

Degree of BEng/MEng in Chemical Engineering

CP203/CP211 Thermodynamics and Chemical Principles

Date: Friday 11th May 2018

Time: 14:00-17:00

Duration: 3 hours

Answer All Questions

The paper is divided into TWO sections

Answer each section in a separate booklet

There are 100 marks available in each section of the paper

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

Remember to clearly state any assumptions you make when solving each question.

Equation sheets and periodic table are provided at the end of the paper.

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Section A: Answer All Questions

- QA1.** A heat engine produces 40 kJ mol^{-1} of work with an overall efficiency of 47%, following the cyclic path shown on the temperature/entropy diagram of **Figure A1.1**. Knowing that step 3 of that cycle takes place at a temperature of 20°C and involves an entropy change of $50 \text{ J mol}^{-1} \text{ K}^{-1}$, calculate the enthalpy of vapourisation of the engine fluid. [12 marks]

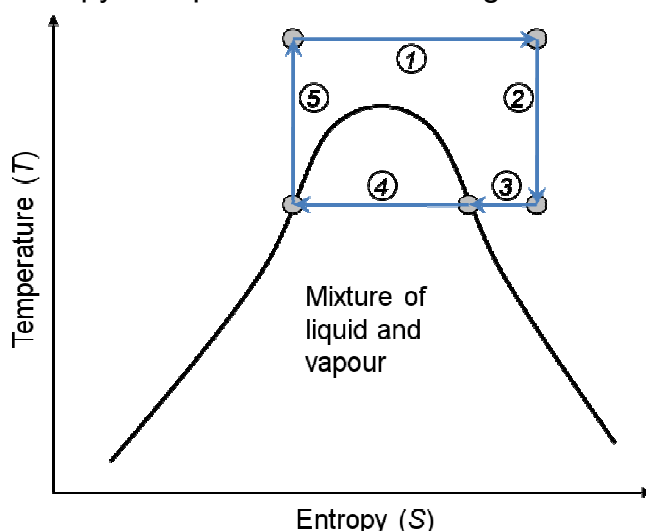


Figure A1.1 - Temperature/Entropy diagram showing the cyclic path of an engine. The arrows show the direction of each step, numbered from 1 to 5.

- QA2.** The boiling point of water at 1 bar is 99.63°C . At 2.5 bar, water boils at 127.43°C . Estimate the saturated vapour pressure of water at 115°C as accurately as possible, making use of thermodynamic principles and stating clearly any assumptions made. [12 marks]
- QA3.** An ideal gas, initially at 3 bar, is expanded adiabatically in a slow steady flow process from an initial volume of 1 m^3 to a final volume of 2.5 m^3 . The ratio of heat capacities for this gas is $\gamma = 1.35$. Calculate the enthalpy change for the expansion process. [15 marks]
- QA4.** The molar enthalpy in a system composed of a binary mixture of two components, A and B, is given by:

$$h = 18x_A + 24x_B - 16x_Ax_B$$

- a) Derive expressions for the partial molar enthalpy of each component of the mixture. [12 marks]
- b) Does the system show positive or negative deviations from ideal mixture behaviour? Give an example of a mixture of two real substances that might show similar qualitative behaviour, and explain why. [5 marks]

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- QA5.** Calculate the molar entropy change when a gas is compressed isothermally, from an initial pressure of 1 bar to a final pressure of 5 bar. Under these conditions, the behaviour of the gas is accurately described by the virial equation of state: $Z = 1 + BP$, with $B = 0.075 \text{ bar}^{-1}$.

[15 marks]

- QA6.** 80 moles of hexane, 30 moles of heptane and 50 moles of octane are mixed together at a constant temperature of 300 K and a constant pressure of 1 bar. **Table A6.1** provides selected physical property data for these three compounds, at 1 bar. Calculate the total heat evolved during the mixing process, making sure to explain clearly any assumptions made.[14 marks]

Table A6.1: Physical properties of alkanes at a pressure of 1 bar (enthalpy of vapourisation, heat capacity at constant pressure, and boiling point).

Component	Hexane	Heptane	Octane
ΔH_{vap} (kJ mol ⁻¹)	28.85	36.0	41.2
C_P (J mol ⁻¹ K ⁻¹)	197.66	224.64	255.68
T_b (K)	341.85	371.53	398.7

- QA7.** An adiabatic turbine operates at steady state with an efficiency of 64%, using air as a working fluid. The air stream enters the turbine at 4.5 bar and 450 K, and leaves at 1.5 bar. Calculate the molar work produced by the turbine.

