# 16.1 The shape of a redox titration curve

Now let Reaction 16-1 come to equilibrium:

$$\underset{\text{Ceric titrant}}{Ce^{4+}} + \underset{\text{Ferrous analyte}}{Fe^{2+}} \rightarrow \underset{\text{Cerous}}{Ce^{3+}} + \underset{\text{Ferric}}{Fe^{3+}}$$

$$Fe^{3+} + Ce^{3+} \rightleftharpoons Fe^{2+} + Ce^{4+} \qquad \text{( reverse of Reaction 16-1)}$$

At any time, Reactions 16-2 and 16-3 are both in equilibrium at the Pt electrode.

$$\text{Indicator half-reaction:} \quad Fe^{3+} + e^- \rightleftharpoons Fe^{2+} \qquad E^\circ = 0.767\ \text{V} \qquad (16\text{-}2)$$

$$\text{Indicator half-reaction:} \quad Ce^{4+} + e^- \rightleftharpoons Ce^{3+} \qquad E^\circ = 1.70\ \text{V} \qquad (16\text{-}3)$$

# 16.1 The shape of a redox titration curve

At the equivalence point,

$$E_+ = 0.767 - 0.059\ 16 \log\left(\frac{[Fe^{2+}]}{[Fe^{3+}]}\right)$$

$$E_+ = 1.70 - 0.059\ 16 \log\left(\frac{[Ce^{3+}]}{[Ce^{4+}]}\right)$$

$$2E_+ = 0.767 + 1.70 - 0.059\ 16 \log\left(\frac{[Fe^{2+}]}{[Fe^{3+}]}\right) - 0.059\ 16 \log\left(\frac{[Ce^{3+}]}{[Ce^{4+}]}\right)$$

$$2E_+ = 2.46_7 - 0.059\ 16 \log\left(\frac{[Fe^{2+}][Ce^{3+}]}{[Fe^{3+}][Ce^{4+}]}\right)$$

But, because $[Ce^{3+}] = [Fe^{3+}]$ and $[Ce^{4+}] = [Fe^{2+}]$ at the equivalence point,

→ the ratio of concentrations in the log term is ***unity***.

→ Therefore, the logarithm is 0

# 16.1 The shape of a redox titration curve

$$2E_+ = 2.46_7 - 0.059\ 16 \log\left(\frac{[Fe^{2+}][Ce^{3+}]}{[Fe^{3+}][Ce^{4+}]}\right)$$

$$2E_+ = 2.46_7\ \text{V} \Rightarrow E_+ = 1.23\ \text{V}$$

The cell voltage is

$$E = E_+ - E(\text{calomel}) = 1.23 - 0.241 = 0.99\ \text{V}$$

In this particular titration,

→ the equivalence-point voltage is independent of the concentrations and volumes of the reactants.

# 16.1 The shape of a redox titration curve

## Region 3: After the Equivalence Point

Now virtually all iron atoms are $Fe^{3+}$.

The moles of $Ce^{3+}$ equal the moles of $Fe^{3+}$

There is a known excess of unreacted $Ce^{4+}$.

At the Pt electrode:

$$E = E_+ - E(\text{calomel}) = \left[1.70 - 0.059\,16 \log\left(\frac{[Ce^{3+}]}{[Ce^{4+}]}\right)\right] - 0.241$$

# 16.1 The shape of a redox titration curve

The calculations above allow us to plot the titration curve in Figure 16-2, which shows potential as a function of the volume of added titrant.

The equivalence point is marked by a steep rise in voltage.

**See Figure 16-2**

# 16.1 The shape of a redox titration curve

**EXAMPLE** **Potentiometric Redox Titration**

Suppose that we titrate 100.0 mL of 0.050 0 M $Fe^{2+}$ with 0.100 M $Ce^{4+}$, using the cell in Figure 16-1. The equivalence point occurs when $V_{Ce^{4+}} = 50.0$ mL. Calculate the cell voltage at 36.0, 50.0, and 63.0 mL.

