

Chapter 1 STUDY GUIDE

How do living systems transcend lifeless molecules? In what sense are living systems more than a collection of molecules obeying the laws of P & C?

They need to have purposefulness and reproductive invariance, complicated and highly organized, biological structures serve functional purposefulness and living systems are actively engaged in energy transformations. Living systems also have a remarkable capacity for self replication. Growth, metabolism, stimulus response, and replication.

Distinguish between vitalism and systems theory.

New properties emerge at each level due to interactions between lower level components because..

Vitalism: because some non-material, vitalistic spirit has been added

Systems Theory: because the potential has been built into components...at every level

Explain that a living system is one that is able to avoid many, many non-living organizational states.

The living state is characterized by the flow of energy through the organism. Energy and material are consumed by the organism and used to maintain stability and order.

How common is organization in Nature? (refer to the "Powers of Ten" reference below)

Explain the implications of the "Bioxerox machine"?

If you take Joe and make an atomic replicate, that is scan all the inorganic precursors CHNOPS and put them all back together and form Joe prime then will Joe Prime be living? Yes because if the atomic level is organized then all following levels as we expand outward will be organized that is the inorganic precursors will be able to form Metabolites which can then form building blocks such as amino acids and nucleotides which will then form the macromolecules → supramolecules complexes → organelles → cells → etc.

Make a hierarchical list of the levels of Nature.

The Inorganic precursors → Metabolites → Building blocks → Macromolecules → Supramolecular complexes → Organelles → The cell

In what sense is this an inclusive, or embedded, or nested hierarchy?

Inclusive system: All have different functions but are made up of the same system

Distinguish the holistic "why" question with the reductionistic/mechanistic "how" question.

Why questions go up hierarchy (eg. To what purpose does it have these properties)

How go down hierarchy (eg. By what mechanism)

Explain the covalent-bonding properties of CHNOPS.

Figure 1.6 page 5

Explain the statement: "New properties emerge at each level."

Due to interactions between lower level components

Name the three "primals" of systems theory...and their units of measurement.

- Mass
 - Grams, g
 - Daltons, D
- Energy
 - Cals/kcals
 - Joules/kJoules
- Information
 - bits

Be able to interconvert: grams/daltons and cals/joules.

1 gram = 6×10^{23} daltons (1 gram = rasin)

1 cal = 4.17 Joules

Explain and give examples of three weak chemical forces.

Van der Waals Interactions: Are the result on induced electrical interactions between closely approaching atoms or molecules as their negatively charged electron clouds fluctuate instantaneously

in time. Strength depends on the relative size of the atoms or molecules distance between them. The size factor determines the area of contact between two molecules: The greater the area, the stronger the interaction. Examples include: dipole-dipole interactions, dipole-induced dipole interactions and induced-dipole induced-dipole interactions (London dispersion forces). The People on hockey puck example shown in class! Have **precise fit!**

Hydrogen bonds: Form between a hydrogen atom covalently bonded to an electronegative atom and a second electronegative atom that serves as the hydrogen bond acceptor. Have a strength of **12 to 30 kJ/mol** and are cylindrically symmetrical and tend to be **highly directional**. Relative strength is proportional to the polarity of the H bond donor and the H bond acceptor. More polar atoms form stronger H bonds. Example include: **figure 1.14**

Ionic Interactions: The results of attractive forces between oppositely charged polar functions, such as **negative carboxyl groups and positive amino groups**. Average about **20 kJ/mol** in aqueous solutions, radially distributed charge (lack directionality of hydrogen, precise fit of van der Waals interactions) strength also depends on the relative polarity of the interacting charges species. Some ionic interactions are also H bonds: $-\text{NH}_3^+ \dots \text{OOC}-$ Other examples include oppositely charged groups on amino acid residues in a protein, Histone –DNA complexes in chromosomes.

Compare their sizes with that of thermal agitation.

Table 1.3 page 13

Thermal Agitation:	2.5 kJ/mol
Van der Waals interactions:	0.4- 4.0 kJ/mol
Hydrogen Bonds:	12 – 30 kJ/mol
Ionic interactions:	20 kJ/mol
Hydrophobic interactions:	<40 kJ/mol

Given their sensitivity to thermal agitation, how can weak chemical forces be important in biology?

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Questions to answer:

1. Calculate your mass in grams, in kilograms, in daltons. Based on the result, what is the most appropriate (user-friendly) unit to use?
2. The oxidation of organic matter releases about 4 to 9 kCals/gm. Ignoring the 70% of your body weight that is water, estimate the energy that would be released by your spontaneous combustion. (Give result both in kCals and kJ's.)
3. An average gene has 1000 bases. How much information does this much DNA contain? Assuming (Human Genome Project) 25,000 genes, how much info is that?
4. Give your own examples of: (a) purposefulness, and (b) reproductive invariance
5. If biomolecules were as boringly round and featureless as billiard balls, biological systems would not "work;" you couldn't get purposefulness and reproductive invariance etc. Why not?

