

**Degree of BEng/MEng in Chemical Engineering**

**CP203/CP211 Thermodynamics and Chemical Principles**

**Date: Friday 6th May 2022**

**Time: 14:00-18:00**

**Duration: 4 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 non-ideal gas described by the van der Waals equation of state, with coefficients  $a = 850 \text{ bar L}^2 \text{ mol}^{-2}$  and  $b = 0.4 \text{ L mol}^{-1}$ , is slowly expanded in a closed piston/cylinder device at a constant temperature of 240 K. The molar volume of the gas is initially  $16 \text{ L mol}^{-1}$  and the final volume is  $28 \text{ L mol}^{-1}$ . Calculate the molar work of expansion of the gas in  $\text{J mol}^{-1}$ .

[12 marks]

- QA2.** Air is fed to a perfectly insulated turbine at 6 bar and exits the turbine at 1 bar and 300 K. Under these conditions, the air is well described by a virial equation of state of the form  $Z = 1 - BP$ , with  $B = 0.075 \text{ bar}^{-1}$ . Its heat capacity at constant pressure is  $29 \text{ J mol}^{-1} \text{ K}^{-1}$  and can be assumed to be independent of temperature. Calculate the inlet temperature of the air (in K) under the assumption that the turbine operates reversibly.

[14 marks]

- QA3.** The molar enthalpy of a mixture of two liquids (labelled A and B) is given by the equation:

$$h = 50x_A + 70x_B - kx_A^2x_B$$

where  $k = 25 \text{ J mol}^{-1}$ .

- a) For this mixture, which of the following statements is correct?

- i) Cross-species interactions, i.e. A-B, are stronger than those between pure species, i.e. A-A and B-B;
- ii) Cross-species interactions, i.e. A-B, are weaker than those between pure species, i.e. A-A and B-B;
- iii) Cross-species interactions, i.e. A-B, are identical to those between pure species, i.e. A-A and B-B.

[4 marks]

- b) Calculate the partial molar enthalpy of component A in  $\text{J mol}^{-1}$  when the mole fraction of component A in the mixture is 0.4.

[12 marks]

- QA4.** In a two-phase ideal mixture of *n*-heptane and *n*-octane, the mole fraction of *n*-heptane in the liquid phase is 0.3 and its mole fraction in the vapour phase is 0.6. At the mixture conditions, the saturated vapour pressure of *n*-heptane is 1 bar, while the saturated vapour pressure of *n*-octane in bar is given by the Antoine equation with coefficients  $A = 9.3224$ ,  $B = 3120.3$ , and  $C = 209.517$  for a temperature in  $^{\circ}\text{C}$ . Assuming the mixture falls within the range of validity of the Antoine constants provided, calculate the temperature of the mixture at equilibrium in  $^{\circ}\text{C}$ .

[14 marks]

**PLEASE TURN OVER**

**QA5.** 12 moles of nitrogen undergo a polytropic process from an initial pressure of 1 bar and an initial temperature of 800 K to a final pressure of 0.7 bar and a final temperature of 400 K. Under these conditions, nitrogen has heat capacities of  $c_P = 29.3 \text{ J mol}^{-1} \text{ K}^{-1}$  and  $c_V = 21.0 \text{ J mol}^{-1} \text{ K}^{-1}$ . Calculate:

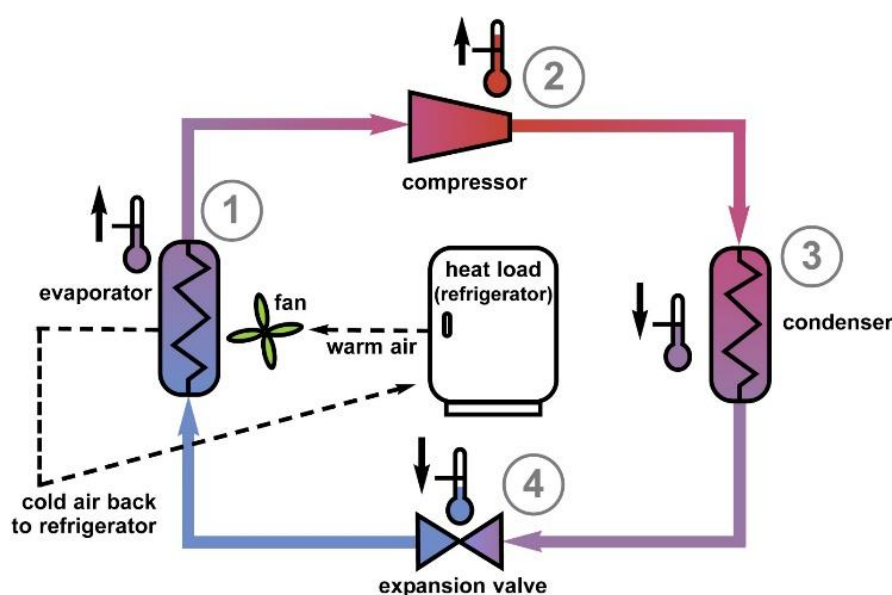
a) The volume change over the process in  $\text{m}^3$ . Clearly state and justify any assumptions made.

