

NATIONAL UNIVERSITY OF SCIENCE AND TECHNOLOGY DEPARTMENT OF APPLIED CHEMISTRY BACHELOR OF SCIENCE HONOURS DEGREE SUPPLEMENTARY EXAMINATIONS – AUGUST 2014 PHYSICAL CHEMISTRY I – SCH 2104 TIME: 3 HOURS

INSTRUCTIONS TO CANDIDATES

Answer ALL questions. Answer each question on a FRESH page. $R = 8.314 JK^{-1} mol^{-1} = 0.08206 dm^3 atm K^{-1} mol^{-1}$ 1 atm = 760 torr = 760 mmHg = 101 325 Pa $lnx = 2.3026 log_{10} x$

1. a) Discuss how the Second Law of Thermodynamics was derived.

[7 marks]

- b) One mole of a monatomic ideal gas is initially at 273 K and 1atm.
 - i) What is the initial internal energy?
 - ii) Find its final internal energy and the work done by the gas when 500 J of heat are added at constant pressure.

iii) Find the same quantities when 500 J of heat are added at constant volume.

[10 marks]

- c) Explain the concept "the higher you go the cooler it becomes". [8 marks]
- 2. a) With the aid of appropriate diagrams, discuss a heat pump. [12 marks]
 - b) Discuss why the Carnot engine is the most efficient engine. [13 marks]
- 3. a) Calculate, q, w and ΔH for the vaporization of 2.5g of liquid water at 2.1 atm and 100°C. Make the following assumptions:
 - (i) density of liquid water at 100° C is 1g/mL.
 - (ii) Water vapour is described by the ideal gas equation.
 - (iii) External pressure is constant at 2.1 atm [12 marks]
 - b) Given that two phases (α and β) are at equilibrium and

 $d\mu_{\alpha} = -S_{m,\alpha}dT + V_{m,\alpha}dP$; derive the Clapeyron equation shown below

$$\frac{dP}{dT} = \frac{\Delta S_m}{\Delta V_m}$$

Hence use it to explain why for some compounds the solid-liquid phase boundary curve has a negative slope while for others the slope is positive. [13 marks]

- 4. a) A mixture of CO(g), H₂ (g), and CH₃OH(g) at 500K with P_{CO} = 10 bar, P_{H₂} = 1 bar and P_{CH₃OH} = 0.1 bar is passed over a catalyst.
 For the reaction, CO(g) + 2H₂(g) ≓ CH₃OH(g); Confirm that the reaction is not spontaneous in the forward direction. What is the minimum temperature required for the reaction to be spontaneous in the forward direction? Given that ΔrG⁰ = 21.21kJ mol⁻¹. [13 marks]
 - b) Considering the Kw data for different temperatures given in the table below:

°C	\mathbf{K}_{w}
10	0.29×10^{-14}
25	1.00×10^{-14}
50	5.48×10^{-14}

Using the following equations discuss whether the autoionization reaction is exothermic or endothermic?

$$\ln K = \frac{-\Delta_R G^0}{RT}$$
, and $G = H - TS$. [12 marks]

End of question Paper!!!