Emergence of new properties at a level requires sophisticated interactive reaction between its components. In the biochemistry of the cell, this means stereo chemical shapes and recognition via weak forces. Boring round and featureless billiard balls don't have that potential.

6. What do you learn from: <http://micro.magnet.fsu.edu/primer/java/scienceopticsu/powersof10/>
That at every level (power of 10) there exists compartments and organization

Chapter 2 STUDY GUIDE

Name and represent (ie, such as =N- for nitrogen)the eleven common bioatoms
CHNOPS

Describe the basis of tetrahedral structure ($4sp^3$ hybrid orbitals)

Distinguish covalent radii and van der Waals radii

Covalent radii are shorter (d/2)

Know average lengths of covalent (0.75 Å) and van der Waals radii (1.5 Å)

Covalent: 0.75 Å

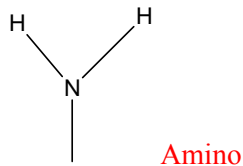
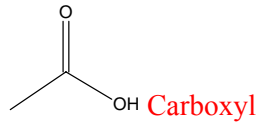
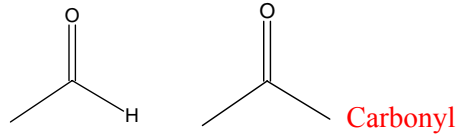
Van der Waals: 1.5 Å

Give approximate strong and weak bond strengths,

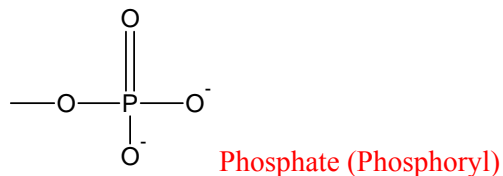
ie, covalent - 400 kJ/mol; weak – 1-80 kJ/mol; vs. thermal - 2.5 kJ/mol

Know the six functional groups

—OH Hydroxyl



—SH Sulfhydryl



Describe the structure and polarity of water

The two hydrogen atoms of water are linked covalently to oxygen, each sharing an electron pair, to give a nonlinear arrangement (bent). In the bent configuration the electronegative O atom and the two H atoms form a dipole that renders the molecule distinctly polar. Can serve as an H donor and an H acceptor.

Figure 2.1

The O-H bonds represent shared pairs of electrons (covalent bond = .095 nm or ≈ 1 Å)

The sharing is unequal

Two lobes of negative charge of the Oxygen atom lie about and below the plane of the diagram

The H-O-H angle is 104 and not 109 (tetrahedral)

Covalent bond length = sum of the covalent radii of O & H

Van der Waals radii define the region of electron density therefore where atoms bounce off each other.

Distinguish liquid water and ice

In ice, the hydrogen bonds form a space-filling, three-dimensional network. These bonds are directional and straight; that is the H atom lies on a directional line between the two O atoms. H bonds in ice are strong and leads to an open lattice structure. They also hold the water molecules apart. **4 H bonds per water molecule, H bond lifetime about 10 microseconds**

In liquid water, pure liquid water consists of H₂O molecules held in a random, three-dimensional network that has a local preference for tetrahedral geometry, yet contains a large number of strained or broken hydrogen bonds. The presence of strain creates a kinetic situation in which H₂O molecules can switch H-bond allegiances; fluidity ensues. The rigidity of ice is replaced by fluidity and the crystalline periodicity of ice gives way to spatial homogeneity. The H₂O moles form a random, H-bonded network. At least half of the hydrogen bonds have nonideal orientations. **2-3 H bonds per water molecule and a H-bond lifetime of 10 psec**

Know the energy, length, and orientation of the hydrogen bond

Between neighboring oxygen atoms linked by a hydrogen bond = 0.274 nm

Covalent H-O is 0.095 nm

The H-O bond in ice is 0.18 nm

←-----0.274nm-----→

O.....H-----O

←-----0.18nm-----→ ←---0.095→

0.18 is less the predicted .14+.10 an indication that the hydrogen bond is shorter and stronger the other weak bonds because the electronic cloud of H is shrunk.

Discuss the basis of solubility

In water it is going to depend on which state minimizes energy...

X bonding to H₂O

X bonding to X and H₂O bonding to H₂O

Which ever state is minimized in energy will determine if the it is soluble

It will be soluble when the attractions between the water molecules interacting with , or hydrating, ions are much greater than the tendency of oppositely charged ions to attract one another.

Ions are always hydrated in water and carry around a hydration shell

Water forms H-bonds with polar solutes

Hydrophobic interactions arise from nonpolar substances

Draw hydrated Na⁺

Show hydrogen bonding of water to the common functional groups

What are hydrophobic compounds? Hydrophilic?

