- 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*

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1.   **a)** A tank is filled with compressed natural gas (assumed to be pure methane, MW 16.0 g mol^{-1}) at 20 °C and a density of 225 grams per liter. $T = (20+273)K = 293\ K$

   i) Calculate the pressure in the tank using the ideal gas equation.

$$\text{molar volume} \quad V_m = \frac{1.00\ L}{(225\ g)/(16.0\ g\ mol^{-1})} = 0.07111\ L\ mol^{-1}$$

$$P = \frac{nRT}{V} = \frac{RT}{V/n} = \frac{RT}{V_m} = \frac{(0.08314\ L\ bar\ K^{-1}mol^{-1})(293\ K)}{0.07111\ L\ mol^{-1}}$$

$$\boxed{P = 343\ bar}$$

   ii) Calculate the pressure in the tank using the van der Waals equation.
   ($a = 2.28$ bar L^2 mol^{-2} and $b = 0.0427$ L mol^{-1})

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

$$= \frac{(0.08314\ L\ bar\ K^{-1}mol^{-1})(293\ K)}{(0.07111 - 0.04273)\ L\ mol^{-1}} - \frac{2.28\ bar\ L^2\ mol^{-2}}{(0.07111\ L\ mol^{-1})^2}$$

$$= 858.4\ bar - 450.9\ bar$$

$$\boxed{P = 408\ bar}$$

   iii) Do attractive intermolecular forces dominate repulsive forces? Justify your answer.

$\boxed{No}$

repulsive methane intermolecular forces dominate

$$\boxed{\begin{array}{cc} P_{real} > P_{ideal} \\ (part\ ii) \qquad (part\ i) \end{array}}$$

   b) Large amounts of methane are transported in liquid form, not as the compressed gas. Why?

Liquefied natural gas is at atmospheric pressure. Does not require thick-wall high pressure tanks or pipelines. Can be shipped economically worldwide.

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$$P_i V_i = P_f V_f = nRT \implies \frac{V_f}{V_i} = \frac{P_i}{P_f}$$

2. 1.00 mole of an **ideal gas** expands isothermally from 8.00 bar to 2.00 bar at 300 **K**:

   a) Calculate w, q, ΔU and ΔH if the expansion is **reversible.** $\boxed{P_{ext} = P}$

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

$$(\text{isothermal})$$

$$w = -\int P_{ext}\, dV = -\int p\, dV = -\int \frac{nRT}{V}\, dV$$

$$w = -nRT \int_{V_i}^{V_f} \frac{1}{V}\, dV = -nRT \ln\!\left(\frac{V_f}{V_i}\right) = -nRT \ln\!\left(\frac{P_i}{P_f}\right)$$

$$w = -(1.00\ \text{mol})(8.314\ \text{J K}^{-1}\text{mol}^{-1})(300\ \text{K}) \ln\!\left(\frac{8.00\ \text{bar}}{2.00\ \text{bar}}\right)$$

$$\boxed{\begin{array}{l} w = -3460\ \text{J} \\ \hline q = 3460\ \text{J} \end{array}} \qquad \left(\begin{array}{l} \Delta U = q + w \\ 0 = q + w \qquad q = -w \end{array}\right)$$

   b) Calculate w, q, ΔU and ΔH if the expansion is **irreversible** with $p_{ext} = 2.00$ bar.

$$\boxed{\Delta U = 0 \quad \text{and} \quad \Delta H = 0}$$

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

$$w = -P_f V_f + P_f V_i = -nRT + \frac{P_f}{P_i} P_i V_i = -nRT + \frac{P_f}{P_i} nRT$$

$$w = nRT\left(\frac{P_f}{P_i} - 1\right) = (1.00\ \text{mol})(8.314\ \text{J K}^{-1}\text{mol}^{-1})300\text{K}\left(\frac{2.00\ \text{bar}}{8.00\ \text{bar}} - 1\right)$$

$$\boxed{w = -1870\ \text{J} \quad q = -w = 1870\ \text{J}}$$

$$\left(\begin{array}{ll} \underline{\underline{\text{or}}}, \text{ use } V_i = RT/P_i = 3.118\ \text{L} & w = -P_f(V_f - V_i) \\ \qquad V_f = RT/P_f = 12.471\ \text{L} & = -2.00(12.471 - 3.118)\ \text{L bar} \\ & w = -1870\ \text{J} \end{array}\right)$$
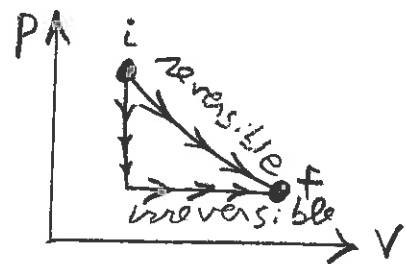
   c) Use the answers to **a** and **b** to illustrate that U and H are state functions, but q and w are path-dependent.

