University of Canterbury

Mid Year Examination and Test Period 2008

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

Time Allowed: ONE HOUR

Number of pages: FIVE

Answer the **ONE** question.

1. This question is worth **60 marks** in all.

All <u>symbols</u> have their usual thermodynamic meaning.

$R = 8.314$ J K^{-1} mol^{-1}

0 K = –273 ˚C

(a) (10 marks)

(i) Give a statement of the First Law of thermodynamics.

(ii) Give a statement of the Second Law of thermodynamics.

(iii) Define enthalpy, H.

(iv) **In one sentence**, explain why H is defined.

(v) Define Gibbs free energy, G.

(vi) **In one sentence**, explain why G is defined.

(b) (12 marks)

2.0 mol of He(g) at 500 K has a volume of 200 L. It expands **isothermally** and **reversibly** until it has a volume of 544 L.

(i) Starting from the definition of work (in terms of p and V), show that $w = -nRT \ln(V_f/V_i)$ for this process.

(ii) Calculate w for this process.

(iii) Explain what a (mechanically) reversible process is.

Question 1 continued on following page

Question 1 continued

(c) (12 marks)

(i) Sketch a constant-volume calorimeter, labelling its essential features.

(ii) In an experiment to measure the heat released by a sample of fuel, 0.001 mol of the compound was burned in an oxygen atmosphere inside a constant-volume calorimeter. As a result of this process the temperature rose by 3.78 ˚C. The calorimeter was then allowed to cool down. After this, a current of 1.54 A from an 11.5 V source was flowed through a heater in the calorimeter for 118 s; the temperature rose by 5.11 ˚C.
What is the heat per mole of the combustion reaction?

(iii) Is your answer to (ii) a value of ΔU or ΔH? Explain.

(d) (13 marks)

The first and second ionisation enthalpies of Be are 900 kJ mol^{-1} and 1 760 kJ mol^{-1} respectively.

(i) Why is the second ionisation enthalpy greater than the first?

(ii) Calculate ΔH for $Be(g) \rightarrow Be^{2+}(g) + 2e^{-}(g)$.

(iii) A footnote to the table of ionisation enthalpies in your textbook states:
"Strictly, these are the values of $\Delta_{ion}U(0)$. For more precise work, use $\Delta_{ion}H(T) = \Delta_{ion}U(0) + \frac{5}{2}RT$."
Noting that $C_{V,m} = \frac{3}{2}R$ for monatomic gases and $e^{-}(g)$, prove this equation.

(iv) Verify that $\Delta_{ion}H(T) \approx \Delta_{ion}U(0)$ for $T = 298$ K.

Question 1 continued on following page

Question 1 continued

(e) (13 marks)

(i) Starting from the definition of entropy, show that $\Delta S_m = R \ln(V_f/V_i)$ for an isothermal volume change of a perfect gas.
[Hint: use the result of (b) (i).]

(ii) Starting from the definition of entropy, show that $\Delta S_m = C_{V,m} \ln(T_f/T_i)$ for the temperature change of a material at constant volume. (You may assume that $C_{V,m}$ remains constant.)

(iii) Calculate the change in molar entropy when a sample of argon is simultaneously compressed from 544 L to 200 L and heated from –173 ˚C to –1 ˚C.
[Hint: use a piece of information given in (d) (iii).]

END OF PAPER