National Exams May 2015

04-Chem-A1 Process Balances and Chemical Thermodynamics

Three Hour Duration

NOTES:

1) If doubt exists as to the interpretation of any question, you are urged to submit a clear statement of any assumptions made along with the answer paper.

2) Property data required to solve a given problem are provided in the problem statement or are available in the recommended texts. If you are unable to locate the required data, do not let this prevent you from solving the rest of the problem. Even in the absence of property data, you still have the opportunity to provide a solution methodology.

3) This is an open-book exam.

4) Any non-communicating calculator is permitted.

5) The examination is in three parts – Part A (Questions 1 and 2), Part B (Questions 3 and 4) and Part C (Questions 5-7). Answer **ONE** question from Part A, **ONE** question from Part B and **TWO** questions from Part C. **FOUR** questions constitute a complete paper.

6) The question from Part A is worth 15 marks, the question from Part B is worth 25 marks, and each of the questions in Part C is worth 30 marks, for a total of 100 marks.

PART A: ANSWER ONE OF QUESTIONS 1-2

Note: Four questions constitute a complete paper
(with one from Part A, one from Part B and two from Part C)

1) A gas has a dry-basis composition of 8.5 mol% CO, 10.5 mol% CO_2, 0.5 mol% O_2, and 80.5 mol% N_2. The temperature of the gas is 600°C, its pressure is 1.0 atm, and its dew point temperature is 57°C. The gas must be cooled to 450°C. This is accomplished by spraying water at 20°C into the gas. Assume that this water leaves the cooler as water vapour in the gas stream, which is at 450°C. Calculate the required cooling water feed rate (kg/h) for a feed of 1000 mol of dry gas/h.

2) A liquid mixture at 50°C and 1.0 atm comprised of 20 mol% ethanol and 80 mol% water is fed to a flash vessel at a rate of 100 mol/s. The exiting liquid and vapour streams are in equilibrium at 1.0 atm and 90°C. The temperature in the vessel is maintained at 90°C by adding heat at the rate of Q [kW].

a) Use the *T-xy* diagram below to determine the molar composition and molar flow rate (mol/s) of both the vapour and liquid streams.

b) Calculate the required heat input Q in kW.
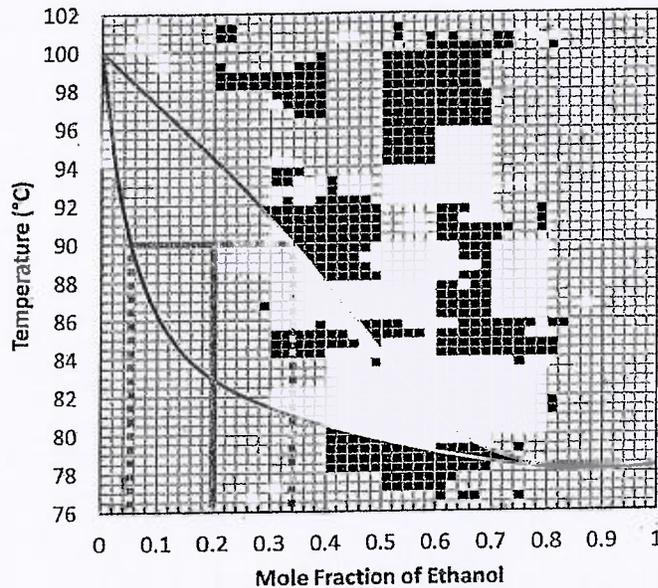
Txy diagram for an ethanol-water mixture at 1 atm.

PART B: ANSWER ONE OF QUESTIONS 3-4

Note: Four questions constitute a complete paper
(with one from Part A, one from Part B and two from Part C)

