

- 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) 5.00 moles of an ideal gas initially at 300 K and 5.00 bar expand reversibly and isothermally to a final pressure of 2.00 bar. Calculate ΔU , q and w .

$$V_i = \frac{nRT}{P_i} = \frac{(5.00 \text{ mol})(0.08314 \text{ L bar K}^{-1} \text{ mol}^{-1})(300 \text{ K})}{5.00 \text{ bar}} = 24.94 \text{ L}$$

$$V_f = \frac{nRT}{P_f} = \frac{nRT}{P_i} \frac{P_i}{P_f} = 24.94 \text{ L} \left(\frac{5.00 \text{ bar}}{2.00 \text{ bar}} \right) = 62.35 \text{ L}$$

$$w = -\int P_{\text{ext}} dV = -\int P dV = -\int \frac{nRT}{V} dV = -nRT \int \frac{1}{V} dV = -nRT \ln \left(\frac{V_f}{V_i} \right)$$

$$w = -(5.00 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(300 \text{ K}) \ln(62.35/24.94) = -11430 \text{ J}$$

$\Delta U = 0$ (isothermal ideal gas) $0 = q + w$ $q = -w = 11430 \text{ J}$

- b) 5.00 moles of an ideal gas initially at 300 K and 5.00 bar expands isothermally against a constant external pressure of 2.00 bar to a final pressure of 2.00 bar. Calculate ΔU , q and w .

$$w = -\int P_{\text{ext}} dV = -P_{\text{ext}} \int dV = -P_{\text{ext}} (V_f - V_i)$$

$$w = -(2.00 \text{ bar})(62.35 - 24.94) \text{ L} = -74.82 \text{ L bar}$$

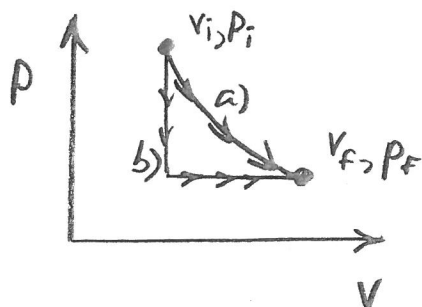
$$w = -(74.82 \text{ L bar})(100 \text{ J L}^{-1} \text{ bar}^{-1})$$

$$w = -7482 \text{ J}$$

$\Delta U = 0$ (isothermal ideal gas)
 $\Delta U = q + w = 0$

$q = -w = 7482 \text{ J}$

- c) Use the results from parts a and b illustrate that the internal energy is a state function but heat and work are path-dependent.



path (a) (rev.) $\Delta U = 0$ path (b) (irrev.) $\Delta U = 0$ ΔU path-independent
 $q = 11430 \text{ J}$ $q = 7482 \text{ J}$
 $w = -11430 \text{ J}$ $w = -7482 \text{ J}$
 q, w path dependent

$$T = (25 + 273.15) \text{ K}$$

2. This question refers to a 25.0 L tank containing methane gas at 25 °C and 1000 bar. $= 298.15 \text{ K}$

a) Use the ideal gas law to calculate the number of moles (n) of methane in the tank.

$$n = \frac{PV}{RT} = \frac{(1000 \text{ bar})(25.0 \text{ L})}{(0.08314 \text{ L bar J K}^{-1})(298.15 \text{ K})}$$

$$n = 1008 \text{ mol}$$

(notice:
molar volume $V_m = V/n$
 $V_m = (25.0 \text{ L}) / (1008 \text{ mol})$
 $V_m = 0.0248 \text{ L/mol}$
Small!

b) The ideal gas law unlikely to give an accurate value of n . Why?

1000 bar pressure is high! Molecules are close together at high pressures \Rightarrow molecular interactions are likely to be important.

$$\text{density} = (16.0 \text{ g}) / (24.8 \text{ cm}^3) = 0.645 \frac{\text{g}}{\text{cm}^3}$$

liquid-like density!

c) Use the compression factors (Z) for methane plotted in the diagram on the next page to calculate a reliable value of n .

$$Z = \frac{PV}{nRT} \quad \text{from the graph (next page), read } Z = 2.00 \text{ at } 1000 \text{ bar, } 25^\circ \text{C}$$

