National Exams    December 2010
04-Chem-A1  Process Balances and Chemical Thermodynamics

Three Hours Duration

NOTES:
1. If doubt exists as to the interpretation of any question, you are urged to submit with the answer paper, a clear statement of any assumptions made.
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 two parts – Part A (Questions 1 – 3) and Part B (Questions 4 – 6). Answer all THREE questions from Part A and any TWO questions from Part B. FIVE questions constitute a complete paper.
6. Questions have the values shown.
PART A: ANSWER ALL THREE OF QUESTIONS 1 – 3

Note: Five questions constitute a complete paper
(with all three from Part A and any two from Part B).

1. Value = 10 marks
In a process for making pure ethanol from an ethanol/water mixture containing 5 mass %
water, a third component, benzene, is added to the feed stream of the distillation column. The
bottoms stream from the column consists solely of ethanol. The overhead product is a
mixture consisting of 18.5 mass % ethanol, 7.4 mass % water and 74.1 mass % benzene.

(a) Perform a degree-of-freedom analysis for the process as described above.
(b) Calculate the mass % benzene in the feed stream entering the column.

2. Value = 20 marks
Formaldehyde is being produced by oxidation of methanol using moist air. With proper
operation of the process, the conversion (defined as moles of formaldehyde in the product
stream per mole of methanol fed) is 30 %. On the day in question, the process operator
observes an unexplained sudden drop in conversion. She orders a complete analysis of the
reactor product stream and the results are as follows: N₂ – 53.1 mole %, O₂ – 13.4 mole %,
H₂O – 5.9 mole %, H₂CO – 4.1 mole %, CH₃OH – 12.3 mole % and HCOOH – 1.2 mole %.
The formic acid in the product stream is formed in reaction (2) below by further oxidation of
some of the formaldehyde produced in reaction (1):

\[
\begin{align*}
\text{(1)} & \quad \text{CH}_3\text{OH} + \frac{1}{2} \text{O}_2 & \rightarrow & \text{H}_2\text{CO} + \text{H}_2\text{O} \\
\text{(2)} & \quad \text{H}_2\text{CO} + \frac{1}{2} \text{O}_2 & \rightarrow & \text{HCOOH}
\end{align*}
\]

Calculate the new conversion corresponding to the above product stream analysis by using
(a) only element material balances, and
(b) only compound material balances.

3. Value = 20 marks
Propane is being burned with 10 % excess air. All of the propane is consumed, but only 70 %
of the propane fed forms carbon dioxide with the remainder burning to carbon monoxide.
The propane enters the furnace at 25 °C, while the entering air is preheated to 100 °C; the
combustion products leave at 500 °C.

Calculate the rate at which heat must be removed from the furnace per mol of propane
burned.
PART B: ANSWER ANY TWO OF QUESTIONS 4 – 6

Note: Five questions constitute a complete paper
(with all three from Part A and any two from Part B).

4. Value = 25 marks
You are doing an extraction that involves removal of a chemical in solution by placing the solution in a semi-permeable membrane container which is immersed in a boiling liquid. The vapours leaving the liquid are then condensed and returned to the boiling flask. A schematic diagram is shown below:

The boiling liquid consists of two liquids (1) and (2) and the temperature is to be maintained at 75 °C. Given the data below, calculate the
(a) concentration (mole fraction) of the two liquids in solution, and
(b) composition of the vapour phase, assuming that the vapour behaves as an ideal gas.

Data available:
- Vapour pressures (mm Hg) of pure components (1) and (2) are given by the Clausius-Clapeyron equations (T in K):

  For (1): $\ln (P_1)_{sat} = -4628/T + 19.7$

  For (2): $\ln (P_2)_{sat} = -4910/T + 21.3$

- Equations which describe the relationship of activity coefficients to liquid mole fractions are:

  $\ln \gamma_1 = -0.632 (X_2)^2$

  $\ln \gamma_2 = -0.205 (X_1)^2$
5. Value = 25 marks
To make use of so-called “stranded” natural gas, it is proposed to fill steel cylinders with the gas and transport many cylinders by boat to the eastern seaboard of North America (e.g. New York City). The gas (100% CH₄) is delivered at 3 °C and 150 bar. However, during delivery, the temperature in the ship might reach a maximum of 40 °C.

(a) Calculate the minimum design pressure for the gas cylinder.
(b) For cylinders that are 30 cm in diameter and 2 m in length, calculate the volume (standard m³) of natural gas contained in one of these cylinders.

6. Value = 25 marks
A group of chemical engineers has been hired to investigate alternatives to the use of petroleum. One area which is being focused on is the manufacture of petrochemicals for polymers, drugs, clothing, etc. It is well known that ethylene is the starting point for many of these chemicals. It is proposed that the following reaction be used to make ethylene in the absence of a petroleum feedstock, the hydrogen being obtained by electrolysis of water. The reaction normally takes place at 800 K.

\[
2 \text{CO}_2 + 6 \text{H}_2 \rightarrow \text{C}_2\text{H}_4 + 4 \text{H}_2\text{O}
\]

(a) Calculate the value of the equilibrium constant at 800 K.
(b) Obtain an equation to determine the conversion of CO₂. It is not necessary to solve the equation for conversion.
(c) Calculate the equilibrium constant if the reaction was run at 100 bar instead of 1 bar.

You may assume that \(C_p\) values are constant and equal to:

\[
\begin{align*}
\text{CO}_2: \quad C_p/R &= 6.20 \\
\text{C}_2\text{H}_4: \quad C_p/R &= 12.0 \\
\text{H}_2: \quad C_p/R &= 3.59 \\
\text{H}_2\text{O}: \quad C_p/R &= 4.60
\end{align*}
\]