$$\Delta U(\text{rev. path}) = \Delta U(\text{irrev. path})$$
$$\Delta H(\quad '' \quad) = \Delta H(\quad '' \quad)$$

$$w(\text{rev. path}) \neq w(\text{irrev. path})$$
$$q(\quad '' \quad) \neq q(\quad '' \quad)$$

3. **a)** Use the thermodynamic equation of state to prove $(\partial U/\partial V)_T = 0$ for ideal gases.

ideal gas: $P = \dfrac{nRT}{V}$

$\left(\text{hint} \quad \left(\dfrac{\partial U}{\partial V}\right)_T = T\left(\dfrac{\partial p}{\partial T}\right)_V - p\right)$

$\left(\dfrac{\partial U}{\partial V}\right)_T = T\left(\dfrac{\partial P}{\partial T}\right)_V - P = T\left(\dfrac{\partial \frac{nRT}{V}}{\partial T}\right)_V - P = T\dfrac{nR}{V}\left(\dfrac{\partial T}{\partial T}\right)_V - P$

$\quad = \dfrac{TnR}{V}(1) - P = \dfrac{nRT}{V} - \dfrac{nRT}{V} = 0$

b) Show $(\partial C_V/\partial V)_T = 0$ for ideal gases. (hint $\quad C_V = (\partial U/\partial T)_V$)

$\left(\dfrac{\partial C_V}{\partial V}\right)_T = \left[\dfrac{\partial}{\partial V}\left(\dfrac{\partial U}{\partial T}\right)_V\right]_T = \left[\dfrac{\partial}{\partial T}\left(\dfrac{\partial U}{\partial V}\right)_T\right]_V$ order of differentiation "doesn't" matter

$\quad = \left[\dfrac{\partial}{\partial T} 0\right]_V = 0 \qquad \left[\left(\dfrac{\partial U}{\partial V}\right)_T = 0 \text{ from part a}\right]$

c) Show $dq = C_V dT + p\,dV$ for reversible processes for ideal gases. (hint $dU = dq + dw$)

ideal gas (U depends only on T): $dU = C_V dT$

reversible expansion/compression: $dw = -p\,dV$
($P = P_{ext}$)

$dU = dq + dw$ — First Law

$C_V dT = dq - p\,dV$ — Ideal Gas

$dq = C_V dT + p\,dV$ — "

d) Use $dq = C_V dT + p\,dV$ to prove the function $q(T,V)$ does not exist for ideal gases.

$dq = g(T,V)dT + h(T,V)dV$

$q(T,V)$ exists if $\left(\dfrac{\partial g}{\partial V}\right)_T \overset{?}{=} \left(\dfrac{\partial h}{\partial T}\right)_V$

$g = C_V$
$h = P$

$\left(\dfrac{\partial g}{\partial V}\right)_T = \left(\dfrac{\partial C_V}{\partial V}\right)_T = 0$ (part b)

$\left(\dfrac{\partial h}{\partial T}\right)_V = \left(\dfrac{\partial P}{\partial T}\right)_V = \left(\dfrac{\partial}{\partial T}\left(\dfrac{nRT}{V}\right)\right)_V = \dfrac{nR}{V}\left(\dfrac{\partial T}{\partial T}\right)_V = \dfrac{nR}{V} \neq 0$

$q(T,V)$ does not exist

4. **a)** 5.00 L of **liquid water** initially at 1.00 bar and 25.0 °C is compressed isothermally. The final pressure is 100.0 bar. For this process:

i) calculate the volume change (use $\kappa = 4.59 \times 10^{-5}$ bar^{-1}, assumed to be constant)

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \implies -\kappa \, dp = \frac{dV}{V} \implies -\int \kappa \, dp = \int \frac{dV}{V}$$

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

$$V_f = V_i \, e^{-\kappa(P_f - P_i)}$$

$$V_f = (5.00 \text{ L}) \, e^{-(4.59 \times 10^{-5} \text{ bar}^{-1})(100-1)\text{bar}} = (5.00 \text{ L}) e^{-0.00454}$$

$$V_f = (5.00 \text{ L})(0.99547) = 4.977 \text{ L}$$

$$\Delta V = V_f - V_i = (4.977 - 5.00)\text{L} = \boxed{-0.023 \text{ L}}$$

ii) explain why is unnecessary to specify if the compression is reversible ($p_{ext} = p$) or irreversible ($p_{ext} = 100.0$ bar) in order to calculate the volume change

