

- please answer all 5 questions in the spaces provided
- allow about 10 minutes per question
- 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 tank contains ethane gas at 350 K. The density of the gas is 174.5 g L^{-1} .

[6]

a) Show that the molar volume of ethane is $0.1723 \text{ L mol}^{-1}$. (The molecular weight of ethane is 30.07 g mol^{-1} .)

$$\text{density } \rho = \frac{\text{mass}}{\text{volume}} = \frac{M}{V_m}$$

$$V_m = \frac{M}{\rho} = \frac{30.07 \text{ g mol}^{-1}}{174.5 \text{ g L}^{-1}} = \boxed{0.1723 \text{ L mol}^{-1}}$$

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

$$p = \frac{nRT}{V} = \frac{RT}{V/n} = \frac{RT}{V_m}$$

$$= \frac{(0.08314 \text{ L bar K}^{-1} \text{ mol}^{-1})(350 \text{ K})}{0.1723 \text{ L mol}^{-1}}$$

$$\boxed{p = 168.9 \text{ bar}}$$

c) Calculate the pressure in the tank using the van der Waals gas equation. (For ethane: $a = 5.58 \text{ L}^2 \text{ bar mol}^{-2}$ and $b = 0.0651 \text{ L mol}^{-1}$)

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

$$= \frac{(0.08314 \text{ L bar K}^{-1} \text{ mol}^{-1})(350 \text{ K})}{(0.1723 - 0.0651) \text{ L mol}^{-1}} - \frac{5.58 \text{ L}^2 \text{ bar mol}^{-2}}{(0.1723 \text{ L mol}^{-1})^2}$$

$$= 271.4 \text{ bar} - 188.0 \text{ bar}$$

$$\boxed{p = 83.4 \text{ bar}}$$

d) For safety reasons, the pressure in the tank should not exceed 100 bar, or it might burst! Is the tank in danger of bursting? Explain.

Probably not - the pressure calculated in part b (including nonideal behavior) is $< 100 \text{ bar}$ and probably more reliable

2. a) 10.0 L of helium initially at 300 K and 4.00 bar expands adiabatically into a vacuum (constant $p_{\text{external}} = 0$). The final volume is 25.0 L.

[6]

Calculate ΔU , ΔH , q and w for this process assuming ideal-gas behavior.

$$q = 0 \quad (\text{adiabatic})$$

$$\begin{aligned} w &= - \int_{V_i}^{V_f} P_{\text{external}} dV \\ &= - P_{\text{external}} \int_{V_i}^{V_f} dV \quad (P_{\text{external}} \text{ constant}) \\ &= - P_{\text{external}} (25.0 - 10.0) \text{ L} \end{aligned}$$

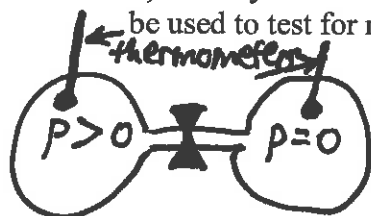
$$w = 0$$

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

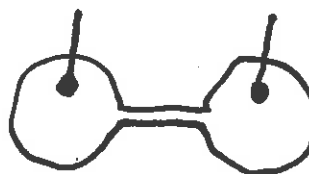
$$\Delta U = 0 \quad \begin{array}{l} \text{isothermal process} \\ U \text{ depends only on } T \text{ (ideal gas)} \\ \text{so } \Delta T = 0 \text{ if } \Delta U = 0 \end{array}$$

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

- b) Briefly describe how a lab experiment based on the process described in part a) could be used to test for nonideal gas behavior.



open
valve



any
temperature
change?

if yes: nonideal gas!

(course notes
and p. 52 in textbook)

3. Data for liquid water 25 °C and 1.00 bar:

[6] $\beta = 0.000204 \text{ K}^{-1}$ $V_m = 18.07 \text{ cm}^3 \text{ mol}^{-1}$ $C_{pm} = 75.3 \text{ J K}^{-1} \text{ mol}^{-1}$

10.00 moles of liquid water is heated from 298 K to 350 K at a constant pressure of 1.00 bar. For this process, calculate:

a) q

$$C_{pm} = \frac{dq_m}{dT}$$

per mole:

$$dq_m = C_{pm} dT$$

$$q_m = \int_{T_i}^{T_f} dq_m = \int_{T_i}^{T_f} C_{pm} dT$$

assume C_{pm} is constant (no other info provided)

$$= C_{pm} (T_f - T_i) = \left(\frac{75.3 \text{ J}}{\text{K mol}} \right) (350 - 298) \text{ K}$$

$$q_m = 3916 \text{ J mol}^{-1}$$

for 10.00 mol: $q = n q_m = (10.00 \text{ mol}) \left(3916 \frac{\text{J}}{\text{mol}} \right) = \boxed{39160 \text{ J}}$

b) ΔV (the volume change)

