

Degree of BEng/MEng in Chemical Engineering

CP203/CP211 Thermodynamics and Chemical Principles

Date: Friday 10th May 2019

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 perfectly sealed piston-cylinder arrangement containing 5 moles of gas undergoes a rapid expansion at a constant temperature of 350 K from an initial volume of 0.03 m³ to a final volume of 0.04 m³. The expansion process takes up 6.5 kJ of heat from the surroundings and produces 3.9 kJ of work on the surroundings. The behaviour of the gas is well described by the following virial equation of state, where $B = 36.4 \text{ cm}^3 \text{ mol}^{-1}$.

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

- a) Calculate the internal energy and the enthalpy changes of the gas inside the cylinder during the expansion process. [10 marks]
- b) Calculate the work produced if the expansion was carried out reversibly. Explain why this value is larger than the work of an irreversible expansion. [10 marks]

- QA2.** The inside of a house is kept at a balmy 28 °C against an average external temperature of 2 °C by action of a heat pump. At steady state, the house loses 4 kW of heat to the outside. Inside the house, there is a large freezer that is always turned on to keep its interior compartment at -7 °C, achieved by absorbing 2.5 kW of heat from that compartment. You can assume that both the heat pump and the freezer are operating at their maximum possible thermodynamic efficiencies. To save energy, the owner is considering:

- a) Increasing the temperature of the freezer to -4 °C;
b) Decreasing the temperature of the inside of the house to 26 °C.

Which of the two above options would be more energetically efficient (i.e. would save more electrical power)? Justify your answer with calculations. [16 marks]

- QA3.** Naphthalene is a substance with a high triple point ($T_t = 353.1 \text{ K}$; $P_t = 1 \text{ kPa}$), so that it sublimates at ambient conditions. **Table QA3** shows vapour pressure data for solid naphthalene at several temperatures. Estimate the enthalpy of sublimation of naphthalene from that data, making use of an appropriate thermodynamic relation and justifying clearly any assumptions made. [16 marks]

Table QA3: Vapour pressure data for naphthalene at several temperatures below the triple point.

Temperature (K)	Pressure (kPa)
350	0.840
340	0.386
330	0.175
320	0.086

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QA4. 2 litres of water are compressed slowly at a constant temperature of 50 °C, starting from a pressure of 1 bar. Calculate the work of compression if the volume of water at the end of the process is 1.97 litres. You can consider the system to be closed and assume a constant value of 4.4×10^{-5} bar for the isothermal compressibility of water at 50 °C. [16 marks]

QA5. A vapour mixture composed of 29% of benzene and 71% of toluene (molar basis), at a temperature of 75 °C, is in equilibrium with a liquid mixture of the same components. The molar entropy of mixing of the vapour phase is $5 \text{ J mol}^{-1} \text{ K}^{-1}$ and the molar enthalpy of mixing of the liquid phase is 0.2 J mol^{-1} . The vapour/liquid equilibrium of each pure component is well described by the Antoine equation with coefficients presented in **Table QA5**. Calculate the pressure and the composition of the liquid phase. [16 marks]

Table QA5: Antoine coefficients (pressure in bar and temperature in K)

Component	A	B	C
Benzene	9.25211	2771.932	-53.226
Toluene	9.39056	3094.543	-53.773
Hexane	9.21647	2697.548	-48.784

QA6. A stream of pure liquid hexane initially at $T = 335 \text{ K}$ and $P = 6 \text{ bar}$ is throttled adiabatically through a valve into a flash drum, such that its temperature drops to 334 K. Determine whether the pressure drop across the valve is sufficient to vaporise part of the liquid stream. If necessary, you may refer to **Tables QA5 and QA6** for physical properties of hexane, which you can consider constant over the relevant ranges of P and T . [16 marks]

Table QA6: Physical properties of hexane. All symbols have the same meaning as given in class materials.

Property	ΔH_{vap}	c_p	T_c	P_c	α	v
Units	kJ mol^{-1}	$\text{J mol}^{-1} \text{K}^{-1}$	K	bar	K^{-1}	$\text{m}^3 \text{mol}^{-1}$
Value	31	195.8	507.6	30.2	0.011	1.3×10^{-4}

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Thermodynamics Equation Sheet

All symbols have the same 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

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

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

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

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

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

Numerical Answers

QA1. a) $\Delta U = 2600 \text{ J}$; $\Delta H = 2579 \text{ J}$

QA1. b) $W = -4207 \text{ J}$

QA2. a) $W_{\text{tot}} = 643 \text{ W}$; b) $W_{\text{tot}} = 631 \text{ W}$

QA3. $\Delta h = 71 \text{ kJ/mol}$

QA4. $W = 517 \text{ J}$

QA5. $P = 0.4 \text{ bar}$; $x_1 = 0.134$

QA6. $P_2 = 0.38 \text{ bar}$; $P^{\text{sat}} = 0.785 \text{ bar}$