

*This assignment is optional.

You lose no marks if you don't hand it in.

*Happy Thanksgiving.*1. For an ideal gas (equation of state $V_m = RT/p$) prove:

[3]

$$\text{a) } (\partial V_m / \partial p)_T = -V_m / p \qquad \text{b) } (\partial p / \partial T)_{V_m} = p / T \qquad \text{c) } (\partial T / \partial V_m)_T = T / V_m$$

2. Use the results from **Question 1** to illustrate the cyclic rule:

[1]

$$(\partial x / \partial y)_z (\partial y / \partial z)_x (\partial z / \partial x)_y = -1$$

3. a) Show that the thermal expansivity (β) of an ideal gas is $1/T$.b) Calculate the thermal expansivity of water vapor at 0 °C and 1.00 bar.c) The thermal expansivity of liquid water at 0 °C and 1.00 bar ($-0.0000680 \text{ K}^{-1}$) is much smaller than that of water vapor. Why? Explain briefly in terms of molecular interactions.

[4]

d) The thermal expansivity of liquid water at 0 °C and 1.00 bar is highly unusual. Why?

4. a) 5.00 L of an ideal gas initially at 1.00 bar is reversibly compressed to a final pressure of 5.00 bar at 25 °C. Calculate w .

[5]

b) 5.00 L of liquid water initially at 1.00 bar is reversibly compressed to 5.00 bar at 25 °C. Calculate w . Use $0.0000459 \text{ bar}^{-1}$ for the isothermal compressibility (κ) of liquid water.

c) The work required to compress water vapor (part a) much larger than the work required to compress liquid water (part b). Why? Explain briefly in terms of interactions between molecules.

5. a) Use the definition of the volumetric thermal expansion coefficient [$\beta = V^{-1}(\partial V / \partial T)_p$] to show $\beta = -\rho^{-1}(\partial \rho / \partial T)_p$ where ρ is the density (mass per unit volume).

[4]

b) The densities of liquid water at 1.00 bar pressure and 15.00 °C, 20.00 °C and 25.00 °C are 0.999103, 0.998207 and 0.997048 gm cm^{-3} , respectively. Use this density data to calculate the volumetric thermal expansion coefficient of liquid water at 1.00 bar and 20.00 °C.

6. Aluminum at 1.00 bar and 20.0 °C initially is heated to a final temperature of 35 °C. Calculate the increase in pressure required to keep the aluminum at constant volume.

[3] Data: $\beta = 0.0000693 \text{ K}^{-1}$ and $\kappa = 0.00000133 \text{ bar}^{-1}$.

Chem 231 Assignment #4

(Q1) $V_m = v/n = RT/P$ (ideal gas)

a) $\left(\frac{\partial V_m}{\partial P}\right)_T = \left(\frac{\partial}{\partial P} \frac{RT}{P}\right)_T = RT \left(\frac{\partial \frac{1}{P}}{\partial P}\right)_T = RT \left(-\frac{1}{P^2}\right)$
 $= -\frac{RT}{P} \frac{1}{P} = -V_m \left(\frac{1}{P}\right)$

b) $\left(\frac{\partial P}{\partial T}\right)_{V_m} = \left(\frac{\partial}{\partial T} \frac{RT}{V_m}\right)_{V_m} = \frac{R}{V_m} = \frac{P}{T}$

$P = \left(\frac{RT}{V_m}\right)$

c) $\left(\frac{\partial T}{\partial V_m}\right)_P = \left(\frac{\partial}{\partial V_m} \frac{PV_m}{R}\right)_P$

$T = \left(\frac{PV_m}{R}\right)$

$= \frac{P}{R} \left(\frac{\partial V_m}{\partial V_m}\right)_P = \frac{T}{V_m}$

(Q2) Cyclic Rule

use:

$x = V_m, y = P, z = T$

$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$

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

$= -1$

(for almost all substances, $\beta > 0$, indicating expansion as T increases)

Q3 a) thermal expansivity $\frac{1}{V_m} \left(\frac{\partial V_m}{\partial T} \right)_P$ of an ideal gas
($V_m = \frac{RT}{P}$)