β is small (only 0.0204 % change in V per degree)

so ΔV is small and $\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \approx \frac{1}{V} \frac{\Delta V}{\Delta T}$

$$\Delta V \approx \beta V \Delta T = \beta n V_m \Delta T \quad (\Delta T = 52 \text{ K})$$

$$= (0.000204 \text{ K}^{-1}) (10.00 \text{ mol}) \left(18.07 \frac{\text{cm}^3}{\text{mol}} \right) (52 \text{ K})$$

$$\Delta V = 1.92 \text{ cm}^3$$

||| 0.2 |||

$$\beta dT = \frac{dV}{V} \Rightarrow \beta \int_{T_i}^{T_f} dT = \int_{V_i}^{V_f} \frac{dV}{V}$$

$$\beta (T_f - T_i) = \ln V_f - \ln V_i = \ln \left(\frac{V_f}{V_i} \right)$$

$$e^{\beta (T_f - T_i)} = \frac{V_f}{V_i}$$

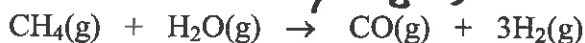
$$V_f = V_i e^{\beta (T_f - T_i)} = (10 \text{ mol}) \left(18.07 \frac{\text{cm}^3}{\text{mol}} \right) e^{0.000204 (52)}$$

$$= 182.63 \text{ cm}^3$$

$$\Delta V = V_f - V_i = 182.63 - 180.7 = 1.93 \text{ cm}^3$$

4. a) Calculate ΔU° , ΔH° , q and w for the following reaction at 25 °C and 1 bar.
(major source of industrial hydrogen)

[6]



product side
reactant side
 $\Delta n_{\text{gas}} = 4 - 2 = 2$

Data at 25 °C:

$\Delta H_{\text{fm}}^\circ(\text{CH}_4, \text{g}) = -74.6 \text{ kJ mol}^{-1}$	$C_{\text{pm}}^\circ(\text{CH}_4, \text{g}) = 35.7 \text{ J K}^{-1} \text{ mol}^{-1}$
$\Delta H_{\text{fm}}^\circ(\text{H}_2\text{O}, \text{g}) = -241.8 \text{ kJ mol}^{-1}$	$C_{\text{pm}}^\circ(\text{H}_2\text{O}, \text{g}) = 33.6 \text{ J K}^{-1} \text{ mol}^{-1}$
$\Delta H_{\text{fm}}^\circ(\text{CO}, \text{g}) = -110.6 \text{ kJ mol}^{-1}$	$C_{\text{pm}}^\circ(\text{CO}, \text{g}) = 29.1 \text{ J K}^{-1} \text{ mol}^{-1}$
$\Delta H_{\text{fm}}^\circ(\text{H}_2, \text{g}) = 0$	$C_{\text{pm}}^\circ(\text{H}_2, \text{g}) = 28.8 \text{ J K}^{-1} \text{ mol}^{-1}$

$$\Delta H = q \quad (\text{constant pressure, only } p\text{-}V \text{ work})$$

$$\begin{aligned} &= \Delta H_{\text{fm}}^\circ(\text{CO}, \text{g}) + 3\Delta H_{\text{fm}}^\circ(\text{H}_2, \text{g}) - \Delta H_{\text{fm}}^\circ(\text{CH}_4, \text{g}) - \Delta H_{\text{fm}}^\circ(\text{H}_2\text{O}, \text{g}) \\ &= -110.6 + 3(0) - (-74.6) - (-241.8) \text{ kJ} \end{aligned}$$

$$\Delta H = q = 205.8 \text{ kJ}$$

$$\begin{aligned} w &= -RT \Delta n_{\text{gas}} \\ &= -(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})(2 \text{ mol}) \end{aligned}$$

$$w = -4955 \text{ J}$$

$w < 0 \Rightarrow$ system expands, pushing back the surroundings $\Delta n = 2$

$$\Delta U = q + w = 205.8 - 4.95$$

$$\Delta U = 200.8 \text{ kJ}$$

- b) Does ΔH° for the above reaction increase if the temperature is raised? Justify your answer.

$$\begin{aligned} \Delta C_p^\circ &= C_{\text{pm}}^\circ(\text{CO}, \text{g}) + 3C_{\text{pm}}^\circ(\text{H}_2, \text{g}) - C_{\text{pm}}^\circ(\text{CH}_4, \text{g}) - C_{\text{pm}}^\circ(\text{H}_2\text{O}, \text{g}) \\ &= 29.1 + 3(28.8) - 35.7 - 33.6 \text{ J K}^{-1} \\ &= 46.2 \text{ J K}^{-1} > 0 \end{aligned}$$

ΔH° increases with temperature

Why? Because $\frac{d\Delta H^\circ}{dT} = \Delta C_p^\circ$

from equation sheet and tutorial

5. a) Why is a minus included in the definition of the isothermal compressibility?

[6]

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

Convenience!

$\left(\frac{\partial V}{\partial p} \right)_T$ is always negative, so κ is always positive (saves tabulating minus signs)

b) Explain why the following result

$$B(T) = b - \frac{a}{RT} \quad \left(\begin{array}{l} \lim T \rightarrow \infty, B = b \\ \lim T \rightarrow 0, B = -\frac{a}{RT} \end{array} \right)$$

shows that repulsive and attractive intermolecular forces dominate at high and low temperatures, respectively.

at high temperature ($T \rightarrow \infty$), $B(T) \rightarrow b$
(a/RT gets small)

at low temperature ($T \rightarrow 0$), $B(T) \rightarrow -\frac{a}{RT}$
($-a/RT$ gets huge)

c) Why is it a good approximation to assume C_{vm} for helium gas is $3R/2$?

↔ monatomic → no rotations or vibrations
only 3 translations @ $\frac{R}{2}$ each

$$C_{vm} = \frac{3}{2} R$$

d) Prove $\beta = 1/T$ for an ideal gas

$$\begin{aligned} \beta &\equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \\ &= \frac{1}{V} \left[\frac{\partial}{\partial T} \left(\frac{nRT}{P} \right) \right]_P \\ &= \frac{1}{V} \frac{nR}{P} \left(\frac{\partial T}{\partial T} \right)_P \rightarrow 1 \\ &= \frac{nR}{PV} = \frac{nR}{nRT} = \frac{1}{T} \quad \text{yes!} \end{aligned}$$

n, R, P constant for this derivative

for an ideal gas

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

substitute