**Solution** *At 36.0 mL:* This is 36.0/50.0 of the way to the equivalence point. Therefore, 36.0/50.0 of the iron is in the form $Fe^{3+}$ and 14.0/50.0 is in the form $Fe^{2+}$. Putting $[Fe^{2+}]/[Fe^{3+}] = 14.0/36.0$ into Equation 16-6 gives $E = 0.550$ V.

*At 50.0 mL:* Equation 16-11 tells us that the cell voltage at the equivalence point is 0.99 V, regardless of the concentrations of reagents for this particular titration.

*At 63.0 mL:* The first 50.0 mL of cerium were converted into $Ce^{3+}$. There is an excess of 13.0 mL of $Ce^{4+}$, so $[Ce^{3+}]/[Ce^{4+}] = 50.0/13.0$ in Equation 16-12, and $E = 1.424$ V.

**TEST YOURSELF** Find $E$ at $V_{Ce^{4+}} = 20.0$ and 51.0 mL (***Answer:*** 0.516, 1.358 V)

# Analytical Chemistry

## Chapter 23. Introduction to Analytical Separations

- In the vast majority of real analytical problems,
  → we must separate, identify, and measure one or more components from a complex mixture.

- This chapter discusses
  → fundamentals of analytical separations.

- The next chapters describe
  → various chromatography methods based on analytical separations.

## 23.1 Solvent Extraction

- **Extraction**

  → the transfer of a solute from one phase to another.

- Common reasons to carry out an extraction in analytical chemistry

  → to isolate or concentrate the desired analyte

  → or to separate it from species that would interfere in the analysis.

- The most common case

  → the extraction of **an aqueous solution with an organic solvent**.

- When aqueous and organic solvents are mixed in any ratio.

  → Two liquids are miscible if they form a single phase

  → Immiscible liquids remain in separate phases.

**See Figure 23-1**

- Organic solvents with low polarity

  → generally immiscible with water, which is highly polar.

- Diethyl ether, toluene, and hexane

  → common solvents that are immiscible with and less dense than water.

  → They form a separate phase that floats on top of the aqueous phase.

- Chloroform, dichloromethane, and carbon tetrachloride

  → common solvents that are denser than water.

- A more realistic treatment

→ considers that most liquids are partially soluble in each other

**See Figure 23-1**

- For simplicity,

→ we assume that the two phases are not soluble in each other.

- Suppose that solute S is partitioned between phases 1 and 2, as depicted in Figure 23-1.
- The **partition coefficient, K**: the equilibrium constant for the reaction.

$$\mathrm{S\ (in\ phase\ 1)} \rightleftharpoons \mathrm{S\ (in\ phase\ 2)}$$

*Partition coefficient:*

$$K = \frac{\mathcal{A}_{S_2}}{\mathcal{A}_{S_1}} \approx \frac{[S]_2}{[S]_1}$$

$$\text{S (in phase 1)} \rightleftharpoons \text{S (in phase 2)}$$

*Partition coefficient:*

$$K = \frac{\mathcal{A}_{S_2}}{\mathcal{A}_{S_1}} \approx \frac{[S]_2}{[S]_1}$$

- $A_{S1}$ : the activity of solute in phase 1.
- Lacking knowledge of the activity coefficients,

  → we will write the partition coefficient in terms of concentrations.
- The larger the partition coefficient,

  → the less solute remains in phase 1.

- Suppose that solute S in $V_1$ mL of solvent 1 (water) is extracted with $V_2$ mL of solvent 2 (toluene).

  → m: the moles of S in the system

  → q: the fraction of S remaining in phase 1 at equilibrium.

  → The molarity in phase 1 = $qm/V_1$.

- The fraction of total solute transferred to phase 2 = (1 – q),

  → the molarity in phase 2 = (1 – q)m/$V_2$.

  → Therefore,

$$K = \frac{[\mathrm{S}]_2}{[\mathrm{S}]_1} = \frac{(1-q)m/V_2}{qm/V_1}$$

- From which we can solve for q:

$$\text{Fraction remaining in phase 1 after 1 extraction} = q = \frac{V_1}{V_1 + KV_2}$$

- The equation above says that

  → the fraction of solute remaining in the water (phase 1) depends on the **partition coefficient** and the **volumes**.

