

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

1. a) Describe how van der Waals modified the ideal gas equation $p = \frac{RT}{V_m}$

i) to include repulsive intermolecular forces

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

ii) to include attractive intermolecular forces

$$p = \frac{RT}{V_m} - \frac{a}{V_m^2}$$

b) The van der Waals a coefficient for Xe ($4.25 \text{ bar L}^2 \text{ mol}^{-1}$) is significantly larger than the van der Waals a coefficient for He ($0.035 \text{ bar L}^2 \text{ mol}^{-1}$). Why?

Xe has more electrons (54) than He (only 2), and therefore stronger dispersion attractions

c) The van der Waals b coefficient for Xe (0.051 L mol^{-1}) is significantly larger than the van der Waals b coefficient for He (0.024 L mol^{-1}). Why?

Xe is a much larger atom than He, less free volume for other Xe atoms to enter

d) A 25.0 L tank contains 100.0 moles of Xe at 300 K. Use the van der Waals equation to decide if attractive Xe-Xe interactions dominate repulsive Xe-Xe interactions in the tank.

ideal gas $p_{\text{ideal}} = \frac{RT}{V_m} = \frac{(0.08314)(300)}{25.0/100.0} = 99.8 \text{ bar if ideal}$

van der Waals gas $p = \frac{RT}{V_m - b} - \frac{a}{V_m^2} = \frac{(0.08314)(300)}{0.250 - 0.051} - \frac{4.25}{(0.250)^2}$

$$= (125.3 - 68) \text{ bar}$$

$$z = \frac{p}{p_{\text{ideal}}} = 0.574$$

$$p = 57.3 \text{ bar van der Waals} \\ < p_{\text{ideal}}$$

$z < 1$ attractive forces dominate

- Q2. a) Monatomic gases (such as He, Ar, and Xe) have the same heat capacities: $C_{vm} = 3R/2$ and $C_{pm} = 5R/2$. Why?

monatomic gases: no rotational or vibration energy, only kinetic energy of motion in the x, y, z directions contributing $3 \frac{R}{2}$ to C_{vm} $C_{vm} = \frac{3}{2}R$

$C_{pm} = C_{vm} + R = \frac{5}{2}R$

- b) 15.0 moles of He (assumed to be an ideal gas) initially at 300 K and 1.00 bar are heated to 400 K at constant pressure. Calculate q , w , ΔU and ΔH .

$dU = C_v dT \Rightarrow \Delta U = \int C_v dT = \int n C_{vm} dT = n C_{vm} (T_f - T_i)$

$\Delta U = (15.0 \text{ mol}) \frac{3}{2} (8.314 \frac{\text{J}}{\text{mol K}}) (400 - 300) \text{ K} = \boxed{\Delta U = 18,710 \text{ J}}$

similarly, using $dH = C_p dT$ gives

$\Delta H = n C_{pm} (T_f - T_i) = (15.0 \text{ mol}) \frac{5}{2} 8.314 \frac{\text{J}}{\text{mol K}} (400 - 300) \text{ K}$

$\Delta H = 31,180 \text{ J} = q$ (pressure constant)

$\Delta U = q + w$ $w = \Delta U - q = 18,710 \text{ J} - 31,180 \text{ J}$
 $w = -12,470 \text{ J}$

- c) 15.0 moles of He (assumed to be an ideal gas) initially at 300 K and 1.00 bar are heated to 400 K at constant volume. Calculate q , w , ΔU and ΔH .

U and H depend only on temperature (ideal gas). Heating at constant pressure from 300 K to 400 K at constant pressure (part a) gives the same values of ΔU and ΔH for heating at constant volume (part c),

$\Delta U = 18,710 \text{ J}$

$\Delta H = 31,180 \text{ J}$

$w = - \int P_{\text{ext}} dV$ (volume constant)

$w = 0$

$\Delta U = q + w = q + 0$

$q = \Delta U = 18,710 \text{ J}$

2 (notice $q \neq \Delta H$ (p not constant))

Q3. a) To illustrate the cyclic rule for an ideal gas ($V_m = RT/p$), prove $\left(\frac{\partial V_m}{\partial T}\right)_p = -\left(\frac{\partial V_m}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_{V_m}$

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

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

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

$$= \frac{RT}{pV_m} \frac{R}{p} = \frac{1}{p} \frac{R}{p} = LS$$

b) Why is it more convenient to define the volumetric thermal expansion coefficient (β) as $V^{-1}(\partial V/\partial T)_p$ instead of $(\partial V/\partial T)_p$? extensive (size-dependent)

$V^{-1}(\partial V/\partial T)_p$ is intensive, so a substance has the same β value for any amount of the substance

c) Show the volumetric thermal expansion coefficient of an ideal gas is $1/T$.

$$\begin{aligned} \beta &= \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p = \frac{1}{\frac{nRT}{p}} \left(\frac{\partial \frac{nRT}{p}}{\partial T}\right)_p \\ &= \left(\frac{1}{\frac{nRT}{p}}\right) \left(\frac{nR}{p}\right) \left(\frac{\partial T}{\partial T}\right)_p = \frac{\frac{nR}{p}}{\frac{nR}{p}} \frac{1}{T} \\ &= \frac{1}{T} \end{aligned}$$

d) The volumetric thermal expansion coefficient of liquid silica (SiO_2) is $-9.7 \times 10^{-5} \text{ K}^{-1}$. This value of β is highly unusual! Why?

