Problems for Premeds, Version 5

These are supplementary end-of-chapter problems designed for premedical students and biology majors taking an introductory chemistry course. Although they are labelled by the chapters in the 8th edition of Principles of Modern Chemistry by Oxtoby, Gillis and Butler, they may be used with any textbook. Faculty are welcome to use these problems in homework and exams, with attribution. However, this material is not for commercial use. (For example, you may not include them in a textbook where copyright is transferred to the commercial publisher.) We wish these problems to be available to students free of charge. Materials contributed by my colleagues are followed by their initials; their names are listed below. If you are a faculty member who wishes to contribute additional original problems, please email me L-Butler@uchicago.edu. Updates to Problems for Premeds are available at http://butlerlab.uchicago.edu/textbook.html.

GE = Prof. Greg Engel, The University of Chicago
PS = Dr. Preston Scrape, PhD, The University of Chicago, 2017
PV = Pablo Vicente, BA, The University of Chicago, 2021
JC = Julia Chael, BS, The University of Chicago, 2020

CHAPTER 1, Section 1.6: The Mole: Counting Molecules by Weighing

P1. Mannitol, $C_6H_{14}O_6$, may be prescribed to reduce swelling of the brain due to acute liver failure. A 100 kg patient is given 0.900 moles of mannitol intravenously over 30 minutes. How many molecules of mannitol is this, and how many moles of O atoms have been transferred to the patient with this infusion?

P2. Amygdalin is a compound found in the seeds of many stone fruits, including cherries. Should someone bite into the seed of a cherry, amygdalin is released, and the body metabolizes it to produced cyanide. The amygdalin content of a red cherry seed is 3.89 mg g^{-1}, and the oral LD_{50} (the amount of substance that is lethal to 50% of a population sampled) for a rat is 0.405 g kg^{-1}. The molar mass of amygdalin is 457.43 g mol^{-1}. **(PV)**

a) How many moles of amygdalin is present in a cherry seed whose mass is 1.49 grams?

b) Is eating this cherry seed likely to be lethal to a rat whose mass is 120 grams?

P3. The f-ATPase pump is a rotary ATPase found in the mitochondrial inner membrane and plays an important role in oxidative phosphorylation. A given f-ATPase is capable of synthesizing 100 molecules of ATP per second. **(PV)**

a) How many molecules of ATP are produced in four hours by a single f-ATPase pump?

b) What is the mass in grams of the number of ATP molecules found in part a) if the relative atomic mass of ATP at physiological pH is 503.1489 on the ^{12}C scale?

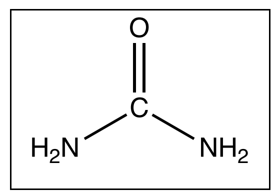
CHAPTER 2: Cumulative Problems for Chemical Formulas, Equations, and Reaction Yields

P4. Theobromine (IUPAC name 3,7-Dimethyl-1*H*-purine-2,6-dione) is a compound found in cocoa beans that is toxic to dogs and cats. This compound has an LD_{50} (the amount of substance that is lethal to 50% of a population sampled) per kg of body mass of 300 mg per kg of body mass for canines. If your dog ingests a toxic dose of theobromine, vomiting should be induced by a veterinarian within two hours as a lifesaving measure.

a) Your beagle with a body mass of 20 lb consumes three bars of dark chocolate. Dark chocolate typically contains 400 mg of theobromine per ounce and a bar is 3.5 oz. Should you take your dog to the vet immediately?

b) Theobromine is 46.66% carbon by mass, 4.48% hydrogen by mass, and 31.10% nitrogen by mass, with the remaining amount consisting of oxygen. What is the empirical formula of theobromine?

P5. Ammonia, NH_3, is toxic to mammals; it is removed from the body by a process called the urea cycle, occurring primarily in the liver, where it is converted to urea (shown in the figure), and ultimately the urea is excreted in the urine. The nitrogen content carried in the other reactants and products in the reaction is not altered in the urea cycle. The density of your urine can increase from 1.010 g/mL (close to that of water, 1.0 g/mL), to 1.040 g/mL if you are dehydrated. If you then excrete 600 grams of urine in a day, calculate the maximum number of moles of ammonia you would be able to remove from your body. Urea is the major nitrogen containing species of urine; with typically 9.30 grams of urea per liter of urine. Assume this value is also a good estimate of the urea content when you are dehydrated (this assumption may be a poor one; we make it for simplicity).

