Analytical Chemistry (分析化學)：Fill in the blanks; 2 points for each blank.
Fill the **final results** in the blanks only; all answers must be **written on the answer sheet.**

1. If $K_{sp}(PbSO_4) = (6.4 \pm 0.5) \times 10^{-9}$, the solubility of $PbSO_4(s)$ in pure water is ________ M. (uncertainty must be included)
2. Four measurements of the percentage of an additive in gasoline yield a mean of 1.64 and a standard deviation of 0.15. The confidence limit at 95% confidence level (t is 3.2 for 3 degrees of freedom) is ________.
3. An unknown sample of Hg^{2+} gives a signal of 0.20 in an AA analysis. Then 1.0 mL of solution containing 400 ppb Hg^{2+} is mixed with 95.0 mL unknown, and the mixture is diluted to 100.0 mL with a volumetric flask. The resulting solution gives a signal of 0.35. The concentration of Hg^{2+} in the unknown is ________
4. A sample of $MCO_3{\cdot}xH_2O(s)$ loses its water content when heated, reducing its mass by 30%. Further heating yields MO; its mass is 1/3 of that of the original sample. (H = 1.0, C = 12, O = 16)
   (a) the molar mass of M is ________ g/mol (b) the value of x is ________
5. If the solubility of $Ag_2CrO_4(s)$ in 0.10 M $AgNO_3(aq)$ is 1.25×10^{-9} M, the solubility of $Ag_2CrO_4(s)$ in pure water is ________ mM. The activity coefficients (at ionic strength of 0.10) for Ag^+ and CrO_4^{2-} are 0.80 and 0.50, respectively.
6. The concentration of a saturated aqueous solution of X is a% (or b m) at t_1°C and 2,5a% (or 4b m) at t_2°C; m is molality. a = ________
7. Consider mixing 50 mL of a solution containing 0.20 M $AgNO_3(aq)$ and 0.30 M $Pb(NO_3)_2(aq)$ with 50 mL of 0.60 M KI(aq) and allows it to reach equilibrium. Given: $K_{sp}(AgI) = 8.0 \times 10^{-17}$; $K_{sp}(PbI_2) = 8.0 \times 10^{-9}$.
   (a) $[Ag^+]$ = ________ M (b) $[Pb^{2+}]$ = ________ M (c) $[I^-]$ = ________ M,
8. The stepwise formation constants for $Ag(NH_3)^+$ and $Ag(NH_3)_2^+$ are 2500 and K_{f2}, respectively. Given that the solubility of AgCl(s) in 2.2 M $NH_3(aq)$ is 0.10 M and $K_{sp}(AgCl) = 2.0 \times 10^{-10}$.
   (a) $[Ag(NH_3)^+]$ = ________ M (b) K_{f2} = ________.
9. The absorbances measured with a 1.0-cm cuvet for an indicator (HIn) at pH = 5.0 at 465 nm (isosbestic point) and 530 nm are 0.80 and 0.68, respectively. Given the molar absorptivity (ε, in $M^{-1}{\cdot}cm^{-1}$) for the indicator: $\varepsilon_{465} = 5000$, $\varepsilon_{530}(HIn) = 8000$, $\varepsilon_{530}(In^-) = 3000$.
   (a) [HIn] = ________ M, (b) $[In^-]$ = ________ M, (c) $K_a(HIn)$ = ________
   (d) give a common light source ________ for these measurements
   (e) give a common detector ________ for these measurements.
10. A battery is constructed as follows: $Zn|Zn^{2+}$ (0.10 M)$||Ag^+$(1.0 M)|Ag; the volume of each electrolyte solution is 100 mL. The battery is allowed to discharge at a constant current of 9.65 A. Given: F = 96500 $C{\cdot}mol^{-1}$; $E°(Zn^{2+}\rightarrow Zn) = -0.76$ V; $E°(Ag^+\rightarrow Ag) = 0.80$ V
    (a) The initial cell potential is ________ V
    (b) The rate for the formation of Zn^{2+} is ________ $M{\cdot}s^{-1}$.
    (c) The time required to discharge the battery until $[Zn^{2+}] = [Ag^+]$ is ________ min.
11. Solvent passes through a 25.0-cm column in 4.0 min; solutes A and B require 10.0 min and 11.1 min, respectively. Width at peak base (W) for peaks A and B are 0.20 min and 0.24 min, respectively.
    (a) The capacity factor k′ for solute A is ________
    (b) The number of theoretical plates for solute A is ________
    (c) The resolution between peaks A and B is ________
12. An electrospray mass spectrum of a protonated protein exhibits a series of peaks (m/z) corresponding to $(MH_z)^{z+}$. Two neighboring peaks are found at 801.0 (peak A) and 841.0 (peak B), respectively.
    (a) The charge for peak A is ________
    (b) The molar mass of the neutral protein is ________ g/mol

