

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

1. The isothermal compressibility is defined as $\kappa = V^{-1}(\partial V/\partial p)_T$.

a) Prove that κ for an ideal gas is $1/p$.

[4]

b) For a nonideal gas obeying the equation of state $p = RT/(V_m - b)$, prove

$$\kappa = \frac{1}{1 + (bp/RT)} \frac{1}{p}$$

c) Explain briefly how the results from parts a and b show that repulsive intermolecular forces make real gases more difficult to compress than ideal gases.

2. At 100 °C and 1.00 bar, the isothermal compressibility of water vapor is 1.00 bar^{-1} and the isothermal compressibility of liquid water is $0.000055 \text{ bar}^{-1}$. Explain briefly, in molecular terms, why the compressibility of liquid water is much smaller than the compressibility of water vapor.

[1]

3. a) 1.00 L of an ideal gas expands reversibly and isothermally from an initial pressure of 5.00 bar to a final pressure of 1.00 bar at 300 K. Calculate the work, w . *Data:* $\kappa = 1/p$.

[5]

b) 1.00 L of liquid water expands reversibly and isothermally from an initial pressure of 5.00 bar to a final pressure of 1.00 bar at 300 K. Calculate the work, w . *Data:* $\kappa = 0.000046 \text{ bar}^{-1}$.

c) Briefly explain how the results from parts a and b illustrate the useful result that work and changes in energy are negligibly small for the isothermal compression or expansion of liquids.

4. The isothermal compressibility is defined as $\kappa = -V^{-1}(\partial V/\partial p)_T$. Starting with this definition, prove that κ in terms of the density ($\rho = \text{mass} / \text{volume}$) is

[2]

$$\kappa = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial p} \right)_T$$

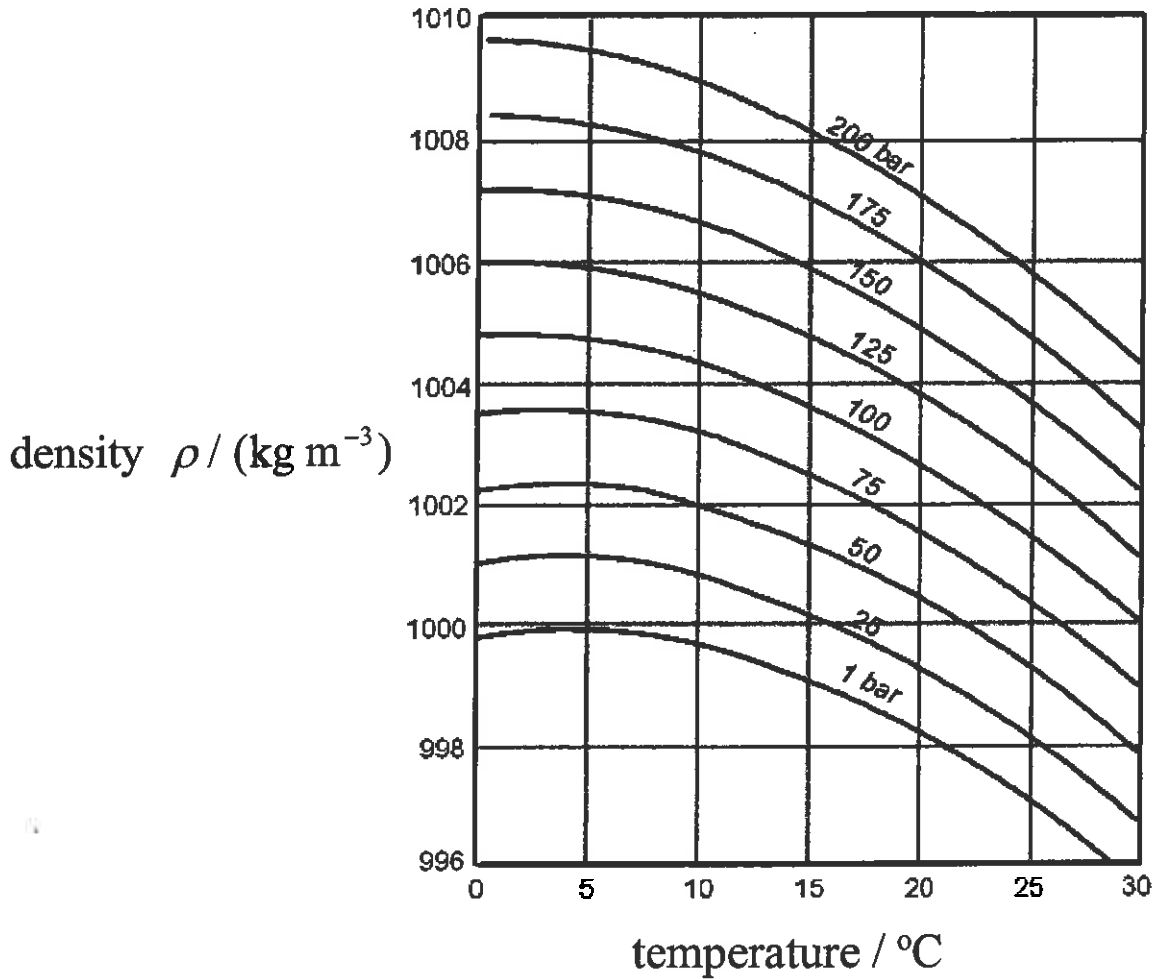
5. The volumetric thermal expansion coefficient is defined as $\beta = V^{-1}(\partial V/\partial T)_p$. Starting with this definition, prove that β in terms of the density is