- If the phases are separated and fresh toluene (solvent 2) is added,

  → the fraction of solute remaining in the water at equilibrium will be

$$\text{Fraction remaining in phase 1 after 2 extractions} = q \cdot q = \left(\frac{V_1}{V_1 + KV_2}\right)^2$$

- After n extractions, each with volume $V_2$,

  → the fraction remaining in the water is

$$\text{Fraction remaining in phase 1 after } n \text{ extractions} = q^n = \left(\frac{V_1}{V_1 + KV_2}\right)^n$$

- Example:

  → If q = ¼ , then ¼ of the solute remains in phase 1 after one extraction.

  → A second extraction reduces the concentration to (¼)(¼) = $^1/_{16}$ of initial concentration.

## pH Effects

- If a solute is in acid or base,
  → its charge changes as the pH is changed.

- Usually, a neutral species is more soluble in an organic solvent;
  a charged species is more soluble in aqueous solution.

- Consider a basic amine whose neutral form, B, has partition coefficient K between aqueous phase 1 and organic phase 2.

$$K = [\mathrm{B}]_2/[\mathrm{B}]_1$$

- Suppose that the conjugate acid, $BH^+$, is soluble only in aqueous phase 1.
- Its acid dissociation constant, $K_a$

$$K_a = [\mathrm{H}^+][\mathrm{B}]_1/[\mathrm{BH}^+]_1$$

- The **distribution coefficient**, D, is defined as

*Distribution coefficient:*

$$D = \frac{\text{total concentration in phase 2}}{\text{total concentration in phase 1}}$$

$$D = \frac{[\mathrm{B}]_2}{[\mathrm{B}]_1 + [\mathrm{BH}^+]_1}$$

$$K = [\mathrm{B}]_2/[\mathrm{B}]_1$$

$$K_a = [\mathrm{H}^+][\mathrm{B}]_1/[\mathrm{BH}^+]_1$$

*Distribution of base between two phases:*

$$D = \frac{K \cdot K_a}{K_a + [\mathrm{H}^+]} = K \cdot \alpha_B \qquad \alpha_B = \frac{[\mathrm{B}]_{aq}}{[\mathrm{B}]_{aq} + [\mathrm{BH}^+]_{aq}}$$

→ where $\alpha_B$ is the fraction of weak base in the neutral form, B, in the aqueous phase.

*Distribution of base between two phases:*

$$D = \frac{K \cdot K_a}{K_a + [H^+]} = K \cdot \alpha_B$$

- The distribution coefficient D is used in place of the partition coefficient K in the equation below

  → when dealing with a species that has more than one chemical form, such as B and $BH^+$.

$$q = \frac{V_1}{V_1 + KV_2}$$

- Charged species tend to be more soluble in water than in organic solvent.

- To extract a base into water,

  → use a pH low enough to convert B into $BH^+$.

- To extract the acid HA into water,

  → use a pH high enough to convert HA into $A^-$.

**See Figure 23-2**

## EXAMPLE Effect of pH on Extraction

Suppose that the partition coefficient for an amine, B, is $K = 3.0$ and the acid dissociation constant of $BH^+$ is $K_a = 1.0 \times 10^{-9}$. If 50 mL of 0.010 M aqueous amine are extracted with 100 mL of solvent, what will be the formal concentration remaining in the aqueous phase **(a)** at pH 10.00 and **(b)** at pH 8.00?

**Solution** **(a)** At pH 10.00, $D = KK_a/(K_a + [H^+]) = (3.0)(1.0 \times 10^{-9})/(1.0 \times 10^{-9} + 1.0 \times 10^{-10}) = 2.73$. *Using D in place of K*, Equation 22-2 says that the fraction remaining in the aqueous phase is

$$q = \frac{50}{50 + (2.73)(100)} = 0.15 \Rightarrow 15\% \text{ left in water}$$

The concentration of amine in the aqueous phase is 15% of 0.010 M = 0.001 5 M.

