

**THE UNIVERSITY OF ZAMBIA**  
**SCHOOL OF NATURAL SCIENCES**  
**DEPARTMENT OF CHEMISTRY**  
**ACADEMIC YEAR 2022**  
**TERM II**  
**CHE 2615: Basic Physical Chemistry**

**ASSIGNMENT 2 - Gases, 1<sup>st</sup> and 2<sup>nd</sup> Laws of thermodynamics - 11<sup>th</sup> September 2023**

**Answer Q1, Q6, Q7 and Q10 the problems and submit before 10:00 hrs on Monday, 18<sup>th</sup> September 2023**

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1.
  - (a) A laboratory gas cylinder filled with nitrogen has a volume of  $0.150 \text{ m}^3$  and contains  $35.0 \text{ kg}$  of gas when delivered. Calculate the pressure in bars inside the cylinder at  $20 \text{ }^\circ\text{C}$ : (a) using the ideal gas equation: and (b) using the van der Waals equation. (The van der Waals constant for nitrogen are  $a = 0.137 \text{ Pa m}^6 \text{ mol}^{-1}$  and  $b = 3.9 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$ .)
  - (b) For nitrogen gas in part (a), work out the percentage reduction in  $V$  due to the term  $nb$  and compare it to the percentage increase in  $p$  due to the  $a(n/V)^2$  term. Which correction factor makes the largest change?
2. Two bulbs A and B, with volumes  $V_A = 1.0 \text{ L}$  and  $V_B = 5.0 \text{ L}$ , are connected through a valve. The volume connecting tubing is negligible. Bulb A contains gas at a pressure of  $6.0 \text{ bar}$  while bulb B contains a vacuum.
  - a) The temperature of the whole apparatus is maintained at  $298 \text{ K}$ . if the valve is opened, calculate the pressure of the gas in the system after opening the tap.
  - b) The tap is closed and bulb B is then immersed in an oil bath at a temperature of  $423 \text{ K}$  while the temperature of bulb A is maintained at  $298 \text{ K}$ . calculate the resulting pressures in each bulb.
  - c) The valve is opened again. What is the final pressure and the number of moles of gas in each bulb.
3. Using the kinetic theory of gases, it can be shown that:

$$PV = \frac{1}{3} nN_A m c^2$$

- a) Explain each of the terms in this equation.
  - b) Show how this equation is equivalent to the ideal gas equation:  $PV = nRT$ .
  - c) Using these equations as examples, explain the difference between an empirical approach and a theoretical approach to modelling a chemical system.
4.
    - a) Liquid water at  $100 \text{ }^\circ\text{C}$  is in equilibrium with water vapour at  $1 \text{ atm}$  pressure. If the enthalpy change associated with the vaporisation of liquid water at  $100 \text{ }^\circ\text{C}$  is  $40.60 \text{ kJ mol}^{-1}$ . What are  $\Delta G$  and  $\Delta S$ .
    - b) Suppose that water at  $100 \text{ }^\circ\text{C}$  is in contact with water vapour at  $0.90 \text{ atm}$ , calculate  $\Delta G$  and  $\Delta S$

5. Given that a gas obeys the modified van der Waals equation

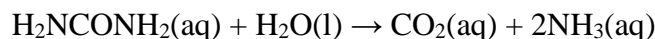
$$P(V_m - b) = RT$$

and that  $b$  has a value of  $0.020 \text{ dm}^3 \text{ mol}^{-1}$ . If  $0.50 \text{ mol}$  of the gas is reversibly compressed from an initial volume of  $2.0 \text{ dm}^3$  to a final volume of  $0.50 \text{ dm}^3$ , how much work is done on the system? How much work would have been done if the gas were ideal? Account for the difference between the two values.

6.

- a)  $1 \text{ mol}$  of an ideal gas is allowed to expand against a piston which supports  $0.041 \text{ MPa}$ , the temperature being constant at  $0 \text{ }^\circ\text{C}$ . The initial pressure is  $1.01325 \text{ MPa}$  and the final pressure is  $0.041 \text{ MPa}$ . Calculate  $W$ ,  $Q$ ,  $\Delta U$  and  $\Delta H$ .
- b) If the change is carried out in such a way that the confining pressure at all time is less than the gas pressure, find the value of  $W$ ,  $Q$ ,  $\Delta U$  and  $\Delta H$

7. Construct the Hess's cycle and use it to calculate the  $\Delta H^\circ$  for the hydrolysis of urea to give carbon dioxide and ammonia in aqueous solution:



Use this data

	$\Delta_f H^\circ / \text{kJ mol}^{-1}$
$\text{H}_2\text{NCONH}_2(\text{aq})$	- 317.77
$\text{H}_2\text{O}(\text{l})$	- 285.85
$\text{CO}_2(\text{aq})$	- 413.80
$\text{NH}_3(\text{aq})$	- 80.71

8. Two moles of water at  $50 \text{ }^\circ\text{C}$  are placed in a refrigerator which is maintained at  $5 \text{ }^\circ\text{C}$ . Taking the heat capacity of water as  $75.3 \text{ J K}^{-1} \text{ mol}^{-1}$  and independent of temperature, calculate the entropy change for the cooling of the water to  $5 \text{ }^\circ\text{C}$ .
9. One mole of super cooled water at  $-10 \text{ }^\circ\text{C}$  and  $1 \text{ atm}$  pressure turns into ice. Calculate the entropy change in the system and in the surroundings and the net entropy change given that the heat capacities ( $C_{p,m}$ ) of water and ice to be constant at  $75.3$  and  $37.7 \text{ J K}^{-1} \text{ mol}^{-1}$ .
10. One mole of liquid water at  $0.0 \text{ }^\circ\text{C}$  and  $1 \text{ atm}$  pressure is turned into steam at  $100 \text{ }^\circ\text{C}$  and  $1 \text{ atm}$  pressure by following two paths:
- a) Heated at constant pressure to  $100 \text{ }^\circ\text{C}$ , and allowed to boil into steam ( $\Delta_{\text{vap}} H^\circ = 40.67 \text{ J mol}^{-1}$  at this temperature).
- b) Pressure lowered to  $0.00602 \text{ atm}$  so that water evaporates to steam at  $0.0 \text{ }^\circ\text{C}$  ( $\Delta_{\text{vap}} H^\circ = 44.92 \text{ J mol}^{-1}$  at this temperature), heated at constant pressure of  $0.00602 \text{ atm}$  to  $100 \text{ }^\circ\text{C}$ , and compressed at  $100 \text{ }^\circ\text{C}$  to  $1 \text{ atm}$  pressure.

Calculate the entropy change along each path and verify that they are the same, thus proving that  $\Delta S^\circ$  is a state property.

$$C_{p,m}(\text{water, liquid}) = 75.48 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$C_{p,m}(\text{water, vapour}) = 30.54 + 10.29 \times 10^{-3} T$$