國立臺灣科技大學
九十三學年度碩士班考試試題

系所組別：化學工程系
科　　目：化工熱力學與動力學

Part I. 化工熱力學

總分 100 分

(1) **(a)** Starting from the differential form of energy balance for a homogeneous closed system $d(U) = dQ + dW$ (where U = internal energy, Q = heat, W = work) and the definition of enthalpy $H = U + PV$ (where P = pressure and V = volume), show that the differential form of entropy change of an ideal gas is $dS = C_P^{ig}\frac{dT}{T} - R\frac{dP}{P}$. (where C_P^{ig} is the ideal gas heat capacity and R is the gas constant). (10%)

(b) A stream of 2 mol/s of air goes from 1000 K and 10 bar to 500 K and 5 bar while doing 5.0 kW of work. Surrounding are 300 K and 1 bar. (see Fig. 1) What is the lost work for this process? (with negligible changes in kinetic and potential energies, for air $C_P^{ig} = 29.1$ J/mol·K, $R = 8.314$ J/mol·K) (10%)

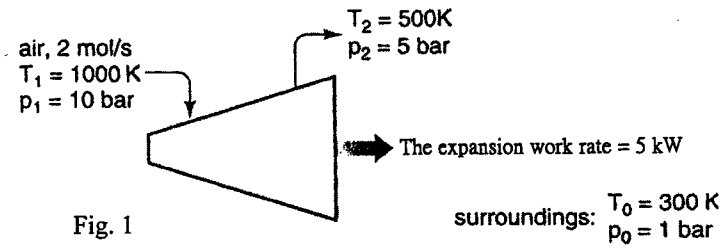

Fig. 1

(2) **(a)** The fugacity of a component in a real mixture (f_i) is defined by $d\mu_i = RT\,d\ln f_i$, where μ_i is the chemical potential of species i, R and T are gas constant and temperature, respectively. What is the definition of fugacity coefficient of species i (ϕ_i) in gas solution if the total pressure is P and the molar fraction of species i is y_i? (3%)

(b) For an ideal liquid mixture, the fugacity of each component (f_i) is linear in molar fraction (x_i), with the proportionality constant equal to the pure component fugacity (f_i^0), i.e., $f_i = f_i^0 x_i$. Please show under what condition can f_i^0 be taken as the pure component vapor pressure (P_i^0). (Under this circumstance, the equation turns to the Raoult's law $f_i = P_i^0 x_i$) (3%)

(c) In the very dilute region, Henry's law applies as $f_i = k_i x_i$, where k_i is Henry's constant. In a binary solution system such as a gas dissolved in a liquid, start from the Gibbs-Duhem equation, i.e., $\sum_i x_i d\mu_i = 0$ to demonstrate that, when one species is in its Henry's law range of concentration, the other species must be in its Raoult's law range. (see Fig. 2) (9%)

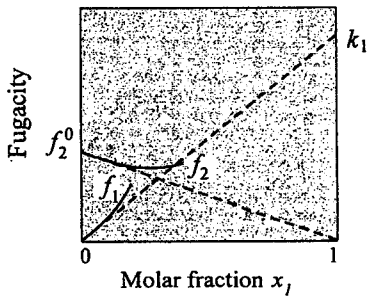

Fig. 2 Limiting fugacity in a binary solution

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(3) **(a)** State the third law of thermodynamics. (5%)

(b) The microscopic definition for entropy (S) is given by $S = k \ln \Omega$, where k is the Boltzmann's constant and Ω is total number of different configurations in which the system can be arranged at constant energy. It is shown that the number of ways to distribute n vacant defect sites and N atoms on $n + N$ sites is $\Omega = \frac{(n+N)!}{n!N!}$. Please calculate the entropy change with introducing 1×10^{18} vacancy defects in a mole of a perfect sold crystal. ($k = 1.38 \times 10^{23}$ J/atom·K) (You can apply Stirling's approximation: $\ln x! \approx x \ln x$, for large x) (10%)

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Part II. 化工動力學

1. (20%)

The exothermic reaction

$$A \rightarrow B + C$$

was carried out adiabatically and the following data recorded:

X Conversion	0	0.2	0.4	0.5	0.6	0.8	0.9
$-r_A$ ($mol/dm^3.min$)	10	16.67	50	50	50	12.5	9.09

The entering molar flow rate of A was 300 mol/min.

