系所組別：化學系

考試科目：物理化學

※ 考生請注意：本試題不可使用計算機

計算與問答題: 每題 10 分 (需寫出計算過程否則不予計分)

1. (a) What is the criterion for a spontaneous change at constant entropy and pressure.(3 %)

   (b) Please explain why the internal energy cannot convert completely to work when a spontaneous change occurs with a decrease in entropy of the system. (3 %)

   (c) Please simply describe the thermodynamic theory of a **heating machine**. (4 %)

   (Hint: Joule-Thomson coefficient (μ))

2. (a) Please briefly describe the isolated method to determine the rate law of a complex reaction. (4 %)

   (b) Derive the rate law of the relaxation method for determination the rate constants k and k'.

   A $\rightleftharpoons$ B (forward: k ; reverse: k') (6 %)

3. (a) Why is the enthalpy of adsorption of gas on solid surface always negative? (4 %)
   (b) How to get the enthalpy of adsorption ($\Delta_{ad}H^0$). (6 %).

4. (a) Derive an equation for calculating the thermodynamic force of a concentration gradient at constant pressure and temperature. (Hint: $\mu = \mu^0 + RT \ln c$) (6 %)
   (b). Please calculate the force and the $\partial c/\partial t$ values of a concentration gradient $c = c_0 x$. (4 %)

5. (a) Derive $\mathbf{dw_{add}}$ (electronic work) = μ_A $\mathbf{dn_A}$ + μ_B $\mathbf{dn_B}$ for a reaction A ➔ B at constant temperature and pressure. (5 %)
   (b) What is Gibbs-Duhem equation? (3 %)
   (c) In a container, 6.0 moles of **A** molecules is mixed with 2.0 moles of **B** molecules. When the change in chemical potential energy of molecule A is decreased 40 kJ after some **A** molecules convert to **B** molecules, please calculate the change in chemical potential of B molecules? (2 %)

(背面仍有題目,請繼續作答)

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6. (a) Why is the triplet (T) state more stable than singlet state (S) when an electron of a chemical bond is excited to the excited electronic state? (6 %)
(b) Give an equation to express the transition dipole moment. Please briefly describe how to use the value of the transition dipole moment to predict a transition is forbidden or allowed. (4 %)

7. (a) Draw a molecular orbital energy level diagram for C_2 molecule. (4 %)
(b) Is the C_2 molecule paramagnetic and antimagnetic? Why? (2 %)
(c) Using that energy level diagram to predict the bond order of C_2^{2+}. (2 %)
(d) Is the C_2^{2+} ion paramagnetic and antimagnetic? Why? (2 %)

8. (a) For a black-body radiation from a source of temperature, T, is given by the Planck distribution: $\rho = (8\pi h\nu^3/c^3)/(\exp(h\nu/kT) - 1)$. Use this result to prove that $A/B = (8\pi h\nu^3/c^3)$ and $B = B'$ (B, B' = coefficients of simulated emission and absorption; A: Einstein coefficient of spontaneous emission). (7 %)
(b) In an NMR spectrum (microwave range), calculate the net rate of the absorption between two sates when the population of two states are equal? (3 %)

9. Write down an proper equation to express the following properties:
(a) Normalization constant for a wavefunction. (3 %)
(b) Orthogonality of ψ_i and ψ_j. (2 %)
(c) Photoelectric effect. (2 %)
(d) $\langle E_k \rangle$ of a wavefunction ψ in 1-dimension. (3 %)

10. (a) What is the thermodynamic criterion for the equilibrium between phase A and phase B? (2%)
(b) In a phase diagram (pressure vs. temperature) of water, please derive the slope of water-ice boundary. (5%)
(c) Is the slope of water-ice boundary negative, positive? Why? (3 %)