國立中正大學八十四學年度碩士班考試試題

所　別：化學工程研究所　　科　目：化工熱力學與化工動力學

Thermodynamics

1. Calculate the theoretical flame temperature (i.e., the maximum attainable temperature) for the following cases:
   (a) when H_2 at 37 °C is burned with the theoretical amount of O_2 at 25 °C;
   (b) when H_2 at 37 °C is burned with the theoretical amount of air at 25 °C;
   assuming complete combustion and N_2 as a nonreactive gas, given

$$H_2 + 1/2\ O_2 \longrightarrow H_2O_{(g)} \qquad H°_{298} = -57798 \text{ cal/g-mole}$$

and

$$C_p = a + bT + c\,T^{-2} \qquad \text{cal/g-mole °C}$$

with (12%)

substance	a	$bx10^3$	$cx10^{-5}$
$H_2O_{(g)}$	7.3	2.46	0
H_2	6.52	0.78	0.12
O_2	7.16	1.00	-0.4
N_2	6.83	0.9	0

2. Two identical bodies have equations of state $U = N C_v T$, with C_v a constant and N and C_v of the same values for each system. The initial temperature are T_1 and T_2, and they are to be used as a source of work by bringing them to a common temperature T_f. (9%)
   (a) What is the range of possible final temperatures ?
   (b) What is the final temperature for a reversible process ?
   (c) What is the maximum amount of delivered work, i.e., W_{rev} ?

3. Find the relation between the number of degrees of freedom F, the number of independent components c_{ind}, and the number of phases p for each of the following systems: (8%)
   (a) rigid, permeable, adiabatic walls separate all the phases of a system.
   (b) movable, permeable, adiabatic walls separate all the phases of a system.
   (c) movable, impermeable, thermal conducting walls separate all the phases of a system.
   (d) movable, permeable, thermal conducting walls separate all the phases of a system.

4. In the study of an engine, one cycle consists of at least the following three steps:
   step 1. An adiabatic compression from P_1, T_1, V_1, to P_2, T_2, V_2.
   step 2. A constant-volume path from P_2, T_2, V_2, to P_3, T_3, V_2 with an input of heat ΔH.
   step 3. An adiabatic expansion from P_3, T_3, V_2, to P_4, T_4, V_1.
   Sketch these steps on a PV diagram, and calculate T_2, P_2, T_3, P_3, T_4, P_4, and W for each of the steps in terms of T_1, V_1, V_2, ΔH, and γ (i.e., C_p/C_v). Assume reversible operation, and take the working substance to be an ideal gas with constant heat capacities. (14%)

5. For binary liquid solutions of components which have comparable molecular volumes, it is observed that the excess Gibbs free energy at constant T and P is represented by

$$\frac{G^E}{RT} = A\,x_1\,x_2$$

where A is independent of x, and the standard states are the states of pure components at T and P. Develope expressions for $\ln\gamma_1$ and $\ln\gamma_2$ as functions of composition, where γ is activity coefficient. (7%)
Hint:

$$\ln\gamma_1 = \frac{\bar{G}^E_1}{RT}$$

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Kinetics

6. The hydrolysis of urea is catalyzed by the enzyme urease. A rate equation, $r=k\,C_u/(K+C_u)$, is expected to be suitable for describing the reaction kinetics. From the following data, evaluate the parameters, K and k, of the rate equation. (15%)

concentration of urea, C_u (mol/L)	initial reaction rate (mol/(L•s))
0.00015	0.060
0.00032	0.130
0.00065	0.226
0.00129	0.362
0.00327	0.600
0.00830	0.846
0.01670	0.975
0.03330	1.030

7. It is proposed for the catalytic oxidation of methanol to formaldehyde

$$\underset{A}{CH_3OH} + \underset{B}{1/2\,O_2} \text{ --------> } \underset{R}{CH_2O} + \underset{S}{H_2O}$$

that the reaction over a ferromolybdenum catalyst proceeds by the following scheme utilizing two type of sites, I and I':

$$A + I \text{ <===> } AI$$
$$B + I' \text{ <===> } BI'$$
$$AI + BI' \text{ -------> } R + SI + I'$$
$$SI \text{ <===> } S + I$$

For irreversible surface reaction (step 3) rate controlling, develop a rate expression for the reaction. (20%)

8. A gas phase reaction, A ----> 2R, is carried out in a tubular plug flow reactor at T = 60 °C and Pt = 4.75 atm. The feed consists of 50 mole % A and 50 mole % inert at a rate of 4000 Kg/hr. The molecular weights of A and inert are 40 and 20, respectively, and the rate coefficient is $k= 2000\ hr^{-1}$. Determine the reactor size for 35% conversion of A by assuming the reaction to be first order. (15%)