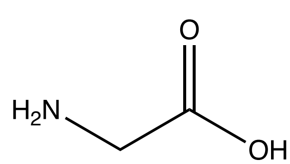


CHAPTER 3, Section 3.1: Representations of Molecules

P6. Two molecules with the molecular formula $C_2H_5NO_2$ are the amino acid glycine and nitroethane, a racing fuel additive. Glycine is important in the formation of α-helices, a three-dimensional structural element, in proteins. It also functions as an inhibitory neurotransmitter; thus, epileptic patients may evidence a shortage of glycine.

a) Write a condensed structural formula for glycine. (Note that the condensed structural formula for formic acid is HC(O)OH.)

b) Organic chemists would typically represent glycine using the simple two-dimensional line drawing below. Add into this structure all C atoms and H atoms, showing the bonds to the H atoms explicitly.

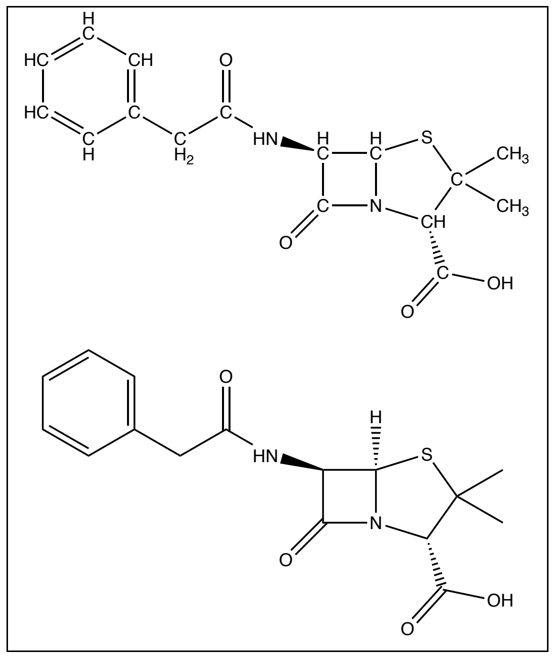


c) At physiological pH a proton is transferred from the OH in glycine to the NH_2 group. Draw this structure showing all the C and H atoms and C–H bonds as you did in part b). It has two resonance structures, so draw both.

d) Draw both resonance structures again for glycine at physiological pH, but this time also show each non-bonding pair of electrons with two dots. Confirm that your drawings show all the valence electrons in the molecule by summing up the number of valence electrons that C, N, O and H atoms have, and then checking that this sum equals the sum of the electrons shown as single or double bonds or as non-bonding pairs in your structures.

CHAPTER 3: Cumulative Problems for Chemical Bonding and Molecular Structure

***P7.** Penicillin G, benzylpenicillin, is a powerful antibiotic that kills a class of bacteria termed gram-positive bacteria. It was discovered in a fortuitously careless laboratory experiment in 1928. Its structure is shown in the figure. The upper graphic shows all the H's and C's in the molecule, while the lower graphic shows the more usual representation by organic chemists, with the C's at vertices (or at the end of a bond) not shown explicitly and the hydrogen atoms attached to carbon atoms not shown unless needed for geometry purposes. The wedge-shaped bonds shown are simply single bonds, with the wedge being a way of indicating whether the bond is angled out of the page toward you (solid wedge), or angled behind the page (dashed wedge).



a) What is the molecular formula for benzylpenicillin?

b) How many valence electrons does benzylpenicillin have?

c) How many of each of the following bonds does penicillin G have in the resonance structure shown: carbon-hydrogen bonds, single bonds between two carbon atoms, double bonds between two carbon atoms, single bonds between carbon and oxygen, double bonds between carbon and oxygen, single bonds between carbon and nitrogen, single bonds between nitrogen and hydrogen, single bonds between oxygen and hydrogen, and single bonds between sulfur and carbon.

d) Using the top graphic in the figure, insert all lone-pair electrons. Please make the dots in each pair large enough so your instructor can see them!

e) Noting that there are two pairs of bonding electrons in each double bond, sum up the electrons in your answer to parts c) and d). Does this sum equal the number of valence electrons in the molecule? If not, check your work.

f) Draw a second resonance structure for benzylpenicillin.

g) Penicillin G is typically sold as a potassium salt, where the H of the carboxylic acid is replaced by a K. Draw this structure. To save time, feel free to photocopy the top graphic, deleting the H and inserting the K.

h) In solution, the potassium salt will break apart into a K^+ ion and a negatively charged ion. What is the molecular formula of this ion and how many resonance structures does it have? (Hint: Consider resonance structures like those for benzene and resonance structures in the part of the molecule similar to $CH_3C(O)O^-$.)

