

**Degree of BEng/MEng in Chemical Engineering [or other]**

**Thermodynamics and Chemical Principles CP203**

**Date:**

**Time:**

**Duration: 3 hours**

**Answer 2 Questions from 3 in Section A**

**Answer 2 Questions from 3 in Section B**

**Calculators must not be used to store text and/or formulae nor be capable of communication. Invigilators may require calculators to be re-set.**

**END OF PAPER**

**[Compilers: Dr M. Jorge, ext. 2825 / Dr A J Fletcher, ext. 2431]**

### **Section A: Answer 2 Questions from 3**

**QA1** A heat engine is used to produce a total of 1 kJ/mol of work in each operation cycle. The operation of the heat engine can be described by a cyclic process with the following steps:

1 – A supercritical fluid, initially at pressure  $P_1$  and volume  $V_1$ , is heated to undergo an isothermal expansion at temperature  $T_A=500$  K to volume  $V_2$ .

2 – The fluid is further expanded adiabatically to a volume  $V_3$  and a temperature  $T_B$ , which is below the fluid's critical temperature.

3 – The fluid, now termed a vapour, is cooled isothermally at temperature  $T_B$  until it reaches the saturated vapour line.

4 – The system is further cooled isothermally and isobarically until all the vapour is condensed into a saturated liquid.

5 – The saturated liquid is compressed adiabatically back to the original state with pressure  $P_1$ , volume  $V_1$ , and temperature  $T_A$ .

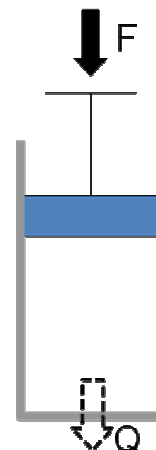
- a) Sketch the cyclic process described above on a PV diagram, taking care to account for any phase changes. [20 marks]
- b) Calculate the heat absorbed in step 1, assuming reversibility and knowing that the final pressure ( $P_2$ ) is one third of the initial pressure ( $P_1$ ). In the range of conditions for this step, the fluid's behaviour is well described by the ideal gas equation of state. [25 marks]
- c) Again assuming ideal gas behaviour, calculate the temperature at the end of step 2 ( $T_B$ ). The final volume ( $V_3$ ) is three times the initial volume ( $V_2$ ). Remember that for an adiabatic process,  $PV^\gamma$  is constant.  $\gamma$  is defined as the ratio of molar heat capacities at constant pressure and constant volume and takes the value of 1.37 for this gas. [20 marks]
- d) Calculate the efficiency of the heat engine and compare it to the efficiency of an ideal Carnot engine operating between the same two temperatures  $T_A$  and  $T_B$ . If you were unable to solve questions A1b) and A1c), assume a value of 5 kJ/mol for the heat absorbed in step 1 and a reasonable value for  $T_B$ . [15 marks]
- e) Calculate the heat discarded in step 3, given that the latent heat of vaporisation of the fluid at  $T_B$  is 1.32 kJ/mol. [20 marks]

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**QA2** One mole of steam is contained within a vertical piston-cylinder arrangement, as shown in Figure A2.1. The system is perfectly sealed and friction can be considered negligible. The steam is initially at a temperature ( $T$ ) of 200 °C and at a pressure ( $P$ ) of 2 bar. Under these conditions, the molar volume ( $v$ ) of the steam is 0.01947 m<sup>3</sup>/mol, and the behaviour of steam is well described by the virial equation of state, where  $Z$  is the compressibility factor and  $B$  is a constant with the value of -200 cm<sup>3</sup>/mol:

$$Z = 1 + \frac{B}{v}$$



**Figure A2.1**

A force of 5000 N is then made to act on the piston, pushing it very slowly downwards (so that the process can be considered reversible).

- a) Consider first that the walls of the cylinder are in perfect thermal contact with the surroundings, so that the final temperature is the same as the initial temperature. If the final volume of the gas inside the cylinder is 0.0177 m<sup>3</sup>/mol, calculate the work exerted on the gas by the piston. [25 marks]

- b) Calculate the radius of the cylinder. If you were unable to solve question A2a), assume a value of 500 J for the work done on the system. [20 marks]

- c) For any system undergoing an isothermal process, the change in internal energy is given by:

$$\left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V - P$$

Making use of this expression, calculate the heat discarded by the system. Again, if you were unable to solve question A2a), assume a value of 500 J for the work done on the system. [25 marks]

