Introduction to Bioelectronics

Spring 2023

Instructors: Prabhakar B

Half-semester course (13 lectures)

General Logistics

- 13 lectures: roughly half theory / background and half lab
- Classroom H101; Tuesday + Friday @ 10:05am-11:30am
- TA: Niteesh
- Grading (will finalize this, but approximately):
  - 25% quizzes + assignments
  - 35% lab work
  - 40% endsem
- Books
  - Introductory Bioelectronics by Pethig & Smith

Theory part: outline

1) Chemistry and biology concepts relevant for bioelectronics

2) Spectroscopy: basic concepts, transitions. Applications.

3) Electrochemistry: Cells. Electrodes and reactions at electrodes.

4) Biosensing: concepts and applications

Basic Chemical and Biochemical Concepts

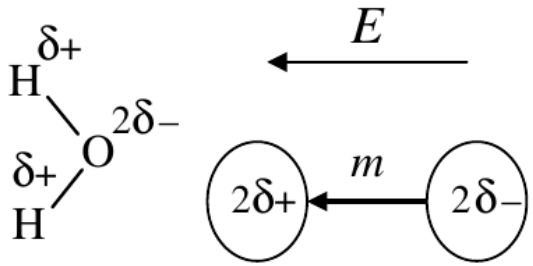
- Atoms
- Molecules:
  - Chemical bonding
  - Nonbonding interactions
    - Nonpolar, polar and ionic bonds
    - Van der Waals Attractions
- Chemical reactions
  - breaking or forming bonds
  - Chemical equilibrium: K_{eq}
  - Free energy associated with chemical reaction

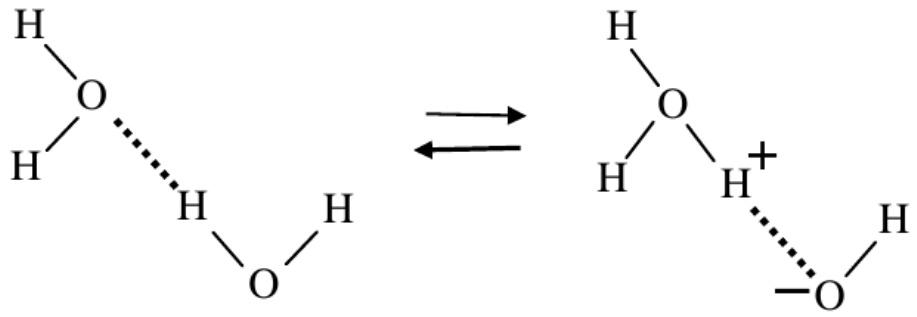
Table 2.1 Approximate chemical composition of a typical bacterium and mammalian cell. (Adapted from Alberts *et al.* [1])

Chemical component	Percentage of total cell weight	
	Bacterium	Animal cell
Water	70	70
Inorganic ions (e.g. Na^{+}, K^{+}, Mg^{2+}, Ca^{2+}, Cl^{2-})	1	1
Amino acids, nucleotides, and other small molecules	1	1
Metabolites (e.g. glucose, fatty acids)	2	2
Macromolecules (proteins, nucleic acids, polysaccharides)	24	21
Lipids	2	5

Major chemical components and interactions

- Water and hydrogen bonds



- 

Transient H-bond formations in water

- Acids, bases and pH

Table 1.8 Acids and Bases

Acids		Bases	
Hydrochloric	$HCl \leftrightarrow H^+ + Cl^-$	Ammonia	$NH_3 + H^+ \leftrightarrow NH_4^+$
Carbonic	$H_2CO_3 \leftrightarrow H^+ + HCO_3^-$	Caustic soda	$NaOH + H^+ \leftrightarrow Na^+ + H_2O$
Acetic	$CH_3COOH \leftrightarrow CH_3\,COO^- + H^+$	Phosphate	$HPO_4^{2-} + H^+ \leftrightarrow H_2PO_4^-$
Water	$H_2O \leftrightarrow H + OH^-$	Water	$H_2O + H^+ \leftrightarrow H_3O^+$

- Law of mass action:

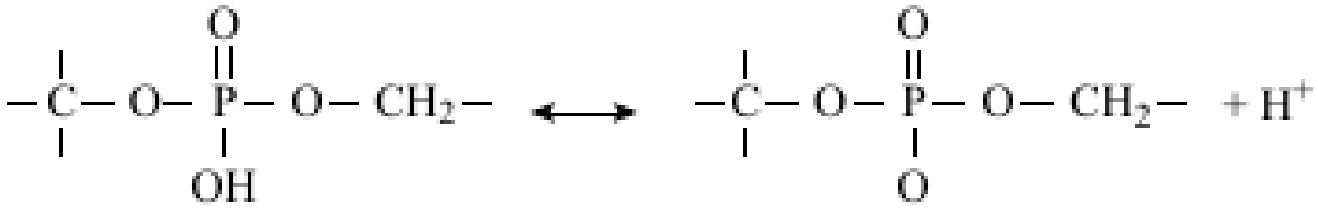
$$\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{A}' + \mathrm{B}'$$

$$K = \frac{[A']^{\alpha'}[B']^{\beta'}\ldots}{[A]^{\alpha}[B]^{\beta}\ldots}$$

$$\mathrm{HA} \rightarrow \mathrm{H}^+ + \mathrm{A}^-$$ and $$2\mathrm{H_2O} \leftrightarrow \mathrm{H_3O}^+ + \mathrm{OH}^-$$

Henderson-Hasselbach equation

$$pH = pK_a + \log\frac{[proton\ acceptor]}{[proton\ donor]}$$



pK_a for the dissociation of the OH proton in DNA and RNA is ~3.0,

$$1^{st}\ \text{Dissociation}: \quad H_3PO_4 \leftrightarrow H_2PO_4^- + H^+ \quad (pK_a = 2.1)$$
$$2^{nd}\ \text{Dissociation}: \quad H_2PO_4^- \leftrightarrow HPO_4^{2-} + H^+ \quad (pK_a = 7.2)$$
$$3^{rd}\ \text{Dissociation}: \quad HPO_4^{2-} \leftrightarrow PO_4^{3-} + H^+ \quad (pK_a = 12.7).$$

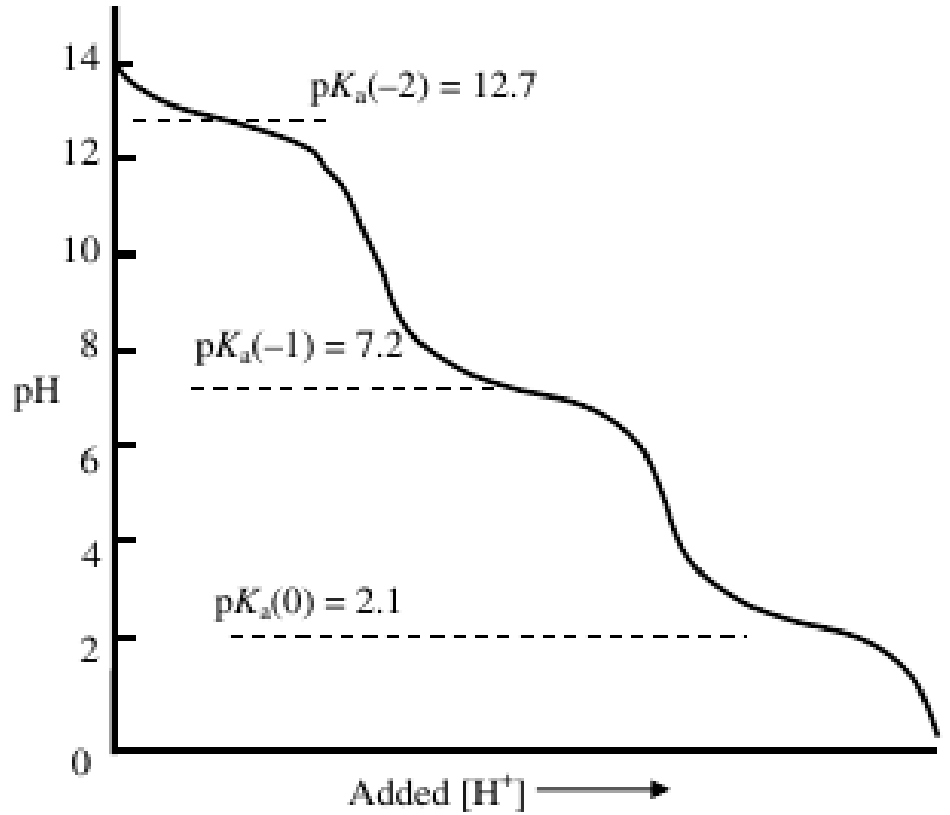


Figure 1.6 The titration curve for phosphoric acid (H_3PO_4) at 298 K, as a function of an added acid. As discussed in the text, the greatest buffering capacity of a conjugate acid-base system is obtained when pH = pK.

Table 2.1 Approximate chemical composition of a typical bacterium and mammalian cell. (Adapted from Alberts *et al.* [1])

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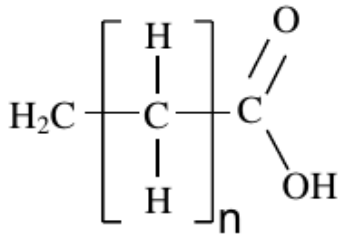
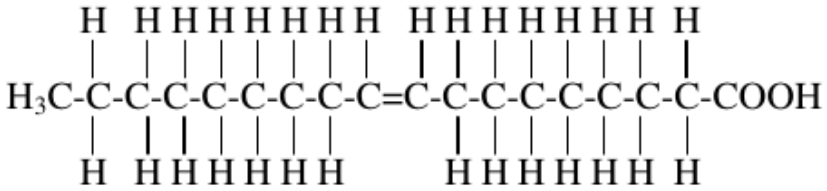
Fatty acids



Chemical structure of saturated fatty acids



Oleic acid

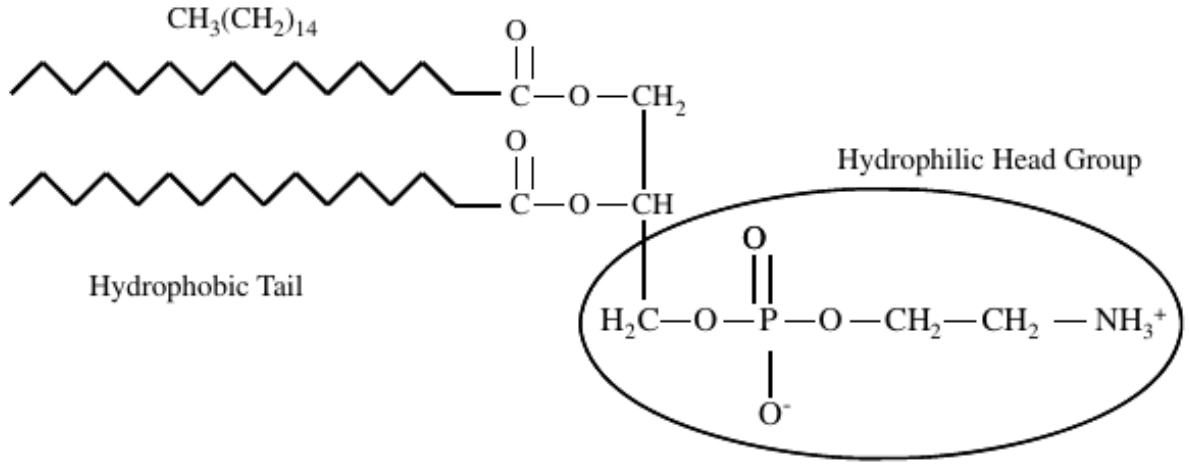


Figure 2.1 The chemical structure of a typical phospholipid (in this case phosphatidylethanolamine) to show its hydrophobic tail and hydrophilic head group.

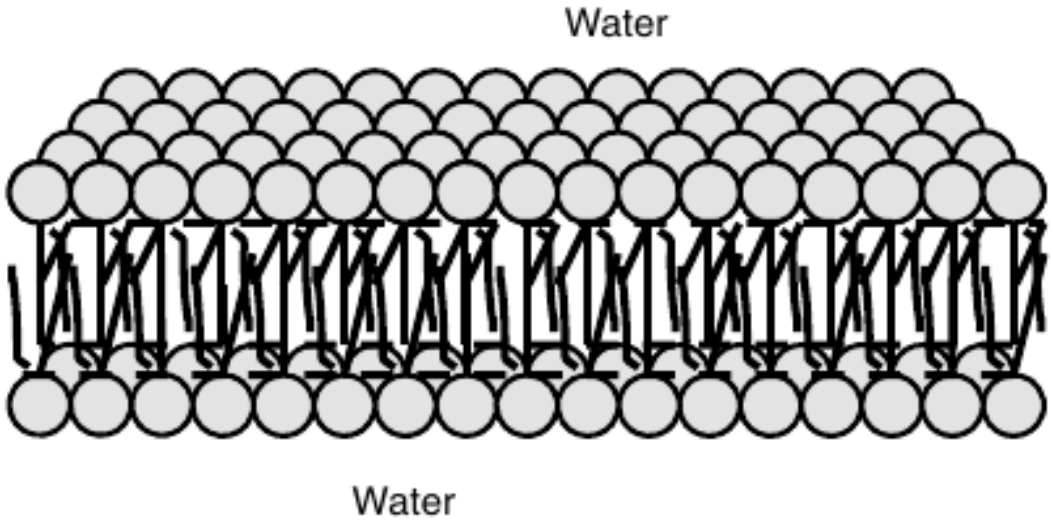


Figure 2.2 Schematic representation of a phospholipid bilayer. The small spheres represent the hydrophilic heads groups, and the lines are the hydrophobic hydrocarbon tails of individual phospholipid molecules.

Fatty acids:
1) precursors to phospholipids forming outer membrane of cell;
2) Important source of energy stored in adipocytes (fat cells)

Carbohydrates & Sugars

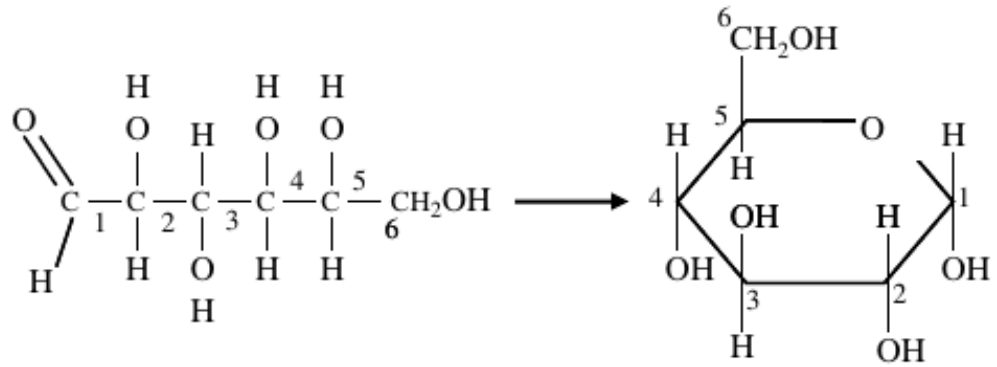
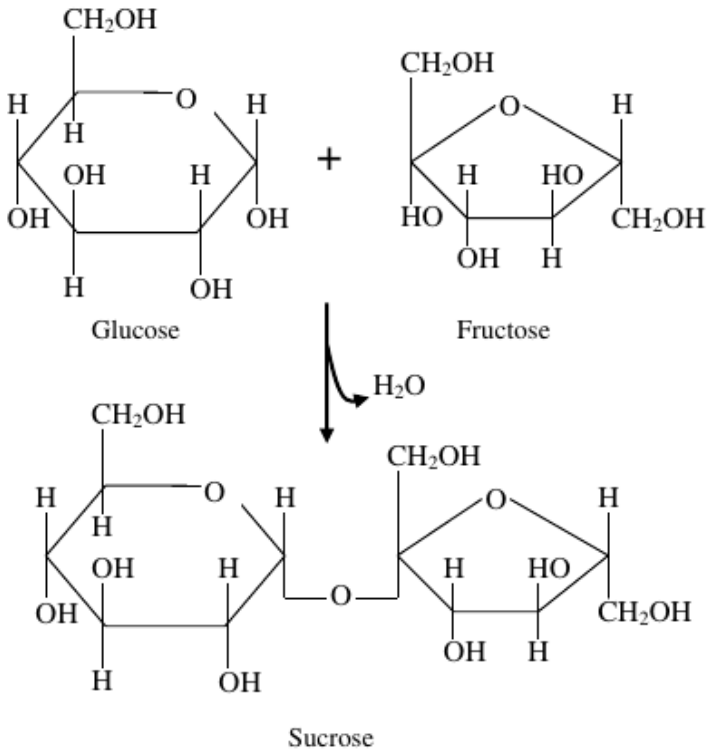


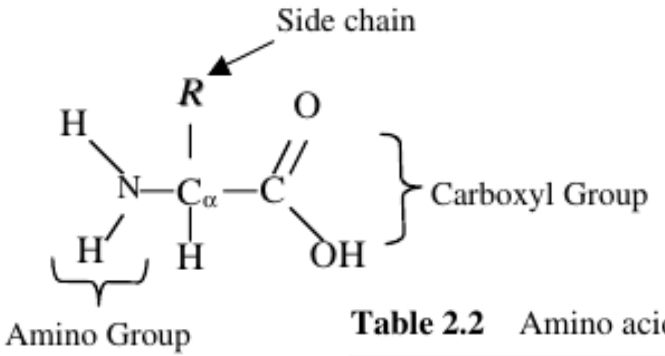
Figure 2.4 The linear and ring form of D-Glucose.



Formation of sucrose from the condensation reaction of glucose with fructose

- Monosaccharide, disaccharide and trisaccharides
- Polysaccharides: hundreds/thousands of sugar subunits,
  - act as energy stores (glycogen in liver)
  - Major component in connective tissue, mucus, slime
  - Cell wall of plants: cellulose is a polysccharide of glucose
  - Attachment to proteins/lipids: solubility of proteins and hence functioning of proteins
  - Blood groups: oligosaccharides linked surface proteins of Red Blood Cells

Aminoacids, polypeptides, proteins



1) Major workhorse of cells (proteins)
2) 20 kinds based on side chain
3) Chiral center only L form is common

Table 2.2 Amino acids with hydrophobic (nonpolar) side chains *R*

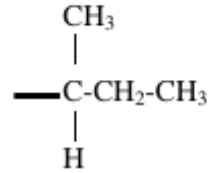
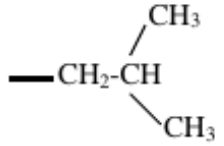
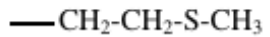
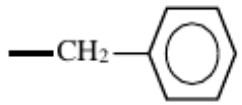
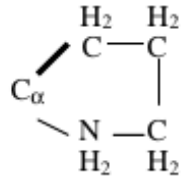
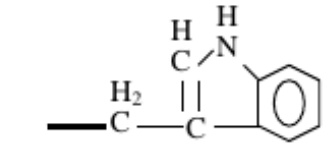
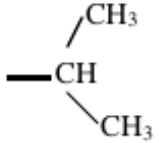
Amino acid	Side chain structure *R*	Amino Acid	Side Chain Structure *R*
Alanine (Ala)	—CH_3	Isoleucine (Ile)	
Leucine (Leu)		Methionine (Met)	
Phenylalanine (Phe)		Proline (Pro)	
Tryptophan (Trp)		Valine (Val)	

Table 2.3 Amino acids with hydrophilic (uncharged, polar) side chains *R*

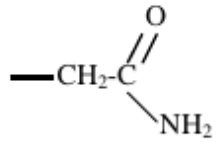
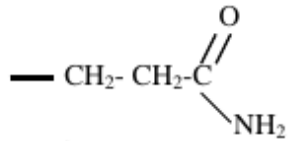
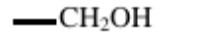
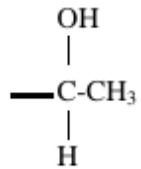
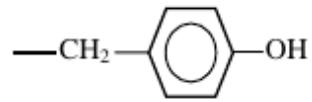
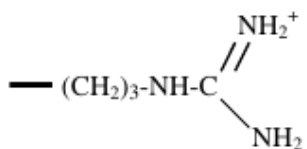
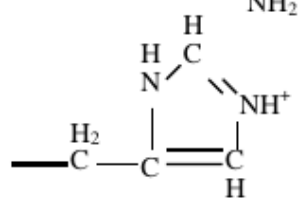
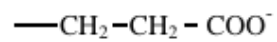
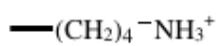
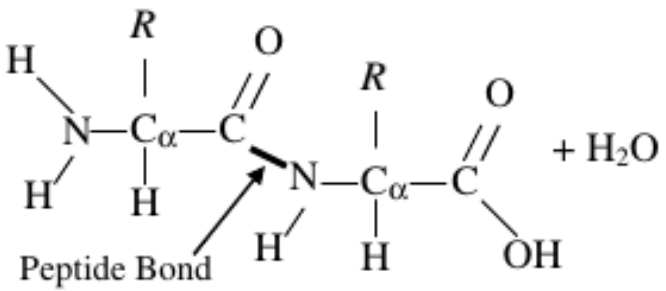
Amino acid	Side chain structure *R*	Amino acid	Side chain structure *R*
Asparagine (Asn)		Cysteine (Cys)	
		Glycine (Gly)	
Glutamine (Gln)		Serine (Ser)	
Threonine (Thr)		Tyrosine (Tyr)	

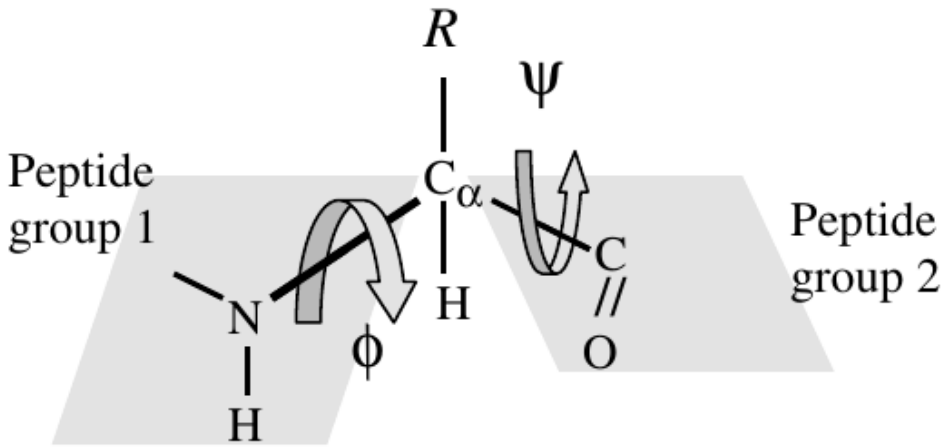
Table 2.4 Amino acids with hydrophilic (charged) side chains *R*

