

University of Canterbury

Mid Year Examination and Test Period 2006

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| Prescription Number(s): | CHEM 233 |
| Paper Title: | Introduction to Physical Chemistry |

Time Allowed: TWO HOURS

Number of pages: 8

Answer **ALL** questions

Question **ONE** is worth **50%** of the marks

Question **TWO** and **THREE** are each worth **25%** of the marks

TURN OVER

Some useful constants:

Molar Gas Constant $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

Faraday Constant $F = 96485 \text{ C mol}^{-1}$

Avogadro's Constant $N_A = 6.023 \times 10^{23} \text{ mol}^{-1}$

$$1 \text{ atm} = 1.01325 \times 10^5 \text{ Pa}$$

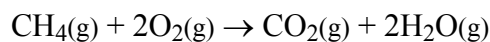
(Question **ONE** is worth **50%** of the marks)

1. (a) The following table lists some symbols used in the study of thermodynamics. Being guided by the given example, complete this table in your answer booklet.

| Symbol | Name of quantity | SI units | State function? |
|------------------|-------------------------|-----------------|------------------------|
| T | temperature | K | yes |
| p | | | |
| V | | | |
| U | | | |
| H | | | |
| S | | | |
| G | | | |
| w | | | |
| q | | | |
| w_p | | | |
| q_{rev} | | | |

TURN OVER

- (b) Give a statement of:
- (i) the first law of thermodynamics;
 - (ii) the second law of thermodynamics;
 - (iii) the third law of thermodynamics.
- (c) To good approximation the **constant-pressure** molar heat capacity for a gas composed of linear molecules is $C_{p,m} = \frac{7}{2}R$ whereas that for a gas composed of nonlinear molecules $C_{p,m} = 4R$.
- (i) For a process in which a sample of acetylene (C_2H_2) gas is heated from $10^\circ C$ to $50^\circ C$ at constant pressure, calculate w , q and ΔU .
 - (ii) Explain whether ΔH for the following reaction will increase or decrease with increasing temperature:



- (d) Camping gas is typically propane (C_3H_8). The standard enthalpy of combustion of propane gas is $-2220 \text{ kJ mol}^{-1}$ and the standard enthalpy of vaporization of the liquid is $+15 \text{ kJ mol}^{-1}$. Calculate:
- (i) The standard enthalpy of combustion of **liquid** propane.
 - (ii) The standard internal energy of combustion of propane **gas**.
- (e) You are required to predict the standard reaction enthalpy of:



- (i) What are the four pieces of thermodynamic data you would require?
- (ii) Explain how you would use these data for the required purpose.

- (f) 1.203 mol of carbon dioxide gas is at 360.9 K and 100 kPa. It expands **isothermally** and **reversibly** to a final state in which its pressure is 36.8 kPa.
- (i) Determine w , q , ΔU , ΔH , ΔS and ΔG for the **system** and also ΔS for the **surroundings**.
[Useful equation: $w = -nRT \ln(V_f/V_i)$.]
- (ii) Is the process spontaneous? Explain.
- (iii) What is the amount of non-expansion work for this process? Explain.

(Question **TWO** is worth **25%** of the marks)

2. (a) Define the following terms which refer to the properties of ionic solutions.
- (i) conductance;
 - (ii) conductivity;
 - (iii) molar conductivity;
 - (iv) transport number;
 - (v) ion mobility.
- (b) The resistance of a series of aqueous KNO_3 solutions, formed by successive dilutions of a sample, were measured in a conductivity cell having a cell constant equal to 15.84 m^{-1} .

| | | | | | | |
|-----------------------|---------|--------|--------|--------|-------|-------|
| $c/\text{mol L}^{-1}$ | 0.00050 | 0.0010 | 0.0050 | 0.0100 | 0.020 | 0.050 |
| R/Ω | 2219 | 1117 | 228.8 | 119.3 | 59.81 | 25.08 |

Using the graph paper provided, verify that the molar conductivity follows the Kohlrausch law and find the limiting molar conductivity of KNO_3 and the Kohlrausch constant, κ .

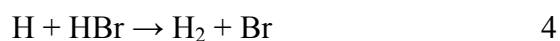
- (c) Briefly explain why a solution of acetic acid does not follow the Kohlrausch law and describe how the acid dissociation constant K_a , can be obtained from conductance measurements.

(Question **THREE** is worth **25%** of the marks)

3. (a) State the assumptions underlying the use of the steady state approximation for the analysis of complicated kinetic mechanisms.
- (b) The rate law for the reaction of hydrogen with bromine to form hydrogen bromide, $\text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr}$, is observed to be of the form,

$$\frac{1}{2} \frac{d[\text{HBr}]}{dt} = \frac{k_A [\text{H}_2] [\text{Br}_2]^{1/2}}{1 + k_B \frac{[\text{HBr}]}{[\text{Br}_2]}}$$

The following mechanism has been proposed for this reaction:



- (i) Write down these equations and label each reaction appropriately (initiation, propagation, linear chain, branched chain, inhibition or termination).
- (ii) Identify all radical intermediate species involved in these reactions.
- (iii) Write down an equation for the rate of formation of HBr, $\left(\frac{d[\text{HBr}]}{dt}\right)$, in terms of the above mechanism.

TURN OVER

- (iv) Assuming the intermediates are in steady state, show that the rate of initiation equals the rate of termination, and that the steady state concentrations of Br is:

$$[\text{Br}] = \left(\frac{k_1}{k_5} [\text{Br}_2] \right)^{1/2}$$

- (v) What further information is required to show that the mechanism is consistent with the observed rate law?
- (c) Explain why the rate of a single-step reaction will increase when the temperature is increased.

END OF PAPER