You may assume that air behaves as an ideal gas and is composed of 79% nitrogen and 21% oxygen (ignoring any other residual components). The heat capacity of nitrogen is $1.049 \text{ J g}^{-1} \text{ K}^{-1}$ and that of oxygen is $0.956 \text{ J g}^{-1} \text{ K}^{-1}$, both independent of temperature in this range.

[15 marks]

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Numerical Answers

QA1. 30.5 kJ/mol

QA2. 1.69 bar

QA3. -317.5 kJ

QA4b. Negative; tetrahydrofuran/chloroform

QA5. -15.9 J/mol.K

QA6. 408.6 kJ

QA7. 2264 J/mol

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Thermodynamics Equation Sheet

All symbols have the meaning as given in class materials.

First Law (general)

$$\Delta U = Q + W - \Delta\left(\frac{1}{2}mv^2\right) - \Delta(mgz)$$

Gibbs phase rule

$$F = 2 - \pi + N$$

Thermal expansion coefficient

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_{P,m}$$

Isothermal compressibility

$$\beta = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_{T,m}$$

Heat capacities

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = T \left(\frac{\partial S}{\partial T} \right)_V$$

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P = T \left(\frac{\partial S}{\partial T} \right)_P$$

$$C_P - C_V = T \left(\frac{\partial V}{\partial T} \right)_P \left(\frac{\partial P}{\partial T} \right)_V$$

Van der Waals equation of state

$$P = \frac{RT}{v-b} - \frac{a}{v^2}$$

Virial equation of state

$$Z = 1 + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^3} + \dots$$

Thermodynamic potentials

$$H = U + PV$$

$$A = U - TS$$

$$G = H - TS$$

Fundamental thermodynamic relations

$$dU = TdS - PdV$$

$$dH = TdS + VdP$$

$$dA = -SdT - PdV$$

$$dG = -SdT + VdP$$

Maxwell equations

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

$$\left(\frac{\partial T}{\partial P} \right)_S = \left(\frac{\partial V}{\partial S} \right)_P$$

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

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

Internal energy and enthalpy

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

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

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

$$\left(\frac{\partial H}{\partial P} \right)_T = -T \left(\frac{\partial V}{\partial T} \right)_P + V$$

Carnot relationship

$$\left| \frac{Q_1}{Q_2} \right| = \frac{T_1}{T_2}$$

Entropy

$$\Delta S = \int_1^2 \frac{dQ_{\text{rev}}}{T}$$

$$dS = \frac{C_P}{T} dT - \left(\frac{\partial V}{\partial T} \right)_P dP$$

$$\Delta S_{\text{IG}} = C_P \ln \frac{T_2}{T_1} - nR \ln \frac{P_2}{P_1}$$

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Thermodynamics Equation Sheet

Joule-Thomson coefficient

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{V}{C_P}(\alpha T - 1)$$

Phase equilibrium

$$\frac{dP^{sat}}{dT_b} = \frac{\Delta h}{T_b \Delta v}$$

$$\frac{dP^{sat}}{dT_b} = \frac{\Delta h P^{sat}}{RT_b^2}$$

$$\ln P^{sat} = A - \frac{B}{T_b + C}$$

Multi-component systems (m or M stand for any extensive property)

$$dU = TdS - PdV + \sum_{i=1} \mu_i dn_i$$

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j}$$

$$m = \sum_i x_i \bar{m}_i$$

$$\Delta M_{\text{Mix}} = \sum_i n_i \bar{m}_i - \sum_i n_i m_i^0$$

$$\sum_i x_i d\bar{m}_i = 0$$

Ideal mixture

$$\mu_i = \mu_i^0 + RT \ln x_i$$

$$U = \sum_i n_i u_i^0$$

$$H = \sum_i n_i h_i^0$$

$$V = \sum_i n_i v_i^0$$

$$S = \sum_i n_i s_i^0 - nR \sum_i x_i \ln x_i$$

$$G = \sum_i n_i \mu_i^0 + nRT \sum_i x_i \ln x_i$$

$$Py_i = P_i^{sat} x_i$$

Relative volatility

$$\alpha_{ij} = \frac{P_i^{sat}}{P_j^{sat}}$$