[10 marks]

b) The internal energy change over the process in kJ. Clearly state and justify any assumptions made.

[10 marks]

**QA6.** A refrigerator operates according to the cycle depicted in **Figure A6**. The working fluid is a fluorinated hydrocarbon refrigerant with an enthalpy of vapourisation of  $15.3 \text{ kJ mol}^{-1}$ . The condensation step (step 3 in the diagram) operates at 300 K and discards  $24 \text{ kJ mol}^{-1}$  of heat to the outside of the refrigerator. Step 1 comprises a complete evaporation of the working fluid at constant pressure and temperature.



**Figure A6** – Diagram of the refrigerator cycle.

a) Calculate the coefficient of performance of the refrigerator.

[10 marks]

b) The vapour pressure of the refrigerant fluid at 300 K is 270 kPa. Knowing that the evaporation step (step 1 in the diagram) takes place at a pressure of 100 kPa, calculate the coefficient of performance of an ideal Carnot refrigerator operating between the same two temperatures.

[14 marks]

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## **Section B: Answer All Questions**

- QB1.** Data for the surface tension of an uncharged surfactant, measured with increasing concentration at 25 °C, is analysed using the Gibbs equation, giving a gradient of  $-18.346 \times 10^{-3} \text{ N m}^{-1}$ , from a plot of  $\gamma$  against  $\log(c)$ .
- i) Calculate the surface excess for the system [8 marks]
  - ii) Explain what the value of the surface excess indicates. [3 marks]
  - iii) Discuss what change would be expected in the area occupied per molecule if the surfactant were charged. [2 marks]
- QB2.** Define the term 'equilibrium vapour pressure'; hence discuss and illustrate, as appropriate:
- i) the molecular basis of this physical quantity [5 marks]
  - ii) the effect of temperature [4 marks]
  - iii) the effect of surface area [4 marks]
- QB3.** Given the data in **Table QB3** for adsorption of ethanol on a mesoporous carbon at 28 °C, at which temperature the saturated vapour pressure for ethanol is 70.9 mbar, and the molar heat of condensation for ethanol is  $-38.56 \text{ kJ mol}^{-1}$ , determine:
- i) the value of the C constant for the process [4 marks]
  - ii) the monolayer coverage [4 marks]
  - iii) the heat of adsorption (in kJ/mol) [4 marks]

**Table QB3:** Molar uptakes for adsorption of ethanol on mesoporous carbon

$p/p^0$	$p/n(p^0-p) / \text{g mmol}^{-1}$
0.05	0.0074
0.15	0.0179
0.25	0.0285
0.35	0.0390

- QB4.** Explain, and illustrate as appropriate, why the phenomenon of capillary rise can be observed. [6 marks]
- QB5.** (i) Why is physisorption always an exothermic process? [5 marks]
- (ii) A carbon adsorbent physisorbs  $12.45 \text{ mmol g}^{-1}$  of nitrogen at 77 K, and  $11.86 \text{ mmol g}^{-1}$  of carbon dioxide at 195 K. Determine the area occupied per molecule of carbon dioxide (in  $\text{\AA}^2$ ) if nitrogen occupies  $1.62 \times 10^{-19} \text{ m}^2 \text{ molec}^{-1}$ . State any assumptions made and comment on the value obtained. [10 marks]

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**QB6.** Increasing amounts of a surfactant are added to water, creating an aqueous solution. For the process that occurs with increasing concentration, the standard free energy varies with temperature according to the data in **Table QB6**.

- Using a graphical method, determine  $\Delta H^\circ$  for this process at 293 K. [6 marks]
- Using the outputs from the graphical method used in (a), determine  $\Delta S^\circ$  for this process at 293 K. [5 marks]
- Comment on the driving force for this process. [3 marks]

**Table QB6:**  $\ln K$  values obtained at set temperatures with increasing concentration

$1/T / K^{-1}$	$\ln K$
$3.44 \times 10^{-3}$	9.071
$3.42 \times 10^{-3}$	9.083
$3.41 \times 10^{-3}$	9.094
$3.40 \times 10^{-3}$	9.107
$3.39 \times 10^{-3}$	9.119

**QB7.** The reaction of compound 1 with methyl chloride under basic conditions is first order. Using the data given in **Table QB7**, determine the activation energy for the reaction (in kJ/mol). [14 marks]