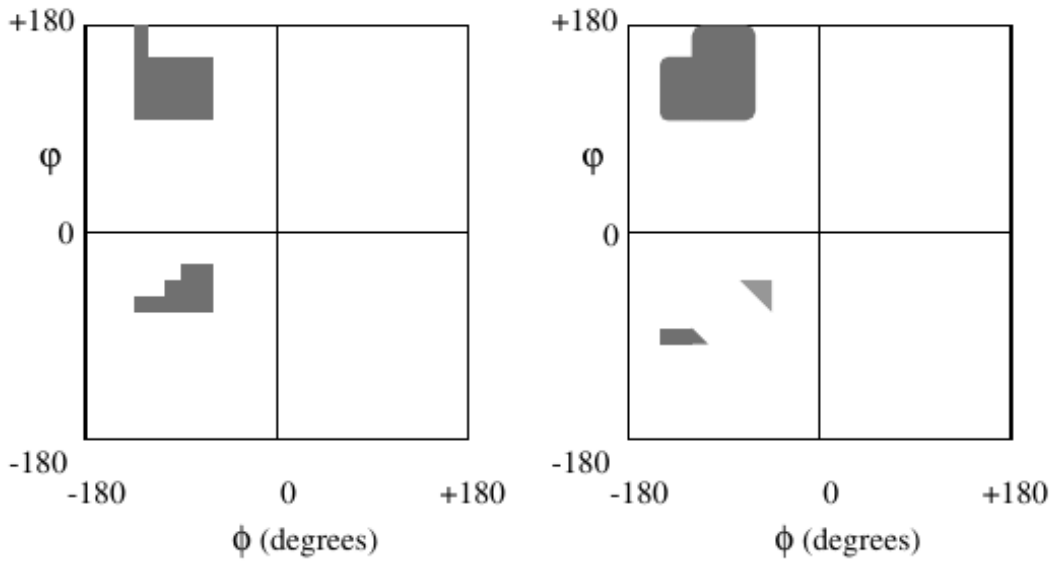
Amino acid	Side chain structure *R*	Amino acid	Side chain structure *R*
	Positively charged (pH < pK)		Negatively charged (pH > pK)
Arginine (Arg) pK ~ 12		Aspartic acid (Asp) pK ~ 4.7	
Histidine (His) pK ~ 6.5		Glutamic acid (Glu) pK ~ 4.7	
Lysine (Lys) pK ~ 10.2			

Peptides, proteins



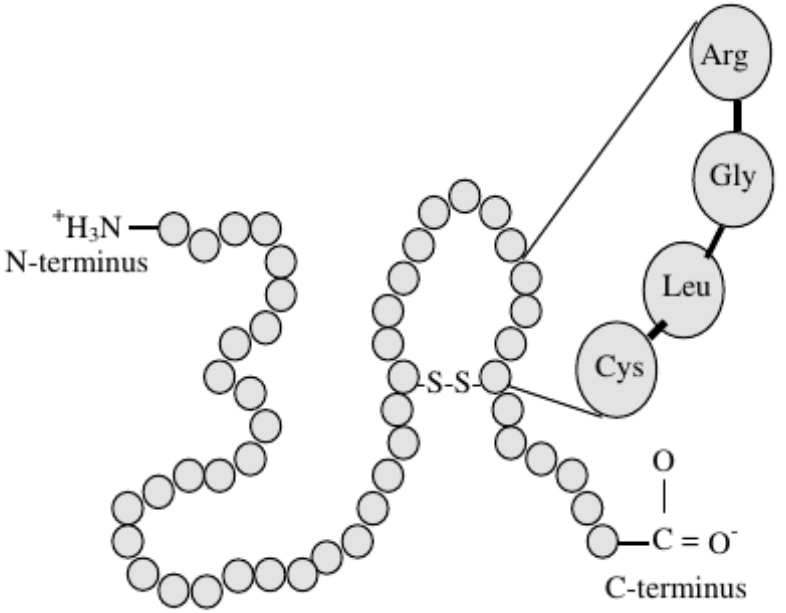
Formation of a Peptide Bond between two Amino Acids and release of water





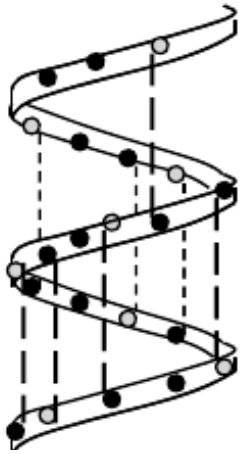
Ramachandran plots to show (left) the permissible conformations of valine and isoleucine

Proteins

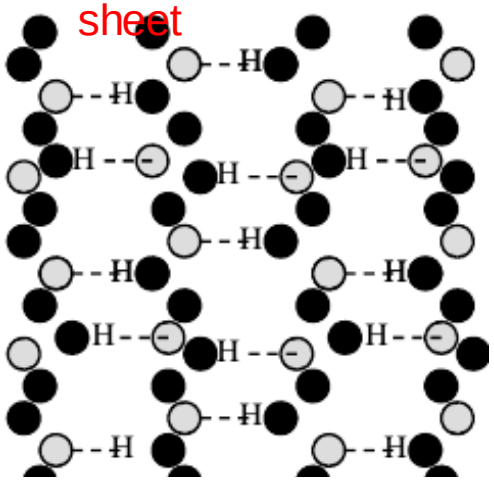


- Primary structure
  - Basically sequence
- Secondary Structure
  - Local structures
  - Alpha helix, beta sheet, loops (next slide)
- Tertiary structure
  - 3D structure of molecule, spatial arrangement, S-S bonds
- Quaternary structure
  - Multiple domains, Protein complexes,

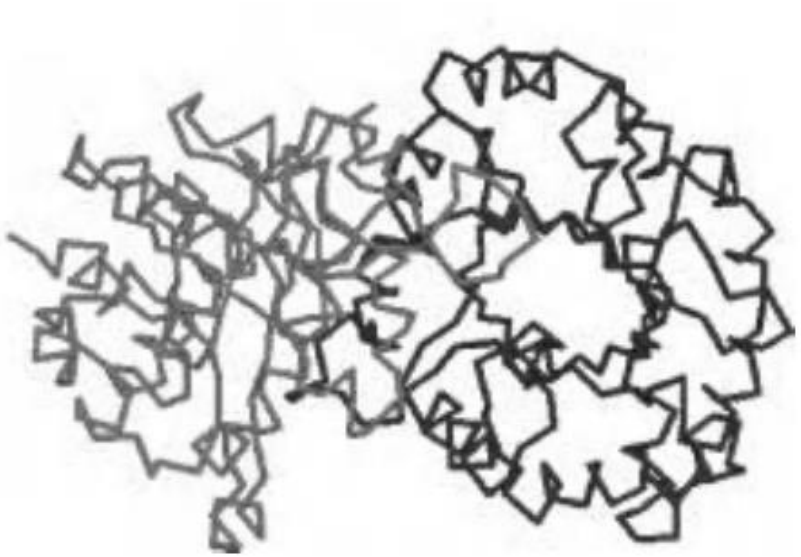
alpha-helix



beta-sheet



Teritiary structure



Quartenery structure: multiple chains

End of lecture overview

- Material from Chap-1+2 of Pethig and Smith
- Basically chemistry overview today
- Next class:
  - Nucleotides, Nucleic acids, DNA, RNA and Genes
  - Central Dogma of Biology
  - Overview of cell structure
  - Transport in/out of cell of molecules
  - Interactions between bio-molecules
  - Overview of Optical and electrochemical properties of biomolecules

Purposefully empty, see next slide

Last class

- Overview of:
- Fatty acids, Lipids
- Carbohydrates, polysaccharides
- Aminoacids, peptides and proteins

Nucleic acid

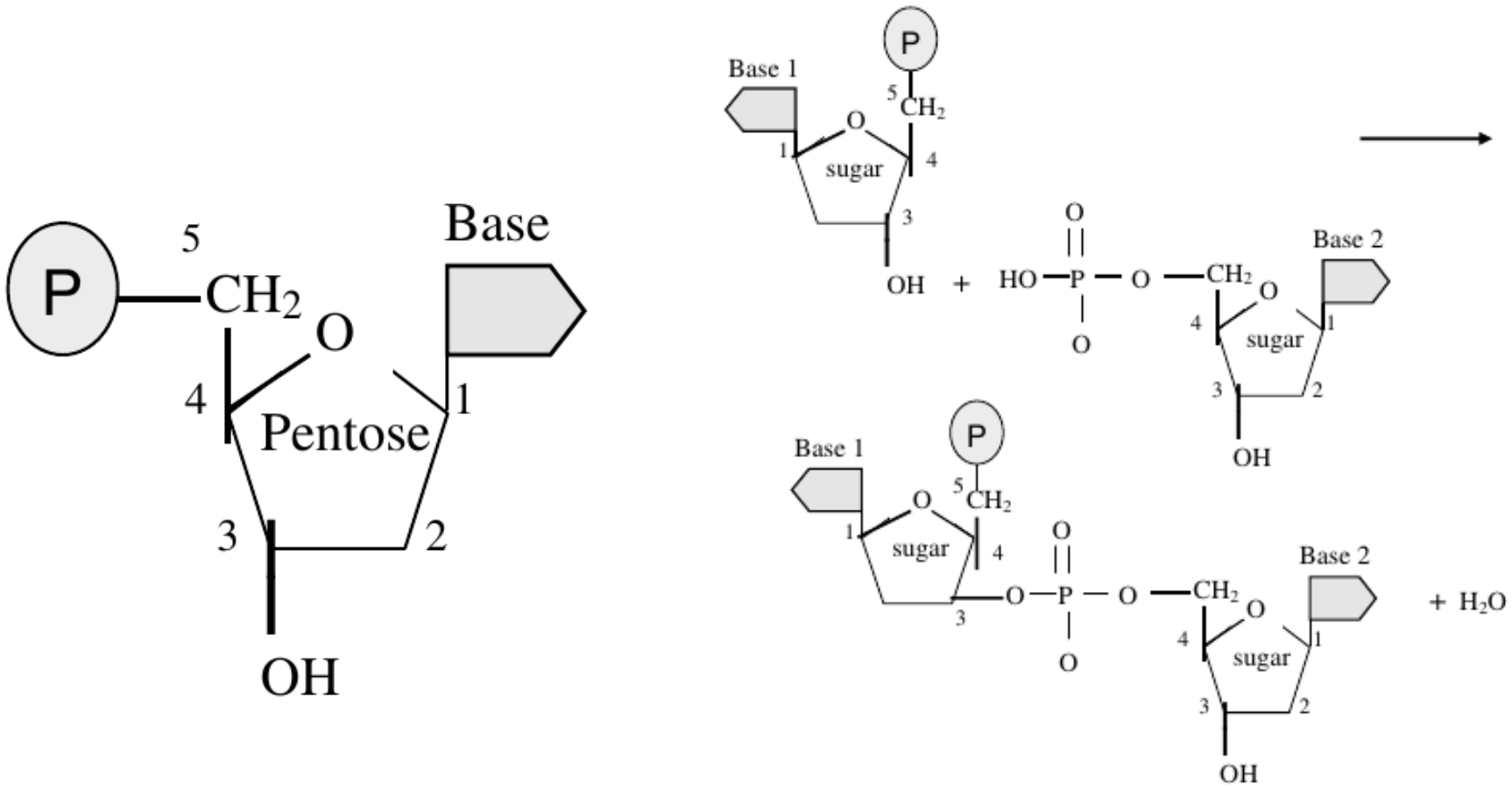
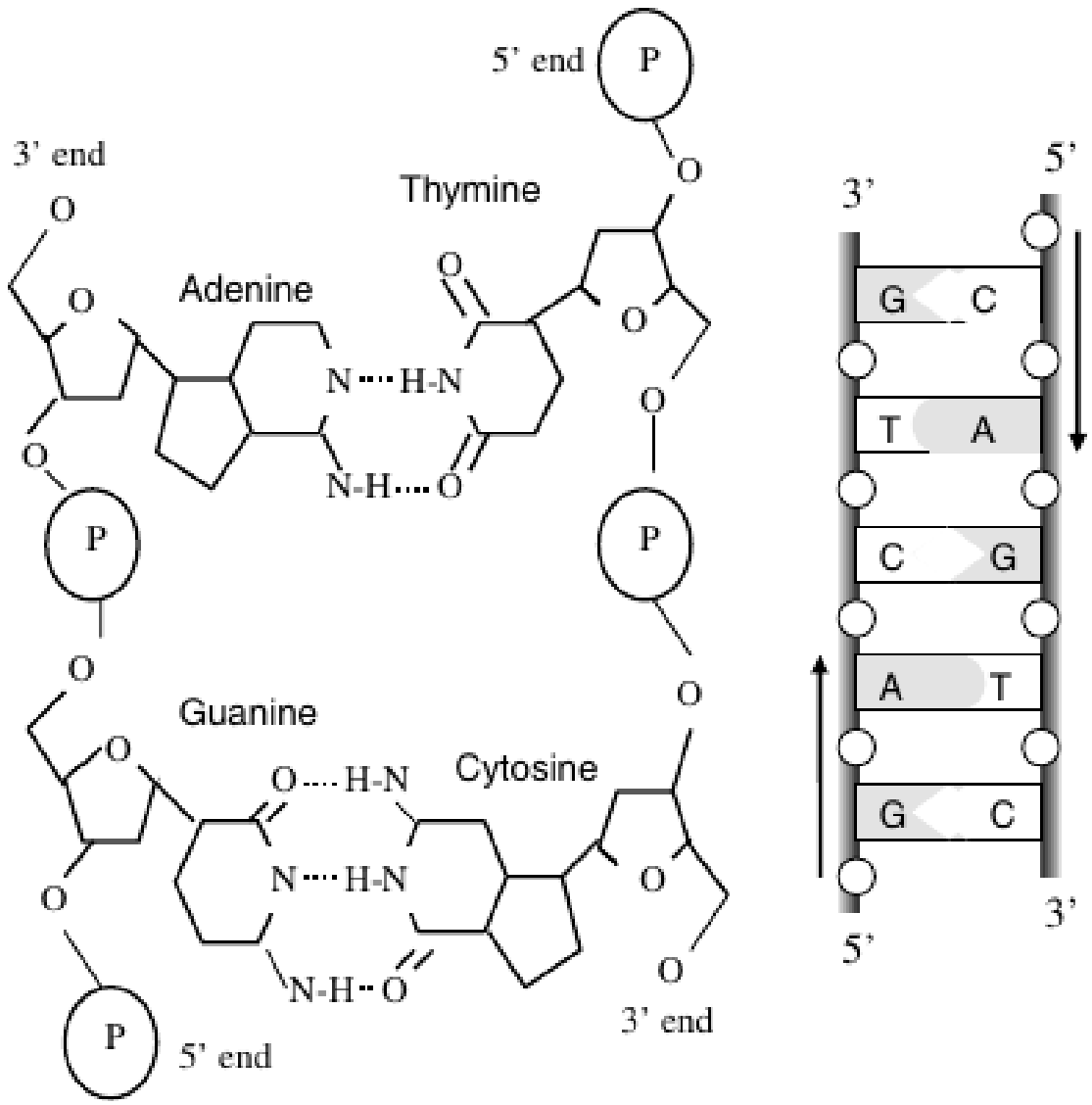
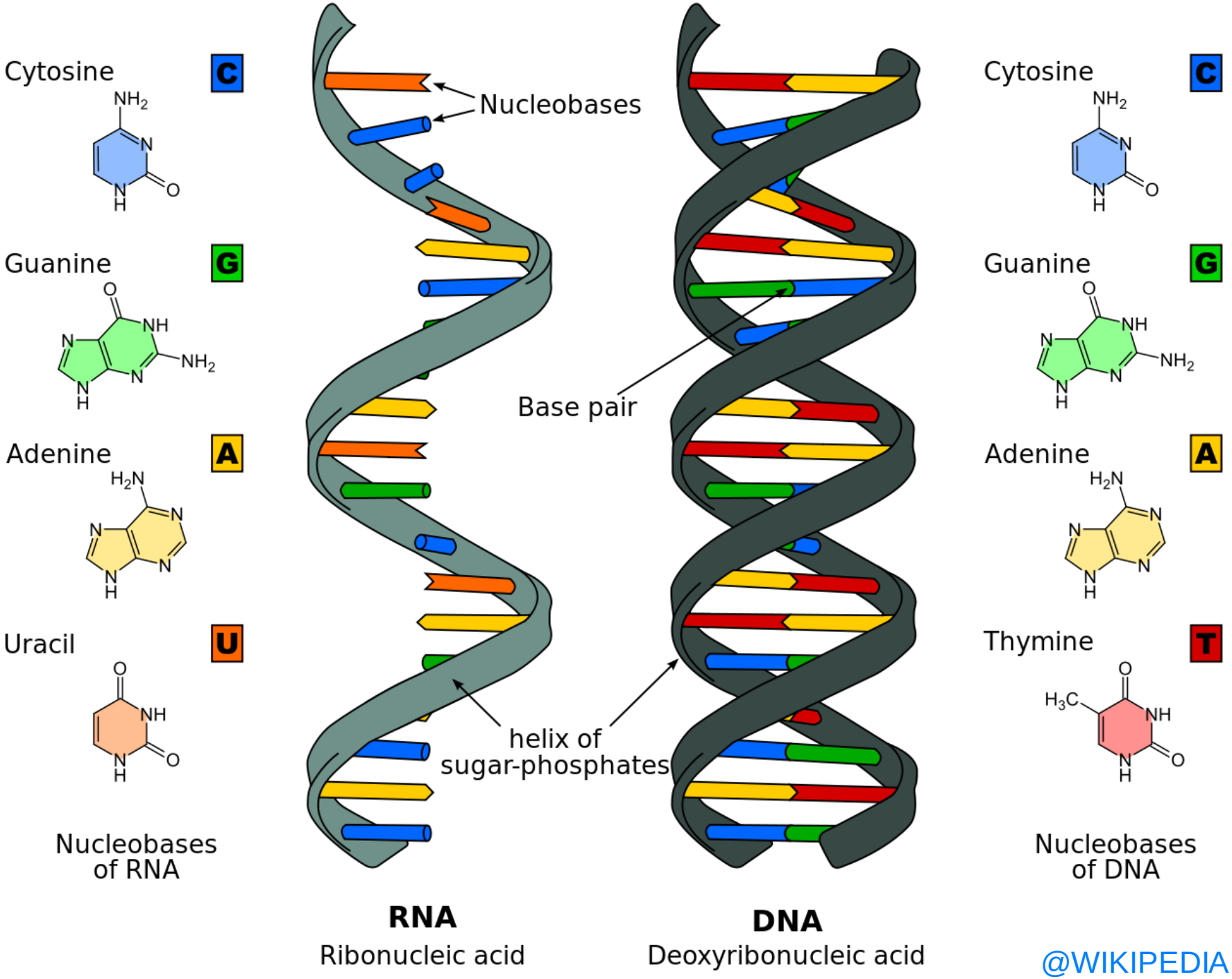


Figure 2.12 The condensation reaction that links two nucleotides with a phosphodiester bond.


5' end
P
3' end
O
Thymine
Adenine
N H-N
N-H O
P
Guanine
Cytosine
O H-N
N H-N
N-H O
5' end
3' end
3'
5'
G C
T A
C G
A T
G C
5'
3'


Cytosine
C
Guanine
G
Adenine
A
Uracil
U
Nucleobases of RNA
Nucleobases
Base pair
helix of sugar-phosphates
RNA
Ribonucleic acid
DNA
Deoxyribonucleic acid
Cytosine
C
Guanine
G
Adenine
A
Thymine
T
Nucleobases of DNA

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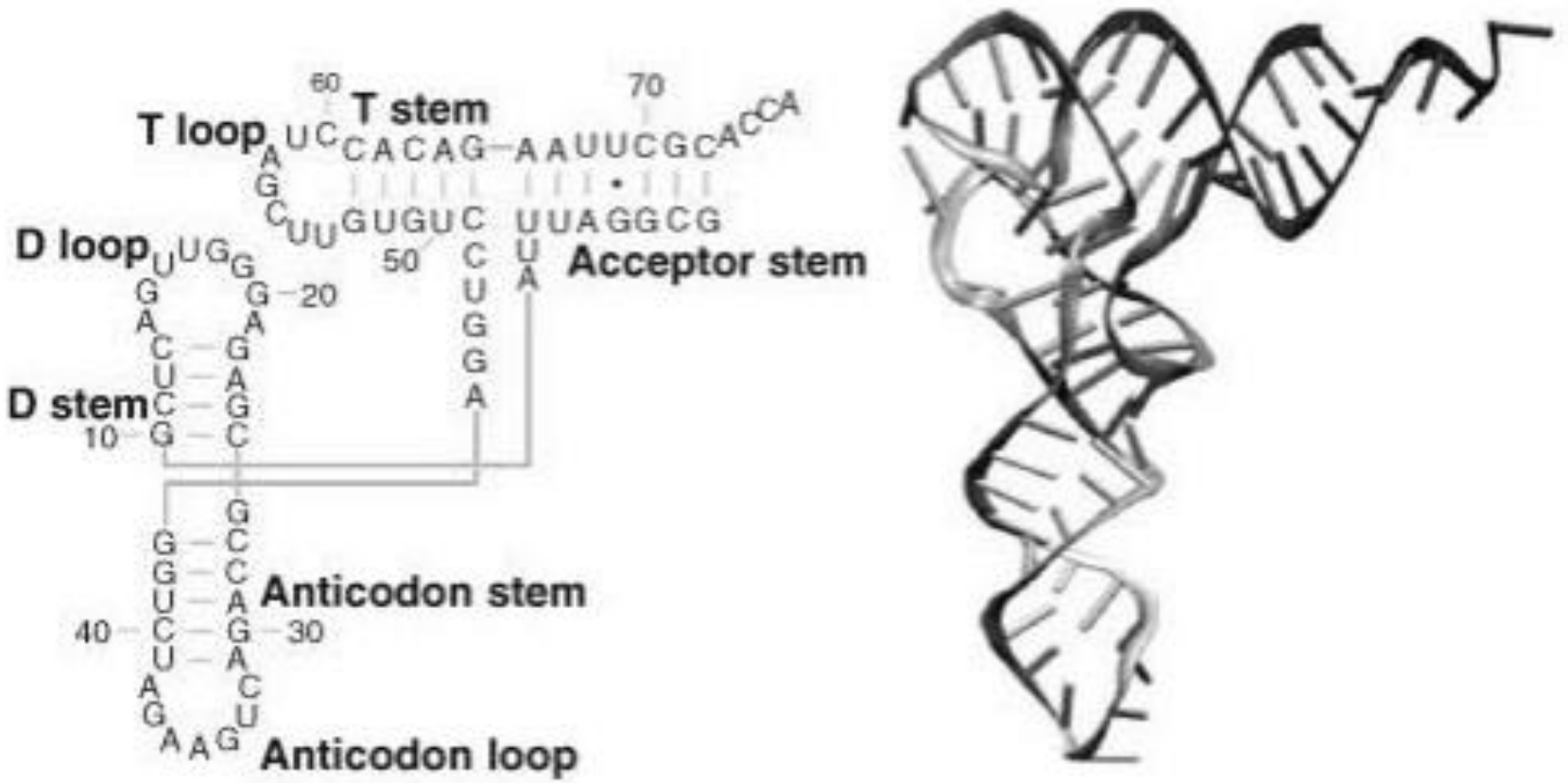
DNA