CHAPTER 4, Section 4.2.2: Atomic Spectra and Transitions between Discrete Energy States

P8. Bone scans are a type of medical imaging used to diagnose osteomyelitis (infections in bones). The photons detected from the patient are emitted from a metastable isotope of technicium, ^{99m}Tc, that is injected into a vein of the patient before the scan. This isotope migrates to the site of injury with the help of a molecule bound to it prior to injection, methylene diphosphonate. When the metastable isotope emits a photon, the normal isotope of Tc, ^{99}Tc is formed. Most of the emitted photons have an energy of 140.5 keV, but there is an excited state of ^{99m}Tc that is 2.1 eV higher in energy than ^{99m}Tc; this excited state of ^{99m}Tc may also emit a photon and produce ^{99}Tc.

a) What is the wavelength of the emitted photon when ^{99m}Tc decays by emitting a photon to produce ^{99}Tc?

b) What is the wavelength of the emitted photon when the excited state of ^{99m}Tc describe above decays by emitting a photon to produce ^{99}Tc?

c) Are the emitted photons visible photons, ultraviolet photons, X-rays, or γ-rays (gamma rays)? (If you are using the 8th edition of Principles of Modern Chemistry, consult Figure 4.3 to see the wavelength ranges of each.)

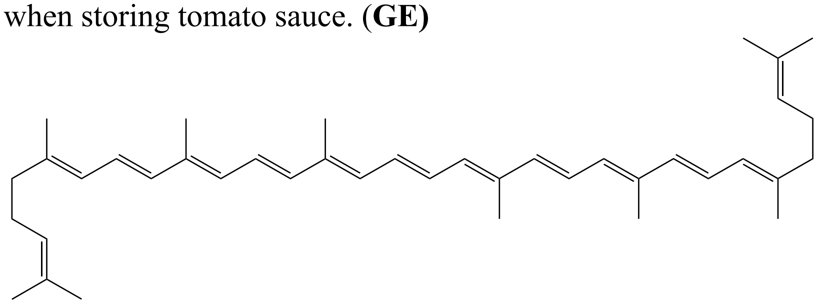
CHAPTER 4: Cumulative Problems for Introduction to Quantum Mechanics

P9. In 2020, 5G networks were rolled out in several countries, which sparked worries about its ability to cause cancer. This is because 5G networks emit electromagnetic radiation in the millimeter range, and 5G frequencies use the high band 24-48 GHz, which largely remained unused for telecommunication. **(PV)**

a) The most direct method of electromagnetic radiation targeting human tissue is by breaking bonds. Ultraviolet light is the region of radiation in which molecular bonds found in DNA begin to dissociate. Qualitatively explain whether microwaves in the millimeter range that are emitted by a 5G tower may dissociate molecular bonds found in DNA.

b) What frequency light (in GHz) would have enough energy in one photon to break a C-C bond. Use the table of bond energies in your textbook (Table 3.5 in the 8th edition of Principles of Modern Chemistry). What wavelength does a photon of this frequency have? Comment if this is in the millimeter range.

P10. There are many important carotenoids in biology; in plants, some carotenoids serve to absorb sunlight in the blue-green region of the spectrum to provide energy for photosynthesis. Lycopene (shown below) is a carotenoid found in tomatoes that is a biosynthetic precursor to β–carotene. It is also the pigment that turns plastic containers orange when storing tomato sauce. **(GE)**



a) One can treat the second pair of electrons in each double bond in the conjugated portion of a molecule with a particle-in-a-box model. Consider the 11 double bonds in the center of the lycopene structure above, each separated by a single bond, in a one-dimensional particle-in-a-box model. Sketch the potential V(x) for a "box" for this portion of the lycopene molecule, giving the width of the box and detailing how you estimated that. You may wish to use the C=C and C–C bond lengths from your textbook. (This is Table 3.6 in the 8th edition of Principles of Modern Chemistry.)

b) For a particle in that potential, sketch superimposed on your potential energy diagram the lowest four energy levels and label the total energy of each. Assign V = 0 to the bottom of the potential well.

c) Near what positions in the box are you most likely to find an electron that is in the $n = 4$ energy level? Assign the left edge of the box as $x = 0$ and be sure to give the units of distance on your answer.