(a) What is the PFR (Plug Flow Reactor) volume necessary to achieve 40% conversion? (10%)

(b) What is the CSTR (Continuous Stirred Tank Reactor) volume necessary to achieve the same conversion as in (a)? (10%)

Show All Your Work.

2. (20%)

Tarzlon is a liquid antibiotic (抗生素) that is taken orally (口服) to treat infections (感染) of the spleen (脾臟). It is effective only if it can maintain a concentration in the blood-stream (based on volume of body fluid) above 0.4 mg per dm^3 of body fluid. Ideally, a concentration of 1.0 mg/dm^3 in the blood would like to be realized. However, if the concentration in the blood exceeds 1.5 mg/dm^3, harmful side effects can occur. Once the Tarzlon reaches the stomach (胃) it can proceed in two pathways, both of which are first order: (1) It can be absorbed into the bloodstream (血液) through the stomach walls; (2) it can pass out through the gastrointestinal tract (腹部的腸道) and not be absorbed into the blood. Both these processes are first order in Tarzlon concentration in the stomach. Once in the bloodstream, Tarzlon attacks bacterial cells (細菌的細胞) and is subsequently degraded by a zero-order process. Tarzlon can also be removed from the blood and excreted in urine (分泌於尿液) through a first-order process within the kidneys (腎臟). In the stomach:

Absorption into blood $k_1 = 0.15\ h^{-1}$

Elimination through gastrointestine $k_2 = 0.6\ h^{-1}$

In the bloodstream:

Degradation of Tarzon $k_3 = 0.1\ mg/dm^3.h$

Elimination through urine $k_4 = 0.2\ h^{-1}$

(a) Write down all of the reaction schemes involving the Tarzlon in the stomach (denoted by A) and the Tarzlon in the blood (denoted by B). (4%)

(b) Derive two differential equations (including initial conditions) describing the variation of the Tarzlon in the stomach, whose concentration can be denoted by C_A, and the Tarzlon in the blood , whose concentration can be denoted by C_B, as a function of time when 1 dose

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(i.e. one liquid capsule) of Tarzlon is taken. (10%)

(c) Solve the ODEs in (b) and obtain C_B as a function of time. Sketch $C_B(t)$ vs. time curve from t = 0 to t = 6 hr using the calculated values of C_B at t = 0, 2, 4, and 6 hr. (6%)

Additional information: One dose of Tarzlon is 250 mg. in liquid form: Volume of body fluid = 40 dm^3.

Show All Your Work.

3. (10%)

Cyclohexanol was passed over a catalyst to form cyclohexene and water:

cyclohexanol → cyclohexene + water

A → B + H

The following data were obtained.

Run	Reaction Rate ($mol/dm^3.s$) x 10^5	Partial Pressure of Cyclohexanol (P_A)	Partial Pressure of Cyclohexene (P_B)	Partial Pressure of Steam (H_2O) (P_H)
1	3.3	1	1	1
2	1.05	5	1	1
3	0.565	10	1	1
4	1.826	2	5	1
5	1.49	2	10	1
6	1.36	3	0	5
7	1.08	3	0	10
8	0.862	1	10	10
9	0	0	5	8
10	1.37	3	3	3

It is suspected that the reaction may involve a dual-site mechanism, but it is not known for certain. It is believed that the adsorption equilibrium constant for cyclohexanol is around 1 and is roughly one or two orders of magnitude greater than the adsorption equilibriums for the other compounds. Using these data, suggest a rate law and mechanism consistent with the data above.

Hint: For the reaction C → D, the surface reaction with a dual-site mechanism can be expressed as CS + S = DS + S, where S is the vacant site, and CS and DS are the species C and D adsorbed on the site S, respectively.

Show All Your Work.