

- please answer all **4 questions** in the spaces provided
- you have **50 minutes** 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

Q1. a) A pressure gauge on 10.0 L tank of xenon reads 30.0 bar at 300 K.

i) Calculate the number of moles of xenon in the tank using the ideal gas law.

$$n = \frac{PV}{RT} = \frac{(30.0 \text{ bar})(10.0 \text{ L})}{(0.08314 \text{ L bar K}^{-1} \text{ mol}^{-1})(300 \text{ K})}$$

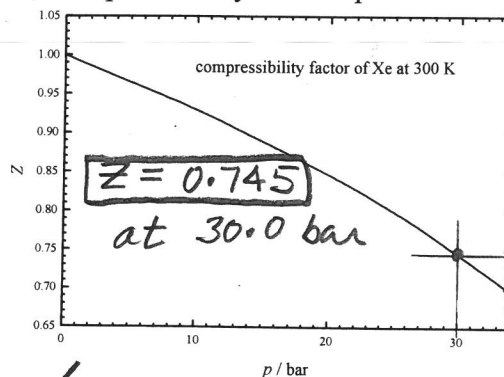
$$n = 12.0 \text{ mol}$$

ii) Calculate a more accurate value of  $n$  using the xenon compressibility factors plotted below.

$$Z = \frac{PV}{nRT}$$

$$n = \frac{PV}{RT} \frac{1}{Z} = (12.0 \text{ mol}) \frac{1}{0.745}$$

$$n = 16.1 \text{ mol}$$



( $Z < 1$  attractive Xe-Xe dominate, "helping" the compression = less work required)

b) 1.00 mole of xenon initially at 1.00 bar and 300 K is reversibly and isothermally compressed to 30.0 bar at 300 K. Assuming ideal-gas behavior, calculate  $w$ .

$$w = -nRT \ln\left(\frac{V_f}{V_i}\right) = -nRT \ln\left(\frac{nRT/P_f}{nRT/P_i}\right) = -nRT \ln\left(\frac{P_i}{P_f}\right) = -(1.00 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(300 \text{ K}) \ln\left(\frac{1.00}{30.0}\right)$$

$$w = 8480 \text{ J}$$

c) Is the actual work required to reversibly compress xenon from 1.00 bar to 30.0 bar at 300 K larger than the work calculated in part b for an ideal gas? Justify your answer.

No.

$$w_{\text{actual}} < w_{\text{ideal}}$$

$$w_{\text{actual}} = - \int \frac{Z nRT}{V} dV$$

$$w_{\text{ideal}} = - \int \frac{nRT}{V} dV$$

$Z < 1$ , so  $w_{\text{actual}} < w_{\text{ideal}}$

$Z < 1 \Rightarrow$  attractive Xe-Xe forces dominate, "helping" to compress the gas

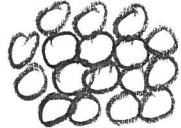
Q2. a) The isothermal compressibility could be defined as  $(\partial V/\partial p)_T$ . Give two reasons why it is more convenient to define the isothermal compressibility as  $-V^{-1}(\partial V/\partial p)_T$ .

- i)  $\kappa$  is always positive (no "-" signs to print)
- ii) dividing by  $V$  gives the fraction change in volume, making  $\kappa$  an intensive quantity

b) Show the isothermal compressibility of an ideal gas is  $1/p$ .

$$\begin{aligned} \kappa &= -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T \\ &= -\frac{1}{V} \left( \frac{\partial}{\partial p} \frac{nRT}{p} \right)_T \\ &= -\frac{1}{V} nRT \left( \frac{\partial \frac{1}{p}}{\partial p} \right)_T \\ &= -p \left( -\frac{1}{p^2} \right) = \frac{1}{p} \end{aligned}$$

c) The isothermal compressibilities of liquids and solids are much smaller than  $1/p$ . Why? Give a molecular interpretation.

○	<u>gases</u>		<u>liquids</u>	
○	"lots" of		<u>solids</u>	
○	free volume		molecules are tightly packed,	
○			~ no free volume to compress into	

d) The change in the internal energy is given by:

$$dU = \left( \frac{\partial U}{\partial T} \right)_V dT + \left( \frac{\partial U}{\partial V} \right)_T dV \quad (1)$$

$$dU = C_V dT + \left( \frac{\beta T}{\kappa} - p \right) dV \quad (2)$$

Both equations are correct, but which equation is more useful for practical calculations? Explain.