d) Noting that each level may contain at most two electrons, and that a ground electronic state lycopene molecule has all its electrons in the lowest available energy level, what is the quantum number n for an electron in the highest occupied level in this portion of lycopene using this particle-in-a-box model?

e) If, when lycopene absorbs a photon, an electron in this highest occupied energy level is promoted to the lowest unoccupied energy level, what is the wavelength of the absorbed photon? (Use the same simple particle-in-a-box model and ignore any electron-electron repulsion.)

f) The peak of lycopene's absorption spectrum in the visible region of the spectrum is near 470 nm. (Note that when a substance absorbs blue-green frequencies of light it appears reddish-orange in color.) Does the particle-in-a-box model above you a good prediction for this portion of the absorption spectrum? (Don't worry if it doesn't, a full quantum mechanical treatment of the electrons in lycopene do give an excellent prediction; the particle-in-a-box model is an oversimplified quantum model.)

CHAPTER 5, Section 5.5: Periodic Properties and Electronic Structure

P11. Although most potassium in your body is intracellular, a healthy person typically has serum K^+ levels of 3.6 to 5.2 millimoles/L of K^+. (Serum is the liquid portion of your blood that has been collected without using an anticoagulant, so has been allowed to clot.) A person with 6 millimoles per liter of K^+ in their serum is at risk of a heart attack.

a) What is the electron configuration of K^+?

b) Is the ionic radius of K^+ smaller or larger than Na^+? Explain.

c) Which neutral atom has a larger atomic radius, K or Na? Explain.

P12. A dog who has recently given birth to a large litter may become calcium deficient due to the high demands of lactation. It is detected in a blood test as lower than normal levels of Ca^{2+}.

a) What is the electron configuration of Ca^{2+}?

b) Which ion has the larger radius Mg^{2+} or Ca^{2+}? Explain.

c) Which neutral atom has the larger radius Mg or Ca? Explain.

P13. The transport of Cl^- ions, across a muscle cell membrane (facilitated by a protein complex that provides an ion specific channel through the membrane) plays an important role in the muscle not being hyperexcitable. Patients with a disease called myotonia typically can't release their grip on an object. Scientists discovered this was due to the inability of the muscle cells to conduct Cl^- across the cell membrane.

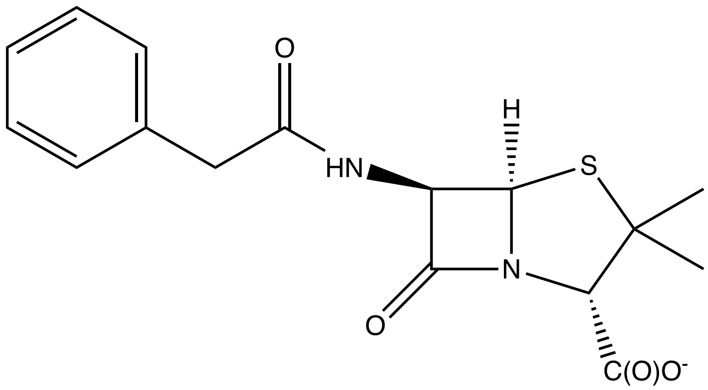
a) What is the electron configuration of Cl^-?

b) Which has the larger radius Cl^- or Ar? Explain.

c) Which neutral atom has the larger radius Cl or Ar? Explain.

CHAPTER 6, Section 6.11: Using the LCAO and Valence Bond Methods Together

P14. Potassium penicillin is a potassium salt with the anion shown below.

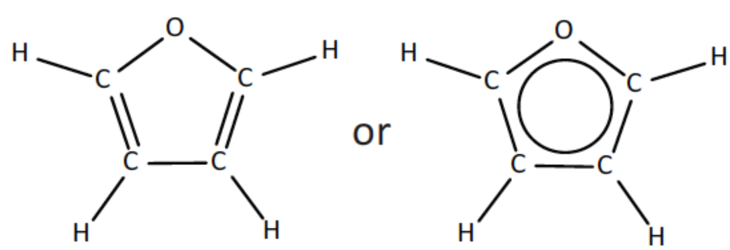


a) The C(O)O⁻ group has two resonance structures, but the bonding is better represented by delocalized π-bonding molecular orbital (MO). Which three atomic orbitals combine constructively to make the π-bonding MO?

b) The benzyl group is also better represented in a delocalized π-bonding representation. The lowest energy π-bonding MO has one nodal plane. The next higher energy level is doubly degenerate. How many nodal planes does each of these MOs have?

c) Are there any electrons in the MOs described in part b? If so, how many electrons in each?