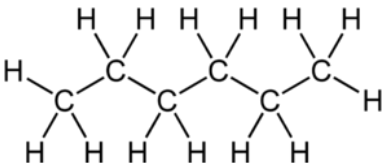
**Table QB7:** Rate constants obtained for reactions at various temperatures

$1/T / K^{-1}$	$k / s^{-1}$
0.00366	1.230
0.00341	4.776
0.00319	15.60
0.00300	44.18

**QB8.** Using the Antoine equation and the data provided in **Table QB8**:

- Calculate the normal boiling point of benzene in  $^\circ\text{C}$ . [3 marks]
- Calculate the normal boiling point of phenol in  $^\circ\text{C}$ . [3 marks]
- Calculate the normal boiling point of benzene in  $^\circ\text{C}$ . [3 marks]
- Explain the trend in boiling points for these three molecules. [4 marks]

**Table QB8:** Antoine constants and chemical structures of chemicals in QB8

Chemical	benzene	phenol	hexane
Chemical structure			
Temperature range/ $^\circ\text{C}$	8 to 103	107 to 182	-29 to 92
A	6.90565	7.1330	6.87601
B	1211.033	1516.79	1171.17
C	220.790	174.95	224.41

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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

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

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## Chemical Principles Equation Sheet

All symbols have the meaning as given in class materials.

$$V = -\frac{\mu_A \mu_B}{4\pi\epsilon R^3} [-2 \cos \theta_A \cos \theta_B + \sin \theta_A \sin \theta_B \cos(\phi_B - \phi_A)]$$

$$\frac{M_t}{M_e} = A_1 [1 - e^{-(k_1 t)^{\beta_1}}] + A_2 [1 - e^{-(k_2 t)^{\beta_2}}]$$

$$F_{electrostatic} = -k \frac{q_1 \cdot q_2}{r^2}$$

$$\eta = \eta_0 e^{\frac{E_a}{RT}}$$

$$E_{electrostatic} = k \frac{q_1 \cdot q_2}{r}$$

$$V = -\frac{\mu Q \cos \theta}{4\pi\epsilon R^2}$$

$$\epsilon_r = \frac{\epsilon}{\epsilon_o}$$

$$V = -\frac{\alpha Q^2 e^2}{32\pi^2 \epsilon^2 R^4}$$

$$E_{electrostatic} = \frac{q_1 \cdot q_2}{4\pi\epsilon_r r}$$

$$V = -\frac{\alpha_B \mu_A^2 (3 \cos^2 \theta_A + 1)}{32\pi^2 \epsilon^2 R^6}$$

$$K.E. = \frac{1}{2} m v^2$$

$$V = -\frac{3h(\nu_A \nu_B) \alpha_A \alpha_B}{512(\nu_A + \nu_B) \pi^4 \epsilon^4 R^6}$$

$$\langle v^2 \rangle^{\frac{1}{2}} = \left( \frac{3RT}{M} \right)^{\frac{1}{2}}$$

$$p = p^* e^{\frac{V_m \Delta P}{RT}}$$

$$\frac{(3RT/M_A)^{\frac{1}{2}}}{(3RT/M_B)^{\frac{1}{2}}} = \left( \frac{M_B}{M_A} \right)^{\frac{1}{2}}$$

$$p = p^* e^{\frac{2\gamma V_m}{rRT}}$$

$$d^2 = 2Dt$$

$$p_{in} = p_{out} + \frac{2\gamma}{r}$$

$$D = \frac{\lambda^2}{2\tau}$$

$$p_{in} = p_{out} + \frac{4\gamma}{r}$$

$$D = D_0 e^{-\frac{E_a}{RT}}$$

$$\gamma = \frac{F}{L}$$

$$D = \frac{k_B T}{6\pi\eta a}$$

$$\frac{2\gamma}{r} = \rho gh$$

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## Chemical Principles Equation Sheet

$$\gamma = \frac{r h \rho g}{2 \cos \theta}$$

$$ratio = \frac{V}{A \cdot L}$$

$$PV = nRT$$

$$\left(p + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

$$\Gamma = \frac{-1}{RT} \left( \frac{d\gamma}{d \ln c} \right)_{p,T}$$

$$\Gamma = \frac{-1}{2.303RT} \left( \frac{d\gamma}{d \log c} \right)_{p,T}$$

$$A = \frac{1}{N_A \Gamma}$$

$$\Delta G = \Delta H - T \Delta S$$

$$Z = \frac{P}{(2\pi m k_B T)^{\frac{1}{2}}}$$

$$T = \frac{\text{Number of sites}}{\text{Collision rate}}$$

$$\frac{P}{n_{ads}} = \frac{1}{K n_m} + \frac{P}{n_m}$$

$$s = n_m A_m L$$

$$\frac{d \ln K}{dT} = \frac{\Delta_f H^\circ}{RT^2}$$

$$\left( \frac{d \ln p}{d \left( \frac{1}{T} \right)} \right)_\theta = \frac{\Delta_{ad} H^\circ}{R}$$