**(b)** At pH 8.00, $D = (3.0)(1.0 \times 10^{-9})/(1.0 \times 10^{-9} + 1.0 \times 10^{-8}) = 0.273$. Therefore,

$$q = \frac{50}{50 + (0.273)(100)} = 0.65 \Rightarrow 65\% \text{ left in water}$$

The concentration in the aqueous phase is 0.006 5 M. At pH 10, the base is predominantly in the form B and is extracted into the organic solvent. At pH 8, it is in the form $BH^+$ and remains in the water.

8th edition

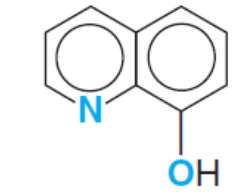
## Extraction with a Metal Chelator

- Most complexes that can be extracted into organic solvents
  → neutral.

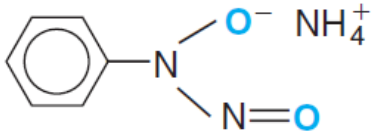
- Charged complexes, such as $Fe(EDTA)^-$ or $Fe(1,10\text{-phenanthroline})_3^{2+}$,
  → not very soluble in organic solvents.

- One scheme for separating metal ions from one another
  → to selectively complex one ion with an organic ligand
  → and extract it into an organic solvent.

- Dithizone, 8-hydroxyquinoline, and cupferron
  → Common ligands.
  → Each is a weak acid, HL, which loses a proton when it binds to a metal ion through atoms shown in bold type.



8-Hydroxyquinoline
(oxine)



Cupferron

$$HL(aq) \rightleftharpoons H^+(aq) + L^-(aq) \qquad K_a = \frac{[H^+]_{aq}[L^-]_{aq}}{[HL]_{aq}}$$

$$nL^-(aq) + M^{n+}(aq) \rightleftharpoons ML_n(aq) \qquad \beta = \frac{[ML_n]_{aq}}{[M^{n+}]_{aq}[L^-]^n_{aq}}$$

- Each ligand can react with many different metal ions,
  → but some selectivity is achieved by controlling the pH.

- Let's derive an equation for the
  distribution coefficient of a metal
  between two phases when
  → essentially all the metal in the
  aqueous phase (aq) is in the form
  $M^{n+}$
  → all the metal in the organic
  phase (org) is in the form $ML_n$

**See Figure 23-3**

- We define the **partition coefficients** for ligand and complex as follows:

$$\mathrm{HL}(aq) \rightleftharpoons \mathrm{HL}(org) \qquad K_{\mathrm{L}} = \frac{[\mathrm{HL}]_{\mathrm{org}}}{[\mathrm{HL}]_{\mathrm{aq}}}$$

$$\mathrm{ML}_n(aq) \rightleftharpoons \mathrm{ML}_n(org) \qquad K_{\mathrm{M}} = \frac{[\mathrm{ML}_n]_{\mathrm{org}}}{[\mathrm{ML}_n]_{\mathrm{aq}}}$$

- The distribution coefficient we seek is

$$D = \frac{[\text{total metal}]_{\mathrm{org}}}{[\text{total metal}]_{\mathrm{aq}}} \approx \frac{[\mathrm{ML}_n]_{\mathrm{org}}}{[\mathrm{M}^{n+}]_{\mathrm{aq}}}$$

$$K_{\mathrm{M}} = \frac{[\mathrm{ML}_n]_{\mathrm{org}}}{[\mathrm{ML}_n]_{\mathrm{aq}}}$$

$$\beta = \frac{[\mathrm{ML}_n]_{\mathrm{aq}}}{[\mathrm{M}^{n+}]_{\mathrm{aq}}[\mathrm{L}^-]_{\mathrm{aq}}^n}$$

$$[\mathrm{ML}_n]_{\mathrm{org}} = K_{\mathrm{M}}[\mathrm{ML}_n]_{\mathrm{aq}} = K_{\mathrm{M}}\beta[\mathrm{M}^{n+}]_{\mathrm{aq}}[\mathrm{L}^-]_{\mathrm{aq}}^n$$