The volume of liquid water is a function of the state variables T, P

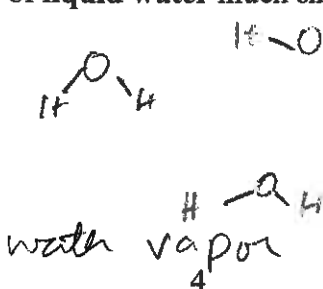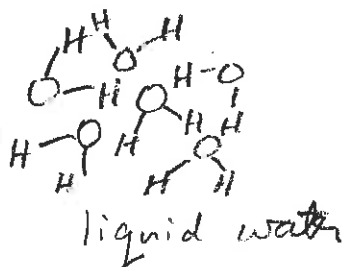$$\Delta V = V(T_f, P_f) - V(T_i, P_i)$$

is therefore path independent

b) Calculate κ for **water vapor** (assumed to be an ideal gas) at 1.00 bar and 25 °C.

ideal gas

$$\kappa = \frac{1}{P} = \frac{1}{1.00 \text{ bar}}$$

$$\boxed{\kappa = 1.00 \text{ bar}^{-1}}$$

c) Why is the compressibility of **liquid water** much smaller than that of **water vapor**?

liquid water

water vapor

liquid water molecules are tightly packed together compared to vapor molecules. ("no free" volume to compress into)
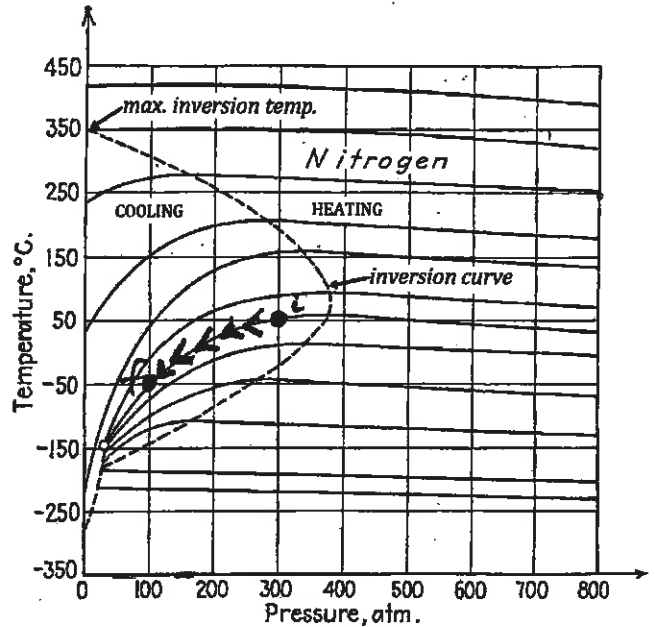
5.

a) Nitrogen gas initially at 300 atm and 50 °C undergoes a Joule-Thomson expansion.

The final pressure is 100 atm.

Use the graph provided to estimate the final temperature.

read from graph:

$$\boxed{-50\ °C}$$

b) Suggest why the Joule-Thomson expansion of an ideal gas is also an isothermal expansion.
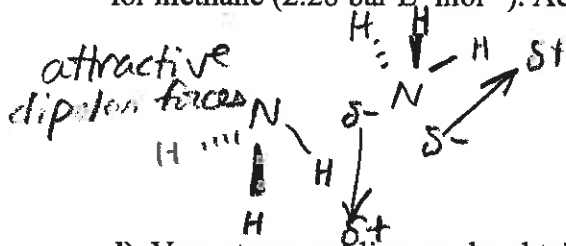
JT expansions are "isenthalpic" (constant H)
For an ideal gas, H depends only on T.
If H is constant, then so is T.

c) Ammonia and methane molecules have the same number of electrons (10) and therefore might be expected to have similar intermolecular dispersion forces.

But the van der Waals a parameter for ammonia (4.24 bar L^2 mol^{-2}) is significantly larger than a for methane (2.28 bar L^2 mol^{-2}). Account for this apparent discrepancy.

attractive
dipole forces

NH_3 molecules have permanent electric dipoles, CH_4 molecules are nonpolar.

electric dipole interactions increase a for NH_3

d) Very strong cooling can be obtained by adiabatically expanding ideal gases (Problem Set #3). But when an ideal gas expands into a vacuum ($p_{ext} = 0$), show there is *no temperature change*!

$$dU = dq + dw \quad \text{First Law}$$

$$C_v dT = dq - P_{ext} dV$$

$$\left(\text{Ideal gas, U depends on T only} \atop dU = C_v dT \right)$$

$$C_v dT = 0 - P_{ext} dV \quad \left(\text{adiabatic} \atop q = 0 \right)$$

$$C_v dT = 0 - 0 \quad (P_{ext} = 0)$$

$$dT = 0$$

$$\boxed{\Delta U = q = w = 0!}$$

Q1
Q2
Q3
Q4
Q5 ___

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