編號： 49

國立成功大學 109 學年度碩士班招生考試試題

系　　所：化學系

考試科目：物理化學

考試日期：0211，節次：1

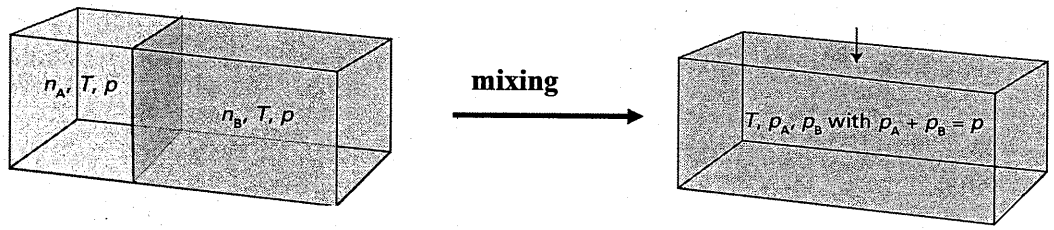
※ 考生請注意：本試題不可使用計算機。　請於答案卷(卡)作答，於本試題紙上作答者，不予計分。

一、簡答題: 每題 5 分, 答案正確才給分 (40 %)

1. For the process involving pure compound B:　B(*s*) → B(*l*), ΔH° = 9.0 kJ/mol, the melting point is 27°C, and = 30.0 J/mol•K. What is the entropy change of this transformation?

2. Write down an equation to prove why heat spontaneously transfers from higher temperature to lower temperature in a closed system?

3. Calculate the value of the ΔG_{mix} for the ideal gases in terms of molar fractions of χ_A and χ_B in the following figure.



4. Suppose the concentration of a solute decays exponentially ($c = c_0 \exp(-x/\lambda)$, λ: decay constant) along the length of a container. Please calculate the thermodynamic force.

5. When a sample of 4-heptanone was irradiated for 100 s with 300 nm radiation with a powder of 100 W under conditions of total absorption, it was found that 3.0 mmol C_2H_4 was formed. Please calculate the quantum yield of C_2H_4 formation. (列出式子即可，無須算出絕對數值)

6. Use the molar partition function (q_m) and the difference in molar energies ($\Delta_r E^0$) of ground states of product (P) and reactant (R) to demonstrate the chemical equilibrium constant for a reaction of R ↔ P.

7. Calculate the energy of a particle in a two dimensional square box of side L in the state with $n_1 = 3$ and $n_2 = 8$.

8. Use the Hückel approximation to set up the Hamiltonian matrix for the π orbitals of cyclobutadiene.

二、問答題 (每題 10 分，須寫出計算或推導過程才予計分) (60 %)

1. In the Eley-Rideal mechanism of a surface catalyzed reaction, a gas-phase molecule (A) colloids with another molecule (B) already absorbed on the surface. The adsorption B follows a Langmuir isotherm. Please calculate the θ_B and derive the Eley-Rideal rate law in terms of P_A, P_B, kr: rate constant and $\alpha = k_a/k_d$)

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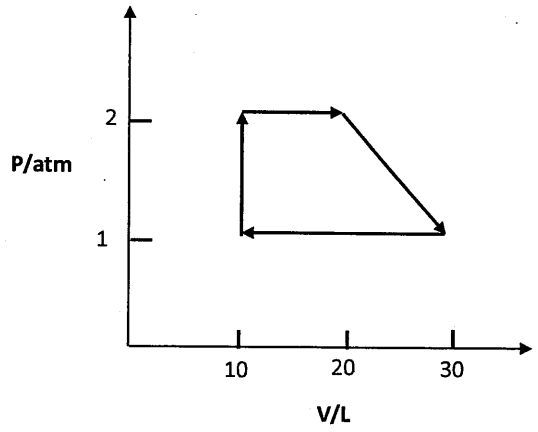
2. (a) A polyester can be regarded as the stepwise condensation from a hydroxyacid HO–M–COOH monomer. We expect the –COOH concentration decreasing to be overall second-order in the concentration of –OH and –COOH (denoted as A) groups. Please derive the integration rate law of the polymerization, in which the rate constant is independent of the chain length. (6 %)

   (b) It is known that the degree of polymerization is $[A]_0/[A]$, please derive the degree of polymerization in terms or rate constant and give a simple method to increase the polymer chain length of the stepwise polymerization? (4 %)

3. Calculate the w, q and ΔS, ΔS(surrounding) and ΔS(universe) of the following cycle when the surrounding temperature is keep at 27°C.



4. (a). Draw a plot of the Gibbs energy vs. temperature of a pure substance in solid, liquid and gas phases and also demonstrate the melting, vaporization and sublimation points. (5 %)

   (b). Derive the equation of $\mathbf{G(p) = G(p_0) + RT \ln (p/p_0)}$ for an ideal gas. (2%)

   (c). Draw a forbidden point of a one-component system. (3 %)

5. (a). Draw a diagram to show the atomic orbital energy levels of H and F atoms and the molecular orbitals they form. From this diagram, please explain why the HF is polar molecule. (6 %)

   (b). The general form of the HF molecular orbital is $\psi = C_H \psi_H + C_F\psi_F$ (C_H and C_F are the coefficients of H and F atoms). In the anti-bonding orbital, which value (C_H or C_F) is larger? Why? (4 %)

6. (a). Use *total* wavefunction including the spin of the particles to prove the Pauli exclusion principle. (6 %)

   (b). The ruby (Al_2O_3 containing small portion of Cr^{3+} ions) laser is an example three-level laser. The ground state is ^4A of the Cr^{3+} ion. The process of pumping a majority of the Cr^{3+} ion into ^4T excited state is followed by a radiationless transition to the ^2E excited state. The laser transition is $^2E \rightarrow {}^4A$, and give rise to 694 nm radiation. Please use the above description to draw the transitions of the energy states in a ruby laser. (4 %)