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

b) water vapor (assumed to be an ideal gas)
 $0^\circ\text{C} \leftrightarrow 273.15\text{ K}$

$$\beta = \frac{1}{T} = \frac{1}{273.15\text{ K}}$$

$$\beta = 0.00366\text{ K}^{-1}$$

c) liquid water at 0°C $\beta = 0.000459\text{ K}^{-1}$

$\beta_{\text{liquid H}_2\text{O}}$ is much smaller than $\beta_{\text{water vapor}}$

because the liquid-phase water molecules are tightly held together and tightly packed together

(e.g., by hydrogen bonds) with little

free volume to expand into when heated (as in the vapor)

d) at 0°C , $\beta_{\text{liquid H}_2\text{O}}$ is negative, so the volume of liquid water shrinks as T increases

Q4 a) Isothermal and reversible compression of an ideal gas (initial volume 5.00 L) from 1.00 bar to 5.00 bar at 298.15 K.

$$\begin{aligned}
 w &= - \int P_{\text{ext}} dV \stackrel{(\text{rev: } P_{\text{ext}} = P)}{=} - \int p dV \stackrel{(\text{isothermal})}{=} - \int \frac{nRT}{V} dV \\
 &= -nRT \int \frac{1}{V} dV = -nRT \ln \left(\frac{V_f}{V_i} \right) \\
 &= -P_i V_i \ln \left(\frac{\frac{nRT}{P_f}}{\frac{nRT}{P_i}} \right) = -P_i V_i \ln \left(\frac{P_i}{P_f} \right) \\
 &= (1.00 \text{ bar})(5.00 \text{ L}) \ln \left(\frac{1.00 \text{ bar}}{5.00 \text{ bar}} \right) \\
 &= 8.047 \text{ L bar} = (8.047 \text{ L bar}) \left(\frac{10^{-3} \text{ m}^3}{\text{L}} \right) \left(\frac{10^5 \text{ Pa}}{\text{bar}} \right) \\
 &= 804.7 \text{ J}
 \end{aligned}$$

b) 5.00 L of liquid water initially at 1.00 bar is reversibly and isothermally compressed to 5.00 bar.

$$\kappa = - \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \quad \text{multiply by } dp_T$$

$$\kappa dp_T = - \frac{1}{V} dV \quad \frac{1}{V} dV = -\kappa dp_T$$

$$\int_{V_i}^{V_f} \frac{1}{V} dV = - \int_{P_i}^{P_f} \kappa dp_T = -\kappa (P_f - P_i) =$$

(Q4 - b cont.)

$$\int \frac{1}{V} dV = \int d \ln V = \ln V_f - \ln V_i = \ln \left(\frac{V_f}{V_i} \right) = -\kappa (P_f - P_i)$$

$$\ln \left(\frac{V_f}{V_i} \right) = -(0.0000459 \text{ bar}^{-1}) (5.00 - 1.00) \text{ bar}$$

$$\ln \left(\frac{V_f}{V_i} \right) = -0.000184 \quad \frac{V_f}{V_i} = e^{-0.000184}$$

$$V_f = e^{-0.000184} V_i = 0.999816 (5.00 \text{ L})$$

$$V_f = 4.9991 \text{ L}$$

* important *
The liquid volume is almost constant.

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

multiply by $pV dp$

$$\kappa p V dp = -\frac{pV}{V} dV$$

$\kappa, V \approx \text{constant}$

$$\int \kappa p V dp = -\int p dV = \text{reversible work } w$$

$$w = \kappa V \int_{P_i}^{P_f} p dp = \kappa V \left(\frac{p^2}{2} \right) \Big|_{P_i}^{P_f} = \kappa V \frac{P_f^2 - P_i^2}{2}$$

$$= (0.0000459 \text{ bar}^{-1}) (5.00 \text{ L}) \frac{5.00^2 - 1.00^2}{2} \text{ bar}^2$$

$$= 0.00275 \text{ L bar} = 0.275 \text{ J}$$

negligibly
small!

(Q4 cont.)