$$K_{\mathrm{a}} = \frac{[\mathrm{H}^+]_{\mathrm{aq}}[\mathrm{L}^-]_{\mathrm{aq}}}{[\mathrm{HL}]_{\mathrm{aq}}}$$

$$[ML_n]_{org} = \frac{K_M \beta [M^{n+}]_{aq} K_a^n [HL]_{aq}^n}{[H^+]_{aq}^n}$$

$$D = \frac{[\text{total metal}]_{org}}{[\text{total metal}]_{aq}} \approx \frac{[ML_n]_{org}}{[M^{n+}]_{aq}}$$

$$D \approx \frac{K_M \beta K_a^n [HL]_{aq}^n}{[H^+]_{aq}^n}$$

$$K_L = \frac{[HL]_{org}}{[HL]_{aq}}$$

- Because most HL is in the organic phase,

  → we substitute $[HL]_{aq} = [HL]_{org}/K_L$ to produce the most useful expression for the distribution coefficient:

*Distribution of metal-chelate complex between phases:*

$$D \approx \frac{K_M \beta K_a^n}{K_L^n} \frac{[HL]_{org}^n}{[H^+]_{aq}^n}$$

- We see that the **distribution coefficient** for metal ion extraction

  → depends on **pH** and **ligand concentration**.

**See Figure 23-4**

$$D \approx \frac{K_M \beta K_a^n}{K_L^n} \frac{[HL]_{org}^n}{[H^+]_{aq}^n}$$

- It is often possible to select a pH
  → where D is large for one metal and small for another.

- For example, Figure 23-4 shows that $Cu^{2+}$ could be separated from $Pb^{2+}$ and $Zn^{2+}$ by extraction with dithizone at pH 5.

## 23.2 What Is Chromatography?

- Chromatography operates on the same principle as extraction,
  → but one phase is held in place while the other moves past it.

- Figure 23-5 shows a solution containing solutes A and B placed on top of a column packed with solid particles and filled with solvent.

**See Figure 23-5**

- When the outlet is opened,
  → solutes A and B flow down into the column.

- Fresh solvent is then applied to the top of the column and the mixture is washed down the column by continuous solvent flow.

- If solute A is more strongly adsorbed than solute B on the solid particles,
  → then solute A spends a smaller fraction of the time free in solution.

- Solute A moves down the column more slowly than solute B and emerges at the bottom after solute B.

- We have just separated a mixture into its components by chromatography.

- The mobile phase (the solvent moving through the column) in chromatography
  → either a liquid or a gas.

- The stationary phase (the one that stays in place inside the column)
  → most commonly a viscous liquid chemically bonded to the inside of a capillary tube or onto the surface of solid particles packed in the column.
  → alternatively, the solid particles themselves may be the stationary phase.

- In any case, the partitioning of solutes between mobile and stationary phases
  → gives rise to separation.

- Fluid entering the column

  → called **eluent**.

- Fluid emerging from the end of the column

  → called **eluate**:


- The process of passing liquid or gas through a chromatography column

  → called **elution**.

- Columns are either ***packed*** or ***open tubular***.

  1) A packed column → filled with particles of stationary phase

  2) An open tubular column

     → a narrow, hollow capillary with stationary phase coated on the inside walls.

