alpha = \frac{1}{V_m} \left( \frac{\partial V_m}{\partial T} \right)_p \approx \frac{1}{V_m(T_1)} \frac{\Delta V_m}{\Delta T} \quad \text{because } \Delta V_m \text{ is small}$$

$$\begin{aligned} \Delta V_m &\approx \alpha V_m(T_1) \Delta T = (0.001273 \text{ K}^{-1}) (80.21 \text{ cm}^3 \text{ mol}^{-1}) (30 \text{ K}) \\ &= 3.06 \text{ cm}^3 \text{ mol}^{-1} \end{aligned}$$

$$\begin{aligned} V_m(T_2) &= V_m(T_1) + \Delta V_m = (80.21 + 3.06) \text{ cm}^3 \text{ mol}^{-1} \\ &= \boxed{83.27 \text{ cm}^3 \text{ mol}^{-1}} \end{aligned}$$

2. a)

$$\begin{aligned} \left(\frac{\partial p}{\partial T}\right)_V &= - \left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P = - \frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial p}\right)_T} = \frac{\frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P}{-\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_T} \\ &= \frac{\alpha}{\kappa} \end{aligned}$$

for liquid mercury at 298 K and 1 bar

$$\alpha = 1.81 \times 10^{-4} \text{ K}^{-1}$$

$$\kappa = 3.91 \times 10^{-6} \text{ bar}^{-1}$$

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{\alpha}{\kappa} = \frac{1.81 \times 10^{-4} \text{ K}^{-1}}{3.91 \times 10^{-6} \text{ bar}^{-1}} = \boxed{46.3 \frac{\text{bar}}{\text{K}}}$$

b) Heating a mercury-in-glass thermometer beyond its temperature scale leaves no mercury vapor space for the liquid to expand into.

Glass has a lower thermal expansivity, so heating the thermometer is almost equivalent to heating liquid mercury in a solid glass container at constant volume.

Glass fails under tension forces, causing the glass to break if the pressure in the mercury reaches only a few bars.

Mercury-in-glass thermometers are banned because they break easily and release toxic mercury.

$$\textcircled{3.} \text{ a) } w = - \overset{\text{const.}}{\int} P_{\text{ext}} dV = -P_{\text{ext}} (V_f - V_i) = -P_{\text{ext}} \left( \frac{nRT_f}{P_f} - \frac{nRT_i}{P_i} \right)$$

$$w = nRT \left( \frac{P_{\text{ext}}}{P_f} + \frac{P_{\text{ext}}}{P_i} \right)$$

$$= (1.00 \text{ mol}) \left( 8.314 \frac{\text{J}}{\text{K mol}} \right) (298 \text{ K}) \left( \frac{-1.00}{1.00} + \frac{1.00}{50.} \right)$$

$$= \boxed{-2430 \text{ J}}$$

$$\text{b) } w = -P_{\text{ext}} \int dV = -P_{\text{ext}} (V_f - V_i) = -P_{\text{ext}} \Delta V$$

$$\kappa = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \approx -\frac{1}{V} \frac{\Delta V}{\Delta P}$$

$$\Delta P = 1.00 - 50.0 \text{ bar}$$

$$\Delta V = -\kappa V \Delta P$$

$$= -(0.000046 \text{ bar}^{-1}) \left( 18.07 \frac{\text{cm}^3}{\text{mol}} \right) (-49 \text{ bar})$$

$$= -0.000046 \text{ bar}^{-1} \left( 0.01807 \frac{\text{L}}{\text{mol}} \right) (-49 \text{ bar})$$

$$= 0.0000407 \text{ L}$$

$$w = -P_{\text{ext}} \Delta V = -(1.00 \text{ bar}) (0.0000407 \text{ L}) = -0.0000407 \text{ L bar}$$

$$\boxed{w = -0.00407 \text{ J}}$$

$$(1 \text{ L bar} = 100 \text{ J})$$

3 c) cont. The volume change for the expanding gas (about 25 L) is much larger than the volume change for the expanding liquid (0.0000407 L).

