九十學年度 化學工程學 系（所） 組碩士班研究生招生考試

科目 化工熱力學及化學反應工程 科號 2102 共 2 頁第 1 頁 *請在試卷【答案卷】內作答

Problem 1 (20%)

Though the Carnot cycle is the most efficient for converting heat to work, it is rarely used because of the large amount of work that must be supplied to a Carnot engine during the isothermal compression step. There are however other cyclic processes used in commercial power generation. The Brayton cycle is one such example. It consists of the following steps: (a) isobaric compression; (b) reversible adiabatic compression; (c) isobaric expansion; and (d) reversible adiabatic expansion. Please develop expressions for its maximum thermodynamic efficiency. Assume that the working fluid is an ideal gas with constant heat capacity.

Problem 2 (20%)

A vessel, divided into two parts by a partition, contains 2 mole of hydrogen gas on one side and 1 mole of oxygen gas on the other. Both sides are at 120℃ and 1 atm. (a) The partition is removed and the gases mix completely. What is the change in enthalpy? What is the change in entropy? What is the change in Gibbs free energy? (b) The gas mixture is then ignited. All the oxygen and hydrogen gases are consumed and $H_2O_{(g)}$ is formed. The system is maintained at 120℃ and 1 atm. What is the change in enthalpy? What is the change in entropy? What is the change in Gibbs free energy? All the above questions concern only the gas system.

Given: (1) $H_{2(g)}+\frac{1}{2}O_{2(g)}=H_2O_{(g)} \quad \Delta H^o_{f,120^oC}=-240\text{kJ}$

(2) Universal gas constant, $R=8.314\frac{J}{gmol\cdot K}$

(3) $\ell n2=0.6931, \ell n3=1.0986, \ell n5=1.6094, \ell n7=1.9459, \ell n10=2.3026$

Problem 3 (20%)

A reversible reaction is shown to have both the forward and reverse reactions to be first order and elementary.

$$A \underset{k'}{\overset{k}{\rightleftharpoons}} B$$

k and k' are the rate constants of the forward and reverse reactions, K is the equilibrium constant and the initial concentrations of A and B are C_{AO} and C_{BO}, respectively.

(1) Show that the rate of disappearance of A can be expressed as

$$-\frac{dC'}{dt}=k_R C'$$

$$\text{where} \quad k_R=k(1+\frac{1}{K})$$

$$C'=(C_A-C_{A,eq})$$

$$\text{and} \quad C_{A,eq}=\frac{C_{AO}+C_{BO}}{K+1}$$

(14%)

(2) If this reaction is an exothermic one, comment on the temperature effect on the reaction rate. And if $k=z_1\exp(-E/RT)$, $K=z_2\exp(H/RT)$, derive an expression for the optimum temperature which maximizes the reaction rate at each C_A, where E is the activation energy for the forward reaction, H is the heat of reaction, both are assumed to be constant. (6%)

Problem 4 (20%)

The phosgene is produced by the reaction as

$$Cl_2 + CO \rightleftharpoons COCl_2$$

At low temperature, the reaction is essentially irreversible. The following experimental data was found in the literature

P_{Cl_2}, mmHg	500	500	300
P_{CO}, mmHg	20	10	10
$t_{1/10}$, min	10	10	21.5

($t_{1/10}$:time for 10% conversion of limiting reactant)

(a) Derive a rate expression from the above data. (15%)

(b) At high temperature, the reaction is reversible. Write backward rate expression. (5%)

Problem 5 (20%)

For a first order irreversible reaction

(a) find the conversion for a plug flow reactor. (3%)

(b) find the conversion for a CSTR with the same reactor volume as that in (a). (3%)

(c) find the conversion for n equal-size CSTRs connected in series. The total reactor volume is equal to that in (a). (4%)

(d) show that if n is very large, the conversion in (c) is very close to that in (a). (5%)

(e) is the statement in (d) still true for other reaction order? Why? (5%)

Use the following notations:

V: reactor volume

F: volumetric flow rate

k: reaction rate constant

τ :average residence time, V/F

X: conversion