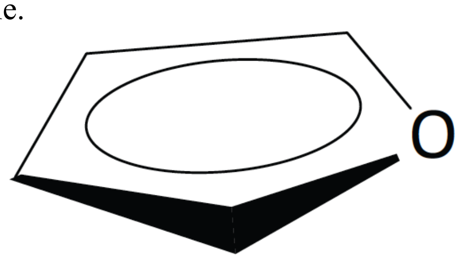
P15. Furan is listed by California as a carcinogen. It is present in coffee and baby food. **(GE)**



a) Specify the hybridization of the oxygen and carbon atoms in the molecule above.

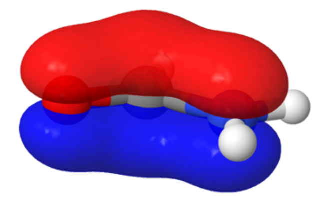
b) How many π electrons are involved in the bonding in the ring and what is the contribution to the bond order in the ring due to the π electrons alone? You may assume that each atom participates equally in the bonding.

c) On the structure below, sketch the shape of the oxygen orbitals that most readily simplify the bonding in this molecule.



CHAPTER 7, Section 7.6.6: Amines and Amides

P16. Amide bonds are the most prevalent structure found in proteins. The Lewis dot structure of an amide gives a poor representation of the bonding; the π bonding is not localized on the C–O bond. Instead, the π bonding is delocalized over the C–N and C–O bonds as shown in the figure of the π orbital of formamide to the right. Formamide is planar (so the N atom is not sp^3 hybridized).



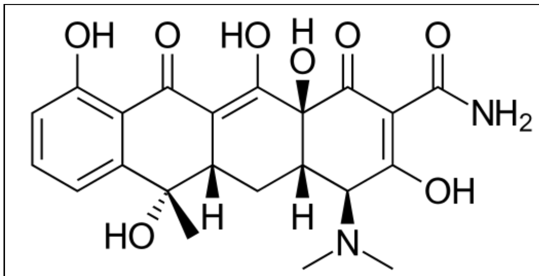
The π bonding MO in formamide. **(PS)**

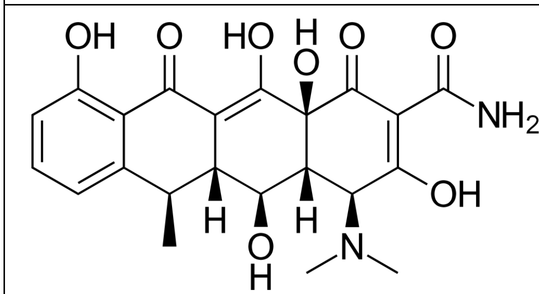
a) In a localized σ bonding, delocalized π bonding model, which three atomic orbitals combine to form the π bonding molecular orbital in the figure? Assume that the CNO plane is the xy plane.

b) What is the hybridization of the C atom and the N atom?

CHAPTER 7, Section 7.7.4: Antibacterial Agents

P17. Tetracycline, shown in the upper frame to the right, is a broad spectrum antibacterial. A similarly acting antibacterial, useful in tick-borne diseases, is doxycycline, shown in the lower frame. (The figures are from Wikipedia.) Each is a substituted tetracene. The IUPAC name of doxycycline is (4*S*,4a*R*,5*S*,5a*R*,6*R*,12a*S*)-4-(dimethylamino)-3,5,10,12,12a-pentahydroxy-6-methyl-1,11-dioxo-4,4a,5,5a,6,7,8,9-octahydrotetracene-2-carboxamide.





a) Which carbon atoms are number 1 and number 4 in the structures? (Make a copy of the structure of doxycycline and label those carbon atoms 1 and 4.)

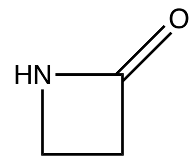
b) What is a carboxamide functional group? Given your answer to part a), do you agree with the 2 in front of carboxamide in the IUPAC name of the compound. (It is correct, so adjust your answer to a) accordingly.)

c) The 3,5,10,12,12a-pentahydroxy portion of the IUPAC name of doxycycline helps you identify carbons 3, 5, 10 and 12. Label those, then identify the carbon labelled by 12a.

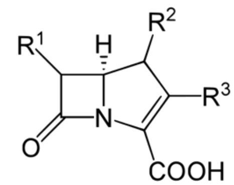
d) What would be the five numbers preceding pentahydroxy be for tetracycline?

