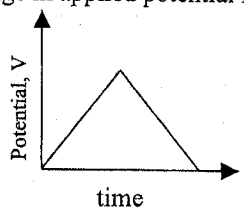
所別：化學學系碩士班 不分組 科目：物理化學與分析化學

1. Which of the following phenomenon during electrolysis at constant applied potential is expected to occur? (5 pts)
   (a) The current is maintained at constant level. (b) The current increases with time. (c) Cathode potential increases with time due to kinetic polarization. (d) IR continues to drop due to decrease in internal resistance. (e) Both the cathode potential and concentration polarization (cathode) increase.

2. To avoid co-deposition of multiple metal ions during electrolysis, draw a schematic diagram for the cell of controlled cathode potential. (5 pts)

3. In anodic stripping method nanomolar detection limits for Pb^{+2} and Ca^{+2} are possible. Which of the following statements is true? (5 pts)
   (a) The potential is fixed at sufficiently negative potential to deposit Pb^{+2} and Ca^{+2} simultaneously.
   (b) The potential is fixed at all times to during stripping. (c) Pb^{+2} has a lower reduction potential than Ca^{+2}, so Pb^{+2} is being stripped first. (d) The change in applied potential is like:



4. In atomic spectrometry determining trace amounts of metal elements, which of the following statements is false? (5 pts)
   (a) X-ray fluorescence is a non-destructive method, but its accuracy and sensitivity is usually poorer than AAS or AES. (b) AAS is more sensitive than ICP-OES, and is a simultaneous multi-element technique. (c) Graphite AA is more sensitive than flame AA due to its longer residence time for the free atoms in the furnace. (d) The lower sensitivity with flame AA than Graphite AA is because its poor efficiency in the nebulization and atomization process. (e) Lambert Beer's law is the quantitative basis for atomic absorption spectrometry.

5. Why is atomic emission more sensitive to flame instability than atomic absorption or fluorescence? (5 pts)
   (a) The population of atoms in the excited state is greater than in the ground states. (b) The population of atoms in the ground states is more sensitive to the flame temperature. (c) The population of atoms in the excited states is more sensitive to the flame temperature than in the ground state. (c) Flame of acetylene and air provides sufficiently high temperature to excite most of the transition metals for atomic emission spectroscopy.

6. Which of the following separation technique does not employ stationary phase for separation? (5 pts)
   (a) Gas liquid chromatography. (b) High performance liquid chromatography. (c) Supercritical fluid chromatography (d) Capillary electrophoresis. (e) Thin layer chromatography.

7. The higher signal-to-noise ratio with FTIR than with dispersive IR is because of: (5 pts)
   (a) Multiplex advantage. (b) The employment of grating and prism. (c) Better detector. (d) High performance monochromator. (e) More optical elements.

8. The comparison between ICP-OES and ICP-MS cannot be adequately described by which of the following statements? (5 pts)
   (a) Both methods use plasma to provide high temperature for either excitation or ionization. (b) Plasma

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source in ICP-MS is used for atomization and excitation. (c) Plasma source in ICP-OES is used for atomization and excitation. (d) Information of isotope abundance can be obtained by ICP-MS. (e) ICP-OES is subject to more severe optical interferences than ICP-MS.

9. Standard addition method is frequently used when matrix interference is a concern. Make a x-y plot of 4 additions to help you explain this method. (5 pts)

10. Calculate the equilibrium constant for the reaction, (5 pts)

$2Fe^{3+} + 3I^- \rightarrow 2Fe^{2+} + I_3^-$;

giving that $2Fe^{3+} + 2e^- \rightarrow 2Fe^{3+}$ $E^0=0.771V$; $I^{3-} + 2e^- \rightarrow 3I^-$ $E^0=0.536V$

11. Determine the overall change in entropy for the following process using 1.00 mole of He:

He (298.0 K, 1.50 atm) → He (100.0 K, 15.0 atm)

The heat capacity of He is 20.78 J/mol • K. Assume the helium acts ideally. (5%)

12. (a) Draw a diagram of a Carnot cycle on a T vs. S plot. (4%);
(b) What is the significance of the area inside a Carnot-cycle PV plot and the T-S plot you have just made. (6%)

13. The z component of angular momentum is defined as follows;

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi}$$

(a) Confirm that the operator $\hat{L}_z$ is a Hermitian operator. (8%)

Hint: Hermitian operator $\int f_m^* \hat{A} f_n d\tau = \int f_n (\hat{A} f_m)^* d\tau$

(b) What is the eigenvalue if $\hat{L}_z$ is operated on a function $\Psi = \frac{\sqrt{70}}{8\sqrt{2\pi}} e^{+3i\phi} \sin^3\theta$? (5%)

14. The operator e^A has a meaning if it is expanded as a power series:

$e^A = \sum_n (\frac{1}{n!}) A^n$.

(a) Show that if |a> is an eigenstate of operator A with an eigenvalue a, then it is also an eigenstate of e^A. (7%);
(b) Find the eigenvalue of e^A. (5%)

15. In a consecutive first-order reaction:

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

Answer the following questions:

(a) Show $[B] = \frac{[A]_0 k_1}{k_2 - k_1}(e^{-k_1 t} - e^{-k_2 t})$ (6%)

(b) At what time will the intermediate B reach its maximum concentration, if $k_1 = 0.25\ s^{-1}$ and $k_2 = 0.15\ s^{-1}$, at what time will the intermediate B reach its maximum concentration? (4%)

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