**QA2 continued overleaf**

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- d) Calculate the change in entropy of the steam during the process. Does this violate the Second Law of thermodynamics? Explain your answer. If you were unable to solve question A2c), assume a value of -400 J for the heat discarded. [15 marks]
- e) Consider now that the cylinder is fitted with a heating jacket and that heat is slowly transferred to the system while the same force as before is acting on the piston, such that the pressure of the steam remains constant at 2 bar. If the heat transferred to the system is 750 J, what is the final temperature of the system? The molar heat capacities of steam are  $c_V = 27.4 \text{ J/mol/K}$  and  $c_P = 36.3 \text{ J/mol/K}$ , and can be assumed to be independent of temperature in this range [15 marks]

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- QA3** Two pure liquid streams, A and B, are fed into a static mixer operating at a temperature ( $T$ ) of 300 K. The molar flow rate of A is 6 mol/hr and that of B is 2 mol/hr. The single outlet stream from the mixer is a homogeneous liquid mixture of the two components, which is then fed into a flash evaporator operating at  $T = 420$  K, as shown in Figure A3.1. The two outlet streams from the evaporator, one liquid and one vapour, are in thermodynamic equilibrium.

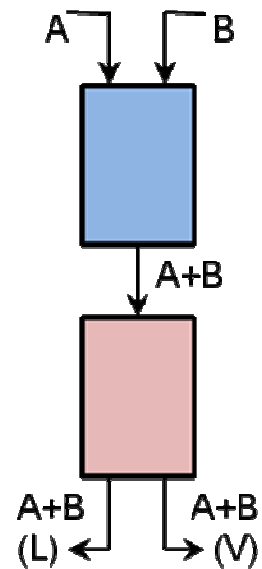


Figure A3.1

The molar volume of the liquid mixture ( $v$ ) as a function of composition ( $x$ ) is given by the equation below, where  $v_i^0$  is the molar volume of pure component  $i$  ( $88 \text{ cm}^3/\text{mol}$  for A and  $130 \text{ cm}^3/\text{mol}$  for B, independent of  $T$ ) and  $K$  is a temperature-dependent constant.

$$v = v_A^0 x_A + v_B^0 x_B + K x_A^2 x_B$$

- a) Derive expressions for the partial molar volume of each component as a function of mixture composition. Recall that the definition of a generic partial molar property  $m$  is:

$$\bar{m}_i = \left( \frac{\partial M}{\partial n_i} \right)_{P,T,n_j} \quad [15 \text{ marks}]$$

- b) The constant  $K$  for this mixture takes the value of  $9 \text{ cm}^3/\text{mol}$  at 300 K and  $0.2 \text{ cm}^3/\text{mol}$  at 420 K. Calculate the molar volume change of mixing at each of these two temperatures, and explain why the mixture can be considered an ideal solution at 420 K. [35 marks]
- c) Explain why the entropy change of mixing always takes a positive value, even when the mixture is ideal. [10 marks]
- d) Knowing that the mole fraction of B in the vapour is 0.3, the saturated vapour pressure of A at 420 K is 26 kPa, and the saturated vapour pressure of B at 420 K is 52 kPa, calculate the equilibrium pressure in the evaporator. You may assume that both liquid and vapour mixtures in the evaporator are ideal. [25 marks]
- e) Calculate the molar flow rate of liquid coming out of the evaporator. If you were unable to solve question A3d), assume a value of 30 kPa for the equilibrium pressure in the evaporator. [15 marks]

**END OF PAPER**

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## NUMERICAL SOLUTIONS

**QA1.b)**  $q_1 = 4.567 \text{ kJ/mol}$

**c)**  $T_B = 333 \text{ K}$

**d)**  $\eta = 0.219$ ;  $\eta_{\max} = 0.334$

**e)**  $q_1 = -2.247 \text{ kJ/mol}$

**QA2.a)**  $W = 370.9 \text{ J}$

**b)**  $r = 0.0872 \text{ m}$

**c)**  $Q = -370.9 \text{ J}$

**d)**  $\Delta S = -0.784 \text{ J/K}$

**e)**  $T = 493.8 \text{ K}$

**QA3.b)**  $\Delta V_{\text{MIX}}^{300\text{K}} = 1.266 \text{ cm}^3/\text{mol}$ ;  $\Delta V_{\text{MIX}}^{420\text{K}} = 0.028 \text{ cm}^3/\text{mol}$

**d)**  $P = 30.6 \text{ kPa}$

**e)**  $n_L = 3.33 \text{ mol/hr}$

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