

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

- 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:

$$\text{Least-squares "best" line} \left\{ \begin{array}{l} \text{Slope: } m = \frac{\left| \begin{array}{cc} \sum(x_i y_i) & \sum x_i \\ \sum y_i & n \end{array} \right|}{D} \\ \text{Intercept: } b = \frac{\left| \begin{array}{cc} \sum(x_i^2) & \sum(x_i y_i) \\ \sum x_i & \sum y_i \end{array} \right|}{D} \end{array} \right.$$



$$\text{Standard deviation of slope and intercept} \left\{ \begin{array}{l} s_m^2 = \frac{s_y^2 n}{D} \\ s_b^2 = \frac{s_y^2 \sum(x_i^2)}{D} \end{array} \right. \quad s_y = \sqrt{\frac{\sum(d_i^2)}{n-2}} \quad (4-20)$$

$$D = \frac{\left| \begin{array}{cc} \sum(x_i^2) & \sum x_i \\ \sum x_i & n \end{array} \right|}{n} \quad (4-18)$$

- 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

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

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

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

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

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

→ 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  $\mu\text{g}$ , and the range of values for the 15.0- $\mu\text{g}$  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- $\mu\text{g}$  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<sub>3</sub>) 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  $\mu\text{g}$  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

$$\begin{array}{lll}
 m = 0.0163_0 & s_m = 0.0002_2 & s_y = 0.005_9 \\
 b = 0.004_7 & s_b = 0.002_6 &
 \end{array}$$

- The equation of the linear calibration line is

$$\begin{aligned}
 \underbrace{\text{absorbance}}_y &= m \times \underbrace{(\mu\text{g of protein})}_x + b \\
 &= (0.0163_0)(\mu\text{g of protein}) + 0.004_7
 \end{aligned}$$

- 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

$$\mu\text{g of protein} = \frac{\text{absorbance} - 0.004_7}{0.0163_0} = \frac{0.302 - 0.004_7}{0.0163_0} = 18.2_4 \mu\text{g} \quad (4-26)$$

**TEST YOURSELF** What mass of protein gives a corrected absorbance of 0.250?  
(Answer:  $15.0_5 \mu\text{g}$ )

- 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<sup>2</sup>

$$d_i^2 = (y_i - \bar{y})^2 = (y_i - mx_i - b)^2$$

- 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



→ 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.

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

- 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.

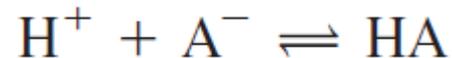
- For the reaction



→ the equilibrium constant,  $K$ ,

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

- For the reverse reaction



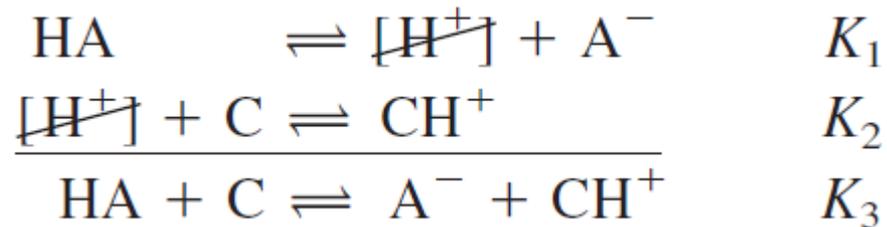
→ the equilibrium constant,  $K$ ,

$$K'_1 = \frac{[\text{HA}]}{[\text{H}^+][\text{A}^-]} = 1/K_1$$

- 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:

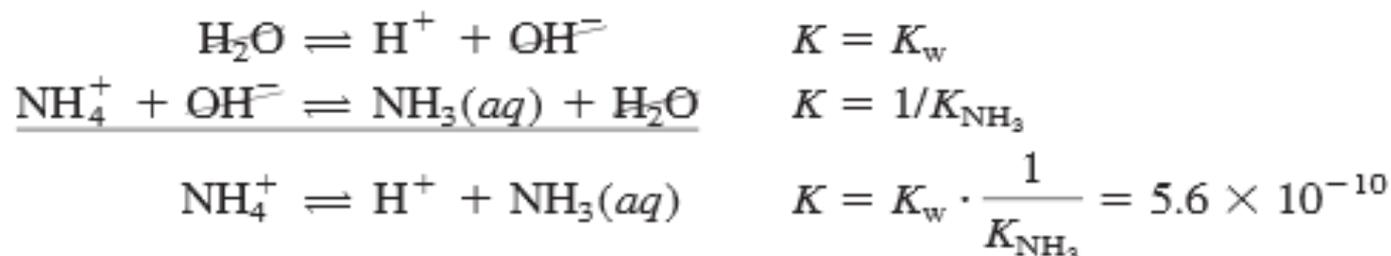


$$K_3 = K_1 K_2 = \frac{\cancel{[\text{H}^+]}[\text{A}^-]}{[\text{HA}]} \cdot \frac{[\text{CH}^+]}{\cancel{[\text{H}^+]}[\text{C}]} = \frac{[\text{A}^-][\text{CH}^+]}{[\text{HA}][\text{C}]}$$

### EXAMPLE Combining Equilibrium Constants

The equilibrium constant for the reaction  $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$  is called  $K_w$  ( $= [\text{H}^+][\text{OH}^-]$ ) and has the value  $1.0 \times 10^{-14}$  at  $25^\circ\text{C}$ . Given that  $K_{\text{NH}_3} = 1.8 \times 10^{-5}$  for the reaction  $\text{NH}_3(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$ , find  $K$  for the reaction  $\text{NH}_4^+ \rightleftharpoons \text{NH}_3(\text{aq}) + \text{H}^+$ .

