## National Exams May 2013

## 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) 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) Crystallization can sometimes be used to separate salts. Sylvinite (a mixed salt containing $42.7 \% \mathrm{NaCl}$, with the remainder KCl ) is dissolved in 1000 kg of water and cooled to induce crystallization. The composition of the crystals is $72.1 \% \mathrm{KCl}, 0.5 \% \mathrm{NaCl}$, and $27.4 \%$ water. A crystal yield of 727 kg is obtained. The mother liquor remaining behind contains $50.0 \%$ water and the remainder is salts.
a) How much sylvinite was originally dissolved?
b) What is the composition of the mother liquor?
c) What is the percent recovery of K Cl ?
2) The vapour from the top tray in a methanol-water distillation column is condensed and sent to an overhead accumulator drum at 5 psig . During a 12 -hour test, 7500 lbm of product was delivered to storage under level control, During the test, the liquid level in the drum fell by 3.5 inches. The average composition of the product was $95.0 \%$ alcohol. How much methanol was condensed during the test?

Data: 1) The liquid volume accumulated in the drum is 50 gallons per change of the liquid level in inches.
2) During the test, the reflux flow rate was held at $80 \%$ of the overhead vapour flow rate.


## PART B:ANSWER ONE OF OUESTIONS 3-4

Note: Four questions constitute a complete paper (with one from Part $A$, one from Part $B$ and two from Part $C$ )
3) In the plant represented by the process flow diagram below, the following reaction occurs in the reactor:

$$
\mathrm{A} \rightarrow \mathrm{~B}
$$

The fresh feed F contains A and some inert material (mole fraction $\mathrm{X}_{\mathrm{i}}$ ). The separation system removes $B$ completely from the reactor effluent. The recycle stream coming from the separator contains A and the inert material, but all of the inert material is removed in the purge stream. The product $P$ is impure, with a mole fraction $X_{A}$ of $A$ in the stream.
a) Suppose that the fresh feed contains 1.5 mole\% inert material and the feed to the reactor is. fixed at $4.5 \mathrm{~mole} \%$ inert. If the ratio $\mathrm{R} / \mathrm{F}=3.0$, what is the ratio of purge to feed $(\mathrm{S} / \mathrm{F})$ ?
b) Is the mole fraction of inert greater in the recycle stream or in the reactor effluent? Explain.
c) Why is the purge not removed directly from the reactor effluent?

4) Propane $\left(\mathrm{C}_{3} \mathrm{H}_{8}\right)$ is catalytically dehydrogenated to propylene $\left(\mathrm{C}_{3} \mathrm{H}_{6}\right)$ in a fixed-bed reactor. As the reaction proceeds, a carbonaceous material is deposited on the catalyst. In a laboratory experiment, 12 kg of pure propane is fed to a fixed-bed reactor. The analysis of the reactor effluent is as follows:

| $\underline{\text { GaS }}$ | $\underline{\text { Mole } \%}$ |
| :--- | :--- |
| $\mathrm{H}_{2}$ | 25.4 |
| $\mathrm{CH}_{4}$ | 3.2 |
| $\mathrm{C}_{2} \mathrm{H}_{4}$ | 0.3 |
| $\mathrm{C}_{2} \mathrm{H}_{6}$ | 5.3 |
| $\mathrm{C}_{3} \mathrm{H}_{6}$ | 21.3 |
| $\mathrm{C}_{3} \mathrm{H}_{8}$ | 44.5 |

An analysis of the deposit on the catalyst indicates that it is $96 \%$ carbon and $4 \%$ hydrogen by mass. Calculate the amount of deposit on the catalyst. Express your answer as a weight percentage of the propane feed.

## PART C: ANSWER TWO OF QUESTIONS 5-7

Note: Four questions consttute a complete paper (with one from Part $A$, one from Part B and two from Part C)
5) Ethylene that is initially at $100^{\circ} \mathrm{C}$ and 30 bar passes through an insulated expansion valve and then a heat exchanger. It emerges from the heat exchanger at $150^{\circ} \mathrm{C}$ and 20 bar. Compute rate of heat addition to the ethylene in the heat exchanger. Assume that the pressure drop across the heat exchanger is negligible, You can use just the $A$ and $B$ terms when expressing $C_{P}$ as a function of temperature.
6) The activity coefficients for a solution of water (1) and acetic acid (2) are given by the Margules equation, where $A_{12}=1.705$ and $A_{2 I}=0.9439$.
a) Calculate the pressure if the bubble point is $100^{\circ} \mathrm{C}$ for a solution with $x_{I}=0.63$.
b) Calculate the pressure if the dew point is $100^{\circ} \mathrm{C}$, and the first drop of condensed liquid has a composition of $x_{I}=0.63$.

Use the following form of the Antoine equation: $\quad \ln \left(P^{s a t}\right)=A-\frac{B}{T+C}$
where $T$ is in K and $P^{s a t}$ is in mm of Hg .

| Species | A | B | $\overline{\mathrm{C}}$ |
| :---: | :---: | :---: | :---: |
| Water | 18.3036 | 3816.44 | -46.13 |
| Acetic Acid | 16.8080 | 3405.57 | -56.34 |

7) Synthesis gas is a mixture of carbon monoxide (CO) and hydrogen gas $\left(\mathrm{H}_{2}\right)$, and is used widely in industry as a fuel and as a precursor to a variety of petrochernical products. Consider the following two simultaneous reversible vapour-phase reactions:

$$
\begin{aligned}
& \mathrm{CH}_{4}+\mathrm{H}_{2} \mathrm{O} \leftrightarrow \mathrm{CO}+3 \mathrm{H}_{2} \\
& \mathrm{CO}+\mathrm{H}_{2} \mathrm{O} \leftrightarrow \mathrm{CO}_{2}+\mathrm{H}_{2}
\end{aligned}
$$

Synthesis gas is produced from methane and water vapour via the first reaction. The second reaction is an unwanted side reaction whereby carbon monoxide can be lost by reacting with the water vapour. Use the data in the table below to answer the questions that follow.

| Species | $\Delta G_{f}^{0}$ at $600 \mathrm{~K}[\mathrm{~J} / \mathrm{mol}]$ | $\Delta G_{f}^{0}$ at $1300 \mathrm{~K}[\mathrm{~J} / \mathrm{mol}]$ |
| :---: | :---: | :---: |
| $\mathrm{CH}_{4}$ | $-22,980$ | $+52,325$ |
| $\mathrm{H}_{2} \mathrm{O}$ | $-214,105$ | $-175,890$ |
| CO | $-164,755$ | $-227,035$ |
| $\mathrm{CO}_{2}$ | $-395,305$ | $-396,310$ |

a) Would an operating pressure of 1.0 bar or 100 bar produce a higher yield of synthesis gas at equilibrium? Why?
b) Which temperature would produce a higher yield, 600 K or 1300 K ? Explain your answer.
c) Calculate the equilibrium constant for the first reaction for the case in which the reaction takes place at the preferable temperature and pressure from parts (a) and (b).
d) Making reasonable assumptions, estimate the equilibrium ratio $\mathrm{H}_{2} / \mathrm{CO}$ for part (c).
e) Estimate $\Delta H_{800 \mathrm{~K}}^{0}$ for the first reaction.

