※ 注意：全部題目均請作答於試卷內之「非選擇題作答區」，請標明題號依序作答。

一、 Physical Chemistry (50 %)

1. (12 %) A thermodynamic system, with internal energy U, is attached to a constant temperature reservoir of temperature T. The system volume V is not fixed. The external pressure P_{ext} is not constant either. The pressure depends on the system volume, as $P_{ext} = P_0 - \alpha(V - V_0)$ where P_0, α, V_0 are positive constants. Find the suitable definition of a (new) free energy such that, by the second law of thermodynamics, it reaches the minima value at the equilibrium.

2. (12 %) A particle, of mass $m = 9.1 \times 10^{-31}$kg, is confined in an infinite potential well -1.0 nm $< x <$ 1.0 nm. At time $t = 0$, the wave function is given as $\Psi(x, t = 0) = N_0 x(1 - x)$ for the positive x, and $\psi = 0$ for the negative x, where N_0 is the normalization constant.
   (a) What is the averaged energy? (Planck constant $h = 6.63 \times 10^{-34}$m^{2}kg/s.)
   (b) At time $t = 0$, expand $\Psi(x, t = 0) = A_1\psi_1(x) + A_2\psi_2(x) + \ldots$ where $\psi_1(x) = \cos(\pi x/2)$ and $\psi_2(x) = \sin(\pi x)$ are the first two energy eigenfunctions. Find A_1 and A_2.
   (c) Approximate $\Psi(x, t)$ as the linear combination of ψ_1 and ψ_2, plot the probability distribution of the particle at the three different times $t = 0$, $t = 2(mL^2/h)$, and $t = 4(mL^2/h)$, where $L = 2$nm.

3. (16 %) Use the Hückel molecular orbital theory to construct the π system of the radical CH_2CHCH_2. The molecule is located on the x-y plane where the middle carbon is at the origin. The x-z plane is also a symmetry plane for the molecule. The MO is approximated as $\psi = c_1\phi_1 + c_2\phi_2 + c_3\phi_3$ where the ϕ_i is the p_z atomic orbital from the ith carbon (i=1, 2, 3). Let $H_{ij} = \int \phi_i^* \hat{H} \phi_j dV$. Assume that $H_{11} = H_{22} = H_{33} = \alpha$, $H_{12} = H_{23} = \beta$, and $H_{13} = 0$. Neglect all the overlap integrals between the neighboring atoms.
   (a) Calculate the MO energies E_n (n=1, 2, 3) and the associated MO wave functions ψ_n.
   (b) An EM wave is propagating toward the positive x direction. If the electric field of the EM wave is along the y direction, can it induce a transition from the lowest energy ψ_1 to the highest energy ψ_3? or can it induce the transition from ψ_1 to the middle ψ_2? Explain your answer with the suitable calculation.

4. (10 %) Given the consecutive first order reactions, with the rate constants k_1 and k_2,

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

   and the initial concentration [A(0)]=A_0, [B(0)]=0, [C(0)]=0,
   (a) Solve the concentrations [A(t)], [B(t)], [C(t)] exactly.
   (b) If $k_1 \gg k_2$, can one apply the steady state approximation on [B(t)], to simplify the calculation? Perform the analysis or explain the difficulty.
   (c) If $k_1 \ll k_2$, can one apply the steady state approximation on [B(t)], to simplify the calculation? Perform the analysis or explain the difficulty.

見背面

二、**Analytical Chemistry** (50 %)

1.(5%) Write down the most important wave property of light based on which the following device/phenomenon is operated: (a) optical fiber, (b) prism (as a wavelength selector), (c) Tyndall effect, (d) grating, (e) Fabry-Perot Etalon

2.(8%) Define the following terms used in analytical chemistry: (a) homogeneous precipitation, (b) mass-absorption coefficient, (c) L'vov platform, (d) Auger emission. (Note: no credit will be given for mere translation)

3.(8%) Sketch the construction and describe the operation of (a) Clark-type sensors for monitoring dissolved oxygen, (b) lithium-drifted detectors for x-ray detection.

4.(7%) An electrochemical cell has two platinum wires acting as the anode and cathode, respectively, and its analyte solution of pH 3.00 contains 0.100 M $CuSO_4$ and sufficient H_2SO_4.
(a) Will oxygen evolve at the anode or cathode when copper deposition takes place?
(b) Calculate the potential of the electrode (i.e., the oxygen electrode) at which oxygen is evolved at 1.00 atm.
(c) Calculate the potential of the copper electrode once the cell is built.
(d) Decide the potential required to initiate deposition of copper for the cell.
(Note: $E°(O_2/H_2O)$ =+1.229 V; $E°(Cu^{2+}/Cu(s))$ =+0.337 V).

5.(22%) Corrosion of household plumbing systems is a major source of copper in drinking water. People drinking water that contains copper in excess of the action level may have gastrointestinal distress (if the exposure is in short time) or liver/kidney damage (if the exposure is in long time). According to US Environmental Protection Agency, the action level for copper is 1.3 mg/L.
(a) Express the copper action level in ppm.
(b) Suggest by giving the names (in English) of one volumetric titrimetric and one electrochemical analysis methods that can analyze copper in drinking water.
(c) For each suggested method listed in (b), describe (i) its chemical working principle and (ii) how the related experiment (including the required experimental condition and reagents) is carried out to obtain quantitative information about copper in drinking water.
(d) Write down (i) the name of the specific statistical test and (ii) the main statistical procedure or equation of the test named in (i) that may be applied to decide if the experimental data of (c)(ii) indicates a drinking water sample in suspect to be less than the action level at the 95% confidence level.
(e) Ultra pure water (UPW) solutions are commonly used by semiconductor manufacturers in post-clean rinse steps. The presence of copper in UPW can cause trace copper metal deposition onto silicon. Suggest one surface analysis method, describe its working principle, and discuss how both the qualitative and quantitative information of copper contamination on silicon may be obtained with your suggested method.

試題隨卷繳回