3) A hot gas stream at 300°C and 2.0 bar is flowing at 100 mol/s and contains 75 mol% N_2 and 25 mol% water vapour. The process depicted in the flowsheet below is to be used to recover as much of the water from the gas as possible before the gas is released to the atmosphere. Each unit operates adiabatically. The gas and liquid streams leaving the phase separators are in equilibrium at the stated temperature and pressure.
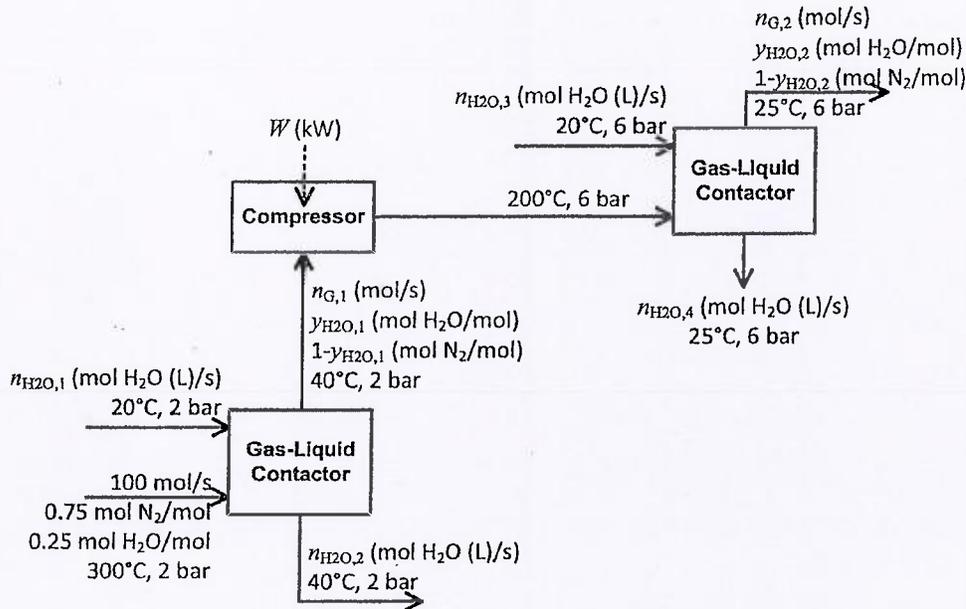
Use the enthalpy data for N_2 is given below. Use steam tables to estimate the enthalpy of the steam and the water. Use units of kJ/mol for all enthalpy values. The molecular weight of water is 0.01802 kg/mol.

a) Complete the following table:

	$\widehat{H}_i$ [kJ/mol]				
	300°C	200°C	40°C	25°C	20°C
N_2	8.12	5.13	0.438	0	--
H_2O (vapour)					--
H_2O (liquid)	--	--			

b) Calculate the flow rate of liquid water entering the first gas-liquid contactor and the flow rates and compositions of the gas and liquid streams leaving the first gas-liquid contactor.

c) Calculate the compressor power required.

d) Calculate the flow rate of liquid water entering the second gas-liquid contactor and the flow rate and compositions of the gas and liquid streams leaving the second gas-liquid contactor.

4) Ethylbenzene (C_8H_{10}) is produced commercially through the direct addition reaction of ethylene and benzene,

$$C_2H_4 + C_6H_6 \rightarrow C_8H_{10}$$
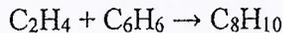
A side reaction between ethylene and benzene also produces di-etylbenzene ($C_{10}H_{14}$),

