$$\sigma_y \approx s_y = \sqrt{\frac{\sum(d_i - \bar{d})^2}{(\text{degrees of freedom})}}$$

- For Equation 4-19, we began with n points.

- Two degrees of freedom were lost in determining the slope and the intercept.

  → Therefore, n – 2 degrees of freedom remain.

- Equation 4-19 becomes

$$s_y = \sqrt{\frac{\sum(d_i^2)}{n-2}}$$

$$\text{Vertical deviation} = d_i = y_i - y = y_i - (mx_i + b)$$

- Uncertainty analysis for Equations 4-16 and 4-17 leads to the following results:

Least-squares "best" line

Slope: $$m = \begin{vmatrix} \Sigma(x_i y_i) & \Sigma x_i \\ \Sigma y_i & n \end{vmatrix} \div D$$

Intercept: $$b = \begin{vmatrix} \Sigma(x_i^2) & \Sigma(x_i y_i) \\ \Sigma x_i & \Sigma y_i \end{vmatrix} \div D$$

Standard deviation of slope and intercept

$$s_m^2 = \frac{s_y^2 n}{D}$$

$$s_b^2 = \frac{s_y^2 \sum (x_i^2)}{D}$$

$$s_y = \sqrt{\frac{\sum(d_i^2)}{n-2}} \quad (4\text{-}20)$$

$$D = \begin{vmatrix} \Sigma(x_i^2) & \Sigma x_i \\ \Sigma x_i & n \end{vmatrix} \quad (4\text{-}18)$$

- where s_m is an estimate of the standard deviation of the slope,

  s_b is an estimate of the standard deviation of the intercept,

  s_y is given by Equation 4-20,

  D is given by Equation 4-18.

- At last, we can assign significant figures to the slope and the intercept in Figure 4-11.

- In Table 4-6, we see that

$$\Sigma(d_i^2) = 0.076\,923$$

- Putting this number into Equation 4-20 gives $s_y = \sqrt{\frac{\Sigma(d_i^2)}{n-2}}$

$$s_y^2 = \frac{0.076\,923}{4-2} = 0.038\,462$$

- Now, we can plug numbers into Equations 4-21 and 4-22 to find

(4-21) $$s_m^2 = \frac{s_y^2 n}{D} = \frac{(0.038\,462)(4)}{52} = 0.002\,958\,6 \Rightarrow s_m = 0.054\,39$$

(4-22) $$s_b^2 = \frac{s_y^2 \sum (x_i^2)}{D} = \frac{(0.038\,462)(62)}{52} = 0.045\,859 \Rightarrow s_b = 0.214\,15$$

- Combining the results for m, s_m, b, and s_b, we write

$$\text{Slope:} \quad \begin{matrix} 0.615\,38 \\ \pm 0.054\,39 \end{matrix} = 0.62 \pm 0.05 \quad \text{or} \quad 0.61_5 \pm 0.05_4$$

$$\text{Intercept:} \quad \begin{matrix} 1.346\,15 \\ \pm 0.214\,15 \end{matrix} = 1.3 \pm 0.2 \quad \text{or} \quad 1.3_5 \pm 0.2_1$$

→ The first digit of the uncertainty is the last significant figure.

Calibration Curves

- A calibration curve shows the response of an analytical method to known quantities of analyte.
- Table 4-8 gives real data from a protein analysis that produces a colored product.

See Table 4-8

- A spectrophotometer measures the absorbance of light,
  → which is proportional to the quantity of protein analyzed.

- Solutions containing known concentrations of analyte are called **standard solutions**.

- Solutions containing all reagents and solvents used in the analysis, but no deliberately added analyte,
  → are called **blank solutions**.

- Blanks measure the response of the analytical procedure to impurities or interfering species in the reagents.
  → Absorbance of the blank can arise from the color of starting reagents, reactions of impurities, and reactions of interfering species.
  → Blank values can vary from one set of reagents to another, but corrected absorbance should not.

- When we scan across the three absorbance values in each row of Table 4-8,
  → the number 0.392 seems out of line:

- It is inconsistent with the other values for 15.0 μg, and the range of values for the 15.0-μg samples is much bigger than the range for the other samples.

See Table 4-8

- The linear relation between the average values of absorbance up to the 20.0-μg sample also indicates that
  → the value 0.392 is in error (Figure 4-12).
  → We choose to omit 0.392 from subsequent calculations.