- Information storage
- E Coli: just less than 5 million base pairs
- Human: 46 chromosomes, 3.2 billion base pairs
  - As a linear chain, about 2 meters in length
- In all higher organisms, DNA wrapped around histone protein molecules and packed into nucleus
- Gene is a small part of DNA
- Large percentage of DNA does NOT code for any genes

RNA



7 The nucleotide sequence and 3-Dimensional structure of a transfer RNA (tRNA)

RNA

- mRNA obtained from DNA template codes
- mRNA move from nucleus to cytoplasm, to be read by proten complex called ribosomes to translate the mRNA code to proteins using tRNA. (next slide)
- Noncoding RNA (ncRNA): transfer-RNA (tRNA),
- ribosomal RNA (r-RNA), regulartory RNA
- Area of active research

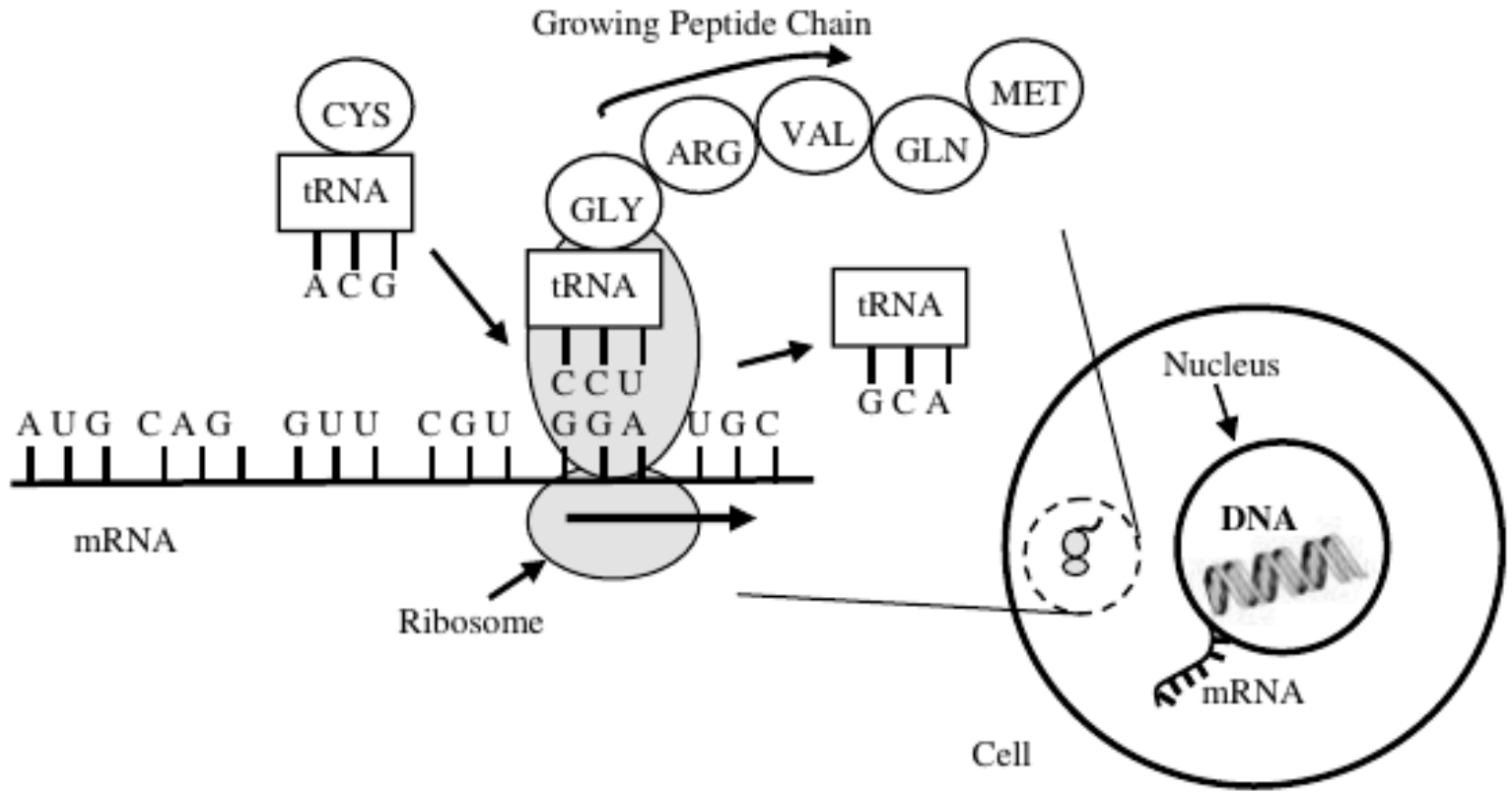


Figure 2.18 Translation of mRNA (from right to left) into a peptide chain. The ribosome begins at the start triplet codon (AUG) at the 3′ end of the mRNA, which also codes for methionine. The triplet codons (CAGGUUCGUGGA) that follow produce glutamine, valine, arginine and glycine in the growing peptide chain. A transfer RNA molecule, with its anticodon ACG, brings cystine towards the codon UGC site on the mRNA.

Central Dogma of Biology

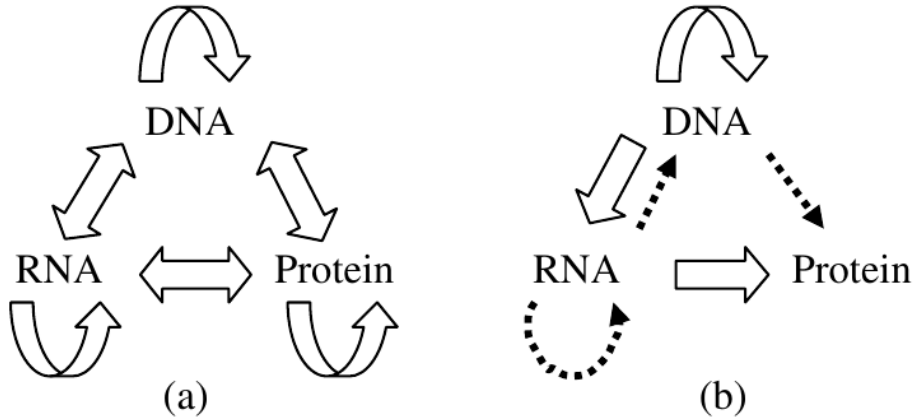


Figure 2.19 (a) The 9 conceivably possible direct transfers of information between DNA, RNA and proteins. (b) The central dogma of molecular biology states that only the transfers represented by the block arrows are possible. The dotted arrows indicate special transfers under specific conditions, such as those involving retroviruses or artificially in a test-tube.

Eukaryote, Prokaryote

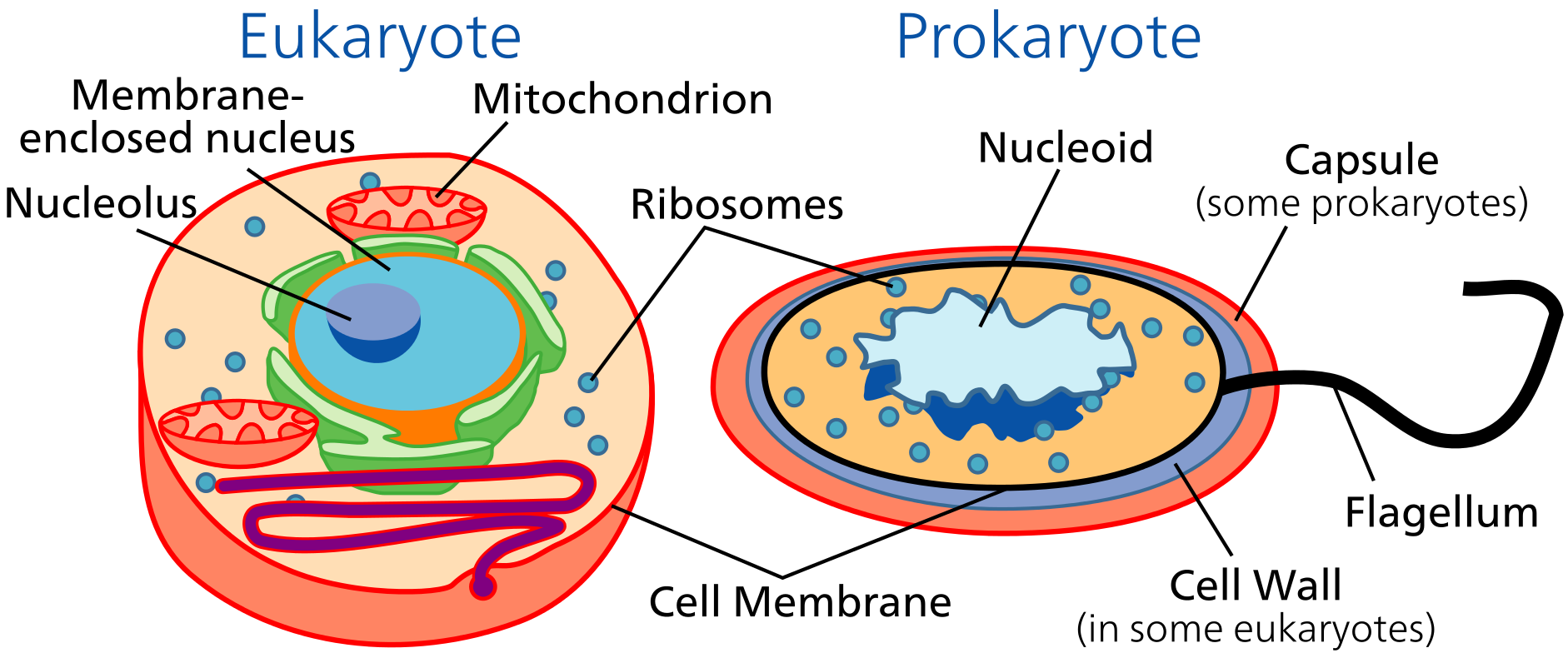


Table 2.7 The characteristic differences between prokaryotic and eukaryotic cells

Feature	Prokaryote	Eukaryote
Size	Small: 0.5 $\sim$ 5 μm	5 $\geq$ 50 μm
Genetic material	Circular DNA (in cytoplasm)	DNA in form of linear chromosomes (in nucleus)
Organelles	Few present	Many organelles
Cell walls and other structures	Rigid, formed from glycoproteins. (Bacteria also contain flagellum, plasmid and capsule)	Fungi: Rigid, formed from polysaccharides (chitin). Plant: Rigid, formed from polysaccharides (e.g. cellulose). Animals: No cell wall

Cell to cell communication

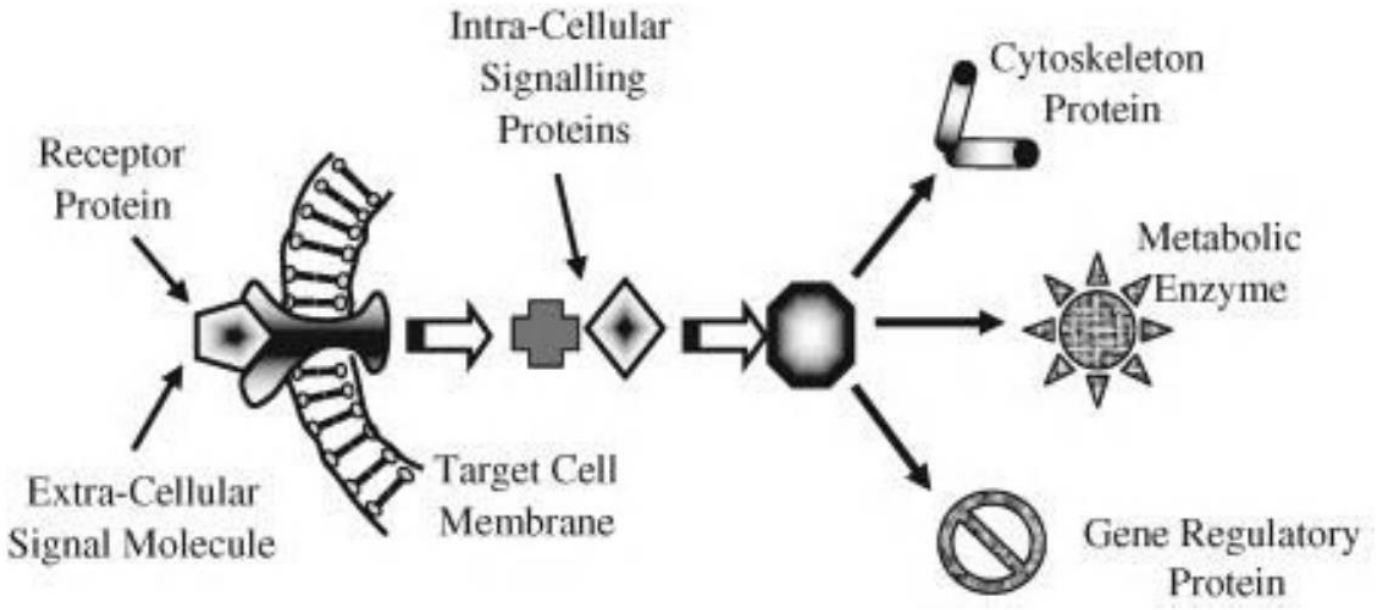


Figure 2.22 This binding of a signalling protein to a membrane receptor protein can activate a sequence of intracellular signalling proteins that are designed to influence the activity of a target effector protein inside the cell. Depending on the type of effector protein, this can result in a change of the shape or motility of a cell, alter cell metabolism or the regulation of gene expression, for example.

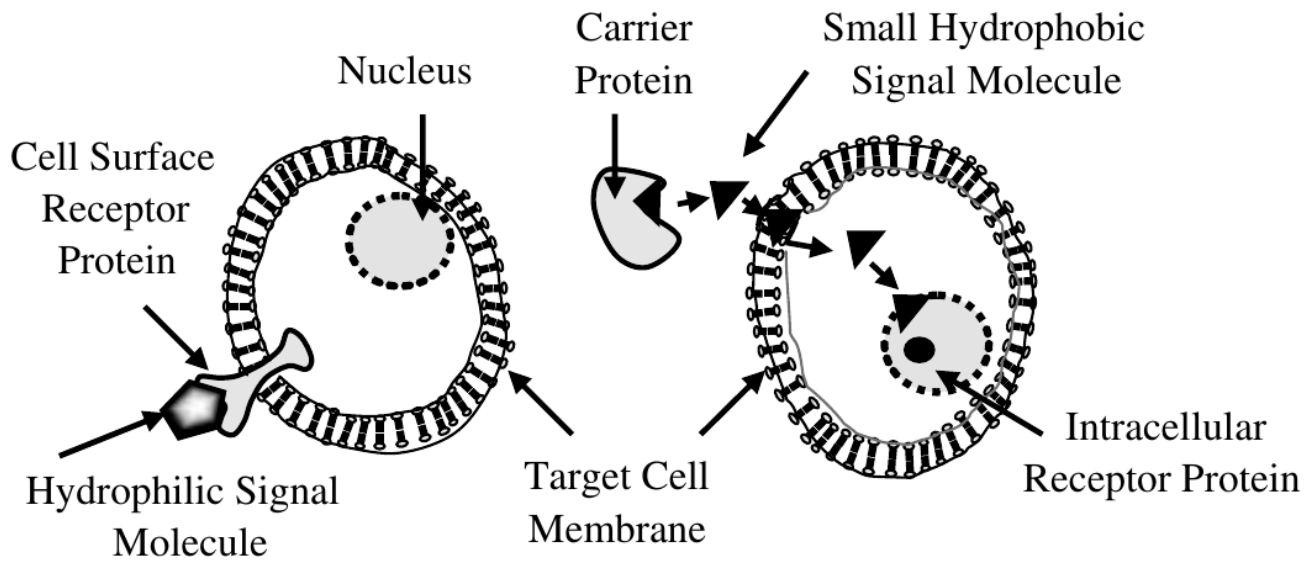
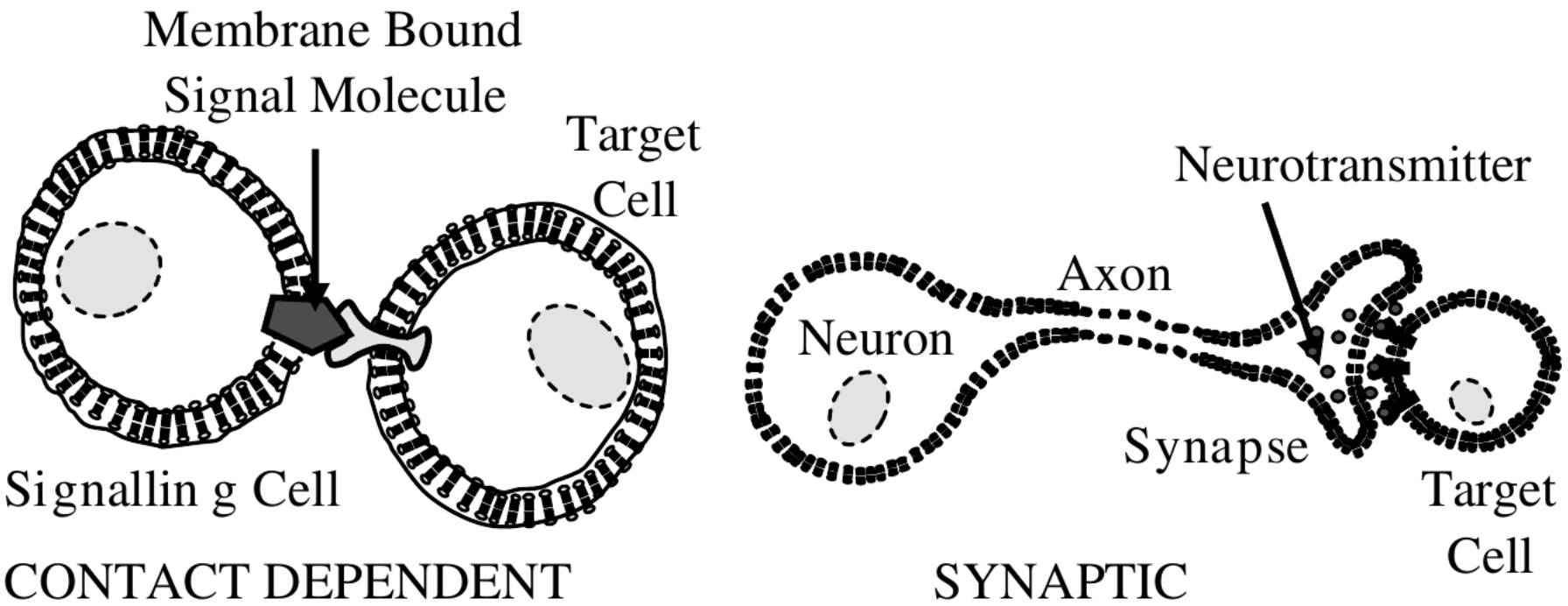
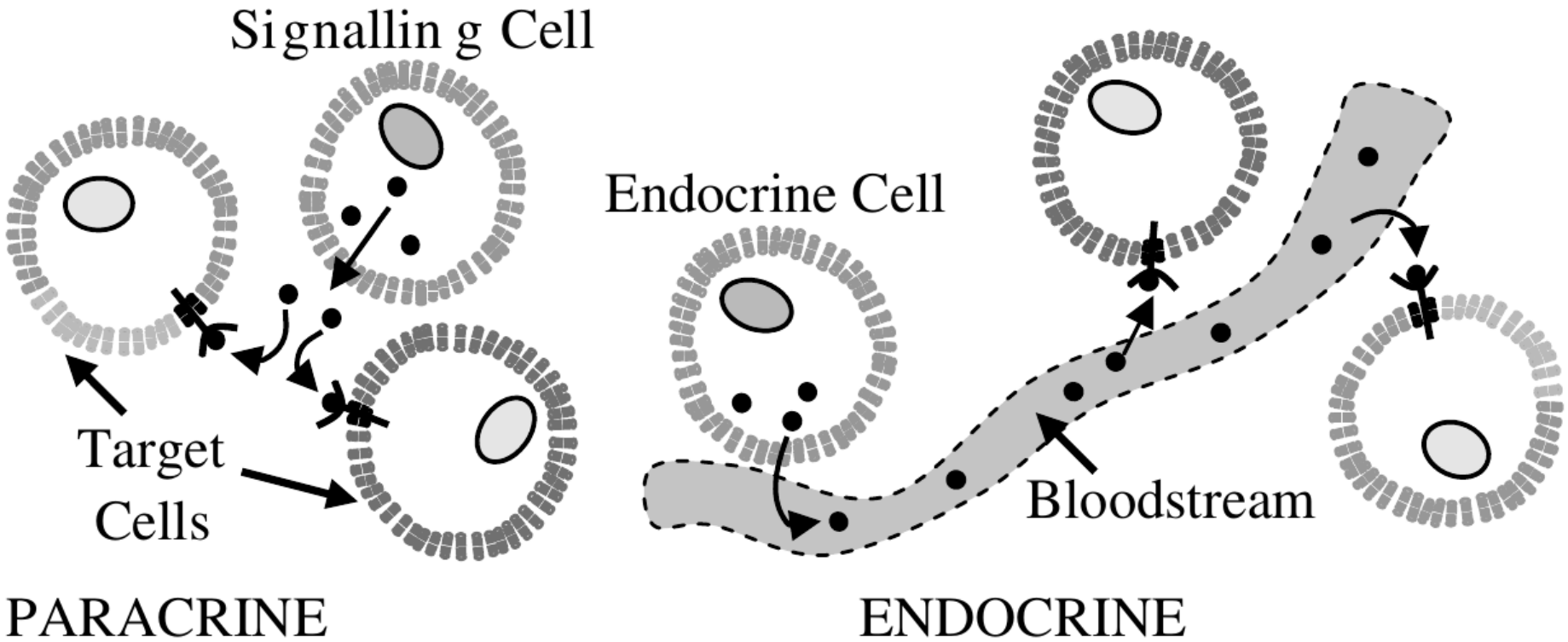


Figure 2.23 Hydrophilic signal molecules released into the extracellular medium can bind directly to cell-surface receptor proteins, but small hydrophobic signal molecules are transported by proteins to the target cell, where they can then diffuse across the cell membrane to interact directly with an internal effector protein.