## Types of Chromatography

- Chromatography is divided into categories

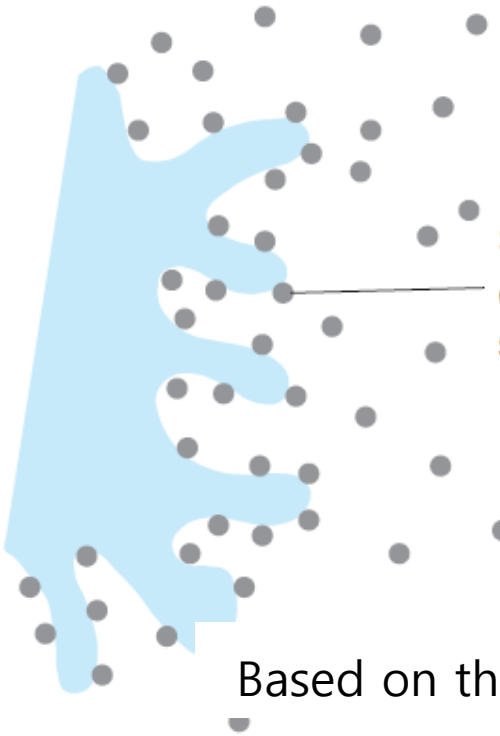
  → on the basis of the mechanism of interaction of the solute with the stationary phase

### 1) Adsorption chromatography

- A solid stationary phase;
  a liquid or gaseous mobile phase.

- Solute is adsorbed on the surface of the solid particles.

- The more strongly a solute is adsorbed, the slower it travels through the column.




Based on the "**adsorption**"

Adsorption chromatography

## 2) Partition chromatography

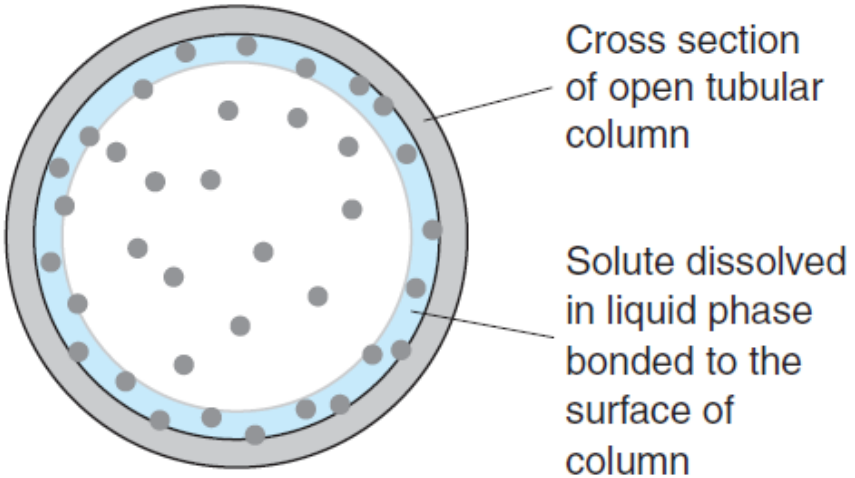
- A liquid stationary phase is bonded to a solid surface,

  → which is typically the inside of the silica ($SiO_2$) chromatography column in gas chromatography.

- Solute equilibrates between the stationary liquid and the mobile phase,

  → which is a flowing gas in gas chromatography.

Based on the "**solubility**"



