CHAPTER 5: SUPPLEMENTARY PROBLEMS CALIBRATION METHODS

- **S5-1.** (a) Use the method of least squares to calculate the equation of the best straight line going through the points (1,3), (3,2), and (5,0). Express your answer in the form $y = [m(\pm \sigma_m)]x + [b(\pm \sigma_b)]$, with a reasonable number of significant figures.
 - (b) Find the uncertainty in x for y = 1.00.
- **S5-2.** The signal (peak area) measured for different standard concentrations of silver in atomic absorption is given below:

Ag (μ g/mL):	0	8.0	16.0	32.0
Peak area:	0.002	0.076	0.147	0.282

- (a) Construct a calibration curve and find the slope and intercept .
- (b) Find the concentration of an unknown that gives a peak area of 0.160 when the blank peak area is 0.004. That is, the corrected absorbance is 0.156.
- **S5-3.** *Propagation of uncertainty with a calibration curve.* Refer to the data in the previous problem. Find the concentration (and its uncertainty) of an unknown with a corrected peak area of $0.156 (\pm s_v)$.
- S5-4. Standard addition. An unknown sample of dopamine gave a current of 34.6 nA in an electrochemical analysis. Then 2.00 mL of solution containing 0.015 6 M dopamine was mixed with 90.0 mL of unknown, and the mixture was diluted to 100.0 mL in a volumetric flask. The signal from the new solution was 58.4 nA.
 - (a) Denoting the initial, unknown concentration as [dopamine]_i, write an expression for the final concentration, [dopamine]_f, after dilution.
 - (b) In a similar manner, write the final concentration of added standard dopamine, designated as [S]_f.
 - (c) Find $[dopamine]_i$ in the unknown.
- S5-5. Internal standard. A mixture containing 80.0 nM iodoacetone (designated A) and 64.0 nM p-dichlorobenzene (designated B) gave the relative detector response (peak area of A)/(peak area of B) = 0.71 in a chromatography experiment. A solution containing an unknown quantity of A plus 930 nM B gave a relative detector response (peak area of A)/(peak area of B) = 1.21. Find the concentration of A in the unknown.

S5-6. *Standard addition.* The quantity of acetylene (HC+CH) in a gas mixture was measured by mass spectrometry, in which the signal for mass number 26 is proportional to the volume percent of acetylene.

Gas	Signal (mV)
Blank containing no acetylene	0.2
Unknown	10.8
Unknown + 0.072 vol % C_2H_2	17.1
Unknown + 0.121 vol % C_2H_2	20.2
Unknowsn + 0.200 vol % C_2H_2	30.0
Unknown + 0.364 vol % C ₂ H ₂	44.6

- (a) Subtract the blank value (0.2 mV) from each measured signal. Prepare a graph to find the volume percent of acetylene in the unknown.
- (b) Use the method of least squares to find the uncertainties in slope and intercept of your graph and to estimate the uncertainty in the answer to part a.
- **S5-7.** *Derivation of standard addition graphical treatment.* Figure 5-6 is a graph of I_{S+X} vs. $[S]_f$. Rearrange Equation 5-16 to the form $I_{S+X} = m[S]_f + b$, where *m* is the slope and *b* is the intercept. The straight line in Figure 5-6 crosses the *x* axis when $I_{S+X} = 0$. Use your equation to show that when $I_{S+X} = 0$, $[S] = -[X]_f$.
- **S5-8.** The lowest temperature achieved for systems of nuclear spins are listed below:

Year (= x)	Temperature (K)	Log [Temperature] $(= y)$
1979	5 × 10 ⁻⁸	-7.3
1983	2×10^{-8}	-7.7
1989	2×10^{-9}	-8.7
1990	8 × 10 ⁻¹⁰	-9.1

- (a) Make a graph of *y* (= log [temperature]) versus *x* (= year) and find the slope and intercept and their standard deviations.
- (b) Use the slope and intercept to extrapolate the line to predict the temperature expected in the year 2010. (Do not consider uncertainties.) Is there any reason to consider this a valid prediction? (*Extrapolation* means to go beyond the measured data. *Interpolation* means to go between measured data.)