As a result, the expanding gas does much more work on the surroundings than the expanding liquid (2430 J vs. 0.00407 J)

$$(4) \quad \left(\frac{\partial H}{\partial P}\right)_T = V(1 - \beta T) \quad \beta = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{V_m} \left(\frac{\partial V_m}{\partial T}\right)_P$$

for an ideal gas ( $PV_m = RT$ ):

$$\beta = \frac{1}{V_m} \left[ \frac{\partial}{\partial T} \left( \frac{RT}{P} \right) \right]_P = \frac{R}{PV_m} \left( \frac{\partial T}{\partial T} \right)_P = \frac{R}{PV_m} = \frac{1}{T}$$

$$\left(\frac{\partial H}{\partial P}\right)_T = V \left( 1 - \frac{1}{T} T \right) = 0$$

(5) prove  $\left(\frac{\partial P}{\partial T}\right)_{V_m} = - \left(\frac{\partial P}{\partial V_m}\right)_T \left(\frac{\partial V_m}{\partial T}\right)_P$  for an ideal gas ( $PV_m = RT$ )

$$\begin{aligned} \text{LS} &= \left(\frac{\partial P}{\partial T}\right)_{V_m} = \left[ \frac{\partial}{\partial T} \left( \frac{RT}{V_m} \right) \right]_{V_m} = \frac{R}{V_m} \left(\frac{\partial T}{\partial T}\right)_{V_m} = \frac{R}{V_m} \\ &= \frac{P}{T} \end{aligned}$$

(5 cont.)

$$RS = - \left( \frac{\partial p}{\partial V_m} \right)_T \left( \frac{\partial V_m}{\partial T} \right)_p$$

$$= - \left[ \frac{\partial}{\partial V_m} \left( \frac{RT}{V_m} \right) \right]_T \left[ \frac{\partial}{\partial T} \left( \frac{RT}{p} \right) \right]_p$$

$$= - RT \left( \frac{\partial \frac{1}{V_m}}{\partial V_m} \right)_T \frac{R}{p} \left( \frac{\partial T}{\partial T} \right)_p$$

$$= - RT \left( -\frac{1}{V_m^2} \right) \frac{R}{p} 1$$

$$= \frac{RT}{V_m} \frac{R}{pV_m}$$

$$= p \frac{1}{T}$$

$$= \frac{p}{T}$$

$$LS = RS$$

⑥

$$v = \frac{m}{e}$$

$m = \text{mass (fixed)}$

$$\beta = \frac{1}{v} \left( \frac{\partial v}{\partial T} \right)_p = \frac{1}{\frac{m}{e}} \left( \frac{\partial \frac{m}{e}}{\partial T} \right)_p = \frac{e}{m} m \left( \frac{\partial \frac{1}{e}}{\partial T} \right)_p$$

$$= e \left( \frac{\partial \frac{1}{e}}{\partial e} \frac{\partial e}{\partial T} \right)_p = e \left( -\frac{1}{e^2} \right) \left( \frac{\partial e}{\partial T} \right)_p = -\frac{1}{e} \left( \frac{\partial e}{\partial T} \right)_p$$

7. a) i)  $\beta$  at  $0^\circ\text{C}$

don't use  
 $\frac{\rho(10^\circ\text{C}) - \rho(0^\circ\text{C})}{10\text{K}}$

this gives  $\beta$  at  $5^\circ\text{C}$   
(the average temperature)

$$\beta \approx -\frac{1}{\rho} \left( \frac{\Delta\rho}{\Delta T} \right) = -\frac{1}{\rho(0^\circ\text{C})} \left( \frac{\rho(10^\circ\text{C}) - \rho(-10^\circ\text{C})}{20\text{K}} \right)$$

$$= -\frac{1}{999.8395 \text{ kg m}^{-3}} \frac{999.7026 - 998.1173 \text{ kg m}^{-3}}{20\text{K}}$$

$$\beta = -0.0000792 \text{ K}^{-1} \text{ at } 0^\circ\text{C}$$

ii)  $\beta$  at  $25^\circ\text{C}$

$$\beta \approx -\frac{1}{\rho(25^\circ\text{C})} \frac{\rho(30^\circ\text{C}) - \rho(20^\circ\text{C})}{10\text{K}}$$