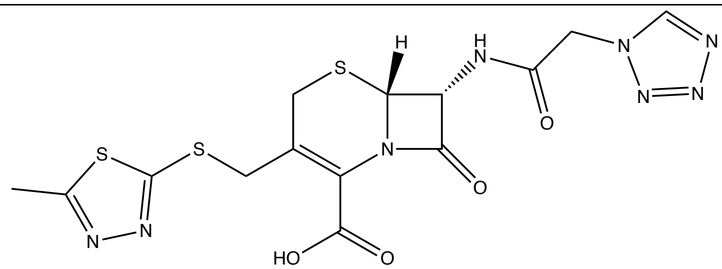
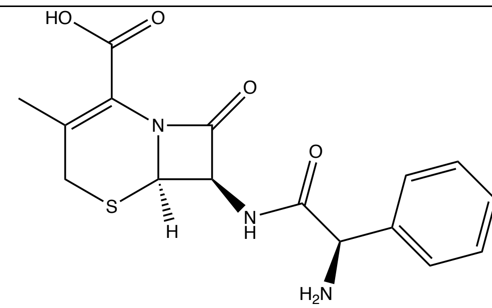
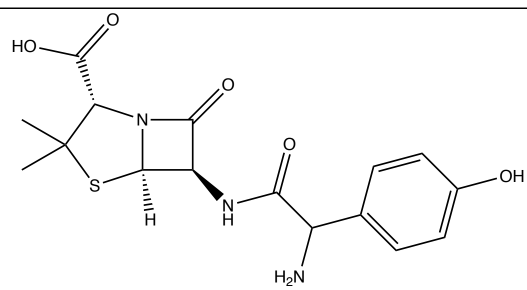
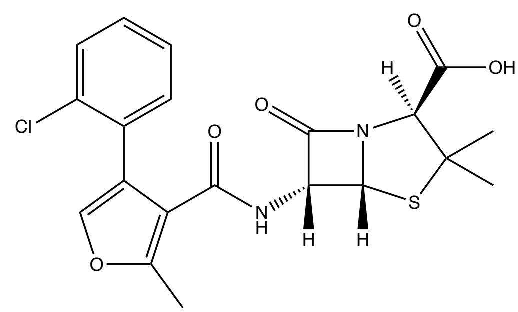
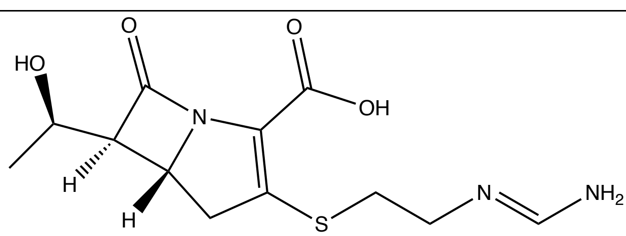
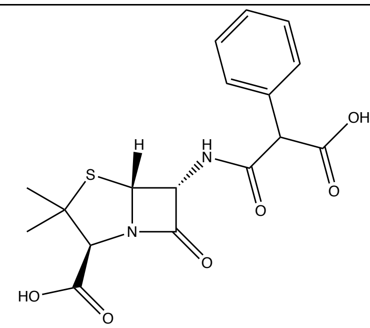
P18. Penicillin and other β-lactams are good antibiotics, but resistance to them is increasing. For example, some gram-negative bacteria have enzymes that hydrolyze the β-lactam ring.

a) The β-lactam group is shown in the figure to the right. (The symbol β here refers to the ring being five-membered.) Identify all the β-lactams below.



b) Carbapenems are a newer class of β-lactam antibiotics that deactivate the enzyme in the bacteria that destroys the β-lactam ring. They have a β-lactam ring connected to a five-membered ring without a sulfur atom but with a carboxylic acid (see figure to right). Find an example antibiotic below that has this functionality.



 cefazolin	 cephalexin
 amoxicillin	 cloxacillin
 imipenem	 carbenicillin

CHAPTER 8: Cumulative Problems for Bonding in Transition Metal Compounds and Coordination Complexes