CHAPTER 6: SUPPLEMENTARY PROBLEMS CHEMICAL EQUILIBRIUM

- S6-1. Write the expression for the equilibrium constant for each of the following reactions. Write the pressure of a gaseous molecule, X, as P_X.
 (a) Cl₂(g) + 2OH⁻(ag) ≈ Cl⁻(ag) + OCl⁻(ag) + H₂O(l) (b) Hg(l) + I₂(g) ≈ HgI₂(s)
- S6-2. Suppose that the following reaction has come to equilibrium: Br₂(l) + I₂(s) + 4Cl⁻(aq) ⇒ 2Br⁻(aq) + 2ICl⁻₂(aq)
 If more I₂(s) is added, will the concentration of ICl⁻₂ in the aqueous phase increase, decrease, or remain unchanged?
- **S6-3.** From the equations $\operatorname{CuN}_3(s) \rightleftharpoons \operatorname{Cu}^+ + \operatorname{N}_3^ \operatorname{HN}_3 \rightleftharpoons \operatorname{H}^+ + \operatorname{N}_3^ K = 4.9 \times 10^{-9}$ $K = 2.2 \times 10^{-5}$

find the value of *K* for the reaction $Cu^+ + HN_3 \rightleftharpoons CuN_3(s) + H^+$. All species are aqueous unless otherwise indicated.

S6-4. For the reaction $H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$, $K = 1.0 \times 10^{-14}$ at 25°C. The concentrations in a system out of equilibrium are $[H^+] = 3.0 \times 10^{-5}$ M and $[OH^-] = 2.0 \times 10^{-7}$ M. Will the reaction proceed to the left or to the right to reach equilibrium?

S6-5. For the sum of two reactions, we know that $K_3 = K_1 K_2$. Show that this implies that $\Delta G_3^\circ = \Delta G_1^\circ + \Delta G_2^\circ$

 $A + B \rightleftharpoons C + D \qquad K_1$ $\underline{D + E \rightleftharpoons B + F} \qquad K_2$ $A + E \rightleftharpoons C + F \qquad K_3$

S6-6. Find ΔG° for the reactions (a) Ca(OH)₂(s) \rightleftharpoons Ca²⁺ + 2OH⁻ $K = 6.5 \times 10^{-5}$

(b) $Mg(OH)_2(s) \rightleftharpoons Mg^{2+} + 2OH^ K = 7.1 \times 10^{-12}$

S6-7. For the reaction $Mg^{2+} + Cu(s) \rightleftharpoons Mg(s) + Cu^{2+}$, $K = 10^{-92}$ and $\Delta S^{\circ} = +18$ J/(K·mol).

(a) Under standard conditions, is ΔG° positive or negative? The term "standard conditions" means that reactants and products are in their standard states.

- (b) Under standard conditions, is the reaction endothermic or exothermic?
- S6-8. Use the solubility product to calculate the solubility of Ag₂CrO₄ (FM 331.73) (→ 2Ag⁺ + CrO₄²⁻) in water expressed as (a) moles per liter, (b) g/100 mL and (c) ppm Ag⁺(≈ µg Ag⁺/mL).

- **S6-9.** The solubility product for CuCl is 1.9×10^{-7} . The equilibrium constant for the reaction $Cu(s) + Cu^{2+} \rightleftharpoons 2Cu^+$ is 9.6×10^{-7} . Calculate the equilibrium constant for the reaction $Cu(s) + Cu^{2+} + 2Cl^- \rightleftharpoons 2CuCl(s)$
- S6-10. How many grams of PbI₂ (FM 461.0) will dissolve in 0.500 L of (a) water and (b) 0.063 4 M NaI?
- S6-11. What concentration of Ca²⁺ must be added to 0.010 M oxalate ($C_2O_4^{2-}$) to precipitate 99.0% of the oxalate?
- **S6-12.** Is it possible to separate 99.90% of 0.020 M Mg²⁺ from 0.10 M Ca²⁺ without precipitation of Ca(OH)₂ by addition of NaOH?
- **S6-13.** Using Equations 6-11 to 6-15, calculate the concentrations of Pb^{2+} , PbI^+ , $PbI_2(aq)$, PbI_3^- and PbI_4^- in a solution whose total I⁻ concentration is somehow fixed at 0.050 M. Compare your answers to Figure 6-2.
- **S6-14.** Consider the following equilibria:

$\operatorname{AgCl}(s) \rightleftharpoons \operatorname{Ag}^+ + \operatorname{Cl}^-$	$K_{\rm sp} = 1.8 \times 10^{-10}$
$\operatorname{AgCl}(s) + \operatorname{Cl}^{-} \rightleftharpoons \operatorname{AgCl}_{2}^{-}$	$K_2 = 1.5 \times 10^{-2}$
$\operatorname{AgCl}_2^- + \operatorname{Cl}^- \rightleftharpoons \operatorname{AgCl}_3^-$	$K_3 = 0.49$

Find the total concentration of silver-containing species in a silver-saturated, aqueous solution containing the following concentrations of Cl⁻:

