國立清華大學 100 學年度碩士班入學考試試題

系所班組別：生命科學院丙組

考試科目（代碼）：物理化學(0603)

1. (10%) Please calculate the pH value of the HCl solution of a concentration of 10^{-7} mol/L at 25°C.

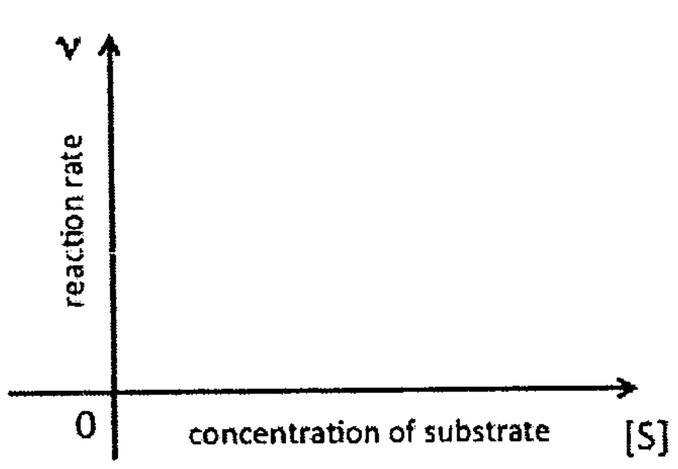
2. (10%) You are making a compound C by using the following reaction:
   $A + B \rightarrow C + D$　　$\Delta G_o' = 120$ kJ/mol
   Can you produce an appreciable amount of C under reasonable experimental condition? Please suggest two ways to improve the yield of C.

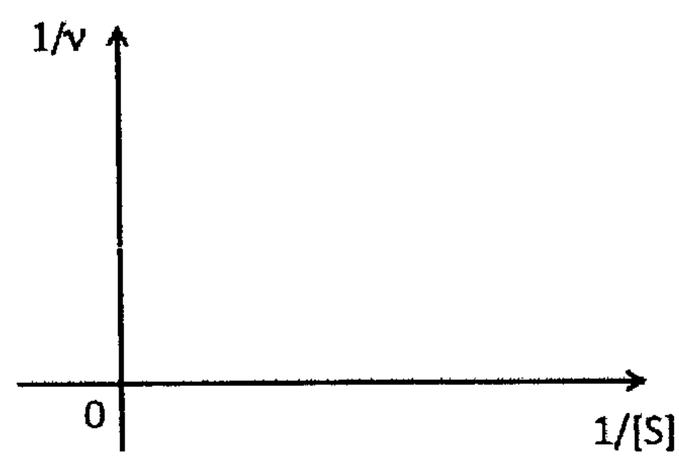
3. (10%) Please briefly explain whether the following statements are true or false.
   (a) If ΔS for a process is positive, this process is spontaneous. (2%)
   (b) If ΔG for a reaction is negative at constant pressure and temperature, the reaction is spontaneous. (2%)
   (c) When a system returns to its original state through a reversible cyclic process, the internal energy of the system $\Delta U_{system} = 0$. (2%)
   (d) The melting of ice below 0°C at 1 atm is forbidden by the first law of thermodynamics. (2%)
   (e) Oxygen gas at standard state has a standard enthalpy of formation of –46.1 kJ/mol. (2%)

4. (15%) We already knew the existing of higher order oligomer of protein A in solution, however we don't know whether it's dimer, tetramer or hexamer. The diffusion coefficient D of monomeric protein A was determined as 10×10^{-7} $cm^2 s^{-1}$. Under the same condition, the diffusion coefficient D of protein A oligomer is 5.5×10^{-7} $cm^2 s^{-1}$. If we assume that the shapes in these two protein states are spheres.
   (a) Please estimate the oligomerization state (dimer, tetramer or hexamer) of protein A by looking at hydrodynamic radius r based on Stokes-Einstein equation:
   $$D = \frac{kT}{6\pi\eta r}$$
   where η is viscosity coefficient and k is Boltzmann constant. (10%)
   (b) Please briefly describe another method you know, no matter chemical or

physical one, which is able to discriminate protein oligomerization state. Please state how it can deal with the measurement. (5%)