[2]

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

6. The densities of liquid water at different temperatures and pressures are plotted below.

[6]



a) Use the plotted density data to estimate the isothermal compressibility $\kappa = -V^{-1}(\partial V/\partial p)_T$ of liquid water at 25 $^{\circ}\text{C}$ and 1 bar. (*Hint:* Refer to question 3.)

b) Use the plotted density data to estimate the volumetric thermal expansion coefficient $\beta = V^{-1}(\partial V/\partial T)_p$ of liquid water at 25 $^{\circ}\text{C}$ and 1 bar. (*Hint:* Refer to question 4.)

c) Intuitively, the volume of a substance is expected to increase as the temperature is raised, due to thermal expansion. Explain how the plotted densities show the unexpected result that the volume of water can actually decrease as the temperature is raised!

Q1 a) Prove that the isothermal compressibility $\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$ is $1/P$ for an ideal gas.

ideal gas: $pV = nRT \Rightarrow V = \frac{nRT}{P}$

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

(substitute)

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

(constants)

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

$$= -\frac{nRT}{V} \left(-\frac{1}{P^2} \right) = \frac{nRT}{pV} \frac{1}{P} = \boxed{\frac{1}{P}}$$

b) Isothermal compressibility for a real gas

with $p = \frac{RT}{V_m - b}$?

b is a positive constant

$$p(V_m - b) = RT \quad \text{so} \quad V_m = \frac{RT}{p} + b$$

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

$$= -\frac{1}{\frac{RT}{p} + b} \left[\frac{\partial}{\partial P} \left(\frac{RT}{P} + b \right) \right]_T = -\frac{RT}{\frac{RT}{p} + b} \left(\frac{\partial \frac{1}{P}}{\partial P} \right)_T$$

$$= -\frac{RT}{\frac{RT}{p} + b} \left(-\frac{1}{P^2} \right) = \left(\frac{RT}{RT + bP} \right) \frac{1}{P} = \frac{1}{1 + \frac{bP}{RT}} \frac{1}{P}$$

(1 cont.)

c) the parameter "b" (also known as the vander Waals b!) represents repulsive intermolecular forces

(Why? The pressure calculated from $P = \frac{RT}{V_m - b}$ is larger than the pressure $\frac{RT}{V_m}$ for an ideal gas.)

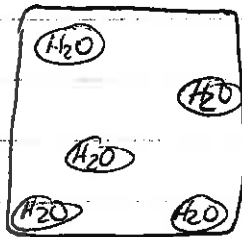
How do repulsive intermolecular forces affect the compressibility?

$$\kappa = \left(\frac{1}{1 + \frac{bP}{RT}} \frac{1}{P} \right)_{\text{real}} \text{ is smaller than } \kappa = \left(\frac{1}{P} \right)_{\text{ideal}}$$

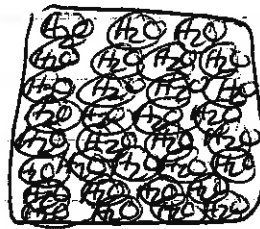
(bP/RT increases the denominator, making κ smaller)

⇒ molecules "pushing each other apart" are more difficult to compress than ideal-gas molecules (no forces between molecules)

Q2



water vapor
(lots of "empty" space)



liquid water
(~ no empty space)

Compressing water vapor is relatively "easy" because there is lots of free space for the molecules to move into. Liquid water molecules, on the other hand, are packed tightly together. Compressing liquid water attempts to cause molecular electron orbitals to overlap ⇒ not allowed!

$$PV = nRT$$

Q3 a) 1.00 L of ideal gas expands reversibly ($P_{ext} = P$) and isothermally (constant T) from 5.00 bar to 1.00 bar at 300 K. Work?

