Chemistry 315
Term Test

March 11, 2014 Time: 75 min

Any type of calculator may be used. A list of equations is appended. No other materials are allowed. Answer all questions in the exam booklet provided. The exam has 9 questions worth 58 marks.

Value (tentative)

(6) 1. What is a liquid junction potential? Explain how such a potential may arise for the case of pure water in contact with an aqueous sodium chloride solution.

A junction potential is a potential difference across the interface between any two dissimilar solutions in contact with each other. In the case or pure water in contact with aqueous NaCl, the potential results from the higher mobility of the chloride ion as compared to the sodium ion. Chloride diffuses into the water at a greater rate than the sodium ion, resulting in excess negative charge in the water, and leaving excess positive charge in the NaCl solution. Charge separation across the interface builds up until it exactly opposes the tendency of chloride to diffuse at a greater rate.

(8) 2. Define the following terms.

a) linear dynamic range

(limit of linearity - limit of quantification) / limit of linearity

b) type I error

a false positive - claiming a species has been detected when it is absent

c) asymmetry potential

a nonzero potential sometimes found to exist across a membrane even though the membrane is separating identical solutions.

d) sensitivity

a measure of how much the instrument response changes per change in concentration - dy/dC where y is instrument response and C is concentration

(4) 3. The standard electrode potential for the half-reaction:

$$Tl^{3+}(aq) + 2e^- \rightleftharpoons Tl^{+}(aq)$$

is $E^o = 1.28$ V. The formal potential in 1.0 M $HClO_4$ is $E^{o'} = 1.26$ V. In 1M HCl, it is $E^{o'} = 0.77$ V. Rationalize why the formal potential in $HClO_4$ is lower than the standard potential, and why the formal potential in HCl is lower than in $HClO_4$.

In the 1.0 M acid solutions, the ionic strength is much higher as compared to conditions for which the standard potential is measured. The higher ionic strength results in lower activities for both Tl species, but moreso for Tl^{3+} as compared to Tl^{+} due to it's higher charge. This causes the half-reaction to shift in favour of Tl^{3+}, putting electrons on the electrode, and shifting the potential in a negative direction. This effect is the same for both perchloric acid and hydrochloric acid solutions since they are both strong acids and hence have the same ionic strength. The potential in hydrochloric acid solution is lower than in perchloric acid because chloride can complex with cations, while perchlorate is a non-complexing anion, at least in aqueous solutions. The chloride complexes with Tl^{3+} more strongly than Tl^{+} due its higher charge. Again, this shifts the half-reaction of favour of Tl^{3+}, causing the potential to shift in a negative direction.

(6) 4. A copper ion selective electrode developed a potential of 87 mV in 100.0 mL of a standard 2.00 ppm Cu^{2+} solution. When 10.00 mL of a solution containing an unknown Cu^{2+} concentration was added to this solution, the potential increased by 16 mV. What was the copper concentration in the unknown solution? (Note that in this case, the standard is spiked with the unknown, rather than the more normal situation where the unknown is spiked with the standard.)

The equation for a single spike can be used except that the reciprocal of the ratio of mass of standard to unknown is used, since the standard was spiked with the unknown, rather than the other way around. Also, for ion selective electrodes, $y = 10^{E/S}$ where, for Cu^{2+}, $S = 59.16 / 2$ mV per decade.

$$\frac{V_t y_t}{V_i y_i} = \frac{n_u}{n_s} + 1 \qquad n_s = 2.0\text{ ppm} \times 100\text{ mL} = 200\ \mu g$$

$$y_t = 10^{\frac{(16+87)2}{59.16}} = 3034.5 \qquad V_t = 110\text{ mL}$$

$$y_i = 10^{\frac{87\times 2}{59.16}} = 873.3 \qquad V_i = 100\text{mL}$$

$$\frac{110 \times 3034.5}{100 \times 873.3} = \frac{n_u}{200} + 1 \qquad n_u = 564.4\ \mu g$$

$$[\text{unknown}] = \frac{564.4\ \mu g}{10.0\text{ mL}} = 56.4\text{ ppm}$$

(6) 5. A particular Na^+ ion-selective electrode gave a potential of 245 mV in a solution containing 1.00 x 10^{-4} M Na^+. When 10.00 mL of 0.100 M HCl were added to 100.0 mL of this solution, the potential increased to 295 mV. Find the selectivity coefficient $k_{Na+,H+}$ for this electrode.