See Fig 4-12

Constructing a Calibration Curve

- We adopt the following procedure for constructing a calibration curve:

Step 1)

→ Prepare known samples of analyte covering a range of concentrations expected for unknowns.

→ Measure the response of the analytical procedure to these standards to generate data like the left half of Table 4-8.

See Table 4-8

Step 2)

→ Subtract the average absorbance (0.099_3) of the blank samples from each measured absorbance to obtain corrected absorbance.

→ The blank measures the response of the procedure when no protein is present.

See Table 4-8

Step 3)

→ Make a graph of corrected absorbance versus quantity of protein analyzed (Figure 4-13).

See Fig 4-13

→ Use the least-squares procedure to find the best straight line through the linear portion of the data, up to and including 20.0 μg of protein (14 points, including the 3 corrected blanks, in the shaded portion of Table 4-8).

→ Find the slope and intercept and uncertainties with Equations 4-16, 4-17, 4-20, 4-21, and 4-22.

→ The results are

$$m = 0.016\,3_0 \qquad s_m = 0.000\,2_2 \qquad s_y = 0.005_9$$
$$b = 0.004_7 \qquad s_b = 0.002_6$$

→ The equation of the linear calibration line is

$$\underbrace{\text{absorbance}}_{y} = m \times \underbrace{(\mu\text{g of protein})}_{x} + b$$
$$= (0.016\,3_0)(\mu\text{g of protein}) + 0.004_7$$

→ where y is the corrected absorbance

(observed absorbance – blank absorbance)

Step 4)

→ If you analyze an unknown at a future time, run a blank at the same time.

→ Subtract the new blank absorbance from the unknown absorbance to obtain corrected absorbance.

EXAMPLE **Using a Linear Calibration Curve**

An unknown protein sample gave an absorbance of 0.406 and a blank had an absorbance of 0.104. How many micrograms of protein are in the unknown?

Solution The corrected absorbance is $0.406 - 0.104 = 0.302$, which lies on the linear portion of the calibration curve in Figure 4-13. Rearranging Equation 4-25 gives

$$\mu g \text{ of protein} = \frac{\text{absorbance} - 0.004_7}{0.016\,3_0} = \frac{0.302 - 0.004_7}{0.016\,3_0} = 18.2_4\ \mu g \qquad (4\text{-}26)$$

TEST YOURSELF What mass of protein gives a corrected absorbance of 0.250? (*Answer:* 15.0_5 μg)

- We prefer calibration procedures with a linear response,
  → in which the corrected analytical signal (signal from sample – signal from blank) is proportional to the quantity of analyte.

- The dashed curve that goes up to 25 μg of protein comes from a least-squares fit of the data to a quadratic equation of the form: $y = ax^2 + bx + c$.

See Fig 4-13

- The linear range of an analytical method is the analyte concentration range over which response is proportional to concentration.

- Dynamic range – the concentration range over which there is a measurable response to analyte, even if the response is not linear.

See Fig 4-14

Good Practice

- Always make a graph of your data.

  → The graph gives you an opportunity

  i) to reject bad data or the stimulus to repeat a measurement

  ii) or decide that a straight line is not an appropriate function.

- It is not reliable to extrapolate any calibration curve, linear or nonlinear, beyond the measured range of standards.

  → Measure standards in the entire concentration range of interest.

- At least six calibration concentrations and two replicate measurements of unknown are recommended.

Recap

- Grubbs test: outlier test
- Method of least squares: Minimizing deviation^2

$$d_i^2 = (y_i - y)^2 = (y_i - mx_i - b)^2$$

- Degree of freedom : (n-2)…the other two used for slope and intercept
- Calibration curve: consisting of standard solutions & blank solutions (use corrected values)

Analytical Chemistry

Chapter 6. Chemical Equilibrium

This chapter introduces equilibria for

i) the solubility of ionic compounds,

ii) complex formation, and

iii) acid-base reactions

Equilibrium constant

- For the reaction

$$aA + bB \rightleftharpoons cC + dD$$

→ the equilibrium constant, K, is written in the form

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

→ The lowercase superscript letters: stoichiometry coefficients

→ Each capital letter: a chemical species.

→ The symbol [A]: the concentration of A relative to its standard state

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

- In the thermodynamic derivation of the equilibrium constant,

  → each quantity in the above equation is expressed as the ratio of the concentration of a species to its concentration in its standard state.

- For solutes,

  → the standard state is 1 M. (moles/liter)

- For gases,

  → the standard state is 1 bar

- For solids and liquids,

  → the standard states are the pure solid or liquid.

$$K = \frac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{A}]^a[\mathrm{B}]^b}$$

- If A is a solute.