$$w = - \int P_{ext} dV \quad \text{(always)} = - \int P dV \quad \text{(reversible)} = - \int \frac{nRT}{V} dV \quad \text{(ideal gas)}$$

$$w = -nRT \int \frac{dV}{V} \quad \text{(isothermal)} = -nRT \ln\left(\frac{V_f}{V_i}\right) = -nRT \ln\left(\frac{\frac{nRT}{P_f}}{\frac{nRT}{P_i}}\right)$$

$$w = -P_i V_i \ln\left(\frac{P_i}{P_f}\right) = - (5.00 \text{ bar})(1.00 \text{ L}) \ln\left(\frac{5}{1}\right)$$

$$w = -8.05 \text{ bar L} = -8.05 \text{ bar L} \left(\frac{10^5 \text{ Pa}}{\text{bar}} \right) \left(\frac{10^{-3} \text{ m}^3}{\text{L}} \right)$$

$$w = -805 \text{ J}$$

b) 1.00 L of liquid water expands reversibly and isothermally from 5.00 bar to 1.00 bar at 300 K.

for a liquid, volume is almost independent of P
Why? liquids are almost (K \approx 0)

$$\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \Rightarrow \text{(incompressible)} \quad -\kappa V dp = dV$$

$$w = - \int P_{ext} dV \quad \text{(reversible, } P = P_{ext}) = - \int P (-\kappa V) dp$$

$$\text{(}\kappa, V \approx \text{constants)} = \kappa V \int P dp = \kappa V \left(\frac{P^2}{2} \right) \Big|_{P_i}^{P_f} = \kappa V \frac{P_f^2 - P_i^2}{2}$$

$$= (0.000046 \text{ bar}^{-1})(1.00 \text{ L}) \frac{(1.00^2 - 5.00^2) \text{ bar}^2}{2}$$

$$= -0.000552 \text{ L bar} = \boxed{-0.0552 \text{ J}}$$

c) -0.0552 J work is negligible

Tiny, compared to -805 J for an ideal gas

Q4 isothermal compressibility defined as $\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$

How are isothermal compressibilities measured?

One popular way = from changes in density ρ measured at different pressures

density $\rho = \frac{\text{mass}}{\text{volume}} = \frac{m}{V}$ constant $\Rightarrow V = \frac{m}{\rho}$

$$\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = -\frac{1}{m/\rho} \left[\frac{\partial (m/\rho)}{\partial P} \right]_T = -\frac{m}{m/\rho} \left(\frac{\partial \frac{1}{\rho}}{\partial P} \right)_T$$

$$\kappa = -\rho \left(\frac{\partial \frac{1}{\rho}}{\partial P} \right)_T = -\rho \left(-\frac{1}{\rho^2} \right) \left(\frac{\partial \rho}{\partial P} \right)_T = \boxed{\frac{1}{\rho} \left(\frac{\partial \rho}{\partial P} \right)_T}$$

very useful!

Q5 volumetric thermal expansion coefficient

defined as $\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$

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

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

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

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

also very useful!

Q6) Can we calculate isothermal compressibilities κ and volumetric thermal expansion coefficients β from graphical data?

isothermal compressibility

a) $\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$ as noted in Q3 and in the course notes, the volumes of liquids are almost constant (because κ is very small)

$\therefore \kappa \approx -\frac{1}{V} \frac{\Delta V}{\Delta P} = \frac{1}{\rho} \frac{\Delta \rho}{\Delta P}$ confirmed by the plotted densities

at 25 °C and 1 bar

($\Delta \rho$ per 25 bar pressure increase \approx constant)

$\kappa \approx \frac{1}{\rho_{25^\circ\text{C}, 1\text{bar}}} \frac{\Delta \rho}{\Delta P} \approx \frac{1}{\rho_{25^\circ\text{C}, 1\text{bar}}} \frac{\rho_{25^\circ\text{C}, 100\text{bar}} - \rho_{25^\circ\text{C}, 1\text{bar}}}{100\text{bar} - 1\text{bar}}$

See graph for $\Delta \rho$, ΔP values

$= \frac{1}{997.2 \text{ kg m}^{-3}} \frac{(1001.2 - 997.2) \text{ kg m}^{-3}}{99 \text{ bar}} = 0.000046 \text{ bar}^{-1}$

volumetric thermal expansion coefficient

b) Similarly: $\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \approx \frac{1}{V} \frac{\Delta V}{\Delta T} \approx -\frac{1}{\rho} \frac{\Delta \rho}{\Delta T}$

the slope $\left(\frac{\partial \rho}{\partial T} \right)_P \approx \frac{\Delta \rho}{\Delta T}$ at 25 °C is $\approx \frac{1003.6 - 997.2 \text{ kg m}^{-3}}{-25 \text{ K}}$