$$(1) \quad 245 = \text{const} + 59.16 \log(1.00 \times 10^{-4})$$

$$(2) \quad 295 = \text{const} + 59.16 \log\left(\frac{100 \times 10^{-4}}{110} + \frac{k \times 10 \times 0.1}{110}\right)$$

$$(2)-(1) \quad 50 = 59.16 \log\left(1.00\times10^{4} \Big/ \frac{100 \times 10^{-4} + k}{110}\right)$$

$$k = 0.067$$

(6) 6. Bi is often used as in internal standard in the determination of Pb by ICP mass spectrometry. Exactly 10.00 mL of a solution containing an unknown concentration of Pb^{2+} and 10.0 mL of 10.0 ppb Bi were added to each of a series of 250 mL volumetric flasks and diluted to volume. Varying volumes of a 10.0 ppb Pb standard were added to the flasks before diluting to volume. The ratio of the Pb to Bi signal was plotted versus the volume of of the Pb standard added, and the regression line for the resulting plot was found to be y = 675x + 3941, where x is in mL. What is the concentration of Pb in the undiluted unknown solution?

The x-intercept is -3941 / 675 = -5.8385 mL. The volume of standard solution containing mass of Pb equal to that due to the unknown is 5.58385 mL. The mass of Pb due to the unknown is 5.8385 x 10.0 ppb = 58.385 ng. This was derived from 10.0 mL of unknown, so the concentration is 58.385 / 10 = 5.84 ppb.

(8) 7. a) What advantage does the method of standard additions have with respect to the method of external standards?

Since the standard and analyte are present in the same solution/matrix, matrix effects are mitigated.

b) What advantage pertains to the use of an internal standard?

Since the ratio of the analyte to internal standard signal volumes, is used, the effects of uncontrollable factors such as fluctuation in injection volume. variation in viscosity, etc. etc. cancel out.

c) What requirements must be met by a compound for it to be useful as an internal standard?

The internal standard must not otherwise be present in the samples to be analyzed.

The internal standard must yield an instrument response uniquely identifiable in the presence of the analyte.

(8) 8. The potential of the following cell is 0.234 V. What is the pH in half-cell on the left?

$Pt|IO_3^-(0.24M),I^-(0.48M),OH^-||I_3^-(0.72M),I^-(0.48M)|Pt$

The relevant half-reactions are:

$I_3^- + 2e^- \rightleftharpoons 3I^-$ $E^o = 0.535$ V

$IO_3^- + 3H_2O + 6e^- \rightleftharpoons I^- + 6OH^-$ $E^o = 0.269$ V

$$E_+ = 0.535 + \frac{.05916}{2} \log \frac{0.72}{(0.48)^3} = 0.55907 \text{ V}$$

$$E_+ - E_- = 0.234 \text{ V} \qquad E_- = 0.32507$$

$$0.32507 = 0.269 - \frac{.05916}{6} \log \frac{0.48}{0.24} - \frac{.05916}{\cancel{6}} \log [OH^-]^{\cancel{6}}$$

$$[OH^-] = 0.10 \text{ M} \qquad pH = 13.00$$

(6) 9. Given the appropriate half-reaction from question 8 and

$I_2(aq) + 2e^- \rightleftharpoons 2I^-$ $E^o = 0.620$ V

find the equilibrium constant for the reaction:

$I_2(aq) + I^- \rightleftharpoons I_3^-$

$$(1) \quad I_{2(aq)} + 2e^- \rightleftharpoons 2I^- \qquad E^o = 0.620$$

$$(2) \quad I_3^- + 2e^- \rightleftharpoons 3I^- \qquad E^o = 0.535$$

$$(1)-(2) \quad I_{2(aq.)} + \cancel{3}I^- \rightleftharpoons I_3^- + \cancel{2I^-}$$

$$I_2 + I^- \rightleftharpoons I_3^- \qquad E^o = 0.620 - 0.535 = 0.085$$

$$0.085 = \frac{.05916}{2} \log K \qquad K = 747$$