- (a) 0.010 M (b) 0.20 M (c) 2.0 M
- S6-15. Identify the Brønsted-Lowry acids on both sides of the reaction NaHSO₃ + NaOH \rightleftharpoons Na₂SO₃ + H₂O
- S6-16. Identify the conjugate acid-base pairs in the reaction

 $H_2NCH_2CH_2NH_2 + H_2O \rightleftharpoons H_3NCH_2CH_2NH_2 + OH^-$ Ethylenediamine

- **S6-17.** Calculate the concentration of H^+ and the pH of:
 - (a) $0.001 0 \text{ M HClO}_4$ (d) 3.0 M NaOH
 - (b) 0.050 M HBr (e) $0.0050 \text{ M} [(CH_3CH_2)_4\text{N}^+]OH^-$
 - (c) 0.050 M LiOH tetraethylammonium hydroxide

S6-18. Write the K_a reaction for formic acid, HCO₂H, and for methylammonium ion, CH₃NH⁺₃.

S6-19. Write the K_b reactions for piperidine and benzoate.



- **S6-20.** Write the K_a and K_b reactions of K₂HPO₄.
- **S6-21.** Write the stepwise acid-base reactions for the following species in water. Write the correct symbol (e.g., K_{b1}) for the equilibrium constant for each reaction.



- **S6-22.** Use Appendix G to decide which is the stronger acid: 3-nitrophenol or 4-nitrophenol. Write the acid dissociation reaction of each.
- **S6-23.** Which is the stronger base: cyclohexylamine or imidazole? Write the base hydrolysis reaction of each. In the case of imidazole, the nitrogen atom without a hydrogen is the one that accepts H⁺.



- **S6-24.** Write the K_b reaction of hypochlorite, OCl⁻. Given that the K_a value for HOCl is 3.0×10^{-8} , calculate K_b for OCl⁻.
- **S6-25.** Write the K_{a2} reaction of H₂SO₄ and the K_{b2} reaction the trisodium salt below.



S6-26. From the K_a values for citric acid in Appendix G, find K_{b1} , K_{b2} and K_{b3} for trisodium citrate.

CHAPTER 7: SUPPLEMENTARY PROBLEMS LET THE TITRATIONS BEGIN

- **S7-1.** How many milligrams of oxalic acid dihydrate, $H_2C_2O_4 \cdot 2H_2O$ (FM 126.07), will react with 1.00 mL of 0.027 3 M ceric sulfate (Ce(SO₄)₂) if the reaction is $H_2C_2O_4 + 2Ce^{4+} \rightarrow 2CO_2 + 2Ce^{3+} + 2H^+$?
- S7-2. A mixture weighing 27.73 mg containing only FeCl₂ (FM 126.75) and KCl (FM 74.55) required 18.49 mL of 0.022 37 M AgNO₃ for complete titration of the chloride. Find the mass of FeCl₂ and the weight percent of Fe in the mixture.
- **S7-3.** The chloride content of blood serum, cerebrospinal fluid or urine can be measured by titration of the chloride with mercuric ion: $Hg^{2+} + 2Cl^- \rightarrow HgCl_2(aq)$. When the reaction is complete, excess Hg^{2+} reacts with the indicator, diphenylcarbazone, which forms a violet-blue color.
 - (a) Mercuric nitrate was standardized by titrating a solution containing 147.6 mg of NaCl, which required 28.06 mL of Hg(NO₃)₂ solution. Find the molarity of the Hg(NO₃)₂.
 - (b) When this same Hg(NO₃)₂ solution was used to titrate 2.000 mL of urine, 22.83 mL was required. Find the concentration of Cl⁻ (mg/mL) in the urine.
- **S7-4.** Consider the titration of 20.00 mL of 0.053 20 M KBr with 0.051 10 M AgNO₃. Calculate pAg⁺ at the following volumes of added AgNO₃:
 - (a) 20.00 mL (b) $V_{\rm e}$ (c) 22.60 mL
- **S7-5.** Consider the titration of 50.00 mL of $0.0246 \text{ M Hg}(\text{NO}_3)_2$ with 0.104 M KSCN. Calculate the value of pHg²⁺ at each of the following points and sketch the titration curve: $0.25V_{\text{e}}, 0.5V_{\text{e}}, 0.75V_{\text{e}}, V_{\text{e}}, 1.05V_{\text{e}}, 1.25V_{\text{e}}.$
- **S7-6.** Calculate the value of pSO_4^{2-} at each of the following points in the titration of 100.0 mL of 0.050 0 M Sr²⁺ plus 0.050 0 M Ra²⁺ with 0.250 M SO₄²⁻. Sketch the titration curve.

