

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 ($\mu\text{g/mL}$):	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 ($\pm s_y$).
- 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 0.0156 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 $[\text{dopamine}]_i$, write an expression for the final concentration, $[\text{dopamine}]_f$, after dilution.
- (b) In a similar manner, write the final concentration of added standard dopamine, designated as $[\text{S}]_f$.
- (c) Find $[\text{dopamine}]_i$ 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 ₂ H ₂	17.1
Unknown + 0.121 vol % C ₂ H ₂	20.2
Unknown + 0.200 vol % C ₂ H 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 $I_{S+X} = 0$, $[S] = -[X]_f$.

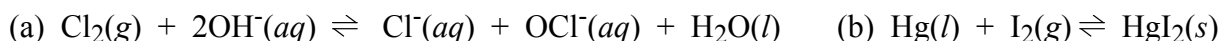
S5-8. The lowest temperature achieved for systems of nuclear spins are listed below:

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

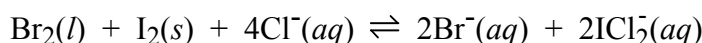
- (a) Make a graph of y (= log [temperature]) versus x (= year) and find the slope and intercept and their standard deviations.
- (b) Use the slope and intercept to extrapolate the line to predict the temperature expected in the year 2010. (Do not consider uncertainties.) Is there any reason to consider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

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 .

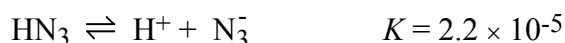


S6-2. Suppose that the following reaction has come to equilibrium:



If more $\text{I}_2(s)$ is added, will the concentration of ICl_2^- in the aqueous phase increase, decrease, or remain unchanged?

S6-3. From the equations $\text{CuN}_3(s) \rightleftharpoons \text{Cu}^+ + \text{N}_3^-$ $K = 4.9 \times 10^{-9}$

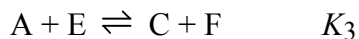
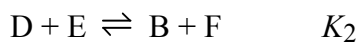
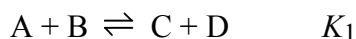


find the value of K for the reaction $\text{Cu}^+ + \text{HN}_3 \rightleftharpoons \text{CuN}_3(s) + \text{H}^+$. All species are aqueous unless otherwise indicated.

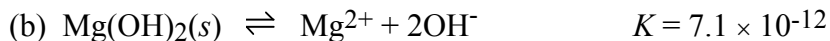
S6-4. For the reaction $\text{H}_2\text{O}(l) \rightleftharpoons \text{H}^+(aq) + \text{OH}^-(aq)$, $K = 1.0 \times 10^{-14}$ at 25°C . The concentrations in a system out of equilibrium are $[\text{H}^+] = 3.0 \times 10^{-5} \text{ M}$ and $[\text{OH}^-] = 2.0 \times 10^{-7} \text{ M}$. Will the reaction proceed to the left or to the right to reach equilibrium?

S6-5. For the sum of two reactions, we know that $K_3 = K_1K_2$. Show that this implies that

$$\Delta G_3^\circ = \Delta G_1^\circ + \Delta G_2^\circ$$



S6-6. Find ΔG° for the reactions



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

(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?

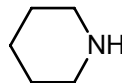
S6-8. Use the solubility product to calculate the solubility of Ag_2CrO_4 (FM 331.73)

($\rightarrow 2\text{Ag}^+ + \text{CrO}_4^{2-}$) in water expressed as (a) moles per liter, (b) g/100 mL and

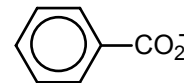
(c) ppm Ag^+ ($\approx \mu\text{g Ag}^+/\text{mL}$).

- S6-9.** The solubility product for CuCl is 1.9×10^{-7} . The equilibrium constant for the reaction $\text{Cu}(s) + \text{Cu}^{2+} \rightleftharpoons 2\text{Cu}^+$ is 9.6×10^{-7} . Calculate the equilibrium constant for the reaction $\text{Cu}(s) + \text{Cu}^{2+} + 2\text{Cl}^- \rightleftharpoons 2\text{CuCl}(s)$
- S6-10.** How many grams of PbI_2 (FM 461.0) will dissolve in 0.500 L of (a) water and (b) 0.063 4 M NaI?
- S6-11.** What concentration of Ca^{2+} must be added to 0.010 M oxalate ($\text{C}_2\text{O}_4^{2-}$) to precipitate 99.0% of the oxalate?
- S6-12.** Is it possible to separate 99.90% of 0.020 M Mg^{2+} from 0.10 M Ca^{2+} without precipitation of $\text{Ca}(\text{OH})_2$ by addition of NaOH?
- S6-13.** Using Equations 6-11 to 6-15, calculate the concentrations of Pb^{2+} , PbI^+ , $\text{PbI}_2(aq)$, 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:
- $$\text{AgCl}(s) \rightleftharpoons \text{Ag}^+ + \text{Cl}^- \quad K_{\text{sp}} = 1.8 \times 10^{-10}$$
- $$\text{AgCl}(s) + \text{Cl}^- \rightleftharpoons \text{AgCl}_2^- \quad K_2 = 1.5 \times 10^{-2}$$
- $$\text{AgCl}_2^- + \text{Cl}^- \rightleftharpoons \text{AgCl}_3^{2-} \quad K_3 = 0.49$$
- 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
- $$\text{NaHSO}_3 + \text{NaOH} \rightleftharpoons \text{Na}_2\text{SO}_3 + \text{H}_2\text{O}$$
- S6-16.** Identify the conjugate acid-base pairs in the reaction
- $$\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{N}^+\text{CH}_2\text{CH}_2\text{NH}_2 + \text{OH}^-$$
- Ethylenediamine
- S6-17.** Calculate the concentration of H^+ and the pH of:
- (a) 0.001 0 M HClO_4 (d) 3.0 M NaOH
 (b) 0.050 M HBr (e) 0.005 0 M $[(\text{CH}_3\text{CH}_2)_4\text{N}^+]\text{OH}^-$
 (c) 0.050 M LiOH tetraethylammonium hydroxide
- S6-18.** Write the K_a reaction for formic acid, HCO_2H , and for methylammonium ion, CH_3NH_3^+ .

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



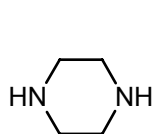
Piperidine



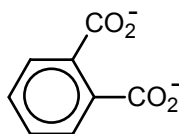
Benzoate

S6-20. Write the K_a and K_b reactions of K_2HPO_4 .

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.



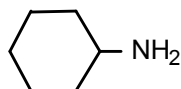
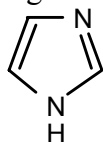
Piperazine



Phthalate ion

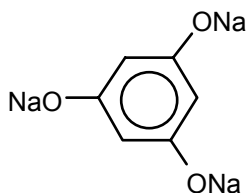
S6-22. Use Appendix G to decide which is the stronger acid: 3-nitrophenol or 4-nitrophenol. Write the acid dissociation reaction of each.

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^+ .

Cyclohexylamine
 $pK_B = 3.36$ Imidazole
 $pK_B = 7.01$

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 H_2SO_4 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.

Total mL Ag ⁺ added	Voltage (mV)	Total mL Ag ⁺ added	Voltage (mV)	Total mL Ag ⁺ added	Voltage (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 (= $\mu\text{g Cl}^-/\text{mL}$). 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 ($\mu\text{g/mL}$)	Fajans titration ($\mu\text{g/mL}$)	Difference
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