Signalling processes: 4 types

- Contact dependent: two cells have to ‘touch’. Immune cells bind to microbes
- Synaptic: Ex. Nerve cells. In addition to contact, additional stimulus (from other neurons) is required for communication (action potential)
- Paracine: signalling molecules are kept in close proximity. Additionally, antogonists are used. Ex. Embryonic signalling
- Endocrine: signal travels through extracellular fluid. Can diffuse over long distances. Ex. Harmones in blood stream

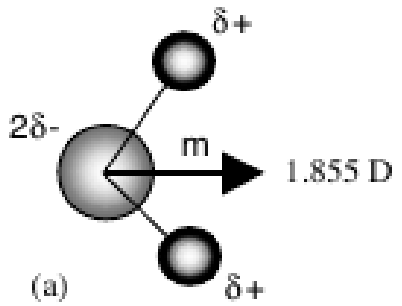

Membrane Bound
Signal Molecule
Target
Cell
Signallin g Cell
CONTACT DEPENDENT
Neurotransmitter
Axon
Neuron
Synapse
Target
Cell
SYNAPTIC

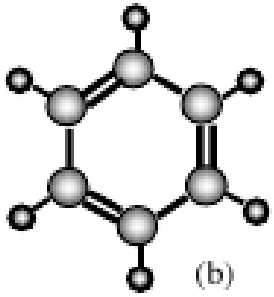

Signallin g Cell
Target
Cells
PARACRINE
Endocrine Cell
Bloodstream
ENDOCRINE

Interactions

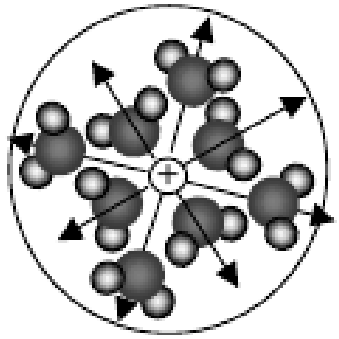
- For today, we will talk (schematically) about
- Electrostatic interactions
  - Ions in water (ion-dipole)
  - Double layer
  - Ion-dipole and dipole-dipole interactions
  - Ions in membrane. Protein (multiple charges moving together)

- Coulombs law: force, energy
- Dipoles

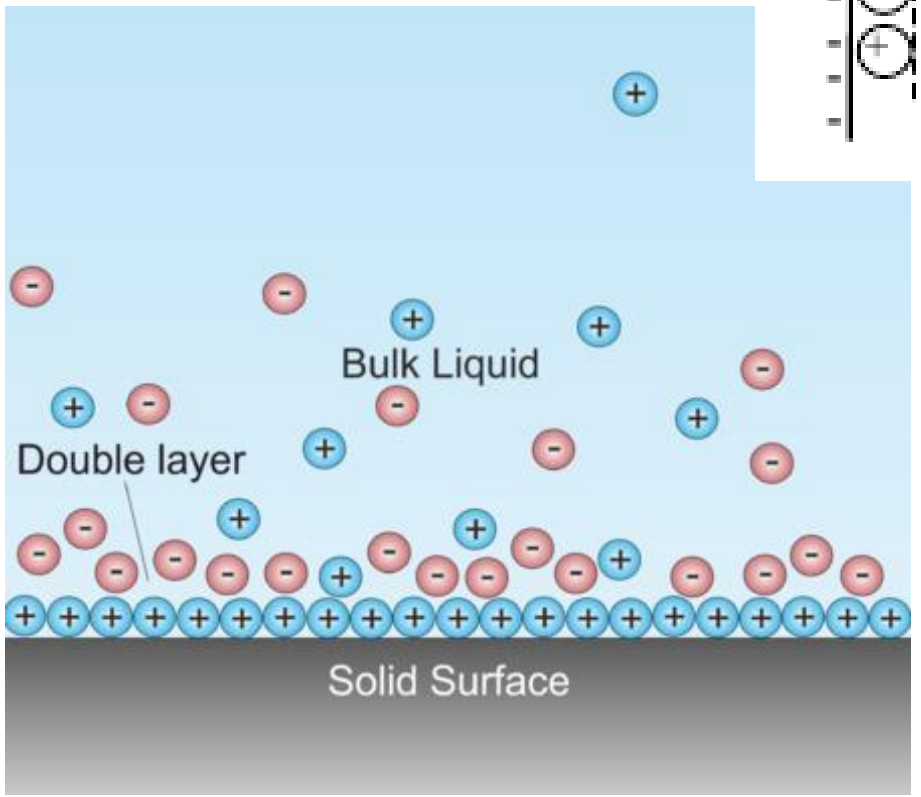


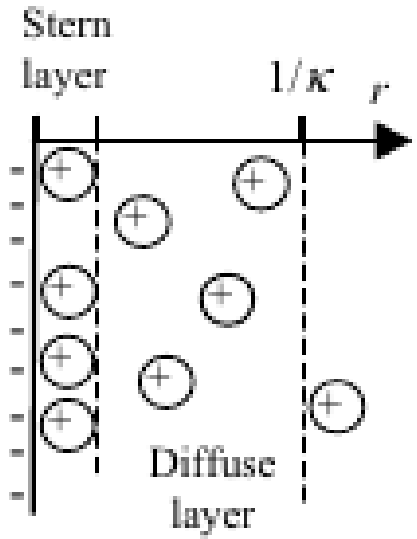


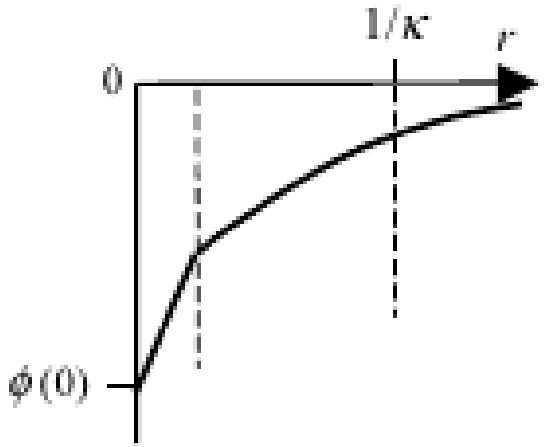
- Ions in water

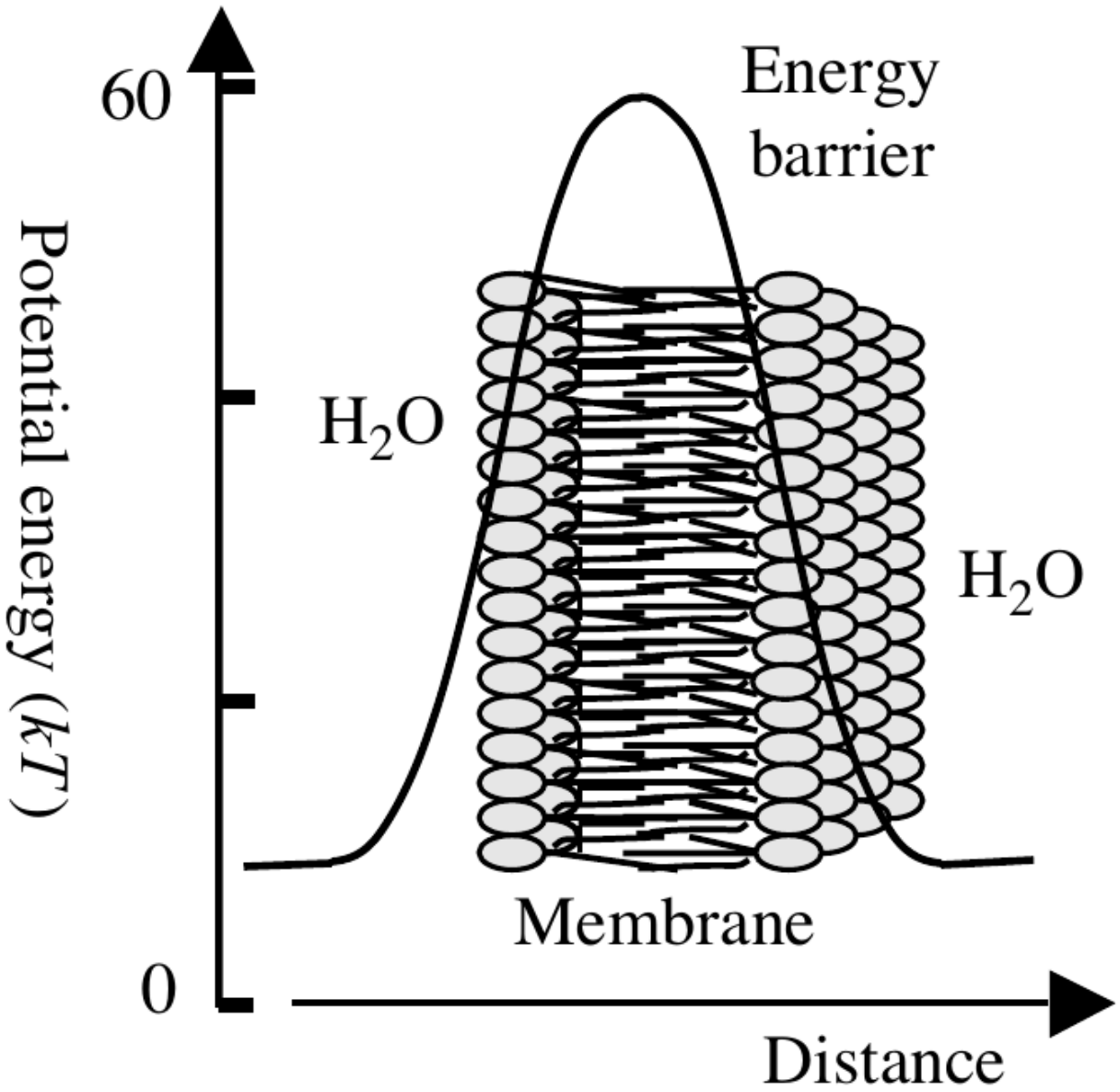


Double layer








60
Potential energy (kT)
0
Energy
barrier
H2O
H2O
Membrane
Distance

Purposefully empty, next slide

Today

- Interactions [Chap 3 till and including 3.7]
- Interactions with light

Interactions

- Electrostatic interactions
  - Ions in water (ion-dipole)
  - Double layer
  - Ion-dipole and dipole-dipole interactions
  - Ions in membrane. Protein (multiple charges moving together)

Ion-ion electrostatic interactions:

$$F = \frac{1}{4\pi\varepsilon_o}\frac{q_1 q_2 (r_1 - r_2)}{|r_1 - r_2|^3} = \frac{1}{4\pi\varepsilon_o}\frac{q_1 q_2}{r^2}\hat{r}_{21}$$

Ion with all other ions:

$$F = \frac{q}{4\pi\varepsilon_o}\sum_{i=1}^{N}\frac{q_i (r - r_i)}{|r - r_i|^3} = \frac{q}{4\pi\varepsilon_o}\sum_{i=1}^{N}\frac{q_i}{R_i^2}\hat{R}_i$$

Work required to bring q1 from Infinity to distance r to q2

$$W = -\int_{\infty}^{r} F\,dr = -\frac{q_1 q_2}{4\pi\varepsilon_o}\int_{\infty}^{r}\frac{1}{r^2}dr = \frac{q_1 q_2}{4\pi\varepsilon_o}\frac{1}{r}$$

Potential energy of interaction

$$U = \frac{q_1 q_2}{4\pi\varepsilon_o}\frac{1}{r} = q_1\phi \qquad \phi = \frac{q_2}{4\pi\varepsilon_o}\frac{1}{r}$$

Electric field due to q2

$$E = \frac{1}{4\pi\varepsilon_o\varepsilon_r}\frac{q_2}{r^2}\hat{r} = -\nabla\phi = \frac{1}{4\pi\varepsilon_o}\frac{q_2}{r^2}\hat{r}$$

Thermodynamics: Internal energy

$$U = H - TS$$

Ions in water: S = $-\partial U/\partial T$, $$S = -\frac{\partial}{\partial T}\left(\frac{q_1 q_2}{4\pi\varepsilon_o\varepsilon_r}\frac{1}{r}\right) = \frac{q_1 q_2}{4\pi\varepsilon_o\varepsilon_r^2 r}\frac{\partial\varepsilon_r}{\partial T} = U\frac{1}{\varepsilon_r}\frac{\partial\varepsilon_r}{\partial T}$$

Formation of Double layer:

Poisson $$\nabla^2\phi(r) = -\frac{\rho(r)}{\varepsilon_o\varepsilon_r}$$

B $$\rho(r) = q\sum\nolimits_i z_i\, c_{i\infty}\exp\left(\frac{-qz_i\phi(r)}{kT}\right)$$

Linearized Poisson-Boltzmann: $$\nabla^2\phi(r) = -\frac{q}{\varepsilon_o\varepsilon_r}\sum\nolimits_i z_i c_{i\infty}\left(1 - \frac{qz_i\phi(r)}{kT}\right)$$

Simplify to: $$\nabla^2\phi(r) = \kappa^2\phi(r) \qquad \kappa^2 = \frac{q^2}{\varepsilon_o\varepsilon_r kT}\sum\nolimits_i z_i^2 c_{i\infty}$$

Screening length: $$1/\kappa = \sqrt{\frac{\varepsilon_o\varepsilon_r kT}{2q^2 I N_A 10^3}}$$

For 10 mM NaCl at 298K, screening length = 3.07 nano meter

REMAINDER: When we are talking about electrical response

Hydrophobic interactions

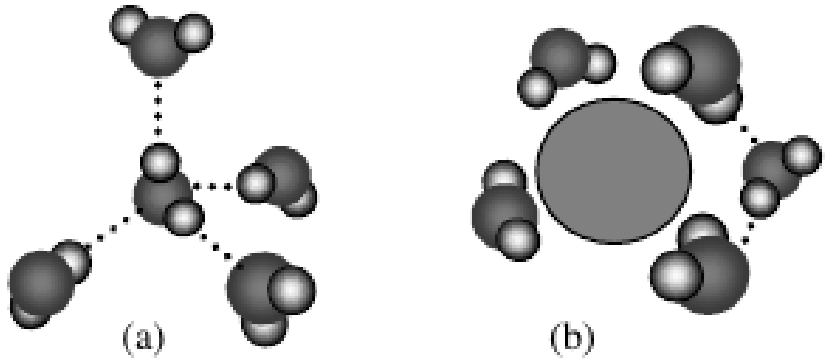


Figure 3.8 (a) Water molecules forming their normal tetrahedral arrangement of hydrogen bonds (dotted lines) in bulk water. (b) Water molecules at the surface of a hydrophobic body are restricted in orientation as they attempt to form hydrogen bonds with other water molecules.

Hydrophobic effect is entropy driven. Hydrogen bond has strength of 20 kJ/mol. Hydrogen bonds 'work around' the hydrophobic surface, restricting the translational and Rotational motion of these molecules.

Hence hydrophobic molecules tend to aggregate to minimize surface area with water

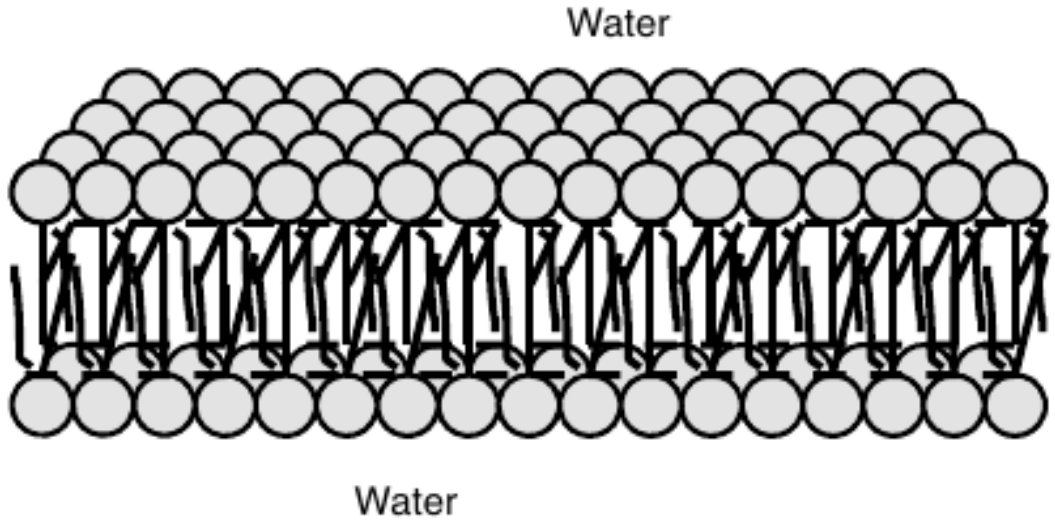


Figure 2.2 Schematic representation of a phospholipid bilayer. The small spheres represent the hydrophilic heads groups, and the lines are the hydrophobic hydrocarbon tails of individual phospholipid molecules.

Osmolarity

- Chemical potential of water is lowered in proportion to the amount of solute present

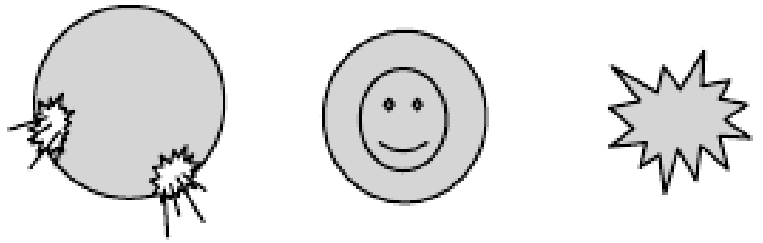


Figure 3.10 Cells suspended in various solutions. (a) Cells swell and burst in a *hypotonic* solution such as pure water. (b) Cells are 'happy' in an *isotonic* solution such as physiological strength saline. (c) Cells shrink and shrivel in a *hypertonic* solution such as a concentrated salt solution.

Transport

- Diffusion: mediated by concentration gradient
- Osmosis: semipermiable membranes, transport of solvent is due to difference in chemical potentials due to concentrations of solute
- Facilatated diffusion: protein channels
- Active transport: consume energy to pump
  - Ex: sodium potassium pump

- Homework: Donnan equilibrium
- Rest of the chapter: after labs

Spectroscopic techniques

- Mainly interaction of molecules with light

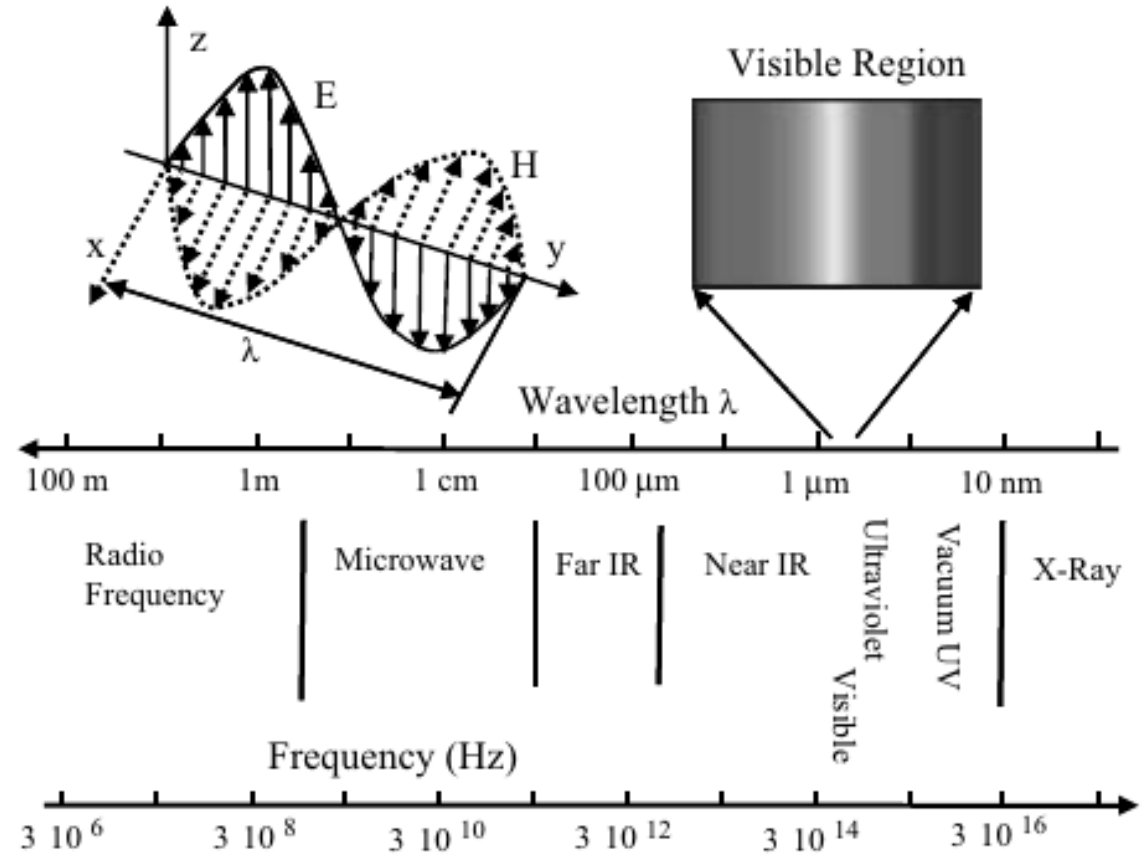


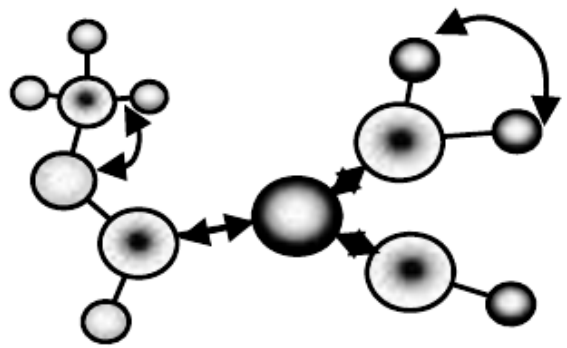
Figure 4.1 Electromagnetic (EM) radiation consists of orthogonal electric (E) and magnetic (H) fields that can propagate as sine waves over a wide range of frequencies. The visible region ($\lambda =$ 400–700 nm) occupies a narrow part of this range.

- Electronic transitions in atoms and molecules

  $10^{14} \sim 10^{17}$ Hz (Visible, UV, X-ray)

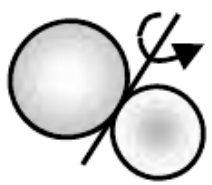
- Bonded nuclei vibrate with respect to each other

  $10^{13} \sim 10^{14}$ Hz (Infrared)



- Molecules rotate

  $10^{10} \sim 10^{12}$ Hz (Microwaves)



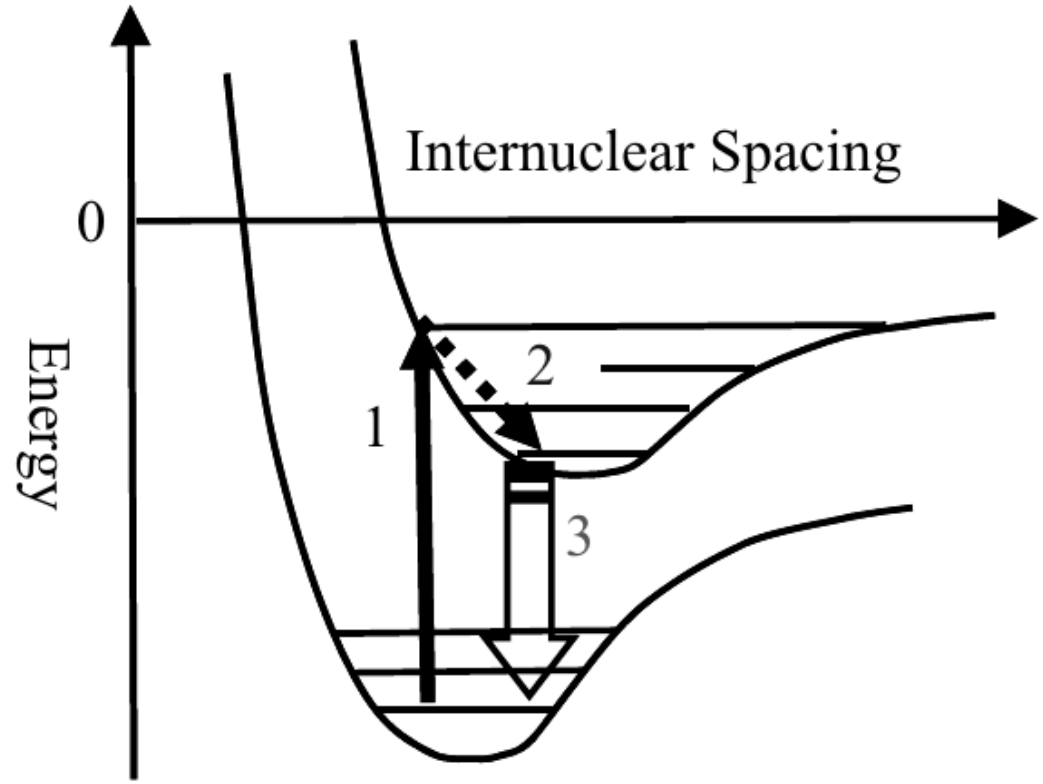


Figure 4.3 Electronic transitions between molecular energy levels can include: (1) absorption of light leading to the excitation of an electron to a higher energy level; (2) relaxation to a lower energy state as a result of energy lost to molecular vibrations; (3) radiative decay (fluorescence) back down to the ground state.