$$2C_2H_4 + C_6H_6 \rightarrow C_{10}H_{14}$$
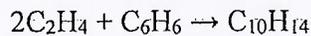
In the process shown below, ethylene gas at 5 bar and 25°C is mixed with a fresh feed of liquid benzene at 5 bar and 25°C. The combined feed stream enters a reactor at 5 bar and 400°C and must contain 80 mol% benzene and 20 mol% ethylene. The conversion of the limiting reactant in the reactor is 90% and the ratio of the extent of the first reaction to the extent of the second reaction is 5. After leaving the reactor, the effluent stream enters a separation system that generates the benzene/ethylene recycle stream and a crude product stream containing all of the ethylbenzene and di-ethylbenzene produced. Use a basis of 100 mol/s feed entering the reactor.
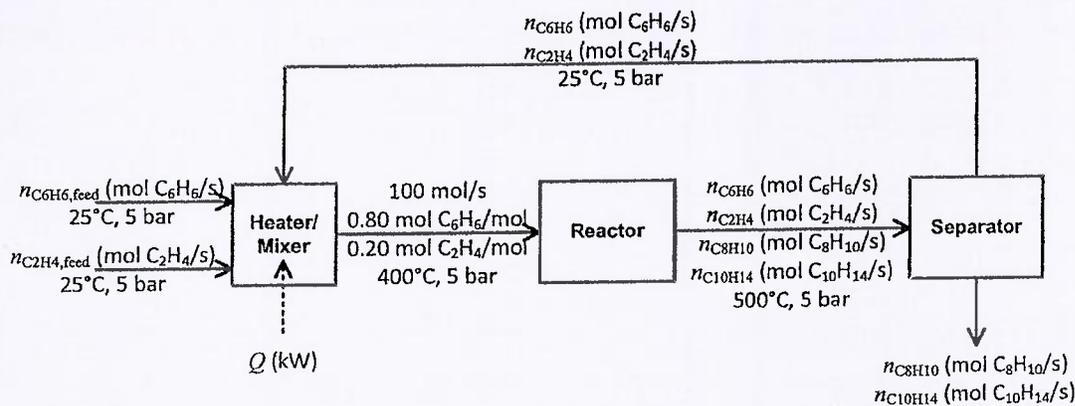
Other useful information: Assume that all gas-phase streams behave as ideal gases.
$(C_p)_{benzene,liquid} = 126.5 \times 10^{-3} + 23.4 \times 10^{-5}T$ [kJ/mol·K]
$(C_p)_{benzene,vapour} = 74.06 \times 10^{-3} + 32.95 \times 10^{-5}T - 25.20 \times 10^{-8}T^2 + 77.57 \times 10^{-12}T^3$ [kJ/mol·K]
$(C_p)_{ethylene,vapour} = 40.75 \times 10^{-3} + 11.47 \times 10^{-5}T - 6.891 \times 10^{-8}T^2 + 17.66 \times 10^{-12}T^3$ [kJ/mol·K]

a) Calculate the flow rates of all components exiting the reactor.
b) Calculate the required heat input to the heater/mixer.

PART C: ANSWER TWO OF QUESTIONS 5-7

Note: Four questions constitute a complete paper
(with one from Part A, one from Part B and two from Part C)

5) At atmospheric pressure, acetone (1) and chloroform (2) form an azeotrope that boils at 64.6°C and which has a mole fraction of acetone in the liquid of $x_1 = 0.335$. The saturation vapour pressures of acetone and chloroform at 64.6 °C are 1.31 and 0.98 atm, respectively. The *T-xy* diagram for acetone and chloroform is shown in the figure below.

T-xy diagram for ACETONE / CHLOROFM
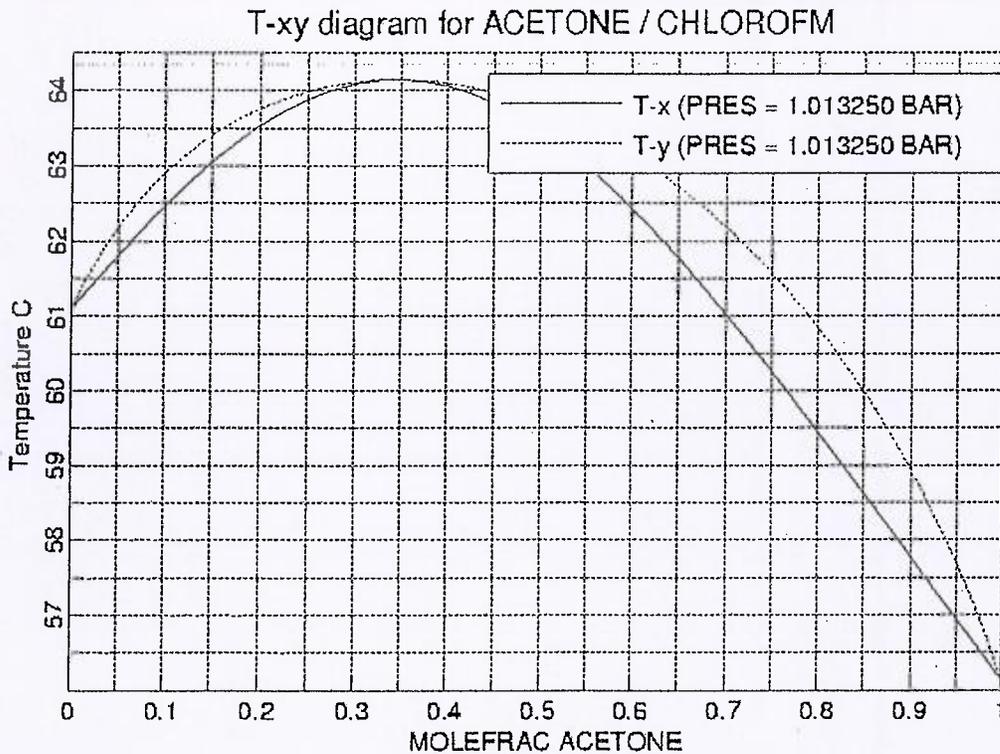
a) Calculate the activity coefficients of acetone and chloroform at the azeotrope.

