

- please answer all 5 questions in the spaces provided
- you have **two hours** to write this test
- a calculator and the equation sheets provided may be used
- all questions are of equal value
- no books or notes are allowed
- no marks for unreadable answers

1. a) Why is the van der Waals equation generally more accurate than the ideal gas equation?
It includes terms to allow for attractive and repulsive forces between molecules found in all real gases, but not included in the ideal gas equation.
- b) For ethane at 350 K and a molar volume of 0.150 L mol^{-1} , use the van der Waals equation and the parameter values $a = 5.38 \text{ bar L}^2 \text{ mol}^{-2}$ and $b = 0.0651 \text{ L mol}^{-1}$ to calculate:

i) the pressure p

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2} = \frac{(0.08314 \text{ L bar K}^{-1} \text{ mol}^{-1})(350 \text{ K})}{(0.150 - 0.0651) \text{ L mol}^{-1}} - \frac{5.38 \text{ bar L}^2 \text{ mol}^{-2}}{(0.150 \text{ L mol}^{-1})^2}$$

$$= 342.7 \text{ bar} - 239.1 \text{ bar}$$

$$p = 104 \text{ bar}$$

ii) the compression factor Z

$$Z = \frac{pV_m}{RT} = \frac{(104 \text{ bar})(0.150 \text{ L mol}^{-1})}{(0.08314 \text{ L bar K}^{-1} \text{ mol}^{-1})(350 \text{ K})}$$

$$Z = 0.536$$

iii) the second virial coefficient $B(T)$

$$B(T) = b - \frac{a}{RT} = 0.0651 \text{ L mol}^{-1} - \frac{5.38 \text{ bar L}^2 \text{ mol}^{-2}}{(0.08314 \text{ L bar mol}^{-1} \text{ K}^{-1})(350)}$$

$$= 0.0651 \text{ L mol}^{-1} - 0.1848 \text{ L mol}^{-1}$$

$$B(T) = -0.120 \text{ L mol}^{-1}$$

or: use

$$Z \approx 1 + \frac{B(T)}{V_m} + \dots$$

$$B(T) = (Z - 1)V_m = -0.070 \frac{\text{L}}{\text{mol}}$$

- c) For ethane at 350 K and a molar volume of 0.150 L mol^{-1} , do attractive intermolecular forces dominate repulsive forces intermolecular forces? Justify your answer.

Yes! $Z = \frac{p}{p_{\text{ideal}}} = 0.536 < 1$

less pressure than for an ideal gas — molecules are "sticking" together

[also, $B(T) < 0$]

2. a) The volumetric thermal expansion coefficient is useful for calculating changes in volume caused by changes in temperature. Why is β defined as $V^{-1}(\partial V/\partial T)_p$ not as $(\partial V/\partial T)_p$?

$\frac{1}{V}(\frac{\partial V}{\partial T})_p$ is more convenient because it is an intensive quantity (the same value for a system of any size)

- b) The isothermal compressibility is useful for calculating changes in volume caused by changes in pressure. Why is κ defined as $-V^{-1}(\partial V/\partial p)_T$ not as $V^{-1}(\partial V/\partial p)_T$? \Rightarrow It's convenient: $(\partial V/\partial p)_T$ is always negative (all systems "shrink" when p increase), so $-\frac{1}{V}(\frac{\partial V}{\partial p})_T$ is always positive \Rightarrow no need to keep using minus signs

- c) Prove that the isothermal compressibility of an ideal gas is $1/p$.

definition:

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

$$= -\frac{nRT}{nRT} \left(\frac{\partial \frac{1}{p}}{\partial p} \right)_T = \left(-\frac{1}{p} \right) \left(-\frac{1}{p^2} \right)$$

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

- d) Liquid mercury initially at 1.00 bar and 300 K is heated at constant volume.