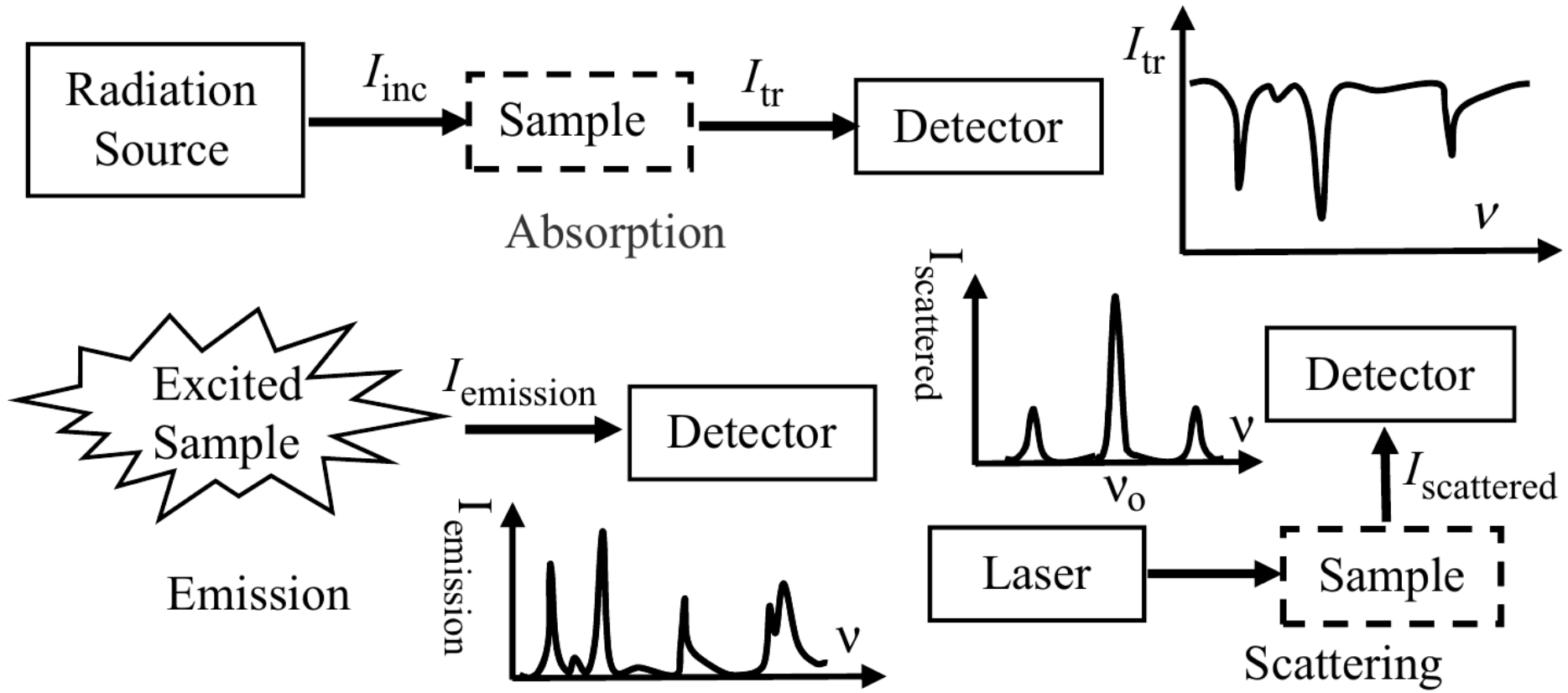
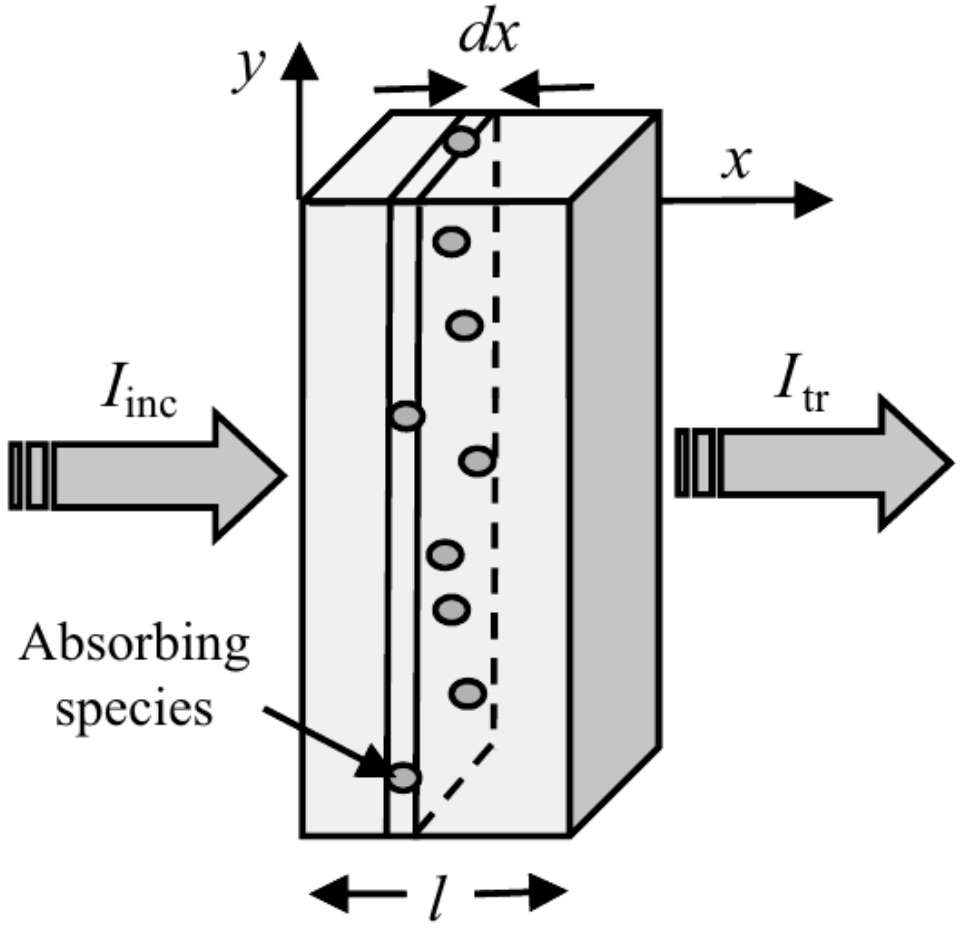


Figure 4.4 The three main classes of spectroscopy (absorption, emission, scattering) differ with respect to their mode of operation and output spectra.

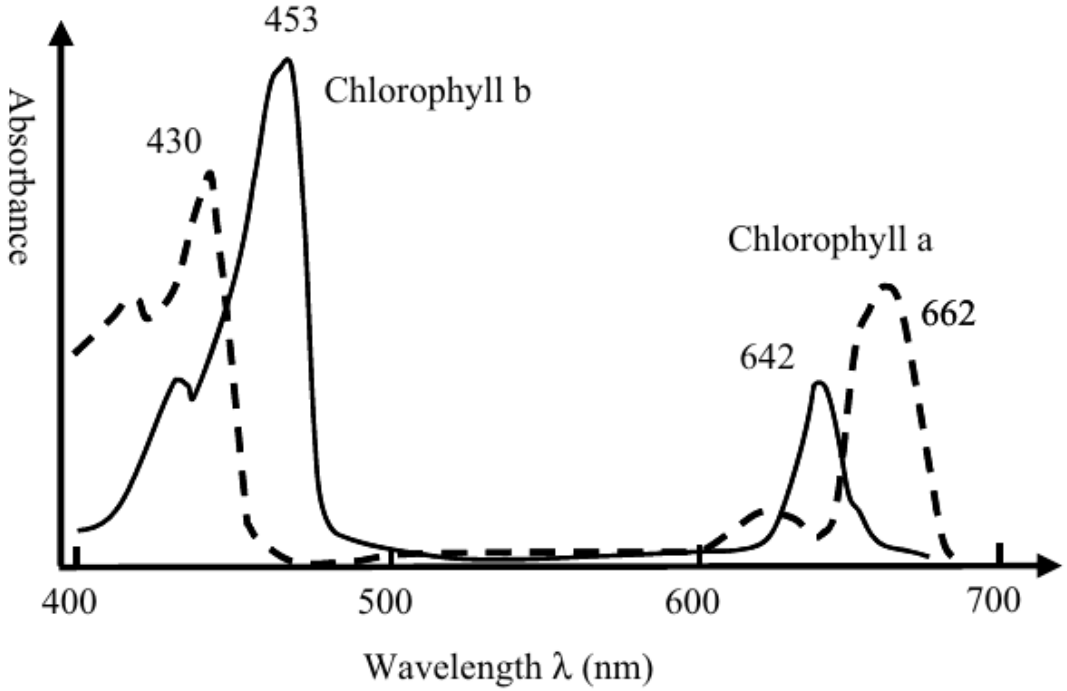
Beer-Lambert Law

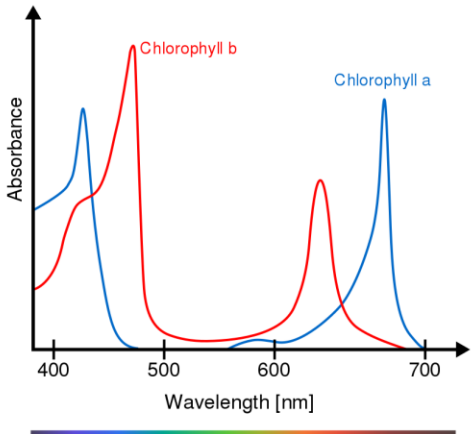


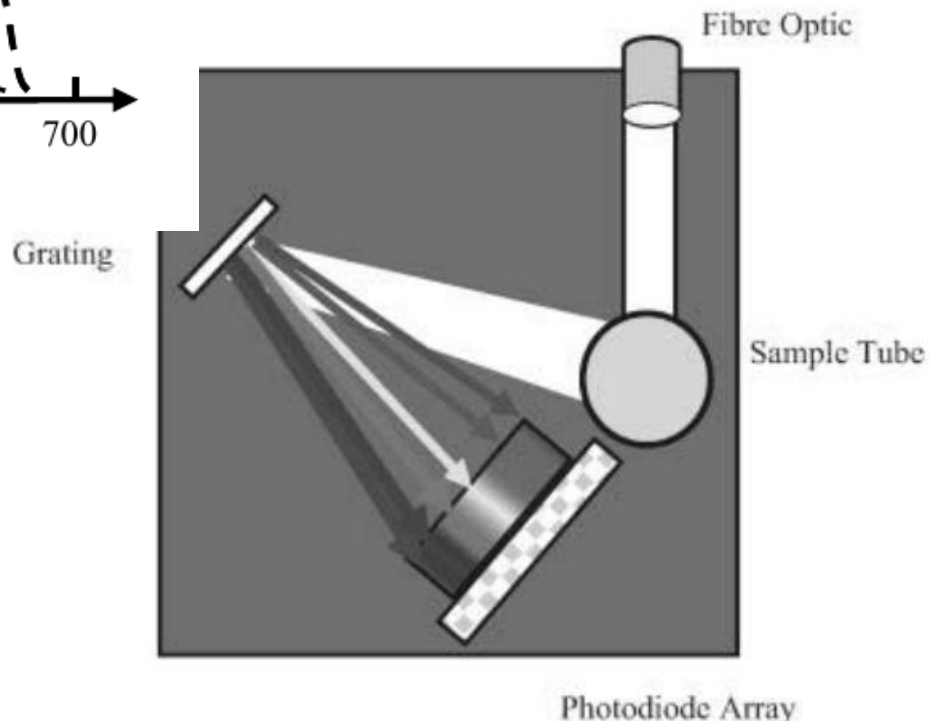
$$\frac{dI}{I_x} = -\sigma N dx.$$

$$-\log_{10}\left(\frac{I_{tr}}{I_{inc}}\right) = \frac{1}{2.303}\sigma N l$$

Electronic spectroscopy (UV-Vis)







Vibrational Spectroscropy (IR)

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k(m_1 + m_2)}{m_1 m_2}} \qquad E_{\text{vibr}} = (n + 1/2)h\nu \quad (n = 0, 1, 2, \ldots)$$

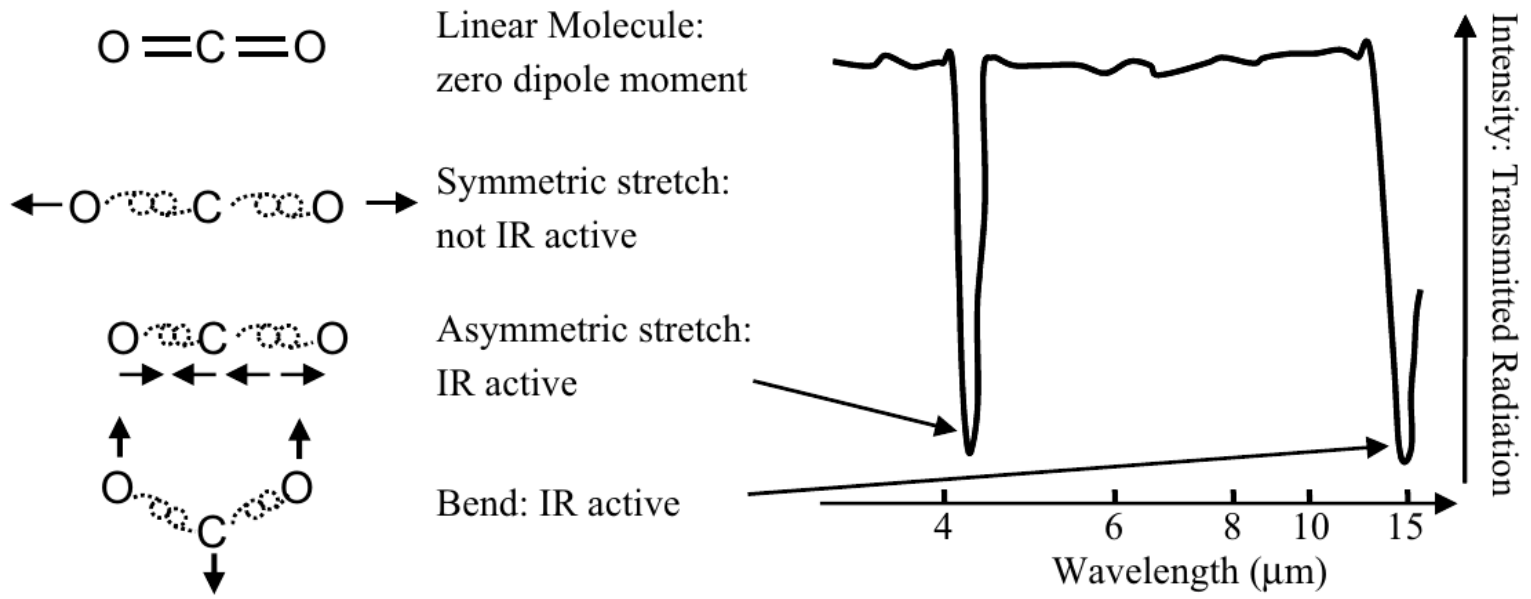


Figure 4.10 A molecule that does not possess a permanent dipole moment can be infrared active. Although the carbon dioxide molecule does not possess a permanent dipole moment, asymmetrical stretching or bending results in a dipole moment and an associated infrared absorption.

Rotational Spectrocopy (microwave)

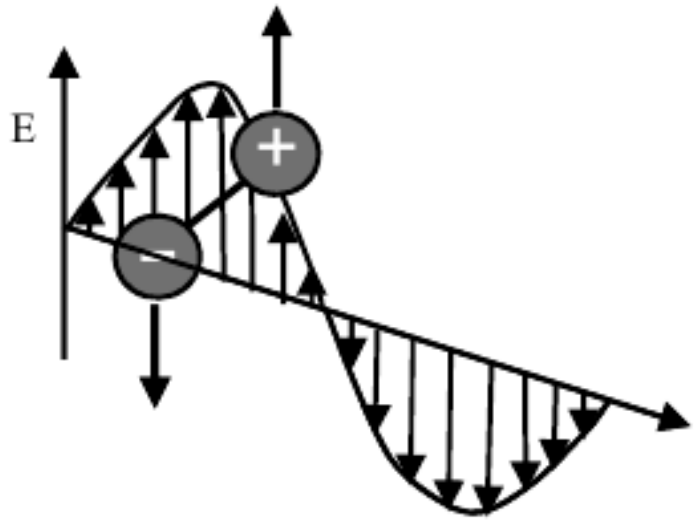


Figure 4.11 A molecule possessing a permanent dipole moment can interact with the electric field component of EM radiation, inducing a rotational torque which can cause its rotation rate to increase or decrease.

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) \quad \text{with } J = 0, 1, 2, \ldots$$

Vib-rotational spectrum

$$E = E_{vibr} + E_{rot} = \left(n + \frac{1}{2}\right)h\nu + \frac{h^2}{8\pi^2}\frac{J(J+1)}{I}$$

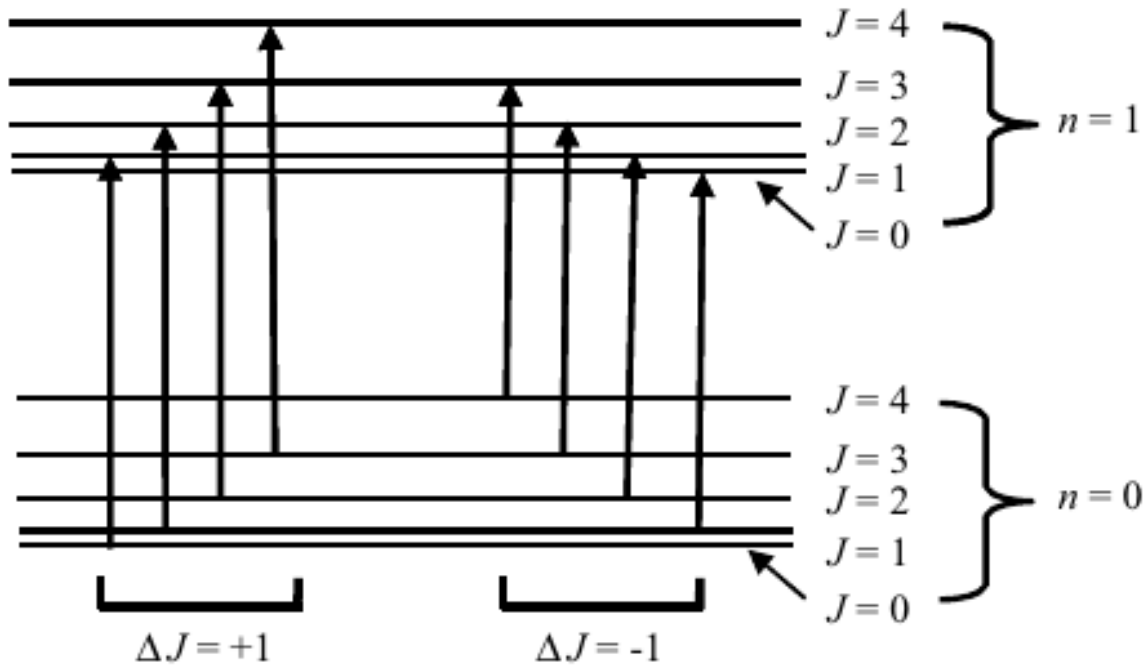


Figure 4.12 The allowed transitions between energy states for molecules experiencing a combination of vibrational and rotational energy changes. The $\Delta l = 0$ transition is forbidden.

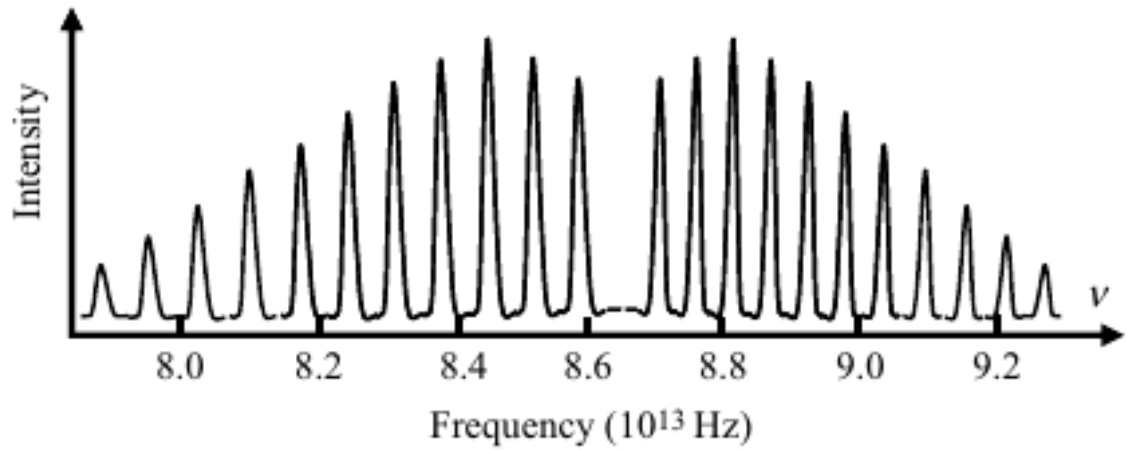


Figure 4.13 A schematic of the combined vibrational-rotational absorption spectrum for HCl, corresponding to the allowed transitions shown in Figure 4.11. The absence of the central frequency peak results from the $\Delta l = 0$ transition being forbidden (based on [2,3]).

