

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

Thermodynamics and Chemical Principles CP203

Date: XXXXdayXX^{xx} May 2015

Time: XX:00-XX:00

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.

PLEASE TURN OVER

Section A: Answer 2 Questions from 3

QA1 A mixture of 12 moles of carbon dioxide and 8 moles of methane is separated in the steady-flow process shown in **Figure A1.1**. The mixture, initially at 1 bar and 25°C, first enters a compressor, after which it passes through a membrane separation unit. One of the outlet streams (stream 3) contains mostly methane with a small amount of carbon dioxide. The other outlet stream (stream 4) contains pure carbon dioxide and passes through a nozzle before exiting the process. All equipment and piping is placed horizontally and you may assume that all steps of the process are reversible. The behaviour of the gas mixture is well described by the following equation of state, with

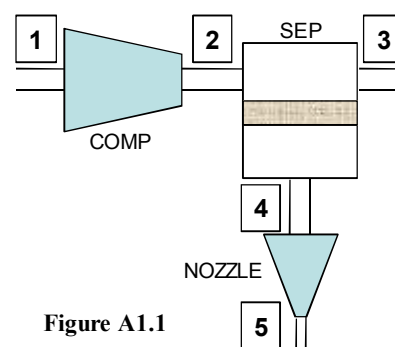


Figure A1.1

coefficient $b=0.002 \text{ m}^3/\text{mol}$:
$$P = \frac{RT}{v - b}$$

- a) Calculate the molar work of compression for the first step of the process. The compressor operates isothermally and the outlet pressure (stream 2) is 20 bar. [15 marks]
- b) Calculate the molar enthalpy change of the gas mixture going through the compressor (i.e., between stream 1 and stream 2). [25 marks]
- c) The membrane separation unit can be assumed to operate adiabatically, under which conditions the product $P(v - b)^{1.35}$ is constant. If the pressure of stream 4 exiting the separator unit is 13 bar, calculate the temperature of the gas in stream 4. [20 marks]
- d) The nozzle also operates adiabatically, and the velocity of the gas in stream 4 is 10 m/s. Passage through the nozzle causes the temperature of the gas to decrease by 20 K. The specific heat capacity of carbon dioxide in this temperature range is 0.8 kJ/kgK. Calculate the velocity of the gas at the exit of the nozzle (stream 5). [25 marks]
- e) Stream 3 contains 2 moles of carbon dioxide and exits the separator at a pressure of 18 bar. The molar volume of the gas mixture under these conditions is well represented by the equation below, where subscript A denotes carbon dioxide, subscript B denotes methane, $v_A=3.8 \text{ dm}^3/\text{mol}$, $v_B=3.3 \text{ dm}^3/\text{mol}$ and $K=-0.4 \text{ dm}^3/\text{mol}$:

$$V = v_A x_A + v_B x_B + K x_A x_B$$

Calculate the temperature of stream 3.

[15 marks]

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QA2 An ideal gas undergoes a Carnot cycle composed of four reversible steps: **i)** isothermal expansion at T_1 ; **ii)** adiabatic expansion to a temperature T_2 ; **iii)** isothermal compression at T_2 ; **iv)** adiabatic compression back to the initial state at T_1 . It is known that the difference in temperature between the hot and cold reservoirs, i.e., $T_1 - T_2$, is 140 K. The entropy change in the first step of the process is $\Delta s_1 = 14 \text{ J/molK}$.

- a)** Starting from the equation for the entropy change of an ideal gas, show that a reversible adiabatic process is isentropic. [20 marks]
- b)** Sketch the Carnot cycle described above on a temperature-entropy (TS) diagram and calculate the molar work produced by the engine. [25 marks]
- c)** In step **ii)**, the pressure of the gas is reduced fourfold. Knowing that the ratio of heat capacities for the gas is 1.4, calculate the efficiency of the Carnot engine. [15 marks]
- d)** Calculate the molar heat absorbed by the engine in step **i)** at high temperature. If you were unable to solve question c), assume an efficiency of 30% for the Carnot engine. [10 marks]
- e)** Consider now a real heat engine that is identical to the Carnot engine described above, except that step **ii)** is irreversible, with an entropy increase of 2 J/molK . Sketch the cyclic process for this real engine on a temperature-entropy (TS) diagram and calculate the efficiency of the real engine. If necessary, you can assume that the real engine absorbs the same amount of heat from the hot reservoir as the Carnot engine considered above. [30 marks]

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- QA3** a) 3 moles of an organic liquid are fed to a closed batch reactor and heated at constant pressure to its boiling point $T_b = 120\text{ }^\circ\text{C}$. If the liquid is initially at $30\text{ }^\circ\text{C}$, calculate the heat necessary to evaporate 40% of the liquid. Notice that the temperature of the whole liquid first needs to be raised to the boiling point, followed by partial evaporation. The latent heat of vaporisation of the liquid is 29 kJ/mol and the molar heat capacity of the liquid is known to depend on the temperature according to the following expression, with T in Kelvin and c_p in J/molK :

$$c_p = 143.5 + 0.141T$$

[20 marks]

- b) Calculate the entropy change for the heating + evaporation process described in question a). [20 marks]
- c) Using the Clausius-Clapeyron equation, calculate the pressure inside the reactor. As a reference point for the integration, you can consider that the boiling temperature of the liquid at 1 bar is $69\text{ }^\circ\text{C}$. [15 marks]
- d) Consider now that the organic liquid mentioned above (component 1) is first mixed with 1.2 moles of another liquid (component 2) before being fed to the reactor and heated to the same temperature, $120\text{ }^\circ\text{C}$. Calculate the entropy of mixing of the two components, assuming that they form an ideal liquid mixture. Explain why you would expect the entropy of mixing to always be positive. [20 marks]
- e) After heating to $120\text{ }^\circ\text{C}$, part of the liquid mixture described in question d) evaporates, forming a vapour phase at the top of the reactor in equilibrium with the liquid. Calculate the pressure and the composition of the vapour phase inside the reactor, assuming that both liquid and vapour mixtures are ideal. You may also assume for simplicity that the vapour volume is small, so that there is no significant change in the liquid composition upon evaporation. The vapour pressure of component 2 is given by the Antoine equation below (P^{sat} in kPa and T in $^\circ\text{C}$):

$$\ln(P^{\text{sat}}) = 15.4869 - \frac{3823.82}{T + 271.69}$$

If you were unable to solve question c), you may assume that the vapour pressure of component 1 at the reactor temperature is 4 bar.

[25 marks]

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NUMERICAL SOLUTIONS

QA1.a) $w = 11.2 \text{ kJ/mol}$

b) $\Delta h = 3.8 \text{ kJ/mol}$

c) $T_2 = 266.5 \text{ K}$

d); $V_2 = 179.2 \text{ m/s}$

e) $T = 289.2 \text{ K}$

QA2.b) $w = -1960 \text{ J/mol}$

c) $\eta_{ID} = 0.327$

d) $q_1 = 5994 \text{ J/mol}$

e) $\eta = 0.231$

QA3.a) $Q = 86.8 \text{ kJ}$

b) $\Delta S = 238.5 \text{ J/K}$

c) $P = 3.75 \text{ bar}$

d) $\Delta S_{\text{mix}} = 20.89 \text{ J/K}$

e) $y_1 = 0.754; P = 3.56 \text{ bar}$

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Thermodynamics Equation Sheet

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

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

Isothermal compressibility

$$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

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

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

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

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

Joule-Thomson coefficient

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

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Thermodynamics Equation Sheet

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

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

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

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

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

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

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

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

END OF PAPER

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