See graph for $\Delta \rho$, ΔT

$\beta \approx -\frac{1}{997.2 \text{ kg m}^{-3}} \frac{(1003.6 - 997.2) \text{ kg m}^{-3}}{-25 \text{ K}}$

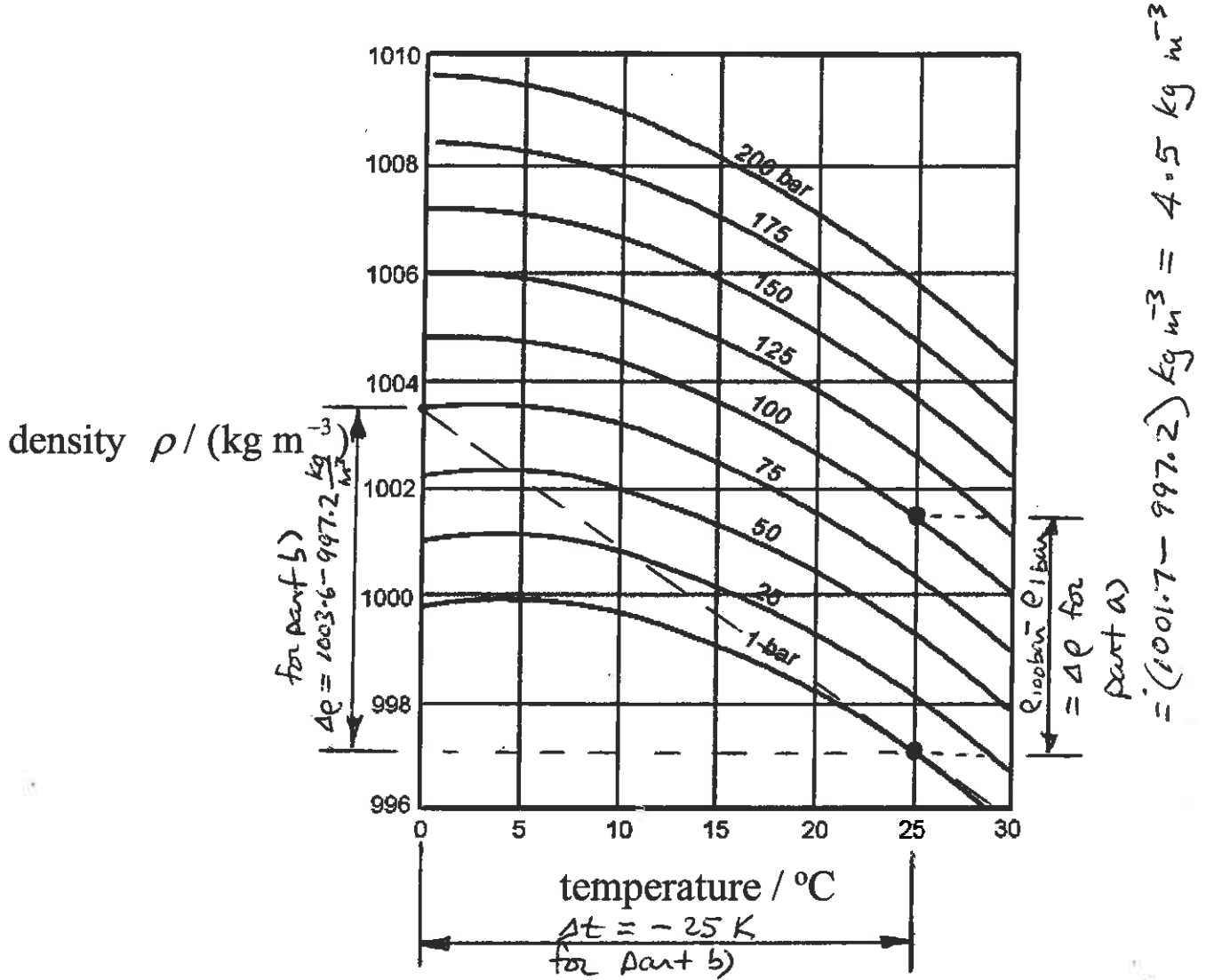
$\beta \approx 0.00026 \text{ K}^{-1}$

c) notice $\left(\frac{\partial \rho}{\partial T} \right)_P > 0$ at 1 bar, 25 bar, $t \leq 4^\circ\text{C} \Rightarrow \beta < 0$

density increase with temp!

6. The densities of liquid water at different temperatures and pressures are plotted below.

[6]



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