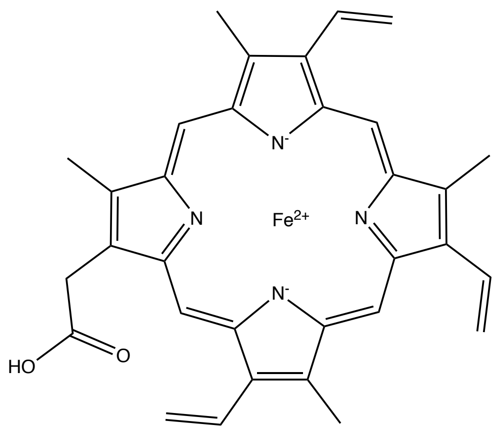
P19. Oxaliplatin is a platinum-based metal complex that is oftentimes used in clinic in combination with other drugs to treat colorectal and pancreatic cancers. Oxaliplatin contains an oxalate group and a trans-1,2-hexanediamine group, and its systematic name is oxalato(trans-1,2-cyclohexanediamine)platinum(II). Note that the ligands in this problem are each bidentate. **(PV)**

a) Write the formula of oxaliplatin, and give the structure geometry of the oxaliplatin (e.g. octahedral, tetrahedral, etc.).

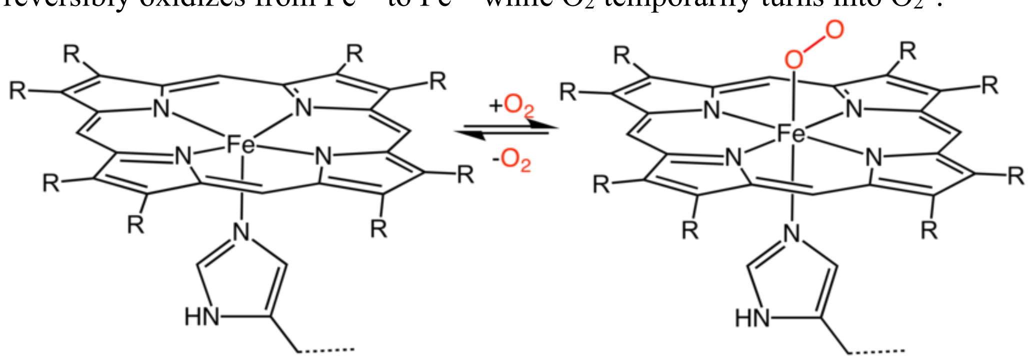
b) Sketch the geometry of the complex showing the Cartesian (xyz) coordinate system superimposed on your sketch, and give the names of the occupied d orbitals of the Pt.

c) Is oxaliplatin paramagnetic or diamagnetic?

P20. Hemoglobin in red blood cells contain four heme units, one of which is shown below. Each consists of Fe^{2+} at the center of a tetrapyrrole ring. Each iron is also bound to deprotonated histidine residue in the surrounding protein (not shown).



The oxidation state of the iron in this complex changes when oxygen binds to a heme unit. The iron reversibly oxidizes from Fe^{2+} to Fe^{3+} while O_2 temporarily turns into O_2^-.



a) In the structure before oxygen is bound to the heme, is the iron Fe(II) or Fe(III)?

b) What is the oxidation state of each of the O atoms in the O–O depicted in red above?

c) What type of ligand is the tetrapyrrole ring, bidentate, tridentate, or another name? Give the name.

d) ATP needed for muscle contraction can come from a reaction of glucose with O_2 that produces CO_2. When CO_2 enters the bloodstream, an enzyme present in red blood cells speeds up a reaction of CO_2 with water that produces H_3O^+. The acidity in the red blood cell results in the hemoglobin releasing more needed O_2 (the *Bohr effect* first described by Christian Bohr in 1904). Write the reaction of one CO_2 molecule with two water molecules that produces one H_3O^+ molecule and one other product molecule.

CHAPTER 9, Section 9.2: Pressure and Temperature of Gases

P21. Atmospheric pressure is 14.7 psi. If you are inflating an automobile tire, the pressure gauge reads the *difference* between the pressure to which you are filling your tire and atmospheric pressure. Thus, a gauge pressure of 32 psi (often called psig, with g for gauge) means you have filled the tire to an absolute pressure of 46.7 psi.

a) When maintaining a patient on gas inhalant anesthesia during surgery, a pop-off valve on the anesthesia machine releases gas pressure from the system if the pressure exceeds 20 cm H_2O (cm H_2O is a pressure unit equal to 98 pascals). This assures that the patient's lungs are never subjected to too high a pressure, risking lung damage. Convert 20 cm H_2O to a pressure in atmospheres.

b) What absolute pressure will the patient's lungs reach when the pop-off valve opens to release pressure?

c) Do you think 20 cm H_2O is a gauge pressure or an absolute pressure? Explain.

