



UNIVERSITY OF
KWAZULU-NATAL
INYUVESI
YAKWAZULU-NATALI

SCHOOL OF ENGINEERING

MAIN EXAMINATIONS: MAY 2025

COURSE AND CODE: THERMODYNAMICS 2 ENCH3TH

DURATION: 2 HOURS

TOTAL MARKS: 100

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DR M. M. LASICH

INTERNAL MODERATOR: PROF W. M. NELSON

EXTERNAL MODERATOR: DR N. NKOSI

INSTRUCTIONS:

1. **ALL** questions should be attempted. Answer in **INK**.
2. Any programmable or non-programmable calculator may be used provided it has been cleared of any information that would subvert the purpose of the examination.
3. Calculations must be shown in sufficient detail to illustrate your understanding of the procedure.
4. **Two answer books are provided. Label them Book A and Book B. Answer Section A in Book A and Section B in Book B.**
5. This examination question paper, together with all associated diagrams, **MUST BE HANDED IN TOGETHER WITH YOUR SCRIPT.**

Student Number:

SECTION A**QUESTION 1**

A single-stage flash vessel is to be designed for the binary system carbon tetrachloride (1) + cyclohexane (2) at 120°C. From limited experimental data it is seen that $y_1 = 0.632$.

- a) Determine an initial estimate for the system pressure (P) and x_1 using only Raoult's Law (10)
- b) Using the initial estimates from part (a), carry out a dew pressure calculation to determine revised estimates of P and x_1 using only the gamma-phi approach (it is not required to revise the initial estimates using modified Raoult's Law). Perform only a single step of the calculation—no iterative procedure is required. You may use generalized correlations (based on the Virial equation of state) to estimate vapour-phase fugacities, and apply Wilson's model to calculate activity coefficients. Assume the Poynting factor is equal to 1. For this system, take $k_{ij} = 0.0$. (40)

$$\ln P^{sat} (kPa) = A - \frac{B}{T(^{\circ}C) + C} \quad \phi_i^{sat} = \exp\left(\frac{B_{ii}P_i^{sat}}{RT}\right)$$

$$B_{ij} = \frac{RT_{c_{ij}}}{P_{c_{ij}}}(B^0 + \omega_{ij}B^1) \quad B^0 = 0.083 - \frac{0.422}{T_r^{1.6}} \quad B^1 = 0.139 - \frac{0.172}{T_r^{4.2}}$$

$$\omega_{ij} = \frac{\omega_i + \omega_j}{2} \quad T_{c_{ij}} = (T_{c_i}T_{c_j})^{0.5} (1 - k_{ij}) \quad P_{c_{ij}} = \frac{Z_{c_{ij}}RT_{c_{ij}}}{V_{c_{ij}}}$$

$$Z_{c_{ij}} = \frac{Z_{c_i} + Z_{c_j}}{2} \quad V_{c_{ij}} = \left(\frac{V_{c_i}^{1/3} + V_{c_j}^{1/3}}{2}\right)^3$$

$$\ln \hat{\phi}_1 = \frac{P}{RT}(B_{11} + y_2^2\delta_{12}) \quad \ln \hat{\phi}_2 = \frac{P}{RT}(B_{22} + y_1^2\delta_{12}) \quad \delta_{12} = 2B_{12} - B_{11} - B_{22}$$

Table 1: Pure component properties for carbon tetrachloride (1) + cyclohexane (2).

Component i	T_{c_i} [K]	P_{c_i} [bar]	V_{c_i} [cm ³ /mol]	Z_{c_i}	ω_i	Antoine Constants			Wilson's Equation Parameters
						A	B	C	Λ_{ij}
1	556.4	45.6	276	0.272	0.19	14.1	2914	232	0.6938
2	553.6	40.73	308	0.273	0.21	13.7	2723	221	0.2412

Further useful information is available on page 2.