  → [A] really means [A]/(1 M)

- If D is a gas,

  → [D] really means (pressure of D in bars)/(1 bar).

- The terms in the above equation are actually dimensionless

  → therefore, all equilibrium constants are dimensionless.

- For the reaction

$$HA \rightleftharpoons H^+ + A^-$$

→ the equilibrium constant, K,

$$K_1 = \frac{[H^+][A^-]}{[HA]}$$

- For the reverse reaction

$$H^+ + A^- \rightleftharpoons HA$$

→ the equilibrium constant, K,

$$K_1' = \frac{[HA]}{[H^+][A^-]} = 1/K_1$$

- If the direction of a reaction is reversed,

  → the new value of K is simply the reciprocal of the original value of K.

- If two reactions are added,

→ the new K is the product of the two individual values:

$$\begin{array}{lll} \mathrm{HA} \rightleftharpoons \cancel{[\mathrm{H^+}]} + \mathrm{A^-} & & K_1 \\ \cancel{[\mathrm{H^+}]} + \mathrm{C} \rightleftharpoons \mathrm{CH^+} & & K_2 \\ \hline \mathrm{HA} + \mathrm{C} \rightleftharpoons \mathrm{A^-} + \mathrm{CH^+} & & K_3 \end{array}$$

$$K_3 = K_1 K_2 = \frac{\cancel{[\mathrm{H^+}]}[\mathrm{A^-}]}{[\mathrm{HA}]} \cdot \frac{[\mathrm{CH^+}]}{\cancel{[\mathrm{H^+}]}[\mathrm{C}]} = \frac{[\mathrm{A^-}][\mathrm{CH^+}]}{[\mathrm{HA}][\mathrm{C}]}$$

EXAMPLE Combining Equilibrium Constants

The equilibrium constant for the reaction $H_2O \rightleftharpoons H^+ + OH^-$ is called K_w ($= [H^+][OH^-]$) and has the value 1.0×10^{-14} at 25 °C. Given that $K_{NH_3} = 1.8 \times 10^{-5}$ for the reaction $NH_3(aq) + H_2O \rightleftharpoons NH_4^+ + OH^-$, find K for the reaction $NH_4^+ \rightleftharpoons NH_3(aq) + H^+$.

Solution The third reaction can be obtained by reversing the second reaction and adding it to the first reaction:

$$\begin{aligned} H_2O &\rightleftharpoons H^+ + OH^- && K = K_w \\ NH_4^+ + OH^- &\rightleftharpoons NH_3(aq) + H_2O && K = 1/K_{NH_3} \\ \hline NH_4^+ &\rightleftharpoons H^+ + NH_3(aq) && K = K_w \cdot \frac{1}{K_{NH_3}} = 5.6 \times 10^{-10} \end{aligned}$$

TEST YOURSELF For the reaction $Li^+ + H_2O \rightleftharpoons Li(OH)(aq) + H^+$, $K_{Li} = 2.3 \times 10^{-14}$. Combine this reaction with the K_w reaction to find the equilibrium constant for the reaction $Li^+ + OH^- \rightleftharpoons Li(OH)(aq)$. (***Answer:*** 2.3)

Equilibrium and thermodynamics

- Equilibrium is controlled by the thermodynamics of a chemical reaction.
- The heat absorbed or released (**enthalpy**) and the degree of disorder of reactants and products (**entropy**) independently contribute to the degree to which the reaction is favored or disfavored.

- **Enthalpy**
- The enthalpy change, $\triangle H$, for a reaction
  → the heat absorbed or released when the reaction takes place under constant applied pressure.
- The standard enthalpy change, $\triangle H^{o}$,
  → the heat absorbed or released when all reactants and products are in their standard states

$$HCl(g) \rightleftharpoons H^+(aq) + Cl^-(aq) \qquad \Delta H^\circ = -74.85 \text{ kJ/mol at } 25^\circ C$$

- The negative sign of △H° indicates
  → that heat is released
  → the solution becomes warmer.

- For other reactions, △H is positive,
  → means that heat is absorbed.
  → Consequently, the solution gets colder during the reaction.

- A reaction for which △H is positive → endothermic.
- A reaction for which △H is negative → exothermic.

Entropy

- The entropy, S, of a substance
  → a measure of its "disorder,"
  → The greater the disorder, the greater the entropy.

- In general, a gas is more disordered than a liquid
  → a gas has higher entropy than a liquid

- A liquid is more disordered than a solid.