(a)	10.00 mL	(c) 21.00 mL	(e) 40.00 mL
(b)	19.00 mL	(d) 30.00 mL	(f) 50.00 mL

S7-7. *Cl⁻ analysis in stream water*. Increments of 4.123 mM AgNO₃ were added to 100.0 mL of stream water and the voltage between a silver electrode and a reference electrode was measured with a pH meter.

Total mL	Voltage	Total mL	Voltage	Total mL	Voltage
Ag ⁺ added	(mV)	Ag ⁺ added	(mV)	Ag ⁺ added	(mV)
20.00	62.8	23.97	75.9	26.97	103.0
20.49	64.2	24.48	77.8	27.49	105.9
20.97	65.1	25.01	81.9	28.47	111.0
21.46	67.1	25.48	87.0	28.99	111.9
21.96	68.0	25.97	92.9	29.50	114.0
23.48	73.0	26.47	98.9	30.00	115.0

G. Lisensky and K. Reynolds, "Chloride in Natural Waters," J. Chem. Ed. 1991, 68, 334.

- (a) Make a graph of millivolts versus milliliters of titrant. Draw a smooth curve through the points. The end point is the steepest part of the curve, but the curve is not nearly so steep as in Figure 7-8. Trace a pencil along the curve and you will feel where the curve is steepest when the slope stops increasing and starts decreasing; this is what is meant by an inflection point. Using this end point, calculate the molarity of Cl⁻ in the stream. Convert the molarity to ppm (= μ g Cl⁻/mL). Compare your answer with the bar graphs at the beginning of Chapter 7 to see if you are in the right ballpark.
- (b) Estimate the uncertainty in the end point based on the uncertainty that you associate with locating the steepest part of the curve. From this uncertainty, estimate the uncertainty in Cl⁻ molarity.
- (c) Students measured Cl⁻ in water from seven locations, using electrodes and a Fajans titration. Are results from the two methods different from each other at the 95% confidence level?

Location	Electrode measurement	rode measurement Fajans titration	
	(µg/mL)	(µg/mL)	
1	63.6	65.1	+1.5
2	42.7	43.3	+0.6
3	133.4	131.9	-1.5
4	82.2	82.7	+0.5
5	79.9	81.0	+1.1
6	44.3	44.8	+0.5
7	48.8	49.2	+0.4

CHAPTER 8: SUPPLEMENTARY PROBLEMS ACTIVITY

S8-1. Find the activity coefficient of each ion at the indicated ionic strength.:

- (a) S^{2-} ($\mu = 0.001 \text{ M}$) (b) PO_4^{3-} ($\mu = 0.001 \text{ M}$) (c) Sn^{4+} ($\mu = 0.05 \text{ M}$) (d) $H_2NCH_2CO_2^-$ ($\mu = 0.01 \text{ M}$)
- **S8-2.** Use interpolation in Table 8-1 to find the activity coefficient of OH⁻ when $\mu = 0.030$ M.
- **S8-3.** Calculate the activity coefficient of formate, HCO_2^- , when $\mu = 0.038$ M by using (a) the extended Debye-Hückel equation (b) linear interpolation with Table 8-1
- **S8-4.** Calculate the solubility of Ag_2CrO_4 (expressed as moles of CrO_4^{2-} per liter) in (a) 0.050 M KClO₄ (b) 0.0050 M AgNO₃
- **S8-5.** Calculate the concentration of Tl⁺ in a saturated solution of TlBr in water.
- **S8-6.** Find the pH of (a) 0.050 M HClO₄ and (b) 0.050 M HClO₄ plus 0.050 M HBr.
- **S8-7.** *Propagation of uncertainty in exponentiation.* An empirical equation for activity coefficients at ionic strengths higher than 0.1 M is

$$\log \gamma = \frac{-A\sqrt{\mu}}{1 + B\sqrt{\mu}} + C\mu$$

where γ is the activity coefficient, μ is the ionic strength, and *A*, *B*, and *C* are constants characteristic of a particular solution. Activity coefficients for Cu²⁺ measured with an ion-selective electrode are described by the parameters *A* = 3.23 (±0.32), *B* = 2.57 (±0.32), and *C* = 0.198 (±0.012). [I. Uemasu and Y. Umezawa, "Chloride Anion Interference in the Spectrophotometric Determination of Arsenazo III" *Anal. Chem.* **1983**, *55*, 386.]

- (a) Ignoring uncertainties in *A*, *B*, and *C*, calculate the activity coefficient of Cu^{2+} at the following ionic strengths: 0.001, 0.01, 0.1, 0.5, 1.0, 1.5, 2.0, and 3.0 M. Make a graph of γ versus μ and compare your values of γ with those in Table 8-1.
- (b) Find the uncertainty in γ when $\mu = 0.1$ M.