Degree of BEng/MEng in Chemical Engineering

CP203/CP211 Thermodynamics and Chemical Principles

Date: Friday 12th May 2017   **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.

Equation sheets, pressure-enthalpy diagram and periodic table are provided at the end of the paper.

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Section A: Answer All Questions

QA1. A gas is compressed isothermally in a steady-flow process from an initial pressure of 1 bar to a final pressure of 3 bar. The work consumed in the compression is 3.5 kJ/mol. Calculate the final temperature of the gas, assuming that its behaviour can be accurately described by the van der Waals equation of state with coefficients a = 0 m^3 J and b = 0.0025 m^3/mol.

[10 marks]

QA2. At a temperature of 110 K, the saturated vapour pressure of methane is 0.9 bar. Under those conditions, the gradient of the vapour-liquid equilibrium line on a pressure vs temperature diagram was estimated as 0.074 bar/K. Using this information, calculate the enthalpy of vapourisation of methane at 110 K. Remember to state clearly any assumptions required in the calculation.

[10 marks]

QA3. 6 moles of hexane vapour, initially at a temperature of 315 K and a pressure of 0.2 bar, undergo a thermodynamic process composed of three successive steps: 1) isothermal compression up to the saturated vapour pressure at 315 K; 2) complete condensation of the vapour into liquid; 3) isobaric cooling of the liquid to the final temperature. The vapour phase is well described by the following virial equation of state:

$Z = 1 + BP$, with B = 0.002 bar/mol, and P in units of bar.

The vapour/liquid equilibrium of hexane is well described by the Antoine equation with coefficients presented in **Table A1**. The enthalpy of vapourisation at 315 K is 30 kJ/mol, and the heat capacity of liquid hexane is 0.2 kJ/molK and can be assumed to be constant. If the total enthalpy loss during the process is ΔH = -210 kJ, calculate the final temperature of the liquid.

[14 marks]

Table A1: 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

QA4. A vapour mixture containing 60% of benzene and 40% of toluene (molar basis) is in equilibrium with a liquid phase of unknown composition at a pressure of 0.25 bar. The vapour/liquid equilibrium of each pure component is well described by the Antoine equation with coefficients presented in **Table A1**. Assuming that the mixture obeys Raoult's Law, determine the equilibrium temperature and the composition of the liquid phase. Complete at least two iterations of the required numerical procedure.

[16 marks]

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QA5. Using the rules of partial differentiation, derive an expression for the change in density with temperature at constant pressure and mass, expressed as $\left(\dfrac{\partial \rho}{\partial T}\right)_{P,m}$, as a function of the thermal expansion coefficient α. Integrate the obtained expression for a closed system under isobaric conditions, and use it to calculate the density of water at 1 bar and 45 °C. As the reference state for the integration, you can consider the density of water at P_0 = 1 bar and T_0 = 25 °C to be999 kg/m^3. You may also assume that α is constant and equal to 2.1 × 10^{-4} K^{-1} over the range of temperatures considered.

[12 marks]

QA6. A jet airplane is flying at a cruise speed of 900 km/hr. The jet engine is equipped with a diffuser to reduce the air speed before it is further compressed. Air enters the diffuser at the velocity of the aircraft and at atmospheric temperature, and exits the diffuser at a velocity of 10 km/hr and at a temperature of 265 K. The temperature of the atmosphere (and hence of the diffuser inlet) depends on altitude (*z*) according to:

$$T_{atm}(K) = 293 - 6.3 \times z(km)$$

Assuming that the heat capacity at constant pressure of air is constant and equal to 1.005 kJ/kgK, calculate the cruising altitude of the airplane. Clearly state any other assumptions made in the calculation. [12 marks]

QA7. Steam enters a reversible adiabatic turbine at 10 bar and 400 °C, and exits the turbine at 2 bar. Using the pressure-enthalpy diagram provided in the supplementary information (Page 7), calculate the molar work produced by the turbine and the outlet temperature of the steam. You may ignore kinetic and potential energy changes during the process. [14 marks]

QA8. A steam engine accepts heat during isothermal expansion at 250 ºC and discards heat through isothermal compression at 25 ºC. The magnitude of the entropy change during the isothermal compression step is 750 J/K. The efficiency of the steam engine is 65% of the maximum attainable theoretical efficiency. Calculate the total work produced by the engine. [12 marks]

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Numerical Answers

QA1. 328.4 K

QA2. 8272 J/mol

QA3. 290 K

QA4. T = 328.3 K; x_1 = 0.342

QA5. 994.8 kg/m^3

QA6. 9.38 km

QA7. w = -7.29 kJ/mol; T = 460 K

QA8. -87 kJ

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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

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

Thermodynamic potentials

$$H = U + PV$$
$$A = U - TS$$
$$G = H - TS$$

Fundamental thermodynamic relations

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V$$
$$\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}P$$
$$\mathrm{d}A = -S\mathrm{d}T - P\mathrm{d}V$$
$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P$$

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

$$\Delta S = \int_1^2 \frac{\mathrm{d}Q_{\text{rev}}}{T}$$

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

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

Thermodynamics Equation Sheet

Joule-Thomson coefficient

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

Phase equilibrium

$$\frac{\mathrm{d}P^{sat}}{\mathrm{d}T_b} = \frac{\Delta h}{T_b \Delta v}$$

$$\frac{\mathrm{d}P^{sat}}{\mathrm{d}T_b} = \frac{\Delta h P^{sat}}{R T_b^2}$$

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

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

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V + \sum_{i=1} \mu_i\,\mathrm{d}n_i$$

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

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

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

$$\sum_i x_i \mathrm{d}\overline{m}_i = 0$$

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

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

Thermodynamics Pressure-Enthalpy Diagram