b) Determine a value for G^E in J/mol for the azeotrope. If enthalpic factors were to have the dominant influence on G^E for this system (recall that $G^E = H^E - TS^E$), would the adiabatic mixing of pure acetone with pure chloroform (each at 64.6°C) to generate a solution at the composition of the azeotrope ($x_1 = 0.335$, $x_2 = 0.665$) produce a solution that was warmer or cooler than 64.6°C? If you were unable to solve part (a), assume that $G^E/RT = 2$.

c) Using your values from part (a), calculate the composition of the vapour over a liquid solution at 64.6 °C that contains 12 mol percent acetone, i.e. $x_1 = 0.12$. The relationship between activity and composition is given by the following equations:

$$\ln \gamma_1 = A_{12}\left[1 + \frac{A_{12}}{A_{21}}\left(\frac{x_1}{x_2}\right)\right]^{-2} \quad \ln \gamma_2 = A_{21}\left[1 + \frac{A_{21}}{A_{12}}\left(\frac{x_2}{x_1}\right)\right]^{-2}$$

d) Calculate the total pressure over the solution at the condition of part (c). If you do not have numerical values from part (c), you may assume the activity coefficient for acetone is 0.5 and that for chloroform is 0.8.

6) In generating expressions for G^E/RT from vapour-liquid equilibrium data, a convenient approach is to plot values of (G^E/RTx_1x_2) vs x_1 and fitting the results with an appropriate function. Let's say that for a particular system the data are fit by the following expression:

$$\left(\frac{G^E}{RTx_1x_2}\right) = A + Bx_1^2$$

a) From this expression for G^E/RT, provide expressions for $ln \gamma_1$ and $ln \gamma_2$ that are functions of A, B, x_1, and x_2.

b) We use the term *infinite dilution* to refer to the limit approached by the minority species as the mole fraction of the majority species approaches 1. The activity coefficient at this limit is known as the activity coefficient at infinite dilution, γ_i^∞, i.e.

$$\lim_{x_i \to 0} \gamma_i \to \gamma_i^\infty$$

For your expressions in part (a), relate A and B to the parameters $ln \gamma_1^\infty$ and $ln \gamma_2^\infty$, noting your approach. If you were unable to solve part (a), you should still be able to provide an answer to how you would solve this problem.

c) Provide a sketch of $A + Bx_1^2$ on a graph of $\frac{G^E}{RTx_1x_2}$ vs x_1, and indicate the limiting locations of $ln \gamma_1^\infty$ and $ln \gamma_2^\infty$ on this graph. Provide relationships for A and for B to $ln \gamma_1^\infty$ and $ln \gamma_2^\infty$ and any other parameters needed using the plot.

7) Consider the reaction

$$ZnO_{(s)} + CO_{(g)} \leftrightarrow Zn_{(g)} + CO_{2(g)}$$
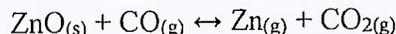
A mixture composed of one mole of CO, one mole of CO_2, one mole of Zn, and 0.75 mole of solid ZnO is equilibrated in a reaction vessel at 1500 K.

a) What will be the pressure at which this mixture reaches equilibrium?
b) What will the pressure need to be to make all of the solid ZnO disappear?

State whatever assumptions you use.

Species	$(\Delta H^0_{298})_f$ [kJ/mol]	$(\Delta G^0_{298})_f$ [kJ/mol]
ZnO	-348.0	-318.4
CO	-110.5	-137.2
CO_2	-393.5	-394.6
Zn	0	0