Fill in the blanks; 2 points for each blank; **Write** all answers **on the answer sheet.**
Fill in the **final results** only; no procedures or calculations required
Use the following parameters if needed:
$K_b(NH_3) = 2.0 \times 10^{-5}$ ($pK_b = 4.70$); $K_a(HF) = 7.2 \times 10^{-4}$ ($pK_a = 3.14$)
$K_{sp}(AgBr) = 4.0 \times 10^{-13}$; malonic acid: $K_{a1} = 1.8 \times 10^{-3}$, $K_{a2} = 2.0 \times 10^{-6}$
Stepwise formation constants: $K_{f1}(Ag(NH_3)^+) = 2500$, $K_{f2}(Ag(NH_3)_2^+) = 4000$
$E°(Fe^{3+} \rightarrow Fe^{2+}) = 0.76$ V; $E°(IO_3^-, Cl^- \rightarrow ICl_2^-) = 1.24$ V

1. The pH of a solution containing (0.80 ± 0.12) M of NH_3(aq) and (0.40 ± 0.08) M of NH_4Cl(aq) is _____ ± _____. (neglect the uncertainty in K_b)
2. Two students, A and B, analyze the glucose content for the same sample; each student performs four measurements. The confidence intervals (at 95% confidence level) of the glucose concentration are (4.85 ± 0.24) mM and (4.62 ± 0.16) mM for A and B, respectively. The ratio of the standard deviations s_A/s_B is _____.
3. An internal standard (Y) is added to the analyte (X) solution in chromatographic analysis. The peak area for 2.0 mM X and 2.0 mM Y are 2.4 and 1.2, respectively. An unknown solution of X containing 4.0 mM Y gives peak area of 7.2 and 1.8 for X and Y, respectively. The concentration of X in the unknown is _____.
4. For 0.10 M NH_4F(aq), pH = _____ ; [HF] = _____.
5. Considering the activity coefficients (γ) in problem 4: $\gamma(H^+) = 0.83$, $\gamma(NH_4^+) = \gamma(F^-) = 0.75$, the concentration of HF is _____.
6. When X ml of 0.10 M NaOH is added to 60 mL of 0.10 M malonic acid (H_2M), $[H_2M]/[M^{2-}] = 100$. X = _____.
7. The solubility of AgBr(s) in 2.0 M NH_3(aq) is _____; the ratio of $[Ag^+]$: $[Ag(NH_3)_2^+]$ in the resulting solution is _____.
8. A Pt electrode and a saturated calomel electrode (S.C.E.) are used for the potentiometric titration of 40.0 mL of 0.010 M Fe^{2+} with 0.010 M IO_3^- in 1.0 M HCl(aq). The formal potential of S.C.E. is 0.244 V, answer the following questions.
   (a) Write the balanced chemical reaction for the titration: _____
   (b) Calculate log K for the reaction in (a): _____
   (c) Write the half-reaction of S.C.E in this potentiometric titration: _____
   (d) Find the cell potential at the equivalence point: _____
   (e) Find the cell potential when 11.0 mL of titrant is added: _____
9. A fluorophore has a lifetime of 5.0 ns and a quantum yield of 0.60. The quantum yield reduces to 0.25 in the presence of a certain quencher (Q). If the rate constant for the quenching process is 2.0×10^{10} $M^{-1} \cdot s^{-1}$, answer the following questions.
   (a) The concentration of quencher Q is _____
   (b) The rate constant for the fluorescence process is _____.
10. For a 5-cm grating ruled at 200 grooves/mm, how close in nm is the closest line to 500.00 nm that can barely be resolved in first-order diffraction: _____
11. In the reaction P + X ⇌ PX, only PX absorbs at 480 nm. To study the reaction, the absorbances at 480 nm (A_{480}) are measured with 1-cm cuvet at fixed $[P]_o$ of 5.0×10^{-5} M and at various $[X]_o$. A plot of $[P]_o/A_{480}$ vs. $1/[X]_o$ yields a straight line when $[X]_o >> [P]_o$; the obtained straight line is $[P]_o/A_{480} = 4.0 \times 10^{-5} + (1.0 \times 10^{-6})/[X]_o$. Answer the following questions.
   (a) write the equation of the straight line (in terms of K and ε_{480}): _____
   (b) the formation constant K = _____
   (c) If 50% of P is complexed, $[X]_o$ = _____
12. In a chromatogram obtained by using a 25.0-cm column, the elution times for the mobile phase and the analyte are 5.0 min and 15.0 min, respectively. Given that the volume of mobile phase is 50 times that of stationary phase and $w_{1/2}$ (width at half-height) for the analyte peak is 0.5 min. Answer the following questions.
   (a) the partition coefficient of the analyte is _____
   (b) the plate height for the analyte peak is _____ mm

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13. Select the type of chromatography from the following list that matches the characteristics described in (a) and (b): (i) adsorption; (ii) affinity; (iii) ion-exchange; (iv) molecular exclusion; (v) partition.
(a) solute equilibrates between mobile phase and a liquid-film bonded to stationary phase: _____
(b) solutes penetrate to voids in stationary phase to different extent; larger molecule elutes faster: _____

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14. (5%) Calculate the hydronium and hydroxide ion concentrations and the pH and pOH of 0.200 M aqueous NaOH at 25°C. At 25°C, the ion-product constant for water is $K_w = 1.00 \times 10^{-14}$.