$$n = \frac{1}{Z} \frac{PV}{RT} = \frac{1}{2.00} (1008 \text{ mol})$$

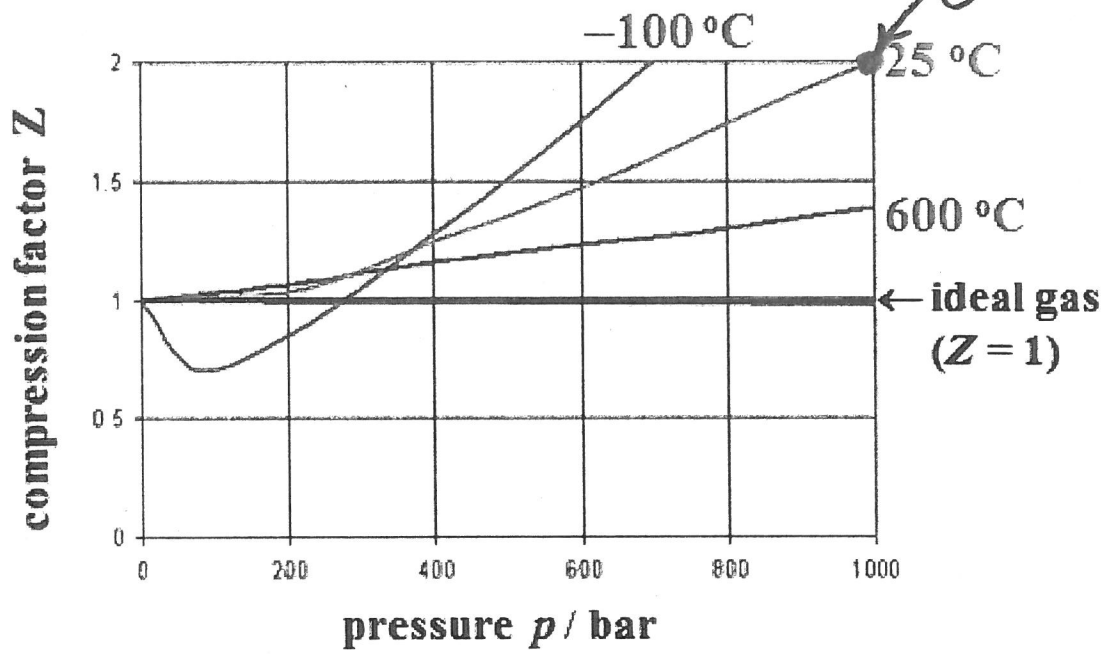
$$n = 504 \text{ mol}$$

e) Explain briefly in terms of molecular interactions why the number of moles methane in the tank is significantly smaller the value of n from the ideal gas equation.

Methane molecules are not point masses, as assumed if the ideal gas law is used. "Real" methane molecules can't be packed closely together without generating repulsive forces that increase the pressure above the value predicted for point masses.

Diagram for Question 2

Compression Factor $Z = pV/nRT$ of Methane



3. 90.0 L of air (assumed to be an ideal gas with $C_{Vm} = 5R/2$) initially at 1.00 bar and 300 K is compressed reversibly and adiabatically to a final volume of 10.0 L.

a) Calculate the final temperature.

$$\text{ideal gas: } C_{pm} = C_{vm} + R = \frac{5}{2}R + R = \frac{7}{2}R$$

$$\gamma = \frac{C_{pm}}{C_{vm}} = \frac{(7/2)R}{(5/2)R} = \frac{7}{5} = 1.40$$

$$\text{reversible adiabatic expansion: } P_i V_i^\gamma = P_f V_f^\gamma$$

$$P_f = \frac{V_i^\gamma}{V_f^\gamma} P_i = \left(\frac{V_i}{V_f}\right)^\gamma P_i = \left(\frac{90.0\text{L}}{10.0\text{L}}\right)^{1.40} (1.00\text{ bar})$$

$$P_f = 21.67\text{ bar} \quad \frac{T_f}{T_i} = \frac{P_f V_f / nR}{P_i V_i / nR}$$

$$T_f = \frac{P_f V_f}{P_i V_i} T_i = \left(\frac{21.67\text{ bar}}{1.00\text{ bar}}\right) \left(\frac{10.0\text{ L}}{90.0\text{ L}}\right) 300\text{K} = \boxed{722\text{ K}}$$

(449 °C)
HOT!

b) Calculate ΔU , ΔH , q and w for one mole of air.

$$dU_m = C_{vm} dT \text{ (ideal gas)}$$

$$\Delta U_m = \int dU_m = \int C_{vm} dT = \frac{5}{2}R \int dT = \frac{5}{2}R(T_f - T_i)$$

$$\Delta U_m = \frac{5}{2} (8.314\text{ J K}^{-1}\text{ mol}^{-1}) (722 - 300)\text{K} = \boxed{8770\text{ J mol}^{-1}}$$

$$\Delta H_m = \frac{7}{2}R(T_f - T_i) = \boxed{12280\text{ J mol}^{-1}}$$

$$\boxed{q_m = 0} \text{ (adiabatic)}$$

$$\Delta U_m = q_m + w_m = 0 + w_m$$

$$w_m = \Delta U_m = 8770\text{ J mol}^{-1}$$

c) Use the answer to a) to explain how diesel engines can run without sparkplugs to ignite fuel/air mixtures in the engine cylinders.

compressing air rapidly (and therefore adiabatically) in the engine cylinders gets the air really "hot", hot enough to ignite the diesel fuel injected into the cylinders

4 (no need for electric spark plugs)

4. a) The isothermal compressibility (κ) is defined as $-V^{-1}(\partial V/\partial p)_T$ not as $V^{-1}(\partial V/\partial p)_T$. Why?