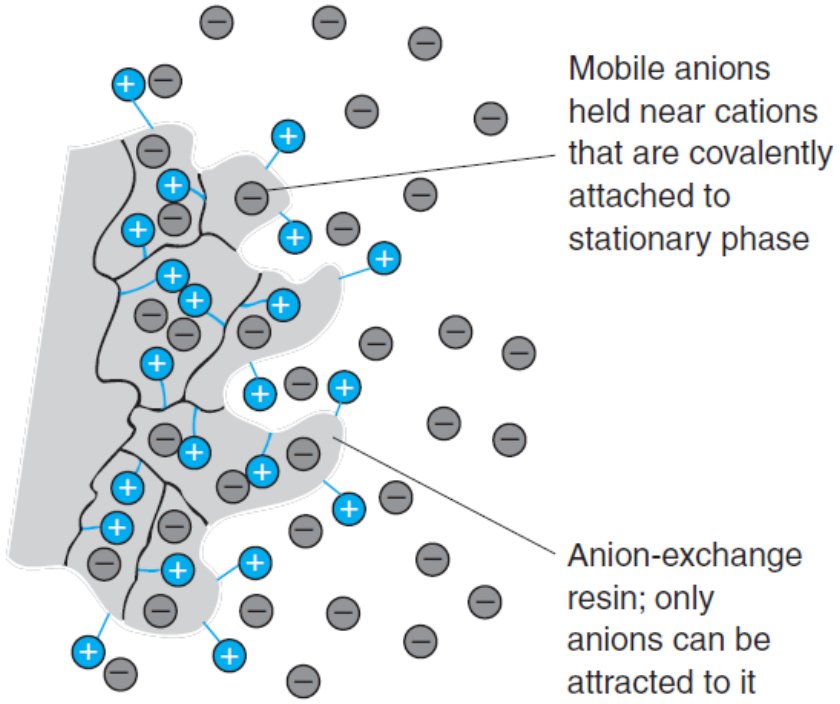

Partition chromatography

## 3) Ion-exchange chromatography

- Anions such as $-SO_3^-$ or cations such as $-N(CH_3)_3^+$
  → covalently attached to the stationary solid phase, usually a resin.

- Solute ions of the opposite charge
  → attracted to the stationary phase.

- The mobile phase
  → liquid.




Ion-exchange chromatography

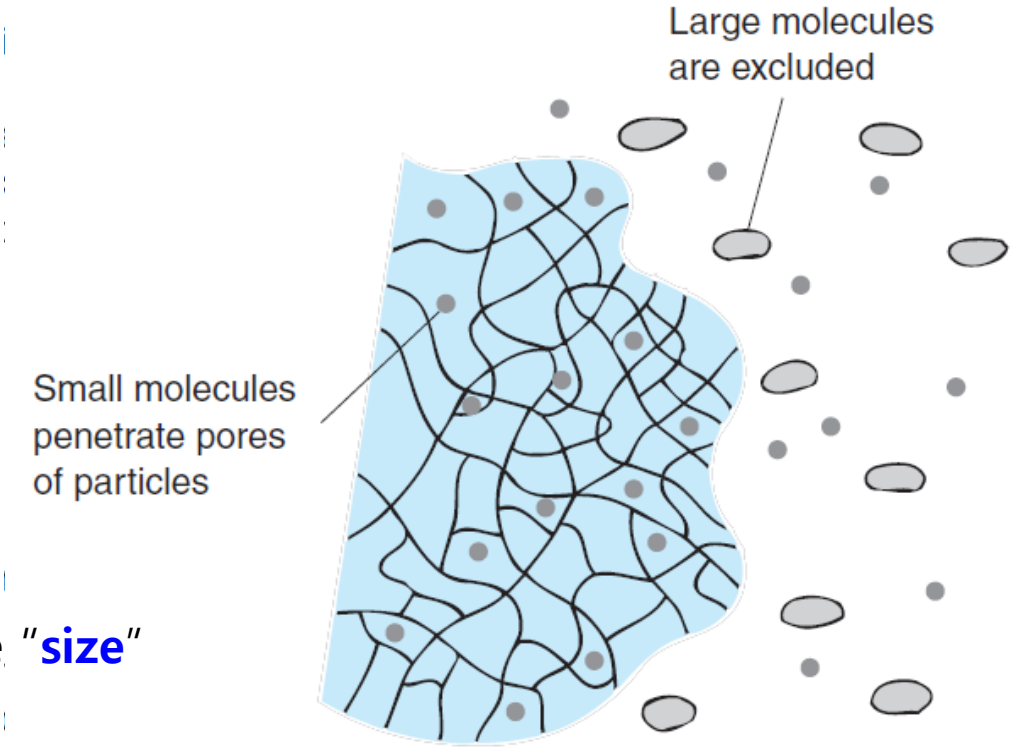
Based on the "**electrostatic interaction**"

## 4) Molecular exclusion chromatography

- Also called size exclusion, gel filtration, or gel permeation chromatography
- This technique separates molecules by size,

  → with the larger solutes passing through most quickly.

Based on the "**size**"




Molecular exclusion chromatography

- In the ideal case of molecular exclusion,
  → there is no attractive interaction between the stationary phase and the solute.

- Rather, the liquid or gaseous mobile phase passes through a porous gel.

- The pores are small enough to exclude large solute molecules
  → but not small ones.