Total Internal Reflection Flouroscence

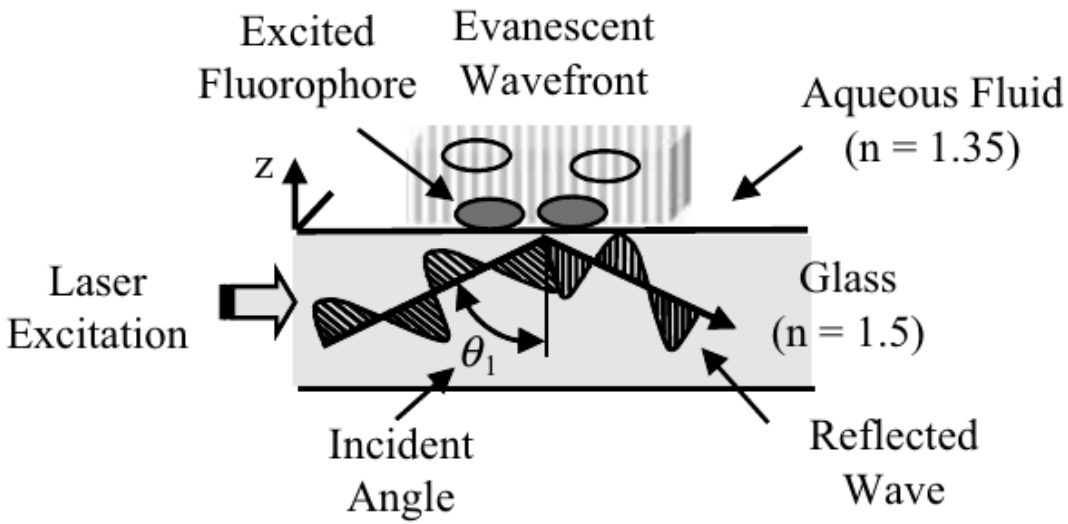


Figure 4.14 Total internal reflection fluorescence (TIRF) makes use of the EM evanescent wave generated by the interference between an incident and reflected light wave. Total internal reflection occurs above a critical angle of incidence, provided that the refractive index n of the light guide is greater than that of the adjacent medium. Excitation of fluorophores by the evanescent wave is confined to a region within $\sim$100 nm from the waveguide-fluid interface. In this case two of the four fluorophores shown are excited.

Next class (or whenever we meet next)

- Raman
- NMR and ESR
- FRET

- Spectroscopy from Chapter 4

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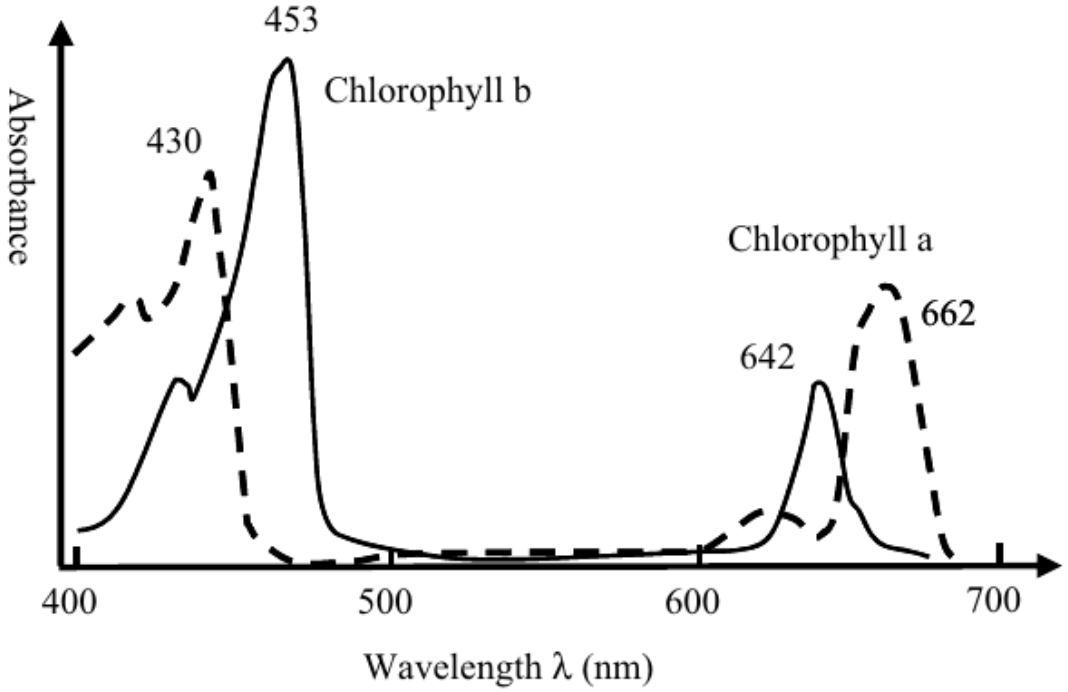
Intro to Bioelectronics

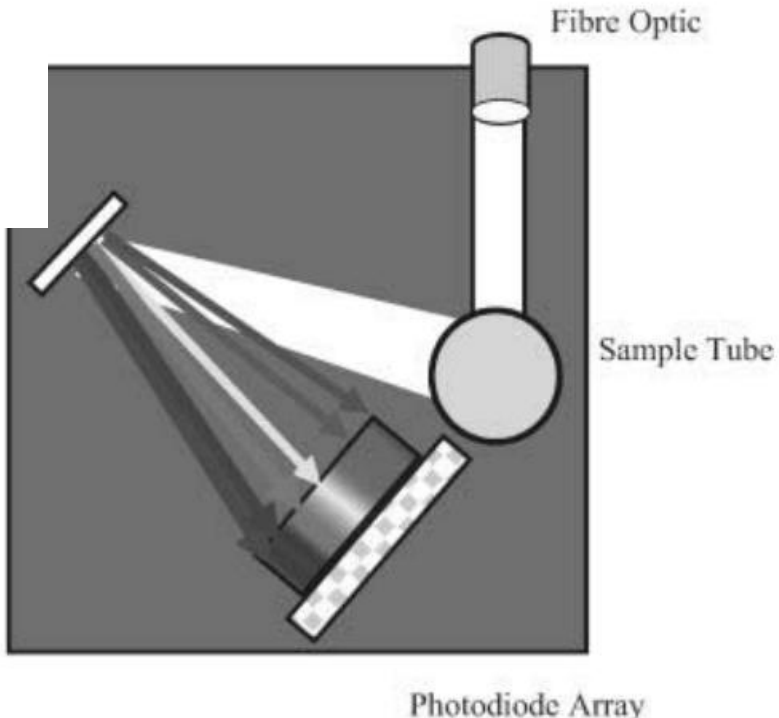
Spring 2023

Lecture-4

Start with uncompleted slides of previous lecture

Electronic spectroscopy (UV-Vis)





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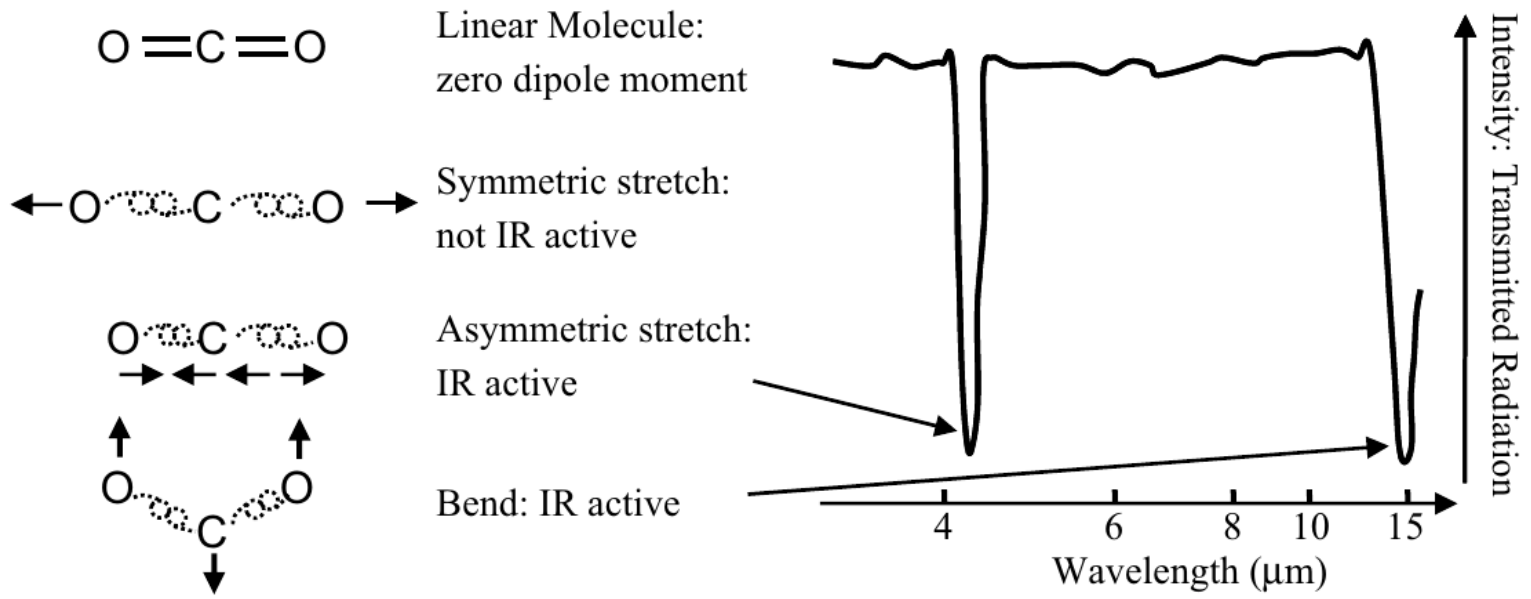

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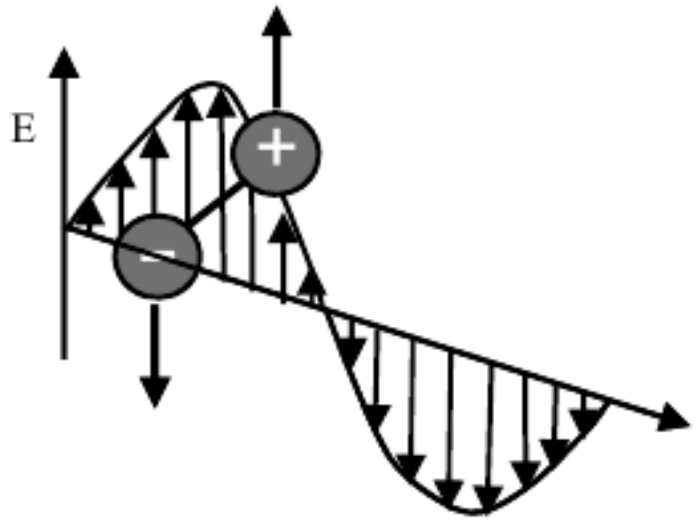
Rotational Spectroscopy (microwave)



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Vib-rotational spectrum

$$E = E_{vibr} + E_{rot} = \left(n + \frac{1}{2}\right)h\nu + \frac{h^2}{8\pi^2}\frac{J(J+1)}{I}$$

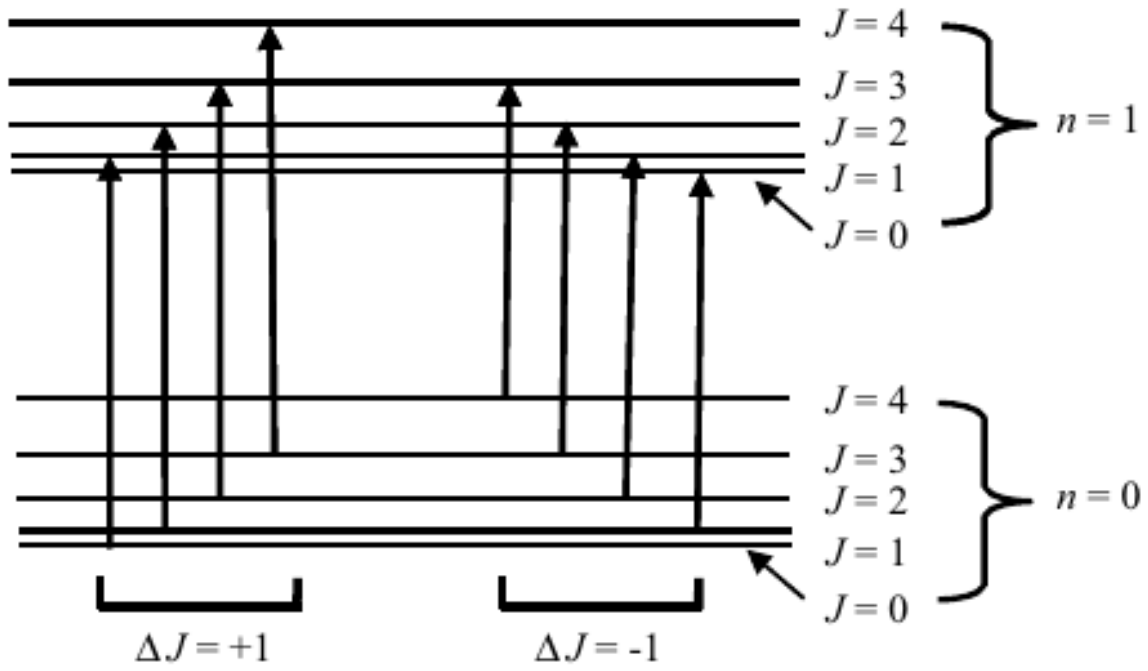


Figure 4.12 The allowed transitions between energy states for molecules experiencing a combination of vibrational and rotational energy changes. The $\Delta l = 0$ transition is forbidden.

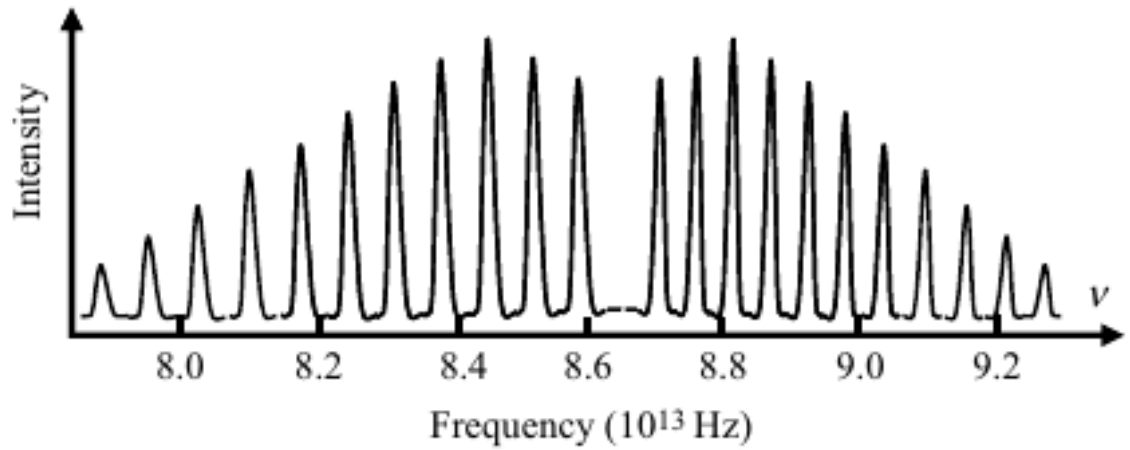


Figure 4.13 A schematic of the combined vibrational-rotational absorption spectrum for HCl, corresponding to the allowed transitions shown in Figure 4.11. The absence of the central frequency peak results from the $\Delta l = 0$ transition being forbidden (based on [2,3]).

Total Internal Reflection Florescence

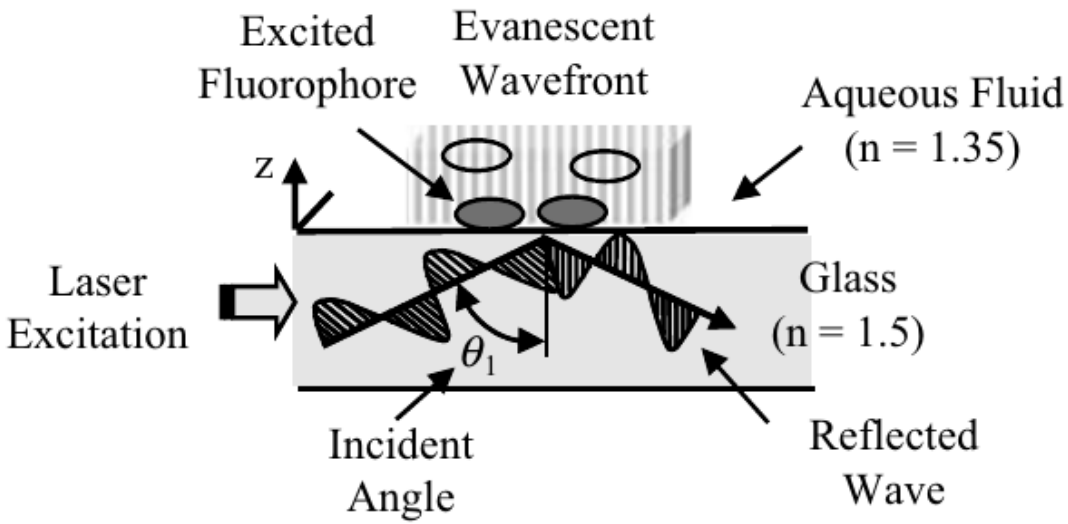


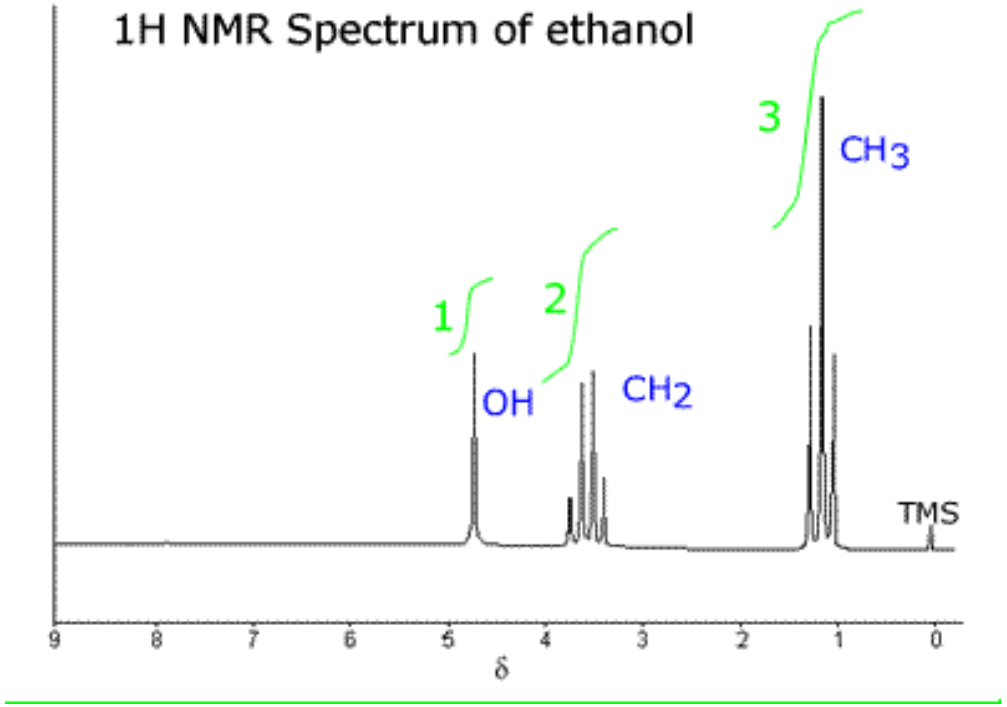
Figure 4.14 Total internal reflection fluorescence (TIRF) makes use of the EM evanescent wave generated by the interference between an incident and reflected light wave. Total internal reflection occurs above a critical angle of incidence, provided that the refractive index n of the light guide is greater than that of the adjacent medium. Excitation of fluorophores by the evanescent wave is confined to a region within $\sim$100 nm from the waveguide-fluid interface. In this case two of the four fluorophores shown are excited.

Nuclear Magnetic Resonance (NMR)

- Nuclei can have magnetic moment. Ex: Hydrogen, Carbon etc
- When placed in an external magnetic field, up spin and down spin have different energy, giving rise to transition with energy

$$\Delta E = \frac{1}{2} B g_I \mu_N - \left(-\frac{1}{2} B g_I \mu_N \right) = B g_I \mu_N$$

- NMR finds ALL such transitions
- Each transition is specific to the
- ‘environment’ of that particular
- nuclei
- 60 - 1000 MHz
- Magnetic Resonance Imaging
- (T1 and T2 modes of relaxation)



Surface Plasmon Resonance

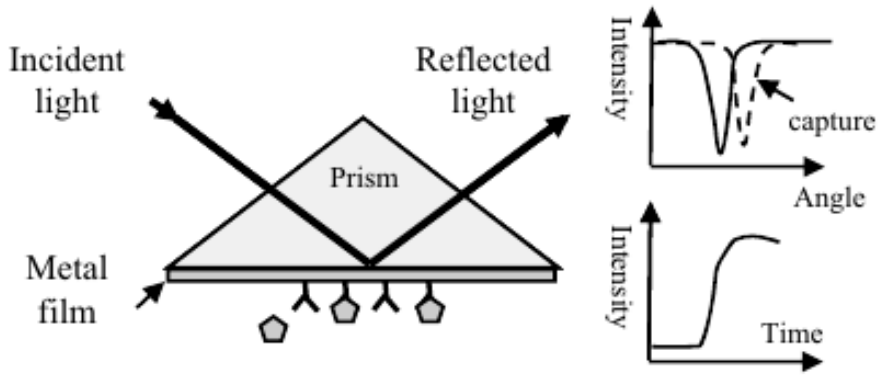


Figure 4.15 At a critical angle of light incidence the photons interact with surface plasmons in a metal film to create polaritons. This critical angle is sensitive to changes of the refractive index of the adjacent medium probed by the created evanescent wave, and changes of this (e.g. caused by analyte capture to an immobilised probe) can be monitored as a change in reflected light intensity.

- Plasmons: quasi-particles arising from harmonic oscillations of free electrons
- Surface Plasmons: plasmons that are confined to surface of metal
- Surface plasmons can couple with light that have matching wave vectors

Froster Resonance Energy Transfer

- Two chromophores: higher energy chromophore transfers energy to lower energy on
- Distance dependent; transfer efficiency inversely dependent on the distance

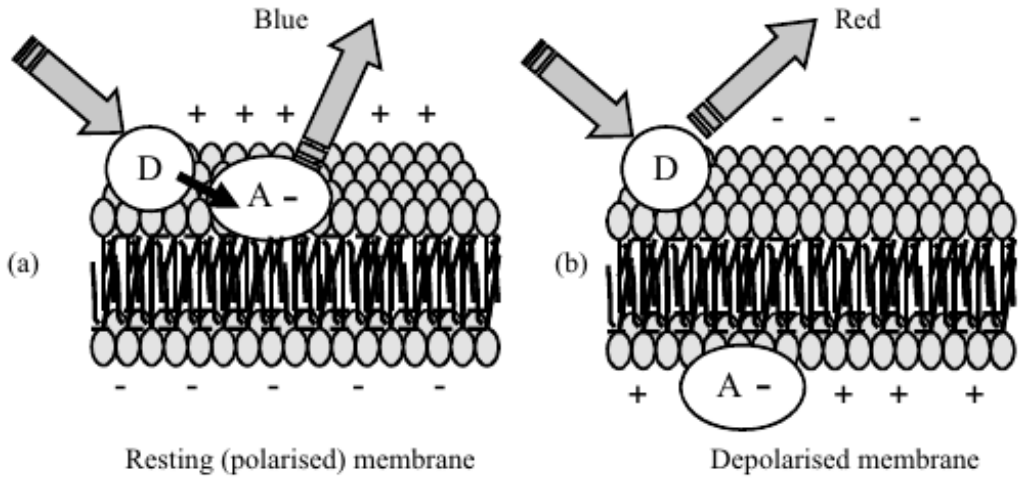


Figure 4.16 The behaviour of electrically excitable cells can be studied by monitoring how the blue fluorescence of a negatively charged acceptor molecule ceases when the membrane potential reverses polarity during an action potential event. The resting state is characterised (in this example) by emitted blue fluorescence arising from FRET from the excited donor molecule, which when energetically uncoupled from the acceptor through their separation being greater than the critical distance fluoresces in the red.