$$= -\frac{1}{997.0479 \frac{\text{kg}}{\text{m}^3}} \frac{995.6502 - 998.2071 \frac{\text{kg}}{\text{m}^3}}{10\text{K}}$$

$$\beta = 0.000256 \text{ K}^{-1}$$

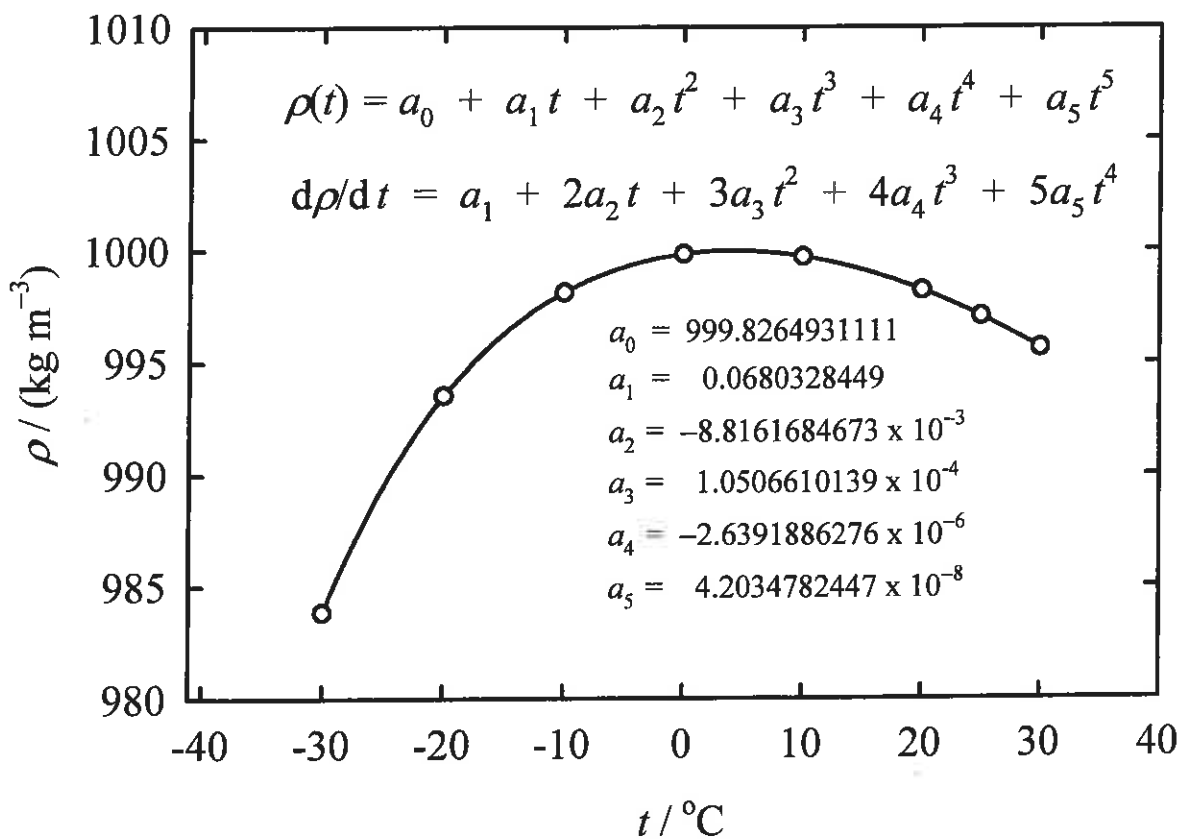
b) At temperatures below  $4^\circ\text{C}$ , the density of liquid water increases as the temperature is raised ( $\beta < 0$ ), meaning that liquid water contracts when heated

(most materials expand when heated ( $\beta > 0$ )).

See Table 3.1



Q7 a graph  $\rho$  vs  $t$  for  $H_2O(l)$



Using the fifth-order polynomial fitted to the density data gives the more accurate thermal expansion coefficients:

$$\beta(0 \text{ } ^\circ\text{C}) = -0.000068 \text{ K}^{-1}$$

$$\beta(25 \text{ } ^\circ\text{C}) = 0.000259 \text{ K}^{-1}$$