Calculate $(\partial p/\partial T)_v$. Data: $\beta = 0.000181 \text{ K}^{-1}$ $\kappa = 0.00000391 \text{ bar}^{-1}$

background information $\left(\frac{\partial p}{\partial T} \right)_v = - \left(\frac{\partial p}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_p = - \frac{(\partial V/\partial T)_p}{(\partial V/\partial p)_T} = \frac{\frac{1}{V}(\partial V/\partial T)_p}{-\frac{1}{V}(\partial V/\partial p)_T} = \frac{\beta}{\kappa}$

from equation sheet:

$$\left(\frac{\partial p}{\partial T} \right)_v = \frac{\beta}{\kappa} = \frac{0.000181 \text{ K}^{-1}}{0.00000391 \text{ bar}^{-1}}$$

$$= 46.3 \frac{\text{K}^{-1}}{\text{bar}^{-1}}$$

$$\boxed{\left(\frac{\partial p}{\partial T} \right)_v = 46.3 \frac{\text{bar}}{\text{K}}}$$

- e) Explain why heating liquids in closed containers can damage the containers, even very strong ones. (Suggestion: use the result from part d.)

Small changes in temperature (a few degrees), can generate very large pressures that will "break" containers [e.g., mercury-in-glass thermometer shatters if heated past its maximum temperature reading]

isothermal: $P_i V_i = P_f V_f = nRT$

3. a) 10.0 L of an ideal gas at 50.0 bar and 300 K expands isothermally to a final pressure of 1.00 bar against a constant external pressure of 1.00 bar. Calculate ΔU , ΔH , w and q .

isothermal ideal gas: $\Delta U = 0$ $\Delta H = 0$

U, H depend only on T : no ΔT then no ΔU no ΔH

next easiest to calculate: $w = \int P_{ext} dV$ (constant)

$V_f = \frac{P_i}{P_f} V_i = \frac{50.0 \text{ bar}}{1.00 \text{ bar}} 10.0 \text{ L} = 500.0 \text{ L}$

$w = -\int_{V_i}^{V_f} P_{ext} dV = -P_{ext} \int_{V_i}^{V_f} dV = -P_{ext} (V_f - V_i)$

$w = -(1.00 \text{ bar})(500.0 - 10.0) \text{ L} = -490.0 \text{ L bar}$

$w = -490 \text{ L bar} (10^{-3} \text{ m}^3 \text{ L}^{-1}) (10^5 \text{ Pa bar}^{-1}) = \boxed{-49,000 \text{ J}}$
 w

$\Delta U = 0 = q + w$

$q = -w$

$q = \boxed{49,000 \text{ J}}$

(1 L bar = 100 J)

- b) 10.0 L of liquid water at 50.0 bar and 300 K expands isothermally to a final pressure of 1.00 bar against a constant external pressure of 1.00 bar. Calculate ΔV and w .

Data: $\kappa = 0.0000459 \text{ bar}^{-1}$

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

$\int_{V_i}^{V_f} \frac{dV}{V} = -\int_{P_i}^{P_f} \kappa dp$

$\ln \frac{V_f}{V_i} = -\kappa (P_f - P_i)$

$= -(0.0000459 \text{ bar}^{-1})(1.00 - 50.0) \text{ bar}$

$\ln \left(\frac{V_f}{V_i} \right) = +0.00225$

$\frac{V_f}{V_i} = e^{+0.00225} = 1.00225$

$V_f = 1.00225 V_i$

$\Delta V = 1.00225 V_i - V_i = 0.00225 V_i$

$\Delta V = 0.00225 (10.0 \text{ L}) = \boxed{0.0225 \text{ L}}$

(1 L bar = 100 J)

$w = -\int P_{ext} dV = -P_{ext} \Delta V = (-1.00 \text{ bar})(0.0225 \text{ L}) = -0.0225 \text{ L bar}$
 $w = \boxed{-2.25 \text{ J}}$

- c) Explain briefly why a leak from a tank of high-pressure gas is much more dangerous than a leak from a tank filled with high-pressure liquid. (Suggestion: use the results from a and b.)