TOTAL /50/

USEFUL RELATIONSHIPS: SECTION A

100 kPa = 1 bar Universal Gas Constant $R = 8.314 \text{ J.mol}^{-1}.\text{K}^{-1}$ $= 8.206 \times 10^{-2} \text{ L.atm.mol}^{-1}.\text{K}^{-1}$ $= 8.314 \times 10^{-2} \text{ L.bar.mol}^{-1}.\text{K}^{-1}$ $= 82.06 \text{ cm}^3.\text{atm.mol}^{-1}.\text{K}^{-1}$	$R = 8.314 \text{ Pa.m}^3.\text{mol}^{-1}.\text{K}^{-1}$ $= 83.14 \text{ cm}^3.\text{bar.mol}^{-1}.\text{K}^{-1}$ $= 1.987 \text{ cal.mol}^{-1}.\text{K}^{-1}$ $= 8314 \text{ cm}^3.\text{kPa.mol}^{-1}.\text{K}^{-1}$
Raoult's Law $y_i P = x_i P_i^{sat}$	Modified Raoult's Law $y_i P = x_i \gamma_i P_i^{sat}$
Fugacity of liquids $\hat{f}_i^l = \phi_i^{sat} P_i^{sat} \exp\left(\frac{V_i^l [P - P_i^{sat}]}{RT}\right)$	Fugacity of liquids $\hat{f}_i^l = x_i \gamma_i P_i^{sat}$
Henry's Law $\hat{f}_i = x_i H_i$	Infinite dilution & Henry's Constant $\gamma_i^\infty = \frac{H_i}{f_i}$
Wilson's Equations $\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2} \right]$ $\ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) - x_1 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2} \right]$	
Gamma-Phi Method $y_i \Phi_i P = x_i \gamma_i P_i^{sat}$	Where $\Phi_i = \frac{\hat{\phi}_i}{\phi_i^{sat}} \exp\left(\frac{-V_i^l [P - P_i^{sat}]}{RT}\right)$
Phi-Phi Method $y_i \phi_i^v = x_i \phi_i^l$	

SECTION B**QUESTION 2**

Narasigadu (2011) measured liquid-liquid equilibrium data for the hexane (1) + acetonitrile (2) system at 350 kPa and obtained the following results for the parameter A for the 2-suffix Margules model:

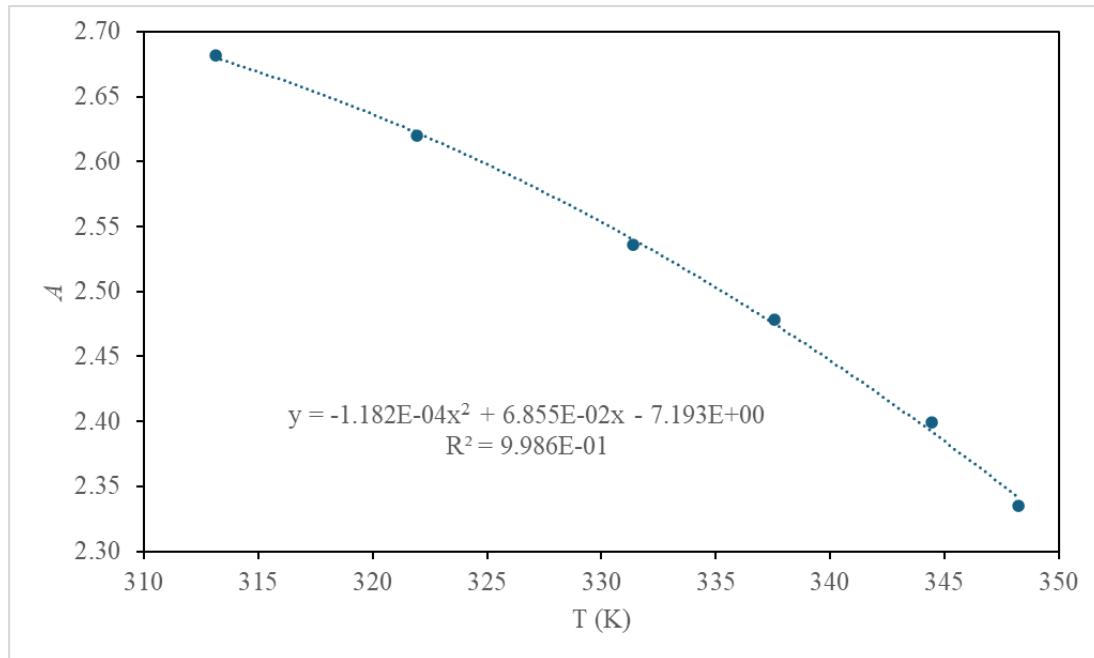


Figure 1: Margules parameter A as a function of temperature (T).

Estimate the composition of both liquid phases at 323 K. It is already known that over the temperature range 313 to 348 K, the hexane-rich phase has a composition ranging from 65 to 92 mol-% hexane while the acetonitrile-rich phase has a hexane content of 6 to 31 mol-%.

The 2-suffix Margules model is given by:

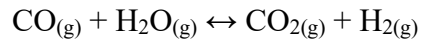
$$\ln \gamma_1 = Ax_2^2 = A(1 - x_1)^2$$

$$\ln \gamma_2 = Ax_1^2$$

TOTAL /20/

QUESTION 3

Consider the water-gas shift reaction:



Initially, a reactor contains 2 moles of CO and 3 moles of H₂O. If the reactor operates at 1 bar and contains 25 mol-% water vapour at equilibrium, estimate the temperature in the reactor and the composition of all species. State all assumptions. The equilibrium constant as a function of temperature for various reactions is given in Figure 2.

TOTAL /15/

QUESTION 4

Sketch a labelled schematic diagram that illustrates a hydrogen fuel cell with an external electrical load. Your diagram must show the flow of reactants and products, as well as the flow of electrons in the system.