$(\partial V/\partial p)_T$ is always negative (systems shrink as p increased)
 so $-V^{-1}(\partial V/\partial p)_T$ is always positive (convenient, κ positive)

b) i) Calculate the change in volume when 10.00 L of liquid water is isothermally compressed from 1.00 bar to 5.00 bar at 25 °C. Data: $\kappa = 0.0000459 \text{ bar}^{-1}$

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

$$-\int \kappa dp = \int \frac{1}{V} dV \quad (\text{have to assume } \kappa \text{ is constant})$$

$$-\kappa(p_f - p_i) = \ln(V_f/V_i) = -(0.0000459 \text{ bar}^{-1})(5.00 - 1.00) \text{ bar}$$

$$\ln(V_f/V_i) = -0.000184 \quad V_f/V_i = e^{-0.000184}$$

$$\frac{V_f}{V_i} = 0.99982 \quad V_f = V_i(0.99982) = 9.9982 \text{ L}$$

$$\Delta V = -0.0018 \text{ L} = -1.82 \text{ mL}$$

ii) If 10.00 L of an ideal gas is isothermally compressed from 1.00 to 5.00 bar, the change in volume is -8.00 L. The volume change for the compression of 10.00 L of liquid water from 1.00 to 5.00 bar is much smaller (< 0.1% of the initial volume). Why? Explain briefly in molecular terms.

ideal gas

"lots" of free volume to compress into

almost incompressible, no free volume, liquid water

c) In class we showed $(\partial U/\partial V)_T = a/V_m^2$ for a van der Waals gas. If a van der Waals gas expands isothermally, does the internal energy increase, decrease or remain constant? Justify your answer.

expansion: V increases

$$dV > 0$$

$$\left(\frac{\partial U}{\partial V} \right)_T = \frac{a}{V_m^2} > 0 \quad \text{so } dU > 0$$

the internal energy increases

d) Prove that the thermal expansivity (β) of an ideal gas is $1/T$.

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad (\text{definition})$$

ideal gas $V = \frac{nRT}{P}$

for an ideal gas
$$\beta = \frac{1}{V} \left(\frac{\partial \frac{nRT}{P}}{\partial T} \right)_P = \frac{nR}{PV} \left(\frac{\partial T}{\partial T} \right)_P = \frac{nR}{PV} (1) = \frac{1}{T}$$

5. a) Give a brief definition of a Joule-Thomson (JT) expansion.

adiabatic expansion of a fluid at constant enthalpy

b) Give two practical applications of JT expansions.

refrigeration, air conditioning (cooling), heat pumps, gas liquefaction

c) Is the Joule Thomson coefficient (μ_{JT}) an extensive quantity? Explain.

No. $\mu_{JT} \equiv \left(\frac{\partial T}{\partial p}\right)_H \sim \frac{\text{intensive } T}{\text{intensive } p} \Rightarrow \boxed{\text{overall intensive}}$

μ_{JT} is independent of the size or mass of the system

d) In class we showed $\mu_{JT} = (V - V\beta T)/C_p$. Use this result to prove the Joule-Thomson coefficient (μ_{JT}) is zero for an ideal gas.

$\mu_{JT} = (V - V\beta T)/C_p$ for any substance

for an ideal gas: $\beta = \frac{1}{T}$ (Question 4 on equation sheet)

$$\mu_{JT}(\text{ideal gas}) = (V - V\frac{1}{T}T)/C_p = 0/C_p = 0$$

e) N_2 gas initially at 300 K and 250 bar expands to a final pressure of 1.00 bar in a JT experiment. Calculate the final temperature of the gas. Data: $\mu_{JT} = 0.340 \text{ K bar}^{-1}$.

$$\mu_{JT} = \left(\frac{\partial T}{\partial p}\right)_H \quad \text{multiply by } dp \text{ (at constant } H)$$

$$\mu_{JT} dp = \left(\frac{\partial T}{\partial p}\right)_H dp$$

$$\Delta T = (0.340 \text{ K bar}^{-1})(1-250) \text{ bar}$$

$$\Delta T = -85 \text{ K}$$

$$T_f = (300 - 85) \text{ K}$$

$$\boxed{T_f = 215 \text{ K}}$$

$$(-56^\circ \text{C})$$

$$\mu_{JT} dp = dT$$

$$\mu_{JT} \int_{p_i}^{p_f} dp = \int_{T_i}^{T_f} dT$$

$$\mu_{JT} \Delta p = \Delta T$$

Q1
Q2
Q3
Q4
Q5