$\beta < 0!$ $\text{SiO}_2(l)$ contracts (does not expand like most materials) when heated

$$P_i V_i = P_f V_f = nRT$$

- Q4. a) 100.0 L of ideal gas at 200.0 bar and 300 K expands isothermally against a constant external pressure of 1.00 bar to a final pressure of 1.00 bar. Calculate ΔV , w , q , ΔU and ΔH .

$$\Delta V = V_f - V_i = \frac{P_i V_i}{P_f} - V_i = \left(\frac{200.0 \text{ bar}}{1.00 \text{ bar}} - 1 \right) 100.0 \text{ L}$$

$$\Delta V = 19,900 \text{ L}$$

$$\Delta U = 0 \quad \Delta H = 0 \quad (\text{isothermal ideal gas})$$

$$w = - \int P_{\text{ext}} dV = - P_{\text{ext}} \int dV = - P_{\text{ext}} \Delta V$$

$$= -(1.00 \text{ bar})(19,900 \text{ L}) = -1.99 \times 10^4 \text{ L bar}$$

$$w = -1.99 \times 10^6 \text{ J}$$

$$\Delta U = 0 = q + w$$

(equivalent to about 2 sticks of dynamite!)

$$q = -w = 1.99 \times 10^6 \text{ J}$$

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

- b) 100.0 L of liquid water at 200.0 bar and 300 K expands isothermally against a constant external pressure of 1.00 bar to a final pressure of 1.00 bar. Calculate ΔV and w .

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

* Can't use $PV = nRT$ ($\text{H}_2\text{O}(l)$ is not an ideal gas)

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

$$\kappa dP = -\frac{dV}{V}$$

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

$$\frac{V_f}{V_i} = e^{-\kappa(P_f - P_i)} = e^{-(4.59 \times 10^{-5} \text{ bar}^{-1})(-199 \text{ bar})} = e^{+0.00913}$$

$$\frac{V_f}{V_i} = 1.00917$$

$$\Delta V = V_f - V_i = (1.00917 - 1) 100.0 \text{ L}$$

$$\Delta V = +0.917 \text{ L}$$

$$w = - \int P_{\text{ext}} dV = -(1.00 \text{ bar})(0.917 \text{ L}) = -0.917 \text{ L bar}$$

$$w = -91.7 \text{ J}$$

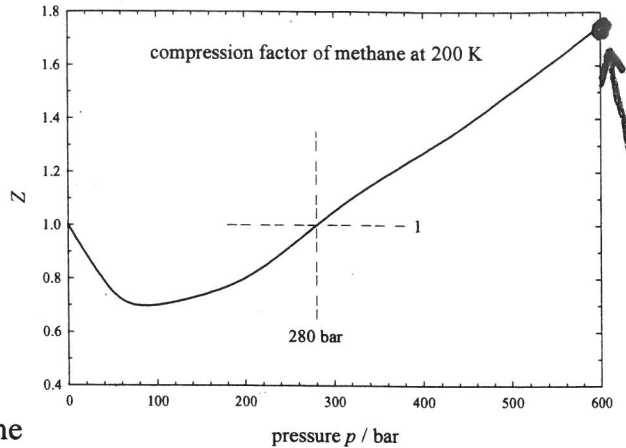
- c) Use the results from a and b to explain why leaks of high-pressure gas are much more dangerous than leaks of high-pressure liquids.

gas leak from 200 bar to 1 bar does $\approx 22,000$ times more work on the surroundings than the correspond liquid leak (change in liquid volume ≈ 0)

Q5. a) The compression factor of methane at 200 K is plotted below.

- i) $Z = 1$ at 200 K and 280 bar. Is methane an ideal gas under these conditions? Explain briefly.

No.
Attractive and repulsive forces cancel here.



- ii) Use the graph to calculate the molar volume and the density of methane (16.0 g mol^{-1}) at 200 K and 600 bar.

from graph, read $Z = 1.75$ at 200 K and 600 bar

$$Z = \frac{pV_m}{RT} \quad V_m = \frac{ZRT}{p} = \frac{1.75 (0.08314)(200)}{600} \frac{\text{L}}{\text{mol}}$$

$$V_m = 0.0485 \frac{\text{L}}{\text{mol}}$$

$$\text{density} = \frac{M}{V_m} = \frac{16.0 \text{ g mol}^{-1}}{0.0485 \text{ L mol}^{-1}}$$

$$\text{density} = 330 \frac{\text{g}}{\text{L}}$$

- b) Use $df = \frac{\partial}{\partial p} \left(\frac{R}{p} dT - \frac{\partial}{\partial T} \left(\frac{RT}{p^2} dp \right) \right)$ to decide if the function $f(T,p)$ exists.

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

$$R_S = \left(\frac{\partial}{\partial T} - \frac{RT}{p^2} \right)_p = - \frac{R}{p^2} \left(\frac{\partial T}{\partial T} \right)_p = - \frac{R}{p^2}$$

$$L_S = R_S \quad f(T,p) \text{ exists (e.g., } f(T,p) = \frac{RT}{p} \text{)}$$

- c) In the design of equipment for refrigeration and cooling, why is it useful to have gases with large positive values of $(\partial T / \partial p)_H$? For cooling.

Want large decrease in T for the expanding gas (pressure dropping) in Joule-Thompson equipment: $dp < 0$ $dT < 0$

$$\text{Then } \left(\frac{\partial T}{\partial p} \right)_H > 0$$