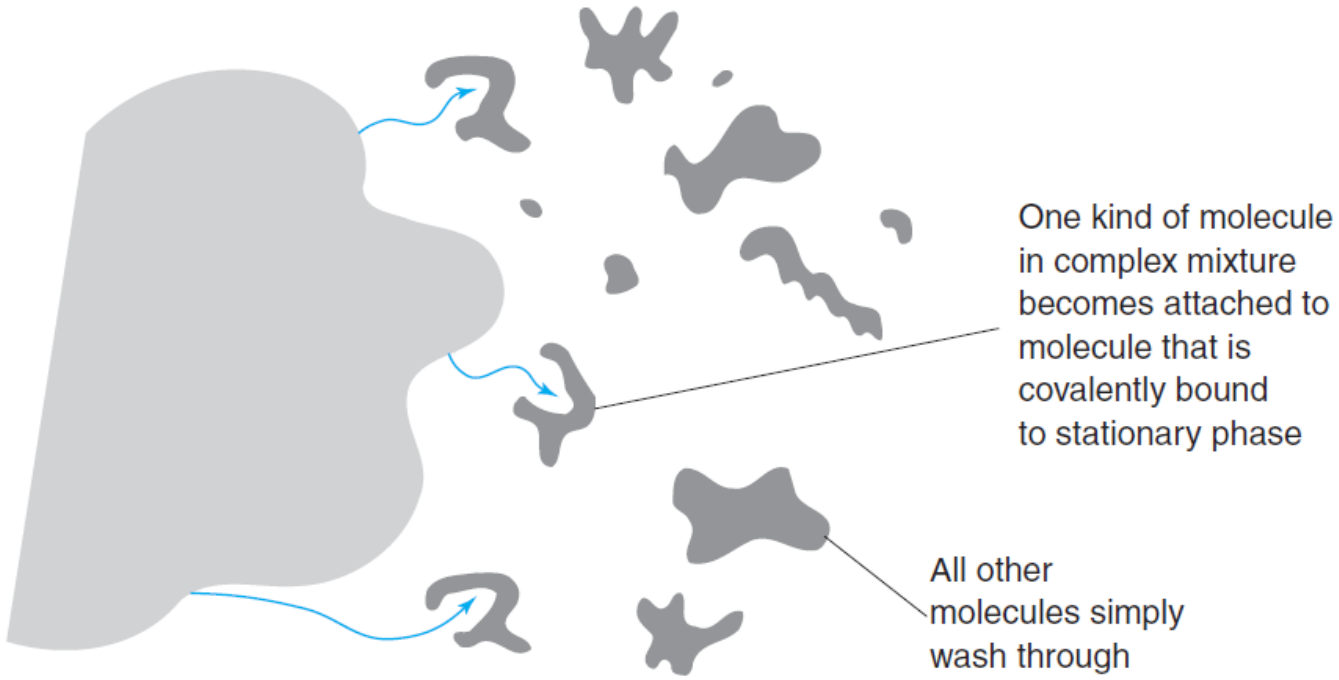
- Large molecules stream past without entering the pores.

- Small molecules take longer to pass through the column
  → because they enter the gel and therefore must flow through a larger volume before leaving the column.

## 5) Affinity chromatography

- This most selective kind of chromatography

  → employs specific interactions between one kind of solute molecule and a second molecule that is covalently attached (immobilized) to the stationary phase.




Affinity chromatography

- For example,

  → the immobilized molecule might be an antibody to a particular protein.

- When a mixture containing a thousand proteins is passed through the column,

  → only the one protein that reacts with the antibody binds to the column.

- After all other solutes have been washed from the column,

  → the desired protein is dislodged by changing the pH or ionic strength.

## 22.3 A Plumber's View of Chromatography

- The speed of the mobile phase passing through a chromatography column is expressed
  → either i) as a volume flow rate
  or ii) as a linear flow rate.

- The volume flow rate
  → tells how many milliliters of solvent per minute travel through the column.

- The linear flow rate
  → tells how many centimeters are traveled in 1 min by the solvent.