(2) is more useful because  $(\partial U/\partial T)_V$  and  $(\partial U/\partial V)_T$  are converted to measurable quantities:

$C_V, \beta, \kappa, T, p$

( $\beta$  can be easily evaluated from equations of state)

Q3. a) For a gas obeying the van der Waals equation  $p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$  show  $\left(\frac{\partial U_m}{\partial V_m}\right)_T = \frac{a}{V_m^2}$ .

Hint: use the thermodynamic equation of state:  $\left(\frac{\partial U_m}{\partial V_m}\right)_T = T \left(\frac{\partial p}{\partial T}\right)_{V_m} - p$

$$\begin{aligned} \left(\frac{\partial U_m}{\partial V_m}\right)_T &= T \left[ \frac{\partial}{\partial T} \left( \frac{RT}{V_m - b} - \frac{a}{V_m^2} \right) \right]_{V_m} - p \\ &= \frac{RT}{V_m - b} \left(\frac{\partial T}{\partial T}\right)_{V_m}^1 - T \left(\frac{\partial \frac{a}{V_m^2}}{\partial T}\right)_{V_m}^0 - p \\ &= \frac{RT}{V_m - b} - \left( \frac{RT}{V_m - b} - \frac{a}{V_m^2} \right) = \frac{a}{V_m^2} \end{aligned}$$

b) If a gas obeying the van der Waals equation expands isothermally, does the internal energy  $U$  of the gas increase? Decrease? Or remain constant? Explain.

$U$  increases because  $\left(\frac{\partial U_m}{\partial V_m}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V_m^2} > 0$

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

Adiabatic expansion of a gas or liquid at constant enthalpy.

d) JT expansions might appear to be a minor thermodynamic curiosity of interest only to physical chemistry instructors. But without JT expansions, *half of the world population would starve!* Explain.

JT expansions are used to produce liquid air from which  $N_2$  is obtained by fractional distillation for the production of ammonia for fertilizers

e) For the operation of air conditioners, freezers and other cooling equipment, why is it not a good idea to use ideal gases as refrigerants?

ideal gas:

$$\mu_{JT} = \left(\frac{\partial T}{\partial p}\right)_H = 0$$

no cooling

(or heating)

- Q4. a) Calculate  $q$ ,  $w$ ,  $\Delta U$  and  $\Delta H$  for the evaporation of 5.00 moles of liquid water at  $100^\circ\text{C}$  and 1.00 bar. Data:  $\Delta H_{\text{vap,m}}(\text{H}_2\text{O},l) = 40.3 \text{ kJ mol}^{-1}$



(constant  $P$ )

$$q = \Delta H = n \Delta H_{\text{vap,m}} = (5.00 \text{ mol}) (40.3 \text{ kJ mol}^{-1})$$

$$q = \Delta H = 201.5 \text{ kJ}$$

$$w = - \int P_{\text{ext}} dV \quad (\text{reversible: } P_{\text{ext}} = P) = - \int p dV$$

$$= -p \int dV = -p(V_f - V_i)$$

$$= -p(nV_m(g) - \underbrace{nV_m(l)}_{\text{negligibly small}}) \rightarrow \approx 0$$

$$= -p n V_m(g)$$

$$= -p n \frac{RT}{p} = -nRT = -(5.00 \text{ mol}) \left( \frac{8.314 \text{ J}}{\text{K mol}} \right) (373.15 \text{ K})$$

$$w = -15,510 \text{ J}$$

$$\Delta U = q + w = 186.0 \text{ kJ}$$

- b) In the calculations for part a, it is an excellent approximation to assume  $V(\text{H}_2\text{O},l) = 0$ . Why?

$$V_m(\text{H}_2\text{O},l) \approx 0.018 \text{ L mol}^{-1} \quad (18 \text{ cm}^3 \text{ mol}^{-1})$$

$$V_m(\text{H}_2\text{O},l) \ll V_m(\text{H}_2\text{O},g) = \frac{RT}{p} = 31.0 \text{ L mol}^{-1}$$

- c) The volumetric thermal expansion coefficient ( $\beta$ ) and the isothermal compressibility ( $\kappa$ ) are positive quantities. Is this statement true or false? Explain.

False

$\beta(\text{H}_2\text{O},l) < 0$  between  $0^\circ\text{C}$  and  $4^\circ\text{C}$