Purposefully empty, see next slide

Intro to Bioelectronics

Electrochemistry
Ref: Ch-5 of "Intro Bioelectronics" by Pethig and Smith

Dr. Prabhakar Bhimalapuram
Center for Computational Natural Sciences and Bioinformatics

HW: remainder "equilibrium electrochemistry"

- Sections 5.0, 5.1, 5.2 and 5.3 of Pethig and Smith

- Basically revision of "Electrochemistry" material in 11th and 12th standard syllabus

Redox Reactions

- Reduction: A + e- -> A- (molecule A receives an electron)
- Oxidation: B -> B+ + e- (molecule B loses an electron)

Electrochemical Cell:

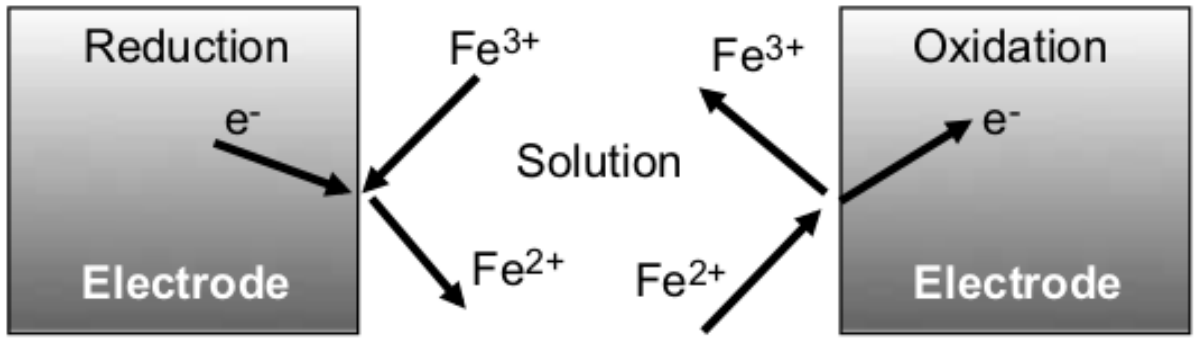


Figure 5.3 The reduction (left) and oxidation (right) reactions shown in Figure 5.2 can each take place at an electrode surface.

If both reduction and oxidation happens naturally (spontaneously), setup is called Galvanic or Voltaic Cell.

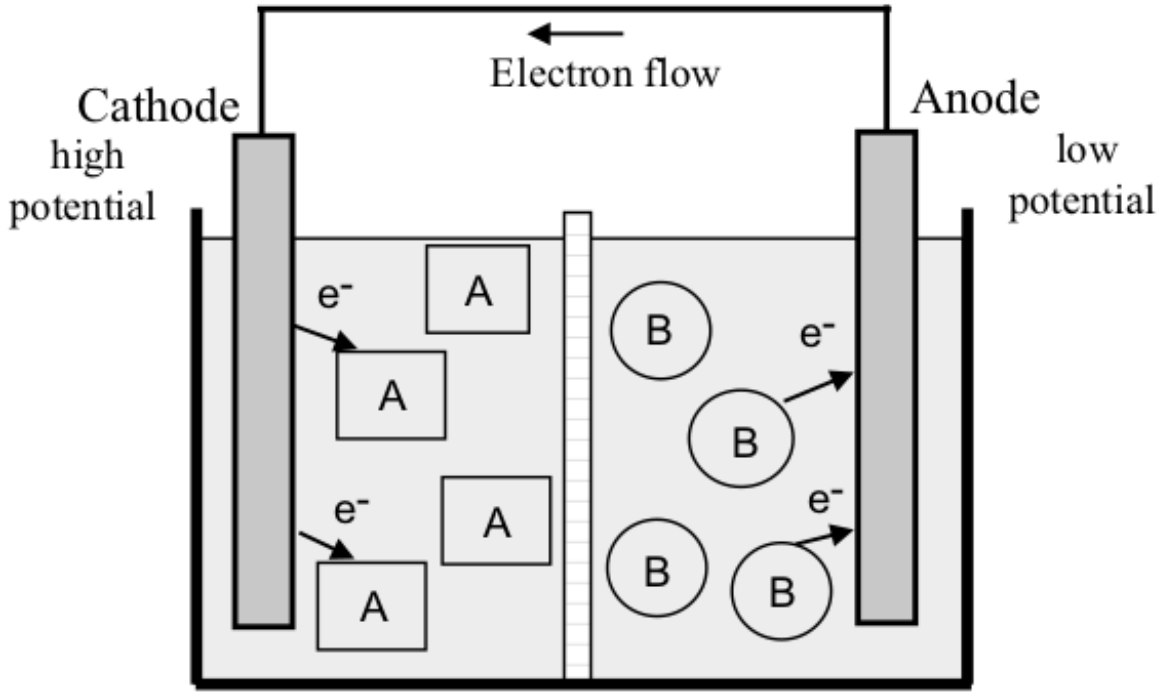


Figure 5.5 In an electrochemical cell the r*eduction* reaction occurs at the *cathode*, inducing a *positive potential* relative to the solution. A *negative potential* relative to the solution is induced at the *anode* as a result of its o*xidation* reaction. An ion porous membrane allows the flow of ions between the two halves of this cell.

Electrochemical cell vs Electrolytic cell

Table 5.1 The definition and electron transfer characteristics of the anode and cathode for an electrochemical cell (battery) and a cell supporting electrolysis

Location	Electrochemical cell	Electrolytic cell
Anode	• Site of oxidation • The negative terminal • Releases electrons to external circuit	• Site of oxidation • The positive terminal • Releases electrons to external circuit
Cathode	• Site of reduction • The positive terminal • Accepts electrons from external circuit	• Site of reduction • The negative terminal • Accepts electrons from external circuit

Reactions at electrodes

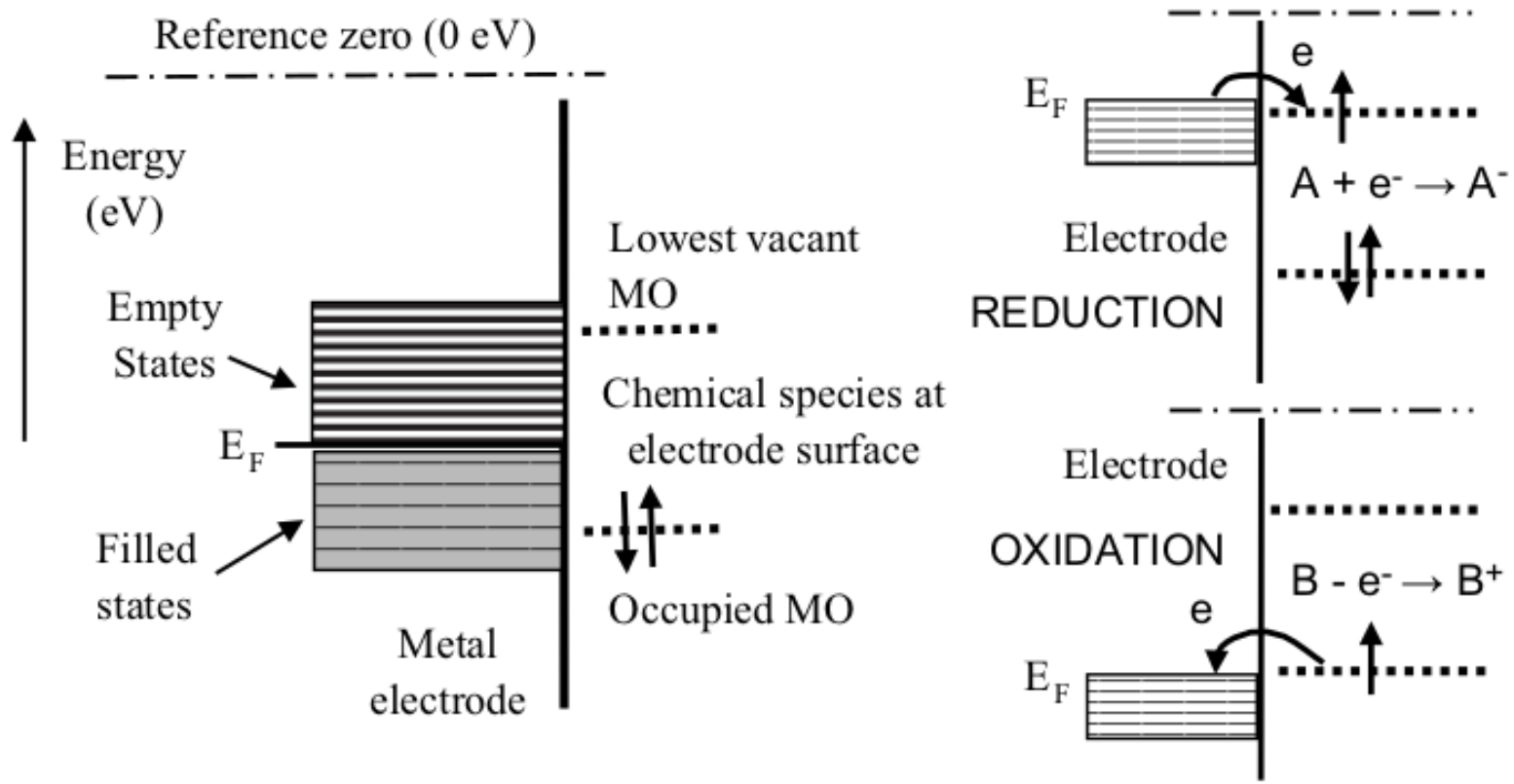


Figure 5.7 Reduction involves the transfer of an electron from the electrode's Fermi level E_F to an unfilled molecular orbital. (MO) of a chemical species situated at the electrode surface. Oxidation involves the transfer of an electron from an occupied MO to an unoccupied level near the Fermi level.

Metal dipped in its salt solution

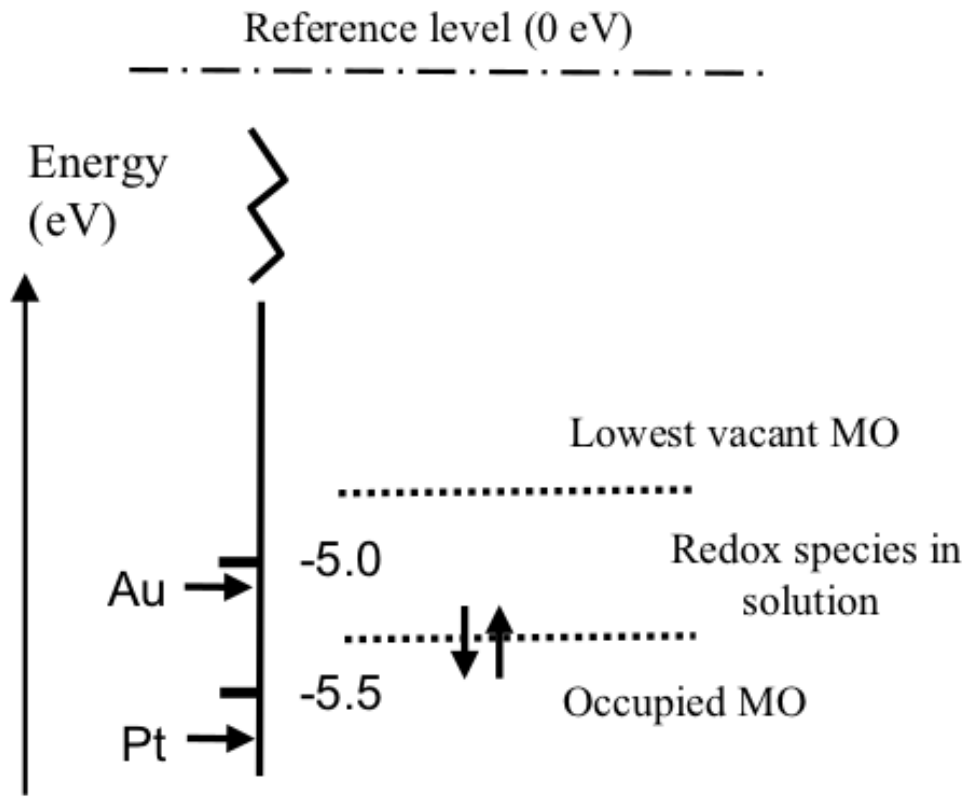


Figure 5.8 The relative Fermi energies for a gold and platinum electrode are shown with respect to the molecular orbital energy levels for a chemical species at the electrode surface (based on Table 5.2 and figure 1.1.3 of [1]). At their equilibrium (zero-current) potentials the chemical will more readily be oxidised by the platinum electrode than by the gold electrode. If their potentials are moved towards more positive values the gold electrode will, on purely thermodynamic grounds, more readily reduce the chemical than the platinum electrode.

Cell setup

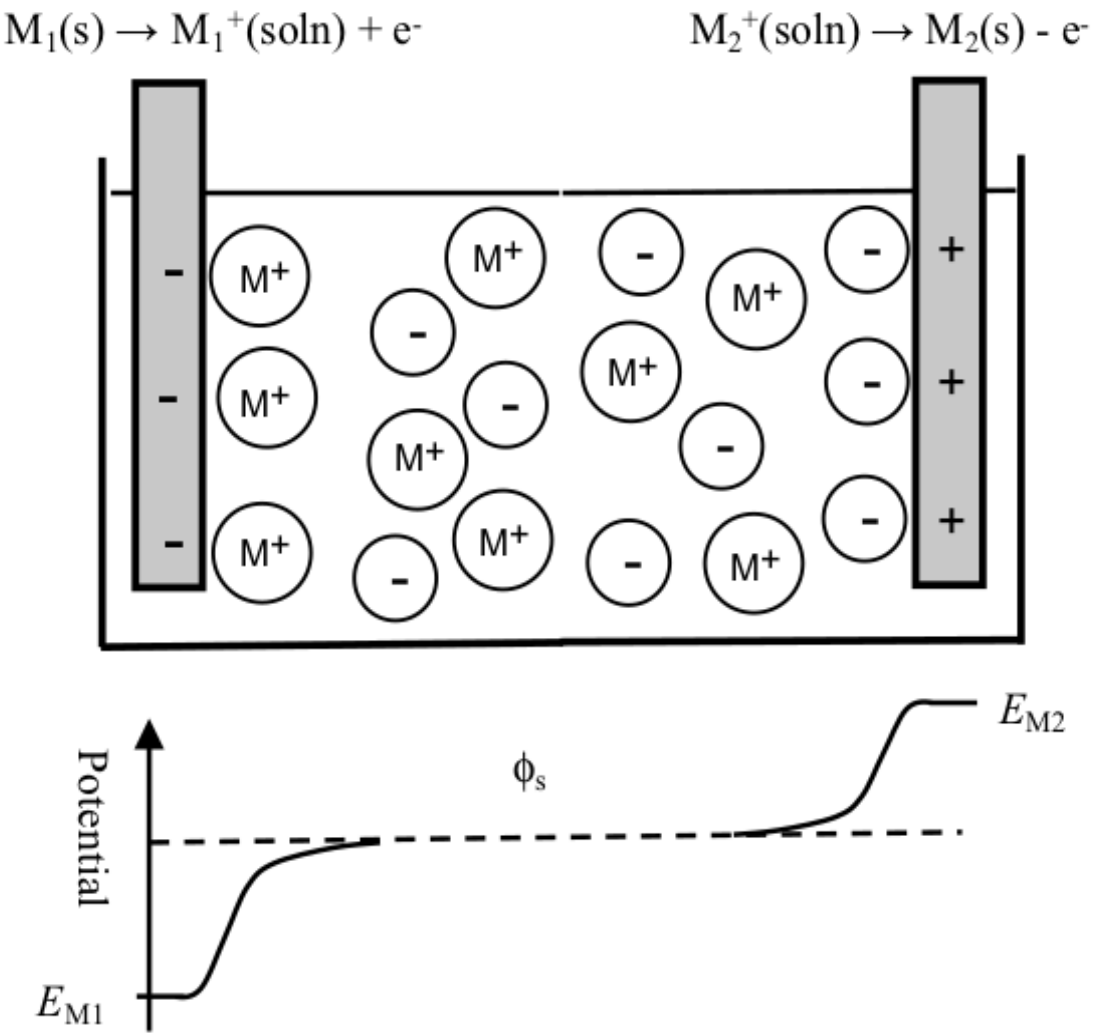


Figure 5.9 The amount and polarity of the net charge on an electrode immersed into a solution containing its metal salt will depend on where the equilibrium lies for the two electrode reactions shown. The potential difference (voltage) appearing between the two electrodes is given by $[(E_{M1} - \phi_s) - (E_{M2} - \phi_s)] = (E_{M1} - E_{M2})$. If E_{M2} is defined as the reference potential, then E_{M1} is the electrode potential of electrode M1 with respect to electrode M2.

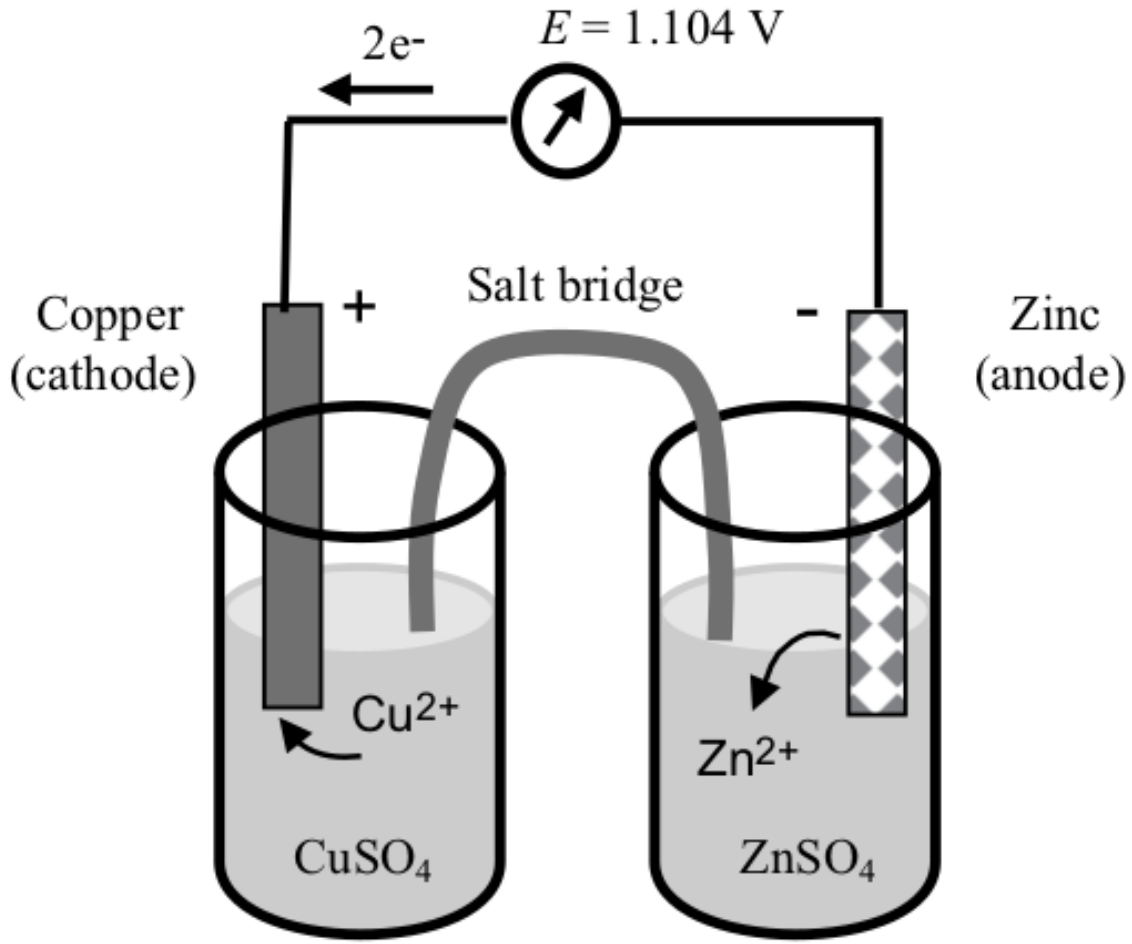
Nernst Equation

- Electrical potential at an electrode is produced by utlising the loss of free energy of the system.
- Free energy change is given by:

$$\Delta G = \Delta G^o + RT \ln\left(\frac{[reduced\,form]}{[oxidized\,form]}\right) = \Delta G^o + RT \ln\left(\frac{[M]}{[M^{Z+}]}\right), \qquad (5.1)$$

- Electrical work is given by n*F*E where F is Faraday constant, E is the electrode potential and n is number of electrons transferred

$$\Delta \mathrm{G} = -nFE, \qquad (5.2)$$



aniell Cell. The electrochemistry of this cell is dis

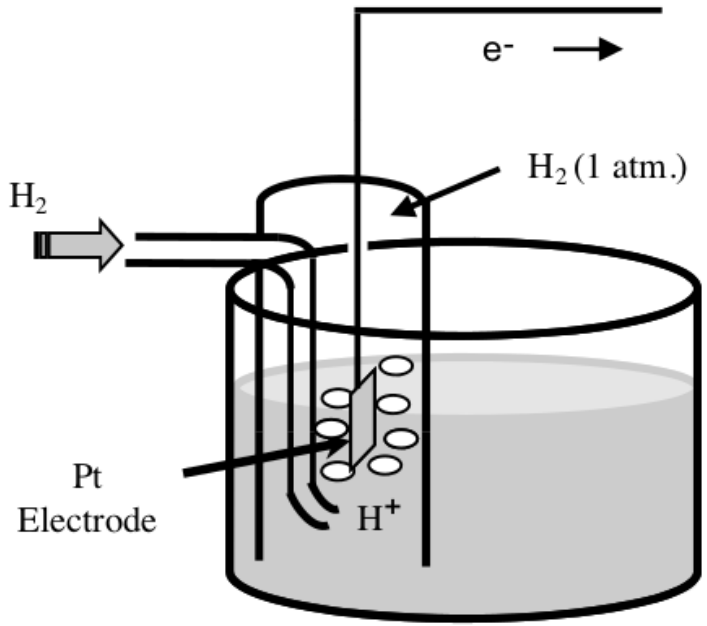


Figure 5.11 The standard hydrogen electrode (SHE) defines the zero reference level for the determi nation of the standard reduction potential of another half-cell system (with a shared electrolyte o hydrochloric aced). The temperature is 25 °C and hydrogen gas is passed at a pressure of one atmo sphere over a pure platinum electrode.

