

**National Exams December 2012**

**04-Chem-A1 Process Balances and Chemical Thermodynamics**

**Three Hour Duration**

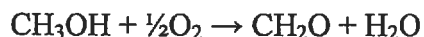
**NOTES:**

- 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. The suggested texts are Elementary Principles of Chemical Processes, 3<sup>rd</sup> edition, by Felder and Rousseau, and Introduction to Chemical Engineering Thermodynamics, 7<sup>th</sup> edition, by Smith, Van Ness, and Abbott.
- 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) Each question is of equal value.

**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) Formaldehyde is made by the catalytic air oxidation of methanol. When the process is operating as designed, the molar ratio of air to methanol in the reactor feed is 6:1 and the single-pass conversion of methanol to formaldehyde is 30%. There is concern that along with the reaction for the synthesis of formaldehyde, i.e.



there is another reaction occurring whereby some of the formaldehyde produced is converted to formic acid, i.e.



An analysis of the reactor effluent (on a dry basis) shows the composition shown in the table below.

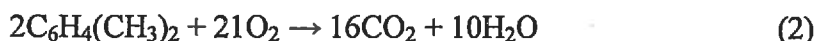
Compound in the Effluent	Mole %
N <sub>2</sub>	67.1
O <sub>2</sub>	14.2
CH <sub>3</sub> OH	13.1
CH <sub>2</sub> O	4.3
CH <sub>2</sub> O <sub>2</sub>	1.3

- Calculate the percent yield. Is it lower than the expected yield?
- Calculate the percent conversion.
- Calculate the selectivity for formaldehyde.

2) Phthalic anhydride can be manufactured by the gas-phase partial oxidation of o-xylene according to Equation 1



During this process, some complete oxidation of o-xylene occurs according to Equation 2



The process can be summarized as follows: Fresh o-xylene is mixed with recycled o-xylene. This mixture is then vapourized, mixed with air, and sent to the reactor. In the reactor, 80% of the o-

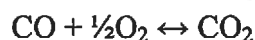
xylene is converted to phthalic anhydride, 2% is completely oxidized, and the remainder is unconverted. Sufficient air is added that the molar ratio of oxygen to o-xylene entering the reactor is 3.00. The reaction products are cooled, the phthalic anhydride crystallizes (all other species remain in the vapour) and is removed. This is the reverse of sublimation. Upon further cooling, the water and o-xylene are condensed. The liquid layers (aqueous and organic) are separated and the o-xylene is recycled. The remaining gases ( $O_2$ ,  $N_2$ ,  $CO_2$ ) are purged from the system. Calculate the following:

- a) the composition (mole %) of the stream leaving the reactor,
- b) the composition of the purge gas,
- c) the number of moles of phthalic anhydride produced per mole of fresh feed,
- d) the number of moles of o-xylene recycled per mole of fresh feed.

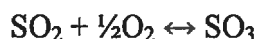
**PART B: ANSWER ONE OF QUESTIONS 3-4**

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

3) Pure CO is burned with 10% excess air. Both fuel and air are pre-heated sufficiently to bring the products of combustion to 2482°C at atmospheric pressure. Calculate the composition of the flue gas if equilibrium is achieved for the following reactions:



4) Consider the oxidation of sulfur dioxide to sulfur trioxide given by



The standard enthalpy change of the reaction is given by

$$H_T^0 = -22,630.14 - 5.2815T + 0.9587 \times 10^{-2}T^2 - 0.5598 \times 10^{-5}T^3 + 1.3826 \times 10^{-9}T^4$$

where  $T$  is in K and  $H_T^0$  is in cal/mole of  $\text{SO}_2$ .

The equilibrium constant  $K$  as a function of temperature is given by

$$\ln K = 3.87 + \frac{11389.10}{T} - 2.6580 \ln T + 0.4825 \times 10^{-2}T - 0.1409 \times 10^{-5}T^2 + 0.2320 \times 10^{-9}T^3$$

where  $T$  is in K.

The standard heat capacity as a function of temperature is given by  $C_p^0 = a + bT + cT^2 + dT^3$ , where  $T$  is in K and  $C_p^0$  is in cal/mole·K. The constants for the relevant compounds are given in the table below:

Compound	a	b x 10 <sup>2</sup>	c x 10 <sup>5</sup>	d x 10 <sup>9</sup>
SO <sub>2</sub>	6.157	1.384	-0.9103	2.057
SO <sub>3</sub>	3.918	3.483	-2.675	7.744
O <sub>2</sub>	6.085	0.3631	-0.1709	0.3133
N <sub>2</sub>	6.903	-0.03753	0.1930	-0.6861

A feed containing 12.0 mole % SO<sub>2</sub>, 9.0 mole % O<sub>2</sub>, and 79.0 mole % N<sub>2</sub> is reacted at atmospheric pressure. If the temperature of the feed to the reactor is 400°C, and the reaction is carried out adiabatically, calculate the final temperature and the final concentration of SO<sub>2</sub>.

**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) The data below give the dew point and bubble point of methanol/ethanol mixtures at 1 bar.

Mole Fraction of MeOH	$T_{\text{Dew}} [^{\circ}\text{C}]$	$T_{\text{Bubble}} [^{\circ}\text{C}]$
0.0	78.00	78.00
0.1	76.95	76.32
0.2	75.85	74.72
0.3	74.70	73.19
0.4	73.49	71.73
0.5	72.20	70.33
0.6	70.82	68.99
0.7	69.35	67.71
0.8	67.76	66.49
0.9	66.05	65.31
1.0	64.20	64.20

a) A liquid solution containing 30 mole % methanol is flashed to 1 bar, 70.82°C. Determine the phase of the system; if there are two phases, report the compositions and relative amounts of each phase.

b) What is the maximum mole fraction of methanol that can be achieved when a solution with 30% methanol is flashed to 1 bar? What is the maximum mole fraction of ethanol?

6) A vapour mixture of acetone (1) and nitromethane (2) ( $y_1 = 0.7$ ) initially at  $P = 1$  bar and  $T = 110^{\circ}\text{C}$  is to be liquefied by compression under constant temperature.

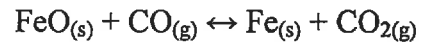
a) At what pressure does the system fully become a liquid?

b) Calculate the composition of the last bubble that condenses.

c) What is the fugacity of nitromethane in the liquid when the system is at the conditions of part (a)?

Assume that the system behaves according to Raoult's law. The saturation pressures of pure acetone and nitromethane at 110°C are 463 kPa, and 132.4 kPa respectively.

7) Ferrous oxide (FeO) is reduced to metallic iron by reacting it with carbon monoxide at 1000°C and 1.0 bar according to the reaction



Assuming that equilibrium is attained, determine the mass of metallic iron produced for one kmol of CO admitted into the reactor. At 1000°C, the equilibrium constant  $K$  is 0.403, with the conventional standard states for gases and solids. The atomic mass of Fe is 55.85,