Hydrophobic: "water fearing" non polar compounds

Hydrophilic: "water loving" polar compounds

What is the basis of the hydrophobic effect?

Nonpolar (oily greasy) molecules are excluded from water, as if they were squeezed out, because they can't form good H-bonds with H₂O.

- A nonpolar solute "organizes" water
- The H-bond network of water reorganizes to accommodate the nonpolar solute
- This is an increase in order of water
- This is decrease in ENTROPY

Why do amphipathic substances aggregate into micelles and bilayers?

Amphilphilic /amphipathic refers to molecules that contain both polar and nonpolar groups (fatty acids)

- They have a long nonpolar hydrocarbon tail and a strongly polar carboxyl head group. The ionic carboxylate functions hydrates readily, whereas the long hydrophobic tail is intrinsically insoluble. The hydrocarbon tails of these structures are joined together in hydrophobic interactions as their polar carboxylate functions are hydrates in typical hydrophilic fashion. The polar ends express their hydrophilicity in ionic interactions with the solvent, whereas their nonpolar counterparts are excluded from the water into a hydrophobic domain constituted from the hydrocarbon tails of many like molecules.
- This is decrease in ENTROPY this is because when the amphipathic molecules come together they displace more water molecules than are bound by the aggregate, thereby causing disorder in the system

Describe/draw micelles and lipid bilayers

Negatively charged carboxylate head groups orient to the micelle surface and interact with the polar H₂O molecules via H bonding. The nonpolar hydrocarbon tails cluster in the interior of the spherical micelle, driven by hydrophobic exclusion from the solvent and the formation of favorable van der Waals interactions. Because of their negatively charged surfaces, neighboring micelles repel one another and thereby maintain a relative stability in solution.

Describe the molecular basis of diffusion

Based on the randomizing effect of thermal agitation, moving an average distance $d \sim t^{1/2}$

Even in a living cell there is no other way for two objects to meet than by random diffusion. A greater directionality would require some long range force. (For ex. Ionic forces are 10 to 40 nm but they are nonspecific.)

Why are bimolecular interactions dependent on random diffusion and stereospecific selection?

“going bump in the night” For example its how a metabolite finds the interior of a bacterial cell to ensure hitting an enzyme’s active site.

How is dialysis used in the biochemical lab?

For separating particles from a solution

Explain the basis of osmotic pressure

Osmotic pressure arises when two aqueous compartments are separated by a semi permeable membrane through which water can pass. If a solute is dissolved in one of the aqueous compartments (and the solute is not freely permeable to the membrane), water will move from the solute-free compartment into the compartment containing the solute. The amount of pressure necessary to prevent this movement of water is the osmotic pressure. Osmotic pressure is a colligative property and as such its magnitude is directly proportional to concentration.

The pressure required to prevent water molecules from moving from a region of higher effective concentration to a region of lower effective concentration.

Describe the ionization of water

Water is capable of ionizing in solution to form hydrogen ions and hydroxyl ions this is because the larger, strongly electronegative oxygen atom strips the electron from one of its hydrogen atoms, leaving the proton to dissociate. Free protons are immediately hydrated to form hydronium ions (H₃O⁺)



Be able to interconvert [H⁺] and pH

$$\text{pH} = -\log[\text{H}^+]$$

See practice problems

Explain the meaning of dissociation constants

States to what extent to which a substance forms ions in water.

Write, explain, and use the Henderson-Hasselbalch eqn

$$\text{pH} = \text{pK}_a + \log_{10} \frac{[\text{A}^-]}{[\text{HA}]}$$

Thus the pH of a solution can be calculated, provided K_a and the concentrations of the weak acid HA and its conjugate base A⁻ are known. When [HA] = [A⁻], pH = pK_a

Provides a general solution to the quantitative treatment of acid-base equilibria in biological systems.

Draw the titration curve of a weak acid (for example, acetic acid, pK_a of 4.76)

Figure 2.11 and figure 2.12 A titration curve will be relatively flat at pH values near the pK_a . In other words the pH changes relatively little as OH^- is added in this region of the titration curve.

What is a polyprotic acid?

A substance that has more than one dissociable proton, will have multiple pK_a 's

How does a buffered solution resist changes in pH?

Being composed of a weak acid and its conjugate base. A solution of weak acid that has a pH nearly equal to its pK_a will by definition contain an amount of the conjugate base nearly equivalent to the weak acid. Addition of H^+ then has little effect because it is absorbed by the following reaction:



Similarly an increase in $[OH^-]$ is offset by the process



List the major blood-buffering compounds

Bicarbonate, Hemoglobin, Proteins, Ionizable groups, especially on histidine, phosphoric acid species