Table 5.3 Standard reduction potentials for some common half-cell reactions. (P. Vanysek, *CRC Handbook of Chemistry and Physics*, 87th edn, Boca Raton, 2007).

$^1/_2$-Cell reaction	Standard potential E^o (Volts)
$F_2 + 2H^+ + 2e^- \leftrightarrow 2HF$	+3.053
$Au^{3+} + 3e^- \leftrightarrow Au$	+1.498
$O_2 + 4H^+ + 4e^- \leftrightarrow 2H_2O$	+1.229
$Br_2 + 2e^- \leftrightarrow 2Br^-$	+1.066
$Ag^+ + e^- \leftrightarrow Ag$	+0.7996
$Fe^{3+} + e^- \leftrightarrow Fe^{2+}$	+0.771
$Cu^+ + e^- \leftrightarrow Cu$	+0.521
$Cu^{2+} + 2e^- \leftrightarrow Cu$	+0.3419
$Hg_2Cl_2 + 2e^- \leftrightarrow 2Hg + 2Cl^-$	+0.26808
$AgCl + e^- \leftrightarrow Ag + Cl^-$	+0.22233
$2H^+ + 2e^- \leftrightarrow H_2$	0.0000
$CO_2 + 2H^+ + 2e^- \leftrightarrow HCOOH$	−0.199
$PbSO_4 + 2e^- \leftrightarrow Pb + SO_4{}^{2-}$	−0.3588
$Fe^{2+} + 2e^- \leftrightarrow Fe$	−0.447
$Cr^{3+} + 3e^- \leftrightarrow Cr$	−0.744
$Zn^{2+} + 2e^- \leftrightarrow Zn$	−0.7618
$2H_2O + 2e^- \leftrightarrow H_2 + 2OH^-$	−0.8277
$Al^{3+} + 3e^- \leftrightarrow Al$	−1.662
$K^+ + e^- \leftrightarrow K$	−2.931
$Ca^+ + e^- \leftrightarrow Ca$	−3.80

Electron transfer reactions at electrode

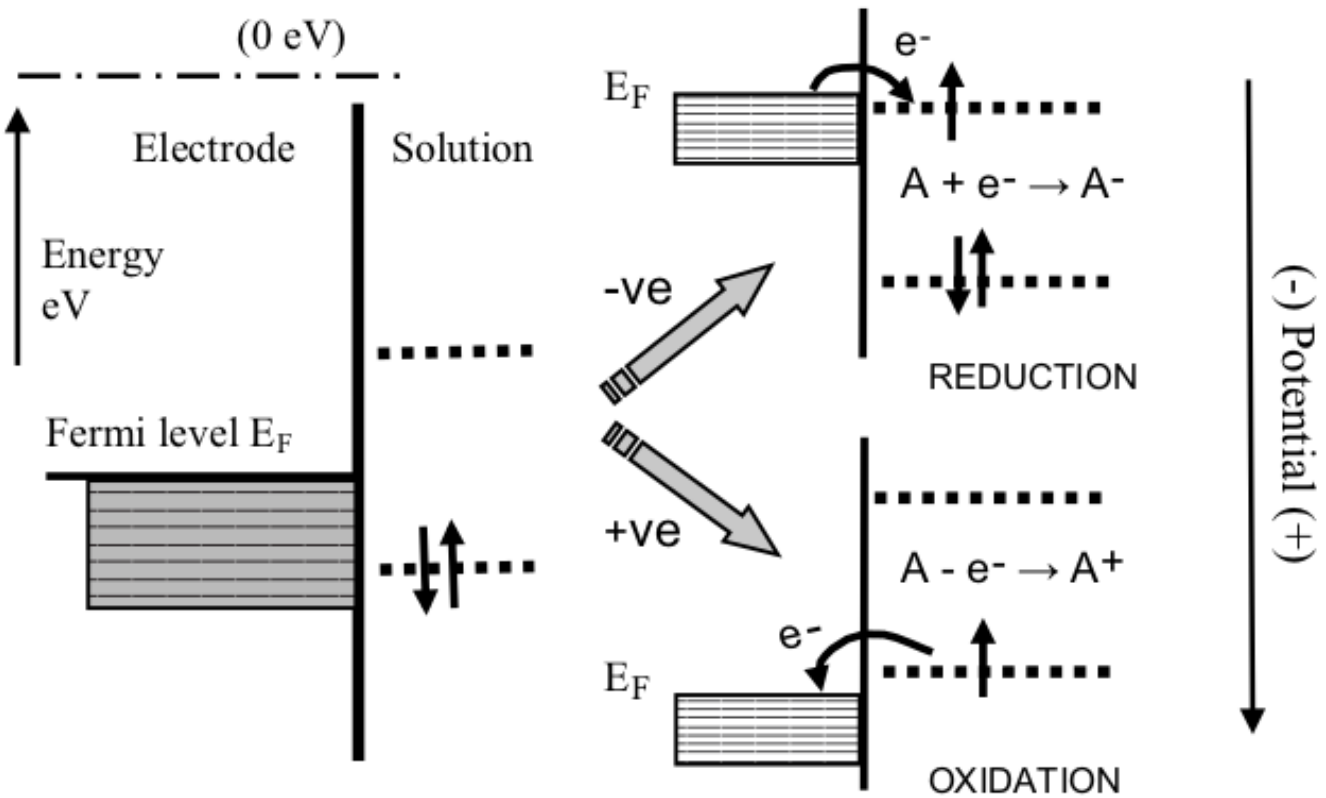


Figure 5.13 Electron transfer reactions at an electrode surface can be controlled by making the electrode potential more positive or negative. The situations shown here correspond to a more positive potential giving rise to the oxidation, and a more negative potential leading to reduction, of a chemical species.

- At electrode dynamical equilibrium between:

Oxidation Current

$$I_{\mathrm{O}} = nF[O]_{\mathrm{s}}\, k_{\mathrm{O}};$$

Reduction Current

$$I_{\mathrm{R}} = -nF[R]_{\mathrm{s}}\, k_{\mathrm{R}};$$

- Net current: I = I_O – I_R

- Butler-Volmer Equation:

$$I = I_o\left[\exp\left(\frac{\alpha_A nF(E-E^o)}{RT}\right) - \exp\left(-\frac{\alpha_C nF(E-E^o)}{RT}\right)\right]. \qquad (5.9)$$

$$\log(I_{OX}) = \log I_o + \frac{\alpha_A nF}{2.3RT}(E-E^o).$$

$$\log(I_R) = \log I_o - \frac{\alpha_C nF}{2.3RT}(E-E^o).$$

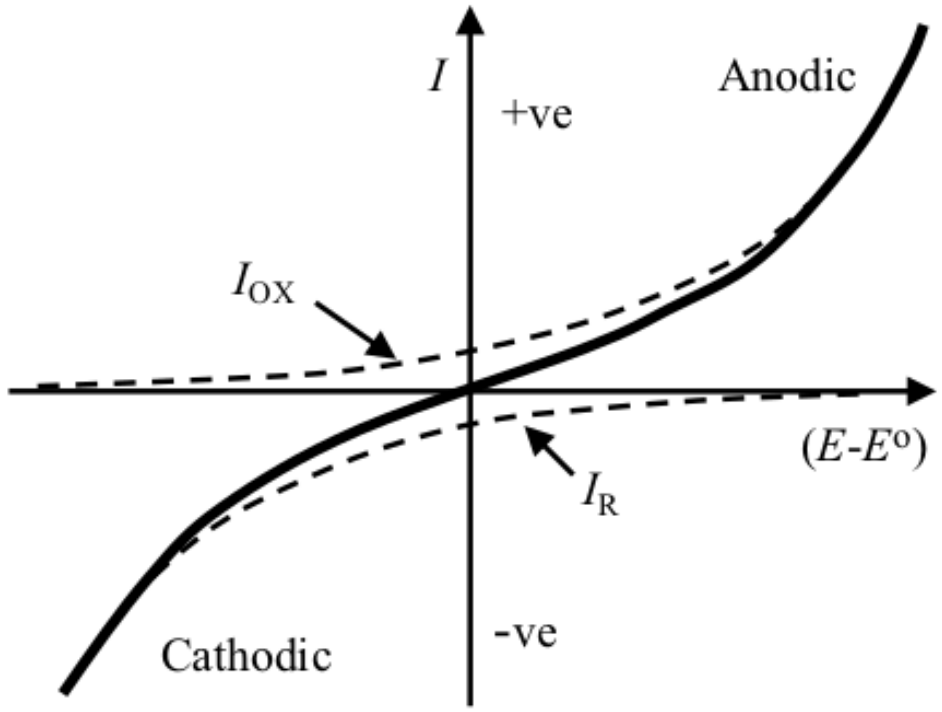


Figure 5.14 The current-potential response of an electrode reaction according to the Butler-Volmer equation (5.9). The total current is the sum of the anodic and cathodic currents given by equations (5.10) and (5.11). Any rate limiting steps associated with the *mass-transfer* of electroactive species between the electrode surface and the bulk electrolyte are not included.

$$I = I_o \left[\frac{[O]_s(t)}{[O]_{bulk}} \exp\left(\frac{\alpha_A nF(E - E^o)}{RT} \right) - \frac{[R]_s(t)}{[R]_{bulk}} \exp\left(- \frac{\alpha_C nF(E - E^o)}{RT} \right) \right]. \qquad (5.$$

Cyclic Voltogramm

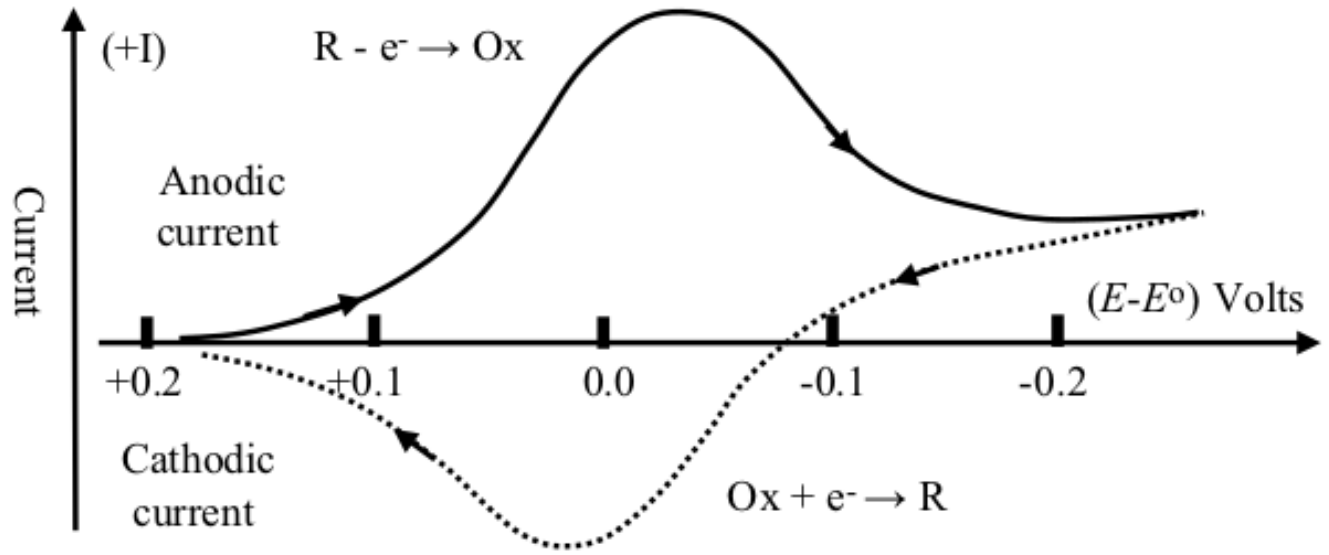


Figure 5.15 A cyclic voltammogram for a reversible redox reaction. Starting at a value above the standard reduction potential E_o, with only the oxidised form of an electroactive species present, the electrode potential E is ramped to a value below E_o, and than back up again. This generates the reduction current peak (solid line) followed by the oxidation current peak (dotted line).

Various processes at electrode

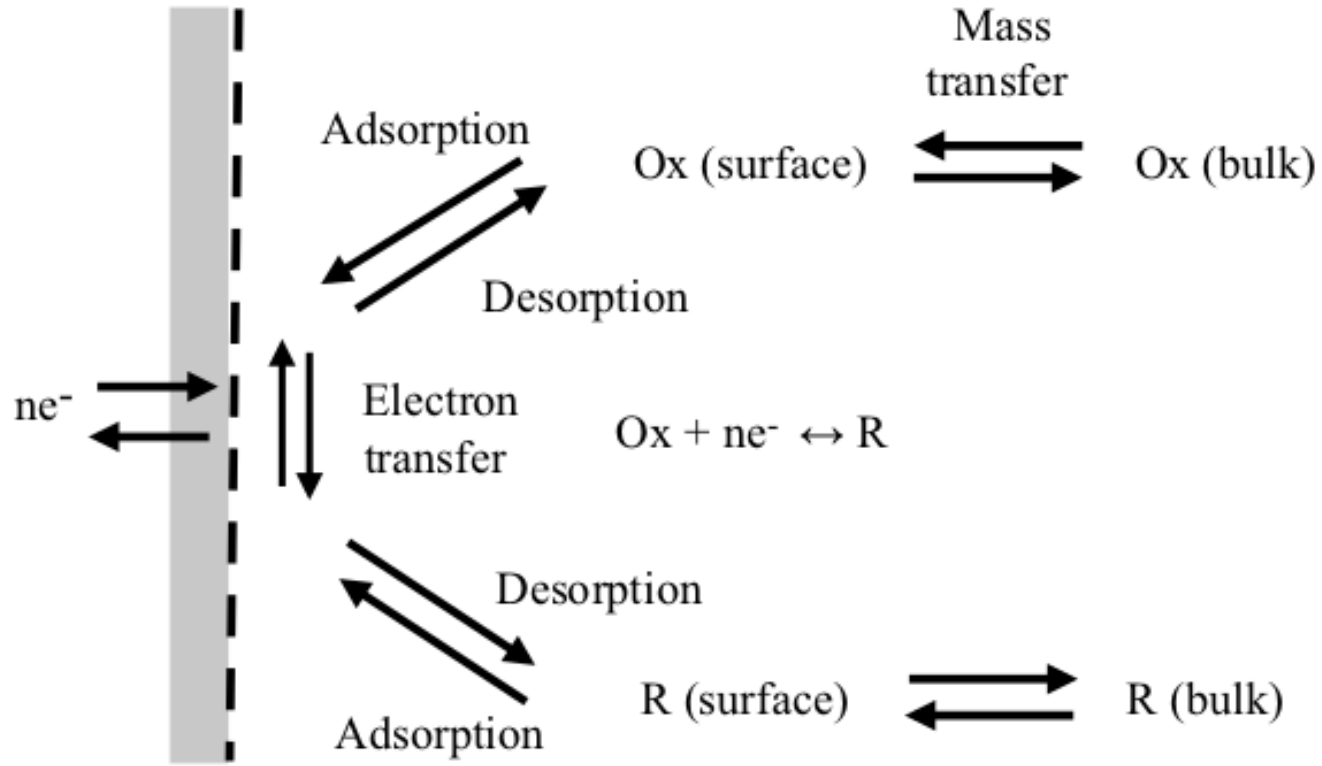


Figure 5.16 The flux of electrons ($-I/nF$) across an electrode surface for a reversible redox reaction is controlled by the kinetics of the electrochemical electron transfer and the mass transport of reduced (R) and oxidised (O) species to and away from the metal surface. The mass transfer involves the diffusion and/or migration of R and O down concentration gradients and electric fields.

Ampherometry

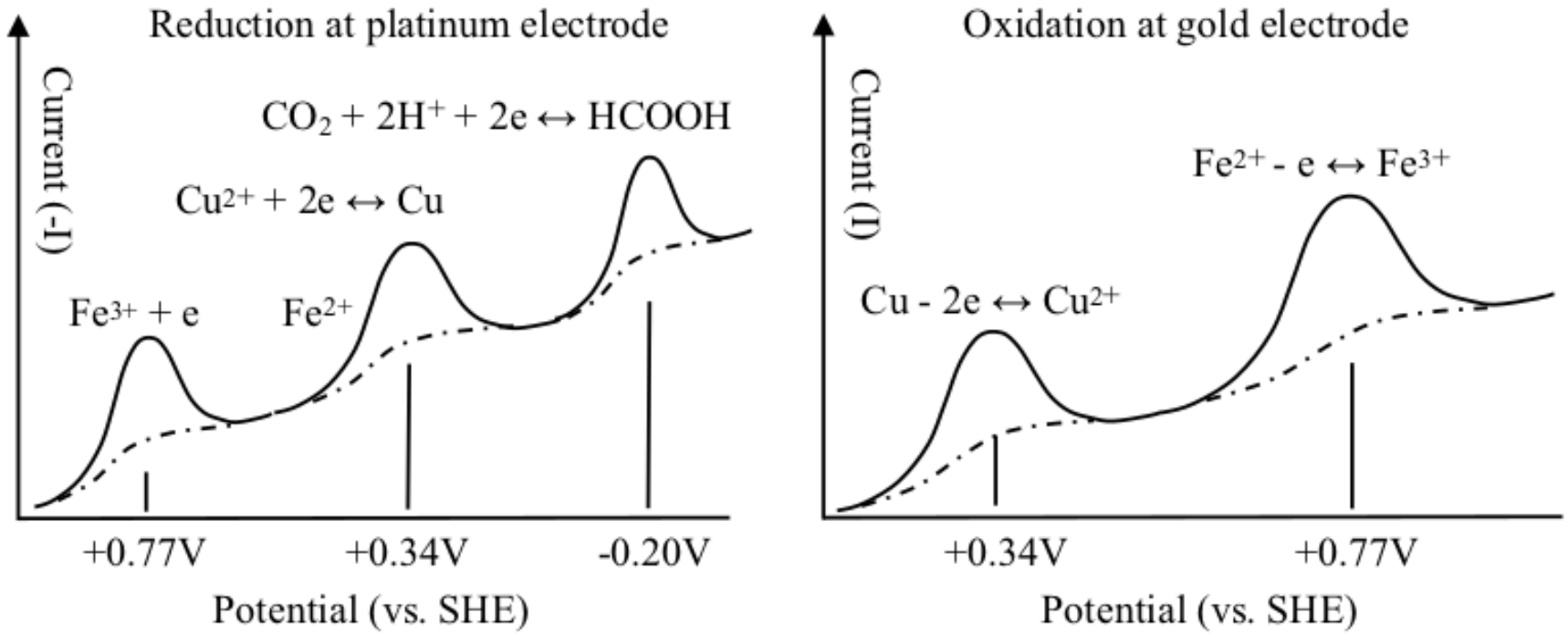


Figure 5.18 Reduction and oxidation currents produced as a function of the potential applied to platinum and gold electrodes, respectively, for the series of redox reactions shown in Figure 5.17 The current peaks are obtained using an applied linear voltage ramp, whilst the dotted curves show the steady-state current.

Three electrode system

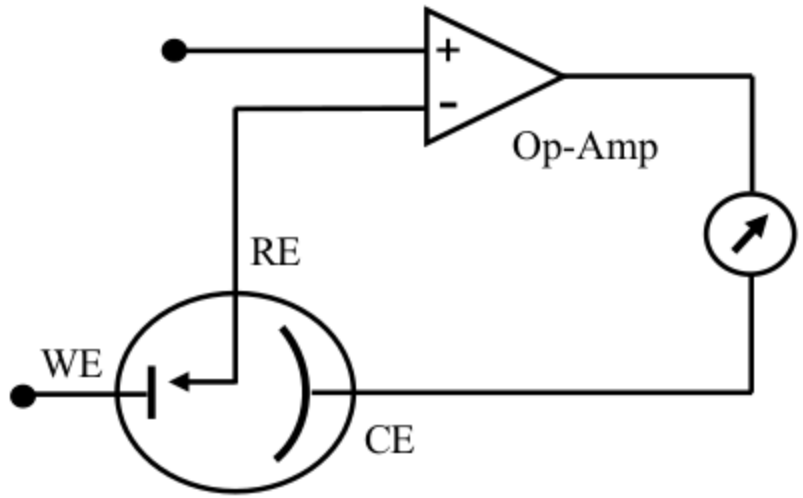


Figure 5.20 A three-electrode electrochemical cell, consisting of the working electrode (WE), a reference electrode (RE) and the counter electrode (CE). The operational amplifier drives the current between the working and counter electrode, but negligible current passes through the reference electrode.

Electrical Impedence Spectroscopy

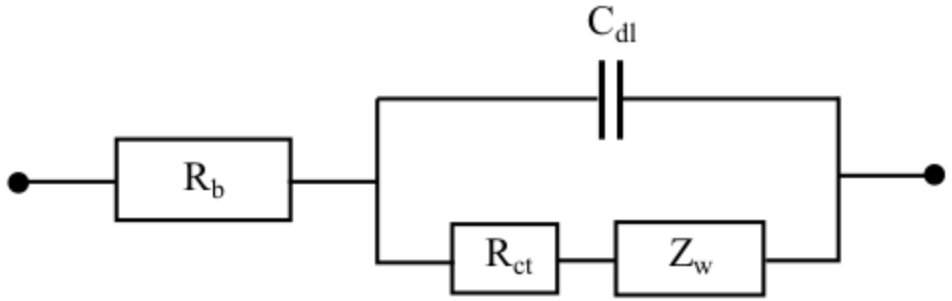


Figure 5.26 Equivalent circuit that includes a charge transfer resistance R_{ct} that controls the kinetics of a simple reversible electrode reaction, together with the Warburg impedance Z_w that controls the mass transport. The resistance R_b of the bulk electrolyte and the capacitance C_{dl} of the electrical double layer at the electrode are also included.

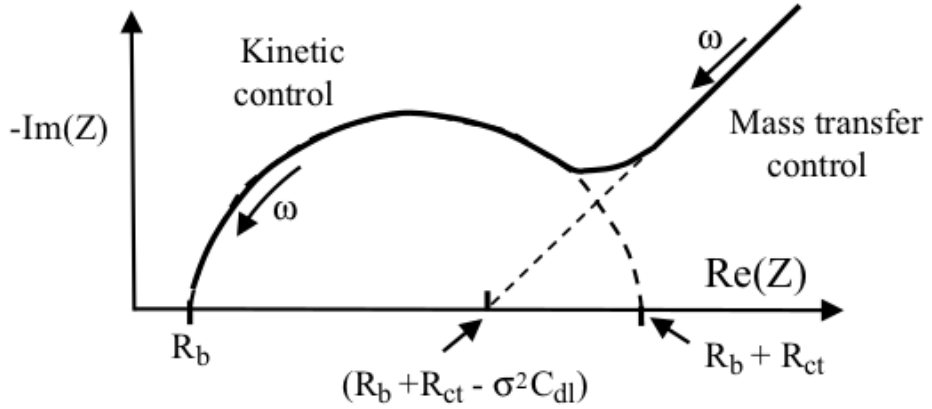


Figure 5.27 Complex impedance plot for the equivalent circuit of an electrode reaction shown in Figure 5.26. Mass transfer control operates at low frequencies, and kinetic control occurs at high frequencies.