

國立清華大學 命題紙

96 學年度 化學工程學 系(所) _____ 組碩士班入學考試

科目 化工熱力學及化學反應工程 科目代碼 0702 共 3 頁第 1 頁 *請在【答案卷卡】
內作答

Problem 1

Consider air (an ideal gas) leaking from a tank. How does the entropy of the gas in the tank change? Use this perspective to develop a relation between the final temperature (T^f) and the final pressure (P^f) of the gas. (10%)

Problem 2

P-V-T behavior of a simple fluid is found to obey the following equation of state: $\frac{PV}{RT} = 1 + (b - \frac{a}{T})(\frac{P}{RT})$.

Derive a formula for the enthalpy departure from the ideal gas behavior of this fluid. (10%)

Problem 3

Two compounds A and B are known to form ideal solutions. Their vapor pressure at 300 K are $P_A^S = 1.2$ and $P_B^S = 1.4$ atm respectively.

- What are the states of pure A and pure B at 300 K and 1 atm (2 points)
- What is the state of a mixture containing 50 mol% A and 50 mol% B at 300 K and 1 atm (2 points)
- What is the bubble point pressure of a liquid mixture containing 50 mol% A and 50 mol% B at 300 K (2 points)
- What is the dew point pressure of a liquid mixture containing 50 mol% A and 50 mol% B at 300 K (4 points)

Problem 4

Two compounds A and B are known to form nonideal solutions. Their vapor pressure at 300 K are $P_A^S = 1.2$ and $P_B^S = 1.4$ atm respectively. The activity coefficients are given by

$$\ln \gamma_A = 0.5x_B^2 \quad \ln \gamma_B = 0.5x_A^2$$

- What are the infinite dilution activity coefficients of A and B (2 points)
- What is the excess Gibbs free energy of mixing per unit mole of a mixture containing 50 mol% A and 50 mol% B (2 points)
- Does the mixture exhibit positive or negative deviation from Raoult's Law? Explain. (2 points)
- Does the mixture forms an azeotrope? If yes, what is the azeotrope composition (4 points)

Given

$$R = 8.314 \frac{J}{mol \cdot K}$$

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Problem 5

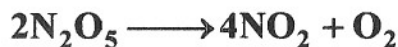
In the original 1824 paper by Sadi Carnot entitled "On the Motive Power of Fire", the basic model for the Carnot heat engine was developed. (a) What is the definition of a Carnot engine? (b) A Carnot cycle consists two isothermal processes and two adiabatic processes. Draw the P-V (pressure-volume) diagram of the cycle traversed by an ideal gas serving as the working fluid in a Carnot engine. (c) Draw the T-S (temperature-entropy) diagram of the cycle as mentioned in (b). (d) What is the mathematic definition of "entropy"? (10%)

Problem 6

(a) Explain the action of a catalyst with a "energy of reaction particles" vs. "reacth path" diagram. (b) Will a catalyst affect the equilibrium constant? Why? (c) Explain why it is easier for a new phase to nucleate on heterogeneous sites than in the homogeneous media. (10%)

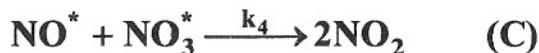
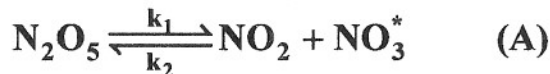
Problem 7

The decomposition of N_2O_5 to NO_2 and O_2 is a simple system and a first order reaction:



$$r_{O_2} = k_{obs} C_{N_2O_5}$$

A proposed mechanism is as follows:



Note the NO_2 does not react in step (B) but it affects the rate of decomposition of NO_3^* .

(a) Show how the mechanism can be made consistent with the overall stoichiometry equation by combination of individual steps. (5%)

(b) Derive the rate law for this mechanism with equilibrium approximation of step (A) so as to show consistency with the observed form. (5%)

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Problem 8

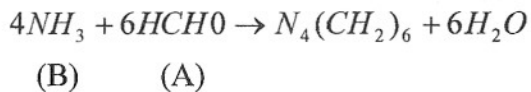
The reaction, $A \xrightarrow{k} B$, was studied in a CSTR. The reactor volume was 1.0 liter. The following experimental data were obtained.

| <u>Q, liter/min.</u> | <u>C_{A0}, g-mole/liter</u> | <u>Conversion,</u> |
|----------------------|-------------------------------------|--------------------|
| 0.25 | 1.0 | 0.5 |
| 0.5 | 1.0 | 0.38 |
| 0.25 | 2.0 | 0.61 |
| 0.5 | 2.0 | 0.5 |

Please use above data to determine the rate expression. (10%)

Problem 9

Hexamethylene tetraamine (HMT) is to be produced in a well-stirred semi-batch reactor by adding aqueous ammonia solution at constant rate to an initial charge of formaline solution:



The reaction is instantaneous, reversible, and exothermic. A cooling rod is immersed in the reaction mixture through which large quantities of cooling water circulate. Therefore, the reactor is operated isothermally. Calculate the time required for complete consumption of formaldehyde.

Data:

Initial charge: $V_0 = 2000 \text{ l}$ $C_{A0} = 15 \text{ mole/l}$ $T_{A0} = 0^\circ \text{C}$

Ammonia: $V_B = 10 \text{ l/min}$ $C_B = 15 \text{ mole/l}$ $T_B = 0^\circ \text{C}$

Heat of reaction: $\Delta H = -75 \text{ kcal/molHMT}$ (10%)

Problem 10

The elementary gaseous reaction $A \rightarrow B$ has a unimolecular reaction rate constant of 0.0015 min^{-1} at 27°C . This reaction is to be carried out in parallel tubes of 3 m long and 2.5 cm inside diameter under a pressure of 10 atm at 127°C . A production rate of 450 kg/hr of B is required. Assuming an activation energy of 25000 cal/mole, how many tubes are needed if the conversion of B is to be 90%? Assume perfect gas laws. A and B each have molecular weights of 58. (10%)