15. (5%) An ideal gas at 300 K has an initial pressure of 15 bar and is allowed to expand isothermally to a pressure of 1 bar. Calculate (a) the maximum work that can be obtained from the expansion, (b) $\Delta_m U$, (c) $\Delta_m H$, (d) $\Delta_m G$, and (e) $\Delta_m S$.

16. (5%) When a reaction is carried out at constant pressure, the entropy change can be used as a criterion of equilibrium by including a heat reservoir as part of an isolated system containing the reaction chamber. Show that $\Delta_r G/T$ is the global increase in entropy for the reaction system plus heat reservoir.

17. (5%) A protein M can bind two molecules of a ligand L, which is a gas. The macroscopic equilibrium constants, written in terms of the partial pressures of the ligand, are defined by

$M + L = ML, \quad K_1 = [ML]/[M][L]$
$ML + L = ML_2, \quad K_2 = [ML_2]/[ML][L]$

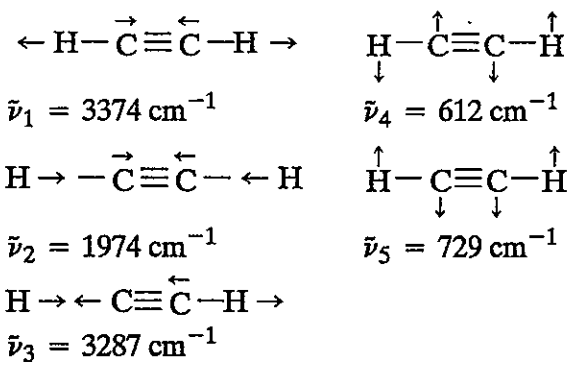
Assume that the two binding sites are different and that ML can be distinguished from LM. How are the microscopic dissociation constants

$M + L = ML, \quad k_1 = [ML]/[M][L]$
$M + L = LM, \quad k_2 = [LM]/[M][L]$
$ML + L = LML, \quad k_3 = [LML]/[ML][L]$
$LM + L = LML., \quad k_4 = [LML]/[LM][L]$

related to the macroscopic dissociation constants K_1 and K_2? How many of the microscopic dissociation constants are independent? If there is a relation between them, what is it?

18. (5%) The delocalization energy of a conjugated molecule is the electron energy minus the electron energy for the corresponding amount of ethylene. Calculate the delocalization energies of 1,3-butadiene and benzene within the Hückel theory.

19. (5%) Acetylene is a symmetrical linear molecule. It has seven normal modes of vibration, two of which are doubly degenerate. These normal modes may be represented as follows:



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(a) Which are the doubly degenerate vibrations? (b) Which vibrations are infrared active? (c) Which vibrations are Raman active?

20. (5%) The pressure in interplanetary space is estimated to be of the order of 10^{-14} Pa. Calculate (a) the average number of molecules per cubic centimeter, (b) the collision frequency, and (c) the mean free path $\lambda=\langle v\rangle/z$. Assume that only hydrogen atoms are present and that the temperature is 1000 K. Assume that the diameter of a hydrogen atom d = 0.2nm. Hint: The collision frequency $z=\rho\pi d^2\langle v\rangle$, where ρ is the number density of hydrogen gas and $\langle v\rangle=(8k_BT/\pi m)^{1/2}$ the mean relative speed. Boltzmann constant $k_B=1.38\times10^{-23}$ J T^{-1}, Avogadro constant $N_A = 6.02\times10^{23}$ mol^{-1}.

21. (5%) The half-life of a first-order chemical reaction A → B is 10 min. What percentage of A remains after 1 h?

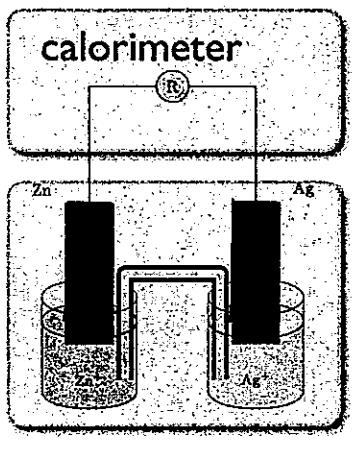
22. (5%) Derive the relation between the relaxation time and the rate constants for the reaction,

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$$

which is subjected to a small displacement from equilibrium.

23. (5%) Suppose we construct an electrochemical cell as shown in the following figure at the standard state ($Zn|Zn^{2+}(1M)||Cl^-(1M)|AgCl|Ag$). Assume that the extent of reaction is small enough to keep the concentrations essentially unchanged. During the discharge, heat will evolve from the resistor and from the cell, and we would measure the heat change by placing the cell and resistor in separate calorimeters. If we take Q_C as the heat change in the cell and Q_R as that in the resistor, we find $Q_C + Q_R = -233\ kJ/mol$ independent of R. In the limit of infinite R, Q_C approaches $-43\ kJ/mol$ and Q_R tends toward $-190\ kJ/mol$.

a) What are the enthalpy, entropy and Gibbs energy changes of the reaction, $Zn + 2AgCl \rightarrow Zn^{2+} + 2Ag + 2Cl^-$.
b) What is the maximal thermodynamic efficiency (i.e. converting the heat released to non-PV work) of this electrochemical cell?



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