THERMODYNAMICS I

QUESTION 1

a) State the *first law of thermodynamics*, and explain what is meant by the term *state function.*

b) Explain clearly the distinction between a *bond dissociation enthalpy* and a *mean bond dissociation enthalpy*.

c) The following enthalpies of combustion have been measured at 298 K.

$W(s) + 1.5\ O_2(g) \rightarrow WO_3(s)$	$\Delta_c H^{\ominus} = -842.9$ kJ mol^{-1}
$W(CO)_6(s) + 4.5\ O_2(g) \rightarrow WO_3(s) + 6CO_2(g)$	$\Delta_c H^{\ominus} = -2242.7$ kJ mol^{-1}
$CO(g) + 0.5\ O_2(g) \rightarrow CO_2(g)$	$\Delta_c H^{\ominus} = -282.8$ kJ mol^{-1}
$C(s) + O_2(g) \rightarrow CO_2(g)$	$\Delta_c H^{\ominus} = -393.5$ kJ mol^{-1}

i) Calculate the enthalpy of formation of $W(CO)_6(s)$.

ii) At 298 K, the enthalpies of sublimation of $W(CO)_6(s)$ and of W(s) are 75.6 and 849.4 kJ mol^{-1} respectively. Calculate the mean (W–CO) bond dissociation enthalpy in $W(CO)_6$.

QUESTION 2

a) From the expression $\mathrm{d}G = V\mathrm{d}p - S\mathrm{d}T$, derive equations for the variation of the vapour pressure of solid and liquid phases with temperature.

b) The vapour pressures, p, of CO_2 at different temperatures are given in the table below.

T / K	186	196	206	226	236	246
p / bar	0.526	1.132	2.447	7.605	11.065	15.579

Determine graphically the latent heats of evaporation and sublimation of CO_2 in this temperature range. What is the latent heat of fusion of CO_2?

QUESTION 3

a) State the second law of thermodynamics

b) For each of the following processes, predict the entropy changes occurring during the process. Briefly justify your answers.

i) 1 mole of calcium carbonate decomposes completely into calcium oxide and carbon dioxide upon heating.

ii) 1 mole of water is frozen rapidly at –5°C and a pressure of 1 atmosphere.

c) Comment on your answer to part ii) in the light of the second law of thermodynamics.

d) The molar heat capacity at constant pressure for He at 298 K is 20.79 JK^{-1}, while that of chlorine at the same temperature is 33.93 JK^{-1}.

i) Predict the molar heat capacity at constant volume of argon at 298 K.

ii) Explain why the molar heat capacities of helium and chlorine differ.

iii) Halogens are often diluted with helium for use in experiments. Calculate the quantity of heat required to raise the temperature of 40 g of a mixture containing (by volume) 5% chlorine and 95% helium from 298 K to 305 K. Assume that the heat capacity of both gases is constant over this small temperature range, that the pressure remains constant, and that the gases do not interact with each other in any way.
[atomic weights: He 4, Cl 35.5]

QUESTION 4

a) Derive, starting from the statements $dU = dq + dw$ and $dS = dq_{rev}/T$, the expression $dG = Vdp - SdT$.

b) i) Use the expression above to derive the Clapeyron equation, $\frac{dp}{dV} = \frac{\Delta_{trs}S}{\Delta_{trs}V}$, for the slope of a phase boundary.

ii) Show how this expression for the phase boundary leads to the Clausius-Clapeyron equation for the vapour pressure curve of a condensed phase.

c) Sketch the appearance of the phase diagram of argon close to its triple point (T_3 = 84 K, p_3 = 0.68 atm), based on your drawing on the Clapeyron equation.

QUESTION 5.

a) i) How is entropy defined thermodynamically?

ii) Starting from the thermodynamic definition of entropy, derive formulae for the entropy change associated with a phase change at constant pressure and with the reversible heating of a pure substance at constant pressure. Assume the heat capacity is independent of temperature.

iii) How may entropy changes be used to determine the direction of spontaneous change?

b) By evaluating the relevant entropy changes, demonstrate that benzene vapour at 343 K and 1.0 atm spontaneously condenses to form the liquid. The normal boiling point of benzene is 353 K and the enthalpy of vaporization of benzene is 30.8 kJ mol^{-1} at this temperature. The molar heat capacities of the liquid and vapour are 136.1 and 81.7 J K^{-1} mol^{-1}, respectively, and may be assumed temperature independent.