gas leak \Rightarrow large $\Delta V \Rightarrow$ large $P_{ext} \Delta V \Rightarrow$ "lots" of work done on surrounding \Rightarrow an "explosion"

(liquids are almost incompressible) liquid leak: $w \approx 0$
 $\Delta V \approx 0$

4. a) Starting with the thermodynamic equation of state $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$

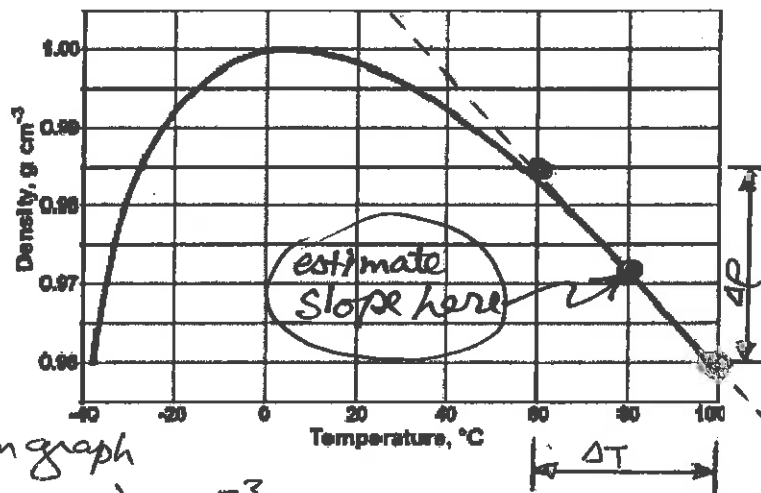
prove $(\partial U/\partial V)_T = 0$ for an ideal gas. $p = \frac{nRT}{V}$

$$\begin{aligned} \left(\frac{\partial U}{\partial V}\right)_T &= T\left(\frac{\partial p}{\partial T}\right)_V - p = T\left[\frac{\partial}{\partial T}\left(\frac{nRT}{V}\right)\right]_V - p = T\left(\frac{nR}{V}\right)\left(\frac{\partial T}{\partial T}\right)_V - p \\ &= \frac{TnR}{V}(1) - p = \frac{nRT}{V} - p = p - p = 0 \end{aligned}$$

b) The density of liquid water at 1.00 bar is plotted against temperature in this diagram. Use the plotted data and

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

to calculate β for liquid water at 80 °C and 1.00 bar.



at 80 °C, 1 bar

read $\rho = 0.972 \text{ g cm}^{-3}$ from graph

tangent slope $\approx \frac{\Delta \rho}{\Delta T} \approx \frac{(0.960 - 0.985) \text{ g cm}^{-3}}{(100 - 60) \text{ K}} = -0.000625 \text{ g cm}^{-3} \text{ K}^{-1}$

$$\beta \approx -\frac{1}{\rho} \frac{\Delta \rho}{\Delta T} = -\frac{1}{0.972 \text{ g cm}^{-3}} (-0.000625 \text{ g cm}^{-3} \text{ K}^{-1})$$

$\beta = 0.00064 \text{ K}^{-1}$

c) 1.00 mole of helium assumed to be an ideal gas ($C_{vm} = 3R/2$) initially at 1.00 bar and 300 K is reversibly and adiabatically compressed to a final pressure of 10.0 bar. Calculate the final temperature of the gas.

ideal gas $C_{pm} = C_{vm} + R = 5R/2$

$$\gamma = \frac{C_{pm}}{C_{vm}} = \frac{5R/2}{3} = \frac{5}{3} \quad \text{use } P_i V_i^\gamma = P_f V_f^\gamma \quad (\text{reversible, const. } \gamma)$$

$$V_i = \frac{nRT_i}{P_i} = \frac{(1.00 \text{ mol})(0.08314 \text{ L bar K}^{-1} \text{ mol}^{-1})(300 \text{ K})}{1.00 \text{ bar}} = 24.94 \text{ L}$$

$$\left(\frac{V_f}{V_i}\right)^\gamma = \frac{P_i}{P_f} = \frac{1.00 \text{ bar}}{10.0 \text{ bar}} = 0.100 \quad \frac{V_f}{V_i} = (0.100)^{1/\gamma} = 0.100^{3/5}$$