TOTAL /15/

DATA SHEET: SECTION B**USEFUL EQUATIONS: SECTION B**

Stability criteria:

$$\frac{d^2(G^E/RT)}{dx_1^2} > \frac{-1}{x_1x_2}$$

$$\frac{d \ln \gamma_i}{dx_i} > \frac{-1}{x_i}$$

$$\frac{d\hat{f}_i}{dx_i} > 0$$

$$\frac{d\mu_i}{dx_i} > 0$$

$$\psi_i = \exp \left[\frac{\Delta H_i^{SL}}{RT_{mi}} \frac{(T - T_{mi})}{T} \right]$$

$$x_i = z_i \psi_i$$

$$y_i = \frac{n_i}{n} = \frac{n_{i0} + v_i \varepsilon}{n_0 + \sum_i v_i \varepsilon}$$

$$y_i = \frac{n_i}{n} = \frac{n_{i0} + \sum_j v_j \varepsilon_j}{n_0 + \sum_j v_j \varepsilon_j}$$

$$\ln \prod_i \left(\frac{\hat{f}_i}{f_i^0} \right)^{v_i} = - \sum_i \frac{v_i G_i^0}{RT} = K$$

$$\ln \left(\frac{K}{K'} \right) = \left(\frac{-\Delta H^0}{R} \right) \left(\frac{1}{T} - \frac{1}{T'} \right)$$

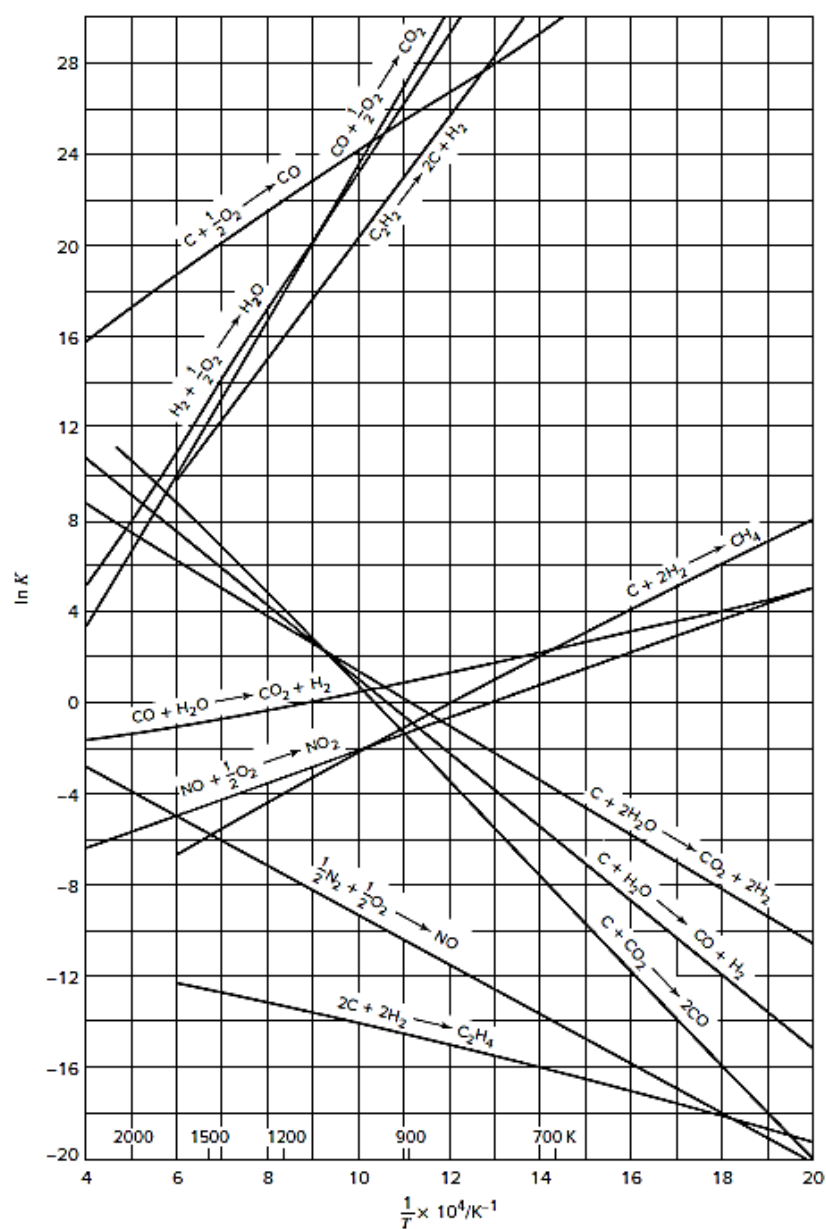


Figure 2: Equilibrium constant as a function of temperature for various reactions.