$$\Delta G = -RT \ln K$$

$$\frac{p}{n(p^o - p)} = \frac{1}{n_m c} + \frac{(c - 1)}{n_m c} \cdot \frac{p}{p^o}$$

$$c = \exp \left( \frac{|\Delta H_A| - |\Delta H_L|}{RT} \right)$$

$$\theta = c_1 \ln(c_2 p)$$

$$\theta = c_1 p^{\frac{1}{c_2}}$$

$$\theta_A = \frac{B_A P_A}{1 + \sum_i B_i P_i}$$

$$V_{ads} = \frac{(K \cdot p)^{\frac{1}{2}} \cdot V_m}{\left[ 1 + (K \cdot p)^{\frac{1}{2}} \right]}$$

$$\log w = \log w_o - D \log_{10}^2 \left( \frac{p^o}{p} \right)$$

$$D = B \left( \frac{T}{\beta} \right)^2$$

$$\frac{M_t}{M_e} = 1 - e^{-kt}$$

$$k = A e^{-\frac{E_a}{RT}}$$

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# Periodic Table

Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18																	
Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18																	
1	1 <b>H</b> 1.008																	2 <b>He</b> 4.003																	
2	3 <b>Li</b> 6.941	4 <b>Be</b> 9.012															9 <b>F</b> 19.00	10 <b>Ne</b> 20.18																	
3	11 <b>Na</b> 22.99	12 <b>Mg</b> 24.31											13 <b>Al</b> 26.98	14 <b>Si</b> 28.09	15 <b>P</b> 30.97	16 <b>S</b> 32.07	17 <b>Cl</b> 35.45	18 <b>Ar</b> 39.95																	
4	19 <b>K</b> 39.10	20 <b>Ca</b> 40.08											21 <b>Sc</b> 44.96	22 <b>Ti</b> 47.87	23 <b>V</b> 50.94	24 <b>Cr</b> 52.00	25 <b>Mn</b> 54.94	26 <b>Fe</b> 55.85	27 <b>Co</b> 58.93	28 <b>Ni</b> 58.69	29 <b>Cu</b> 63.55	30 <b>Zn</b> 65.41	31 <b>Ga</b> 69.72	32 <b>Ge</b> 72.64	33 <b>As</b> 74.92	34 <b>Se</b> 78.96	35 <b>Br</b> 79.90	36 <b>Kr</b> 83.80							
5	37 <b>Rb</b> 85.47	38 <b>Sr</b> 87.62											39 <b>Y</b> 88.91	40 <b>Zr</b> 91.22	41 <b>Nb</b> 92.91	42 <b>Mo</b> 95.94	43 <b>Tc</b> 98	44 <b>Ru</b> 101.1	45 <b>Rh</b> 102.9	46 <b>Pd</b> 106.4	47 <b>Ag</b> 107.9	48 <b>Cd</b> 112.4	49 <b>In</b> 114.8	50 <b>Sn</b> 118.7	51 <b>Sb</b> 121.8	52 <b>Te</b> 127.6	53 <b>I</b> 126.9	54 <b>Xe</b> 131.3							
6	55 <b>Cs</b> 132.9	56 <b>B</b> 137.3											71 <b>Lu</b> 175.0	72 <b>Hf</b> 178.5	73 <b>Ta</b> 180.9	74 <b>W</b> 183.8	75 <b>Re</b> 186.2	76 <b>Os</b> 190.2	77 <b>Ir</b> 192.2	78 <b>Pt</b> 195.1	79 <b>Au</b> 197.0	80 <b>Hg</b> 200.6	81 <b>Tl</b> 204.4	82 <b>Pb</b> 207.2	83 <b>Bi</b> 209.0	84 <b>Po</b> 209	85 <b>At</b> 210	86 <b>Rn</b> 222							
7	87 <b>Fr</b> 223	88 <b>Ra</b> 226											103 <b>Lr</b> 260	104 <b>Rf</b> 267	105 <b>Db</b> 268	106 <b>Sg</b> 271	107 <b>Bh</b> 272	108 <b>Hs</b> 270	109 <b>Mt</b> 276	110 <b>Ds</b> 281	111 <b>Rg</b> 280	112 <b>Uub</b> 285	113 <b>Uut</b> 284	114 <b>Uuq</b> 289	115 <b>Uup</b> 288	116 <b>Uuh</b> 293	117 <b>Uus</b> —	118 <b>Uuo</b> 294							
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