- Ions in aqueous solution

  → are normally more disordered than in their solid salt:

$$KCl(s) \rightleftharpoons K^+(aq) + Cl^-(aq) \qquad \Delta S^\circ = +76.4\ J/(K\cdot mol) \text{ at } 25^\circ C$$

- △S°

  → the change in entropy when all species are in their standard states

  → entropy of products minus entropy of reactants

- The positive value of △S°

  → Products more disordered than reactants

  → indicates that a mole of K^+(aq) plus a mole of Cl^-(aq) is more disordered than a mole of KCl(s).

Free Energy

- At constant temperature, T,

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta S_{tot} = \Delta S_{sys} + \Delta S_{surr}$$

$$T\Delta S_{tot} = T\Delta S_{sys} - \Delta H_{sys} \qquad T\Delta S_{tot} = -\Delta G$$

$$\Delta S_{tot} = \Delta S_{sys} - \frac{\Delta H_{sys}}{T}$$

- The **second law of thermodynamics**

  → In any spontaneous process, the total entropy of a system and its surroundings increases

$$\Delta S_{tot} > 0$$

- At constant temperature, T,

$$\Delta G = \Delta H - T\Delta S$$

- The Gibbs Free Energy is a measure of the total entropy change

- ΔG < 0 → spontaneous
- ΔG > 0 → nonspontaneous
- ΔG = 0 → at equilibrium

- When △H is negative and △S is positive,
  → the reaction is clearly favored.
- When △H is positive and △S is negative,
  → the reaction is clearly disfavored

- For the dissociation of HCl,

$$HCl(g) \rightleftharpoons H^+(aq) + Cl^-(aq)$$

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= (-74.85 \times 10^3\ \text{J/mol}) - (298.15\ \text{K})(-130.4\ \text{J/K·mol}) \\ &= -35.97\ \text{kJ/mol}\end{aligned}$$

- △G° is negative,

  → so the reaction is favored when all species are in their standard states.

- In most reactions, the reactants and products are not in standard states

$$\Delta G = \Delta G^o + RT \ln Q$$

- Q is the reaction quotient – similar in form to K

$$aA + bB \rightleftharpoons cC + dD$$

$$\mathbf{Q} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

- Q « 1, ΔG < 0 → drives towards products
- Q » 1, ΔG > 0 → drives back towards reactants
- At equilibrium, ΔG = 0 (Q = K)

$$\Delta G = \Delta G^o + RT \ln Q = 0 = \Delta G^o + RT \ln K$$

$$\Delta G^o = -RT \ln K \qquad K = e^{-\Delta G^\circ/RT}$$

- For the dissociation of HCl,

$$\mathrm{HCl}(g) \rightleftharpoons \mathrm{H}^+(aq) + \mathrm{Cl}^-(aq)$$

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= (-74.85 \times 10^3\ \mathrm{J/mol}) - (298.15\ \mathrm{K})(-130.4\ \mathrm{J/K \cdot mol}) \\ &= -35.97\ \mathrm{kJ/mol}\end{aligned}$$

$$K = \mathrm{e}^{-\Delta G^\circ/RT}$$

- where R is the gas constant and T is temperature (Kelvin).

$$K = \mathrm{e}^{-(-35.97 \times 10^3\ \mathrm{J/mol})/[8.314\ 472\ \mathrm{J/(K \cdot mol)}](298.15\ \mathrm{K})} = 2.00 \times 10^6$$

- The more negative the value of ΔG°,

  → the larger is the equilibrium constant.

Le Châtelier's Principle

- The direction in which the system proceeds back to equilibrium
  → is such that the change is partially offset.

$$\underset{\text{Bromate}}{BrO_3^-} + \underset{\text{Chromium(III)}}{2Cr^{3+}} + 4H_2O \rightleftharpoons Br^- + \underset{\text{Dichromate}}{Cr_2O_7^{2-}} + 8H^+$$

- Suppose that the equilibrium is disturbed by adding dichromate to the solution to increase the concentration of $[Cr_2O_7^{2-}]$.
  → In what direction will the reaction proceed to reach equilibrium?
  → the reaction should go back to the left to partially offset the increase in dichromate

$$\underset{\text{Bromate}}{BrO_3^-} + \underset{\text{Chromium(III)}}{2Cr^{3+}} + 4H_2O \leftarrow Br^- + \underset{\text{Dichromate}}{Cr_2O_7^{2-}} + 8H^+$$