$V_f/V_i = 0.251$

$$V_f = 0.251(24.94 \text{ L}) = 6.26 \text{ L} = \frac{nRT_f}{P_f}$$

$$T_f = \frac{(6.26 \text{ L})(10.0 \text{ bar})}{1.00 \text{ mol}(0.08314 \text{ L bar K}^{-1} \text{ mol}^{-1})}$$

$T_f = 753 \text{ K}$

gas is not isothermal

$$\frac{P_i}{P_f} = \frac{V_f}{V_i} = \frac{1}{10}$$

can't use

5. a) The van der Waals parameter for NO might be expected to be the average of the a values for N_2 and O_2 , but experiments give:

$$a(N_2) = 1.37 \quad a(O_2) = 1.38 \quad a(NO) = 1.67 \quad (\text{units: } L^2 \text{ bar mol}^{-2})$$

Why is a for NO significantly larger than a for N_2 or O_2 ?

NO has a permanent electric dipole, causing stronger NO-NO attractions than for NN-NN or OO-OO
(N_2 and O_2 are nonpolar)

- b) Is the Joule-Thomson coefficient an extensive quantity? Justify your answer.

$$\mu_{JT} \equiv \left(\frac{\partial T}{\partial P} \right)_H \sim \frac{\Delta T}{\Delta P} \sim \frac{\text{intensive quantity}}{\text{intensive quantity}} \therefore \text{intensive}$$

- b) Use the equation $\mu_{JT} = -V_m(1 - \beta T)/C_{pm}$ derived in class to prove the Joule-Thomson coefficient of an ideal gas is zero. Explain why ideal gases are unsuitable for refrigeration or gas liquefaction applications.

μ_{JT} is proportional to $1 - \beta T$
for an ideal gas $\beta = \frac{1}{T}$

$$1 - \beta T = 1 - \frac{1}{T} T = 0$$

$$\therefore \mu_{JT} = 0 \quad (\text{ideal gas})$$

- c) Joule-Thomson expansions were analyzed in class for gases. What about liquids?

Use the general equation $\mu_{JT} = -V_m(1 - \beta T)/C_{pm}$ derived in class to calculate the Joule-Thomson coefficient for liquid mercury (atomic weight 200.6 g mol^{-1}) at 300 K and 1.00 bar.

Data for liquid mercury: density 13.7 g cm^{-3} , $\beta = 0.000181 \text{ K}^{-1}$, $C_{pm} = 28.0 \text{ J K}^{-1} \text{ mol}^{-1}$

$$V_m = \frac{\text{molar mass}}{\text{density}} = \frac{200.6 \text{ g mol}^{-1}}{13.7 \text{ g cm}^{-3}} = 14.6 \text{ cm}^3 \text{ mol}^{-1}$$

$$V_m = (14.6 \text{ cm}^3 \text{ mol}^{-1}) (10^{-6} \text{ m}^3 \text{ cm}^{-3}) = 14.6 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1} \quad \left(\begin{array}{c} \text{SI} \\ \text{units} \end{array} \right)$$

$$\mu_{JT} = - \frac{(14.6 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}) (1 - (0.000181 \text{ K}^{-1}) (300 \text{ K}))}{28.0 \text{ J K}^{-1} \text{ mol}^{-1}}$$

$$= -4.93 \times 10^{-7} \text{ K Pa}^{-1}$$

$$= -(4.93 \times 10^{-7} \text{ K Pa}^{-1}) (10^5 \text{ Pa bar}^{-1})$$

$$\mu_{JT} = -0.0493 \text{ K bar}^{-1} \quad 5$$

Q1
Q2
Q3
Q4
Q5