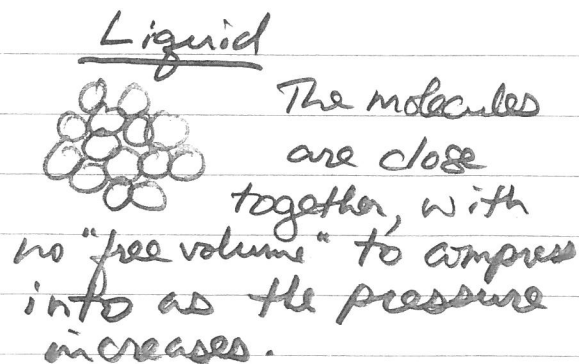
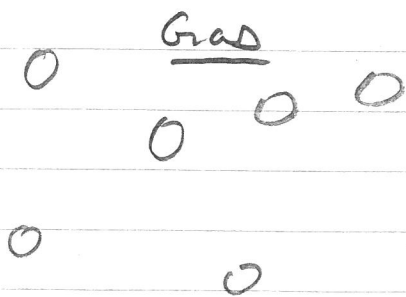
c) The volume change for the vapor (5.00 L to 1.00 L) is much larger than the volume change of the liquid (5.0000 L to 4.9991 L)

$$\Delta V_{\text{gas}} = -4.00 \text{ L}$$

$$\Delta V_{\text{liquid}} = -0.0009 \text{ L} \approx 0$$

$$w_{\text{gas}} = - \int P dV_{\text{gas}} \quad \text{significant}$$

$$w_{\text{liquid}} = - \int P dV_{\text{liquid}} \quad \leftarrow \text{almost zero} \approx 0$$



The molecules are far apart, and easily move closer together as the pressure increases

$$\left(\frac{d\frac{1}{\rho}}{d\rho} = -\frac{1}{\rho^2} \text{ so } d\left(\frac{1}{\rho}\right) = -\frac{1}{\rho^2} d\rho \right)$$

(Q5) a) For a fixed mass^(m) of substance, the volume and density are inversely related.

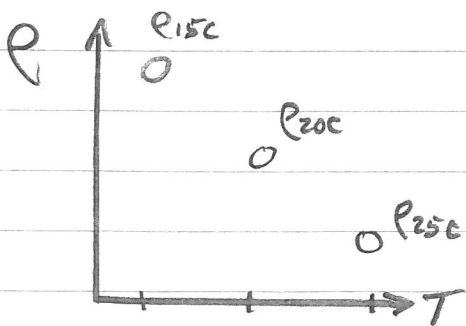
$$\rho = \frac{m}{V} \quad V = \frac{m}{\rho}$$

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = \frac{1}{m/\rho} \left(\frac{\partial \frac{m}{\rho}}{\partial T} \right)_P$$

$$= \left(\frac{m}{m/\rho} \right) \left(\frac{\partial \frac{1}{\rho}}{\partial T} \right)_P = (\rho) \left(-\frac{1}{\rho^2} \right) \left(\frac{\partial \rho}{\partial T} \right)_P$$

$$\beta = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_P$$

b) $\beta = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_P$ ← slope of ρ plotted against T



best estimate of slope
at 20°C :

$$\frac{\rho_{25c} - \rho_{15c}}{T_{25c} - T_{15c}} = \text{slope}$$

$$\text{slope} = \frac{(0.997048 - 0.999103) \text{ g cm}^{-3}}{10 \text{ K}} = -2.055 \times 10^{-4} \frac{\text{g cm}^{-3}}{\text{K}}$$

at 20°C:

$$\beta = -\frac{1}{\rho_{20c}} \left(\frac{\partial \rho}{\partial T} \right)_P \stackrel{\text{slope}}{=} = -\frac{(-2.055 \times 10^{-4} \text{ g cm}^{-3} \text{ K}^{-1})}{0.997048 \text{ g cm}^{-3}}$$

$$\beta = 2.06 \times 10^{-4} \text{ K}^{-1}$$

Q6

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{\beta}{\kappa}$$

assume α, κ
are constants

$$dp = \frac{\beta}{\kappa} dT$$

(no other information)

$$\int dp = \int \frac{\beta}{\kappa} dT = \frac{\beta}{\kappa} \int dT$$

$$P_f - P_i = \frac{\beta}{\kappa} (T_f - T_i)$$

$$= \frac{0.0000693 \text{ K}^{-1}}{0.0000133 \text{ bar}^{-1}} (35 - 20) \text{ K}$$

$$= 781 \text{ bar}$$

pressure increase
to keep the volume
of aluminium constant