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



**TEST YOURSELF** For the reaction  $\text{Li}^+ + \text{H}_2\text{O} \rightleftharpoons \text{Li}(\text{OH})(\text{aq}) + \text{H}^+$ ,  $K_{\text{Li}} = 2.3 \times 10^{-14}$ . Combine this reaction with the  $K_w$  reaction to find the equilibrium constant for the reaction  $\text{Li}^+ + \text{OH}^- \rightleftharpoons \text{Li}(\text{OH})(\text{aq})$ . (*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,  $\Delta H$ , for a reaction
  - the heat absorbed or released when the reaction takes place under constant applied pressure.
- The standard enthalpy change,  $\Delta H^\circ$ ,
  - the heat absorbed or released when all reactants and products are in their standard states



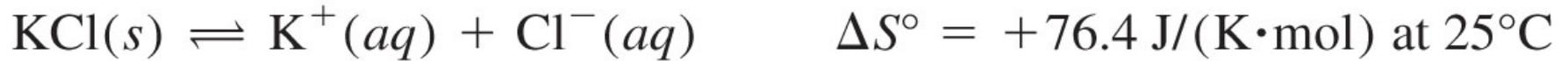
- The negative sign of  $\Delta H^\circ$  indicates
  - that heat is released
  - the solution becomes warmer.
- For other reactions,  $\Delta H$  is positive,
  - means that heat is absorbed.
  - Consequently, the solution gets colder during the reaction.
- A reaction for which  $\Delta H$  is positive → endothermic.
- A reaction for which  $\Delta H$  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:



- $\Delta S^\circ$

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

→ entropy of products minus entropy of reactants

- The positive value of  $\Delta S^\circ$

→ Products more disordered than reactants

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

## Free Energy

- At constant temperature,  $T$ ,

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

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

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

$$T\Delta S_{tot} = -\Delta G$$

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

- The **second law of thermodynamics**

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

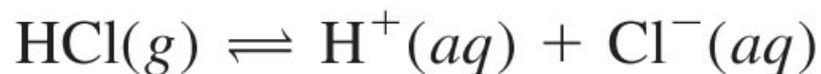
$$\Delta S_{tot} > 0$$

- At constant temperature,  $T$ ,

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

- The Gibbs Free Energy is a measure of the total entropy change
- $\Delta G < 0 \rightarrow$  spontaneous
- $\Delta G > 0 \rightarrow$  nonspontaneous
- $\Delta G = 0 \rightarrow$  at equilibrium
- When  $\Delta H$  is negative and  $\Delta S$  is positive,  
 $\rightarrow$  the reaction is clearly favored.
- When  $\Delta H$  is positive and  $\Delta S$  is negative,  
 $\rightarrow$  the reaction is clearly disfavored

- For the dissociation of HCl,



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

$$= (-74.85 \times 10^3 \text{ J/mol}) - (298.15 \text{ K})(-130.4 \text{ J/K}\cdot\text{mol})$$

$$= -35.97 \text{ kJ/mol}$$

- $\Delta G^\circ$  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

$$\Delta G = \Delta G^{\circ} + RT \ln Q$$

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



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

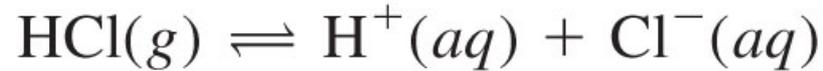
- $Q \ll 1$ ,  $\Delta G < 0 \rightarrow$  drives towards products
- $Q \gg 1$ ,  $\Delta G > 0 \rightarrow$  drives back towards reactants
- At equilibrium,  $\Delta G = 0$  ( $Q = K$ )

$$\Delta G = \Delta G^{\circ} + RT \ln Q = 0 = \Delta G^{\circ} + RT \ln K$$

$$\Delta G^{\circ} = -RT \ln K$$

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

- For the dissociation of HCl,



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

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

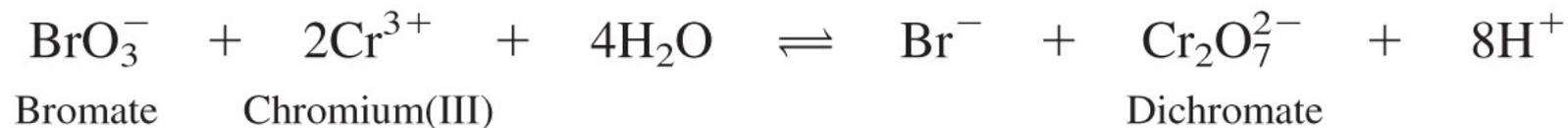
- where R is the gas constant and T is temperature (Kelvin).

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

- The more negative the value of  $\Delta G^\circ$ ,  
→ 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.



- Suppose that the equilibrium is disturbed by adding dichromate to the solution to increase the concentration of  $[\text{Cr}_2\text{O}_7^{2-}]$ .  
→ 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