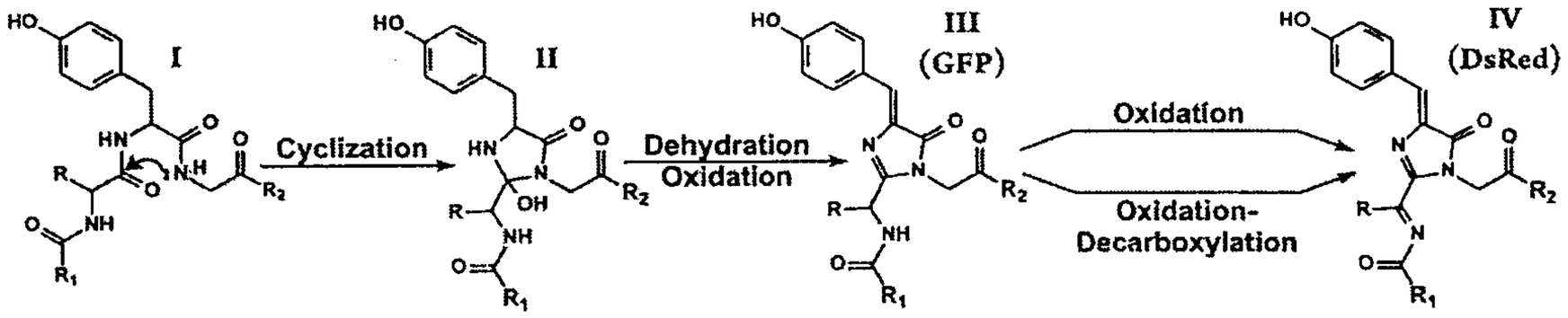
5. (13%) Micaelis-Menten equation:
   (a) Please write down the Micaelis-Menten equation. (3%)
   (b) Please make plots of (i) regular substrate saturation curve and (ii) Lineweaver-Burk plot. Please label the related parameters, such as V_{max}, K_M, x- and y-intercepts and slope in these two plots. (10%)





6. (6%) If you place a charged amino acid (please consider both positive and negative residues) into an unpolar environment, like interior of membrane bilayer, how the residue pKa changes (shift up or down)? State your reason.

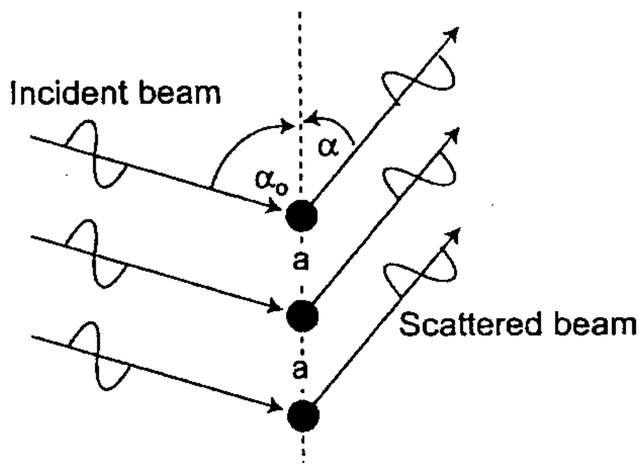
7. (10%) The chromophore of green fluorescent protein (GFP) is formed by cyclization of residues Ser65, Tyr66 and Gly67, through a series of chemical modifications as shown below. One GFP variant, DsRed, undergoes further modification to result in a slightly different chromophore as the final product. Based on the chemical structure of DsRed, explain why the emitted fluorescence is shifted from green to red.



8. (8%) In X-ray crystallography, the von Laue condition for diffraction is given by

$$h\lambda = a\,(\cos\alpha - \cos\alpha_0)$$

where h is an integer, a is the length of one of the sides of the unit cell, λ is the wavelength of the X-ray, α_0 is the angles between the incident beam and the row of the scatterers and α is the angles between the scattered beam and the two of the scatterers, as described in the figure below.



Show that the von Laue condition is analogous to the Bragg's law.

9. (18%) In nuclear magnetic resonance (NMR) spectroscopy, the nuclear magnetic moment of a nucleus is denoted μ. The component of the nuclear magnetic moment on the z-axis, μ_z, is proportional to the component of spin angular moment on that axis, m_I,

$$\mu_z = \gamma \frac{h}{2\pi} m_I$$

where γ is the gyromagnetic ratio (for ^1H, $\gamma = 2.675 \times 10^8\ T^{-1}\ s^{-1}$) and h is the Planck's constant (6.6262×10^{-34} J s). In a magnetic field B in the z-direction, the $2I+1$ orientations of the nucleus have different energies, which are given by

$$E_{m_I} = -\mu_z B$$

(a) Under a magnetic field of 11.7 T, what is the Larmor frequency of the nucleus of a ^1H atom, i.e., a proton? What is the ratio of population difference of the ^1H nuclei being in spin up ($m_I = +1/2$) and spin down ($m_I = -1/2$)? What is the advantage of having a stronger magnetic field in NMR spectroscopy? (6%)

(b) The dimensionless parameter chemical shift δ is an important parameter that has been used to elucidate molecules structures using NMR spectroscopy. For an amide proton that resonates at 8.5 ppm and a methyl proton of tetramethylsilane (TMS) that resonates at 0.0 ppm, what is the difference in local magnetic field between the two protons when the applied field is 11.7 T? What is the frequency separation in Hz? (6%)

(c) Ring current effect plays a dominant role in the neighbouring group effect for chemical shifts. Use the figure below to explain how ring current effect affects chemical shift. What is the relationship between the chemical shift of the ^1H atom and its neighbouring aromatic group? The position of the ^1H atom is described by the separation **r** between the nucleus and the center of the aromatic ring, and the angle θ between applied magnetic field B and the position vector **r**. Please describe the ring effect on chemical shift as a function **r** and θ. (6%)