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13. (16 pts) Consider the gas phase reaction 2X⇄Z. The ideal gases X and Z have the molar heat capacities $\bar{C}_X = (3/2)R$ and $\bar{C}_Z = (5/2)R$ respectively. Both gases obey the ideal gas law for their partial pressures P_X and P_Z.
   (a) (5 pts) For gas X alone, use the first and the second laws of thermodynamics to integrate the entropy. Show that the molar entropy has the form $\bar{S}_X(T, \bar{U}_X, \bar{V}) = \bar{C}_X \ln(\bar{U}_X - \bar{U}^0_X) + R\ln\bar{V} + \bar{S}^0_X$ where $\bar{V}$ is the molar volume, $\bar{U}^0_X$ and $\bar{S}^0_X$ are constants.
   (b) (6 pts) Perform the suitable Legendre transform to get the molar Gibbs' free energy $\bar{G}_X$.
   (c) (5 pts) Find the equilibrium constant K for the reaction 2X⇄Z in terms of the constants $\bar{C}_X$, $\bar{C}_Z$, $\bar{U}^0_X$, $\bar{U}^0_Z$, $\bar{S}^0_X$, and $\bar{S}^0_Z$.

14. (24 pts) Consider the molecular orbitals (MO) of the π system in cyclopropenyl radical C_3H_3 which are formed by the p_z orbitals ϕ_1, ϕ_2, ϕ_3 from the three carbon atoms in the $x-y$ plane.
   (a) (9 pts) Approximate the molecular orbital as $\psi = c_1\phi_1 + c_2\phi_2 + c_3\phi_3$ where c_1, c_2, c_3 are coefficients. Denote $H_{ij} = \int \phi_i^* \hat{H} \phi_j dV$. Here $H_{11} = H_{22} = H_{33} = \alpha$ and $H_{12} = H_{13} = H_{23} = \beta$. Neglect all the overlap integrals. Solve the MO energies and the MO wave functions.
   (b) (5 pts) Analyze the suitable transition dipole moments to explain the expected UV spectrum for this radical.
   (c) (5 pts) Consider the radical C_3H_2X where one hydrogen atom is replaced by a substituent atom X. Suppose that the adjacent carbon is affected to acquire a slightly different $H_{11} = \alpha'$ whereas $H_{22} = H_{33} = \alpha$ and the β remains the same as above in (a). Describe qualitatively how the MO energies and MO shapes change compared with those of cyclopropenyl radical.
   (d) (5 pts) Analyze the suitable transition dipole moments to explain the expected UV spectrum for the radical C_3H_2X.

15. (10 pts) Consider the inert gas as the ideal hard sphere gas with the diameter d. According to the kinetic theory, the collision frequency of a molecule with its neighbors is $z = 4\sqrt{\pi}\rho d^2\sqrt{k_BT/m}$ where ρ is the number density of the gas, k_B is the Boltzmann constant, and m is the mass of the molecule.
   (a) (4 pts) Derive the expression for the mean free path λ.
   (b) (6 pts) Show that the diffusion constant D is proportional to $(k_BT/m)^{1/2}/(\rho d^2)$.

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