CHAPTER 9, Section 9.3: The Ideal Gas Law

P22. A patient can be kept unconscious during an operation using a mixture of O_2 and isoflurane from an anesthesia machine. If the hospital does not have a central gas supply, the O_2 gas delivered to the patient is stored in a compressed gas cylinder attached to the anesthesia machine. The typical gas cylinder used is a "Medical E" cylinder with an internal volume of 4.5 liters. A full tank is one filled to 2200 psi. Assume a room temperature of 20ºC.

a) How many liters of O_2 at atmospheric pressure can a full gas cylinder provide?

b) For a 75 kg patient, gas inhalant anesthesia starts initially with a high O_2 gas flow of 5 L/min and then reduced to 1.0 L/min after 10 min. Using this protocol for the flow rates, how long a surgery can you perform before the gas in your O_2 cylinder is depleted?

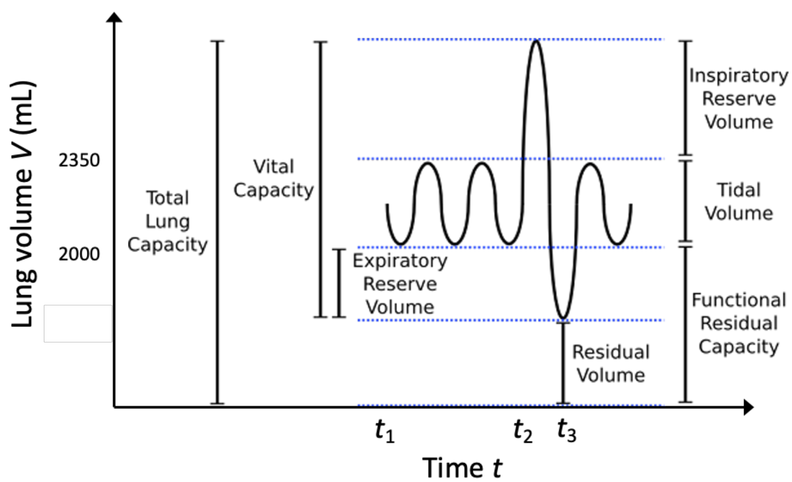
c) If the hospital does have a central gas supply, the O_2 piped into the surgical suite for the anesthesia machine comes from the evaporation of liquid oxygen. How many cubic centimeters of liquid oxygen would be used for a 30 min surgery if one used the flow rates in part b? Liquid oxygen has a density of 1.14 g cm^{-3}.

d) If the surgery in part c instead used a full Medical E gas cylinder initially filled to 2200 psi, what would be the pressure in the gas cylinder at the end of the 30 min surgery? Assume the flow rate is adjusted after 10 min as described in part b.

CHAPTER 9, Section 9.4: Mixtures of Gases

P23. A mixture of O_2 and isoflurane, where the mole fraction of isoflurane is 1.2 %, is typically inhaled by a patient to keep them unconscious during surgery. The total pressure is one atmosphere. What is the partial pressure of isoflurane in the mixture?

P24. The graph below depicts example lung volumes as a female 52 kg patient inhales and exhales normally between times t_1 and t_2, then takes a deep breath in and forces air out of her lungs, then breathes normally. Since the alveolar sacs in one's lungs must not collapse, there is a small residual volume, shown here as about 1200 mL, in the lungs that cannot be exhaled even upon a deep inhalation and forced exhalation cycle. **(JC)**

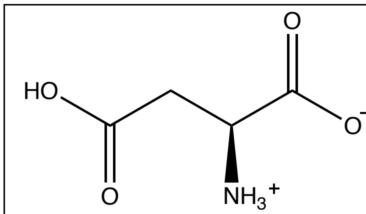


a) Reading the graph above, what is this 52 kg patient's tidal volume, the amount of air inhaled (or exhaled) during a normal breadth? Then calculate her tidal volume in mL/kg.

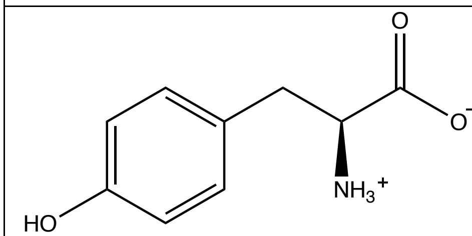
b) The above patient's functional residual capacity is 2000 mL. Her sister has the same tidal volume, but the physician wishes to measure her functional residual capacity. The following experiment is performed. The sister breathes in and out of a warm 6 L gas tank filled before the experiment with a mixture of air and 10% helium at a total pressure of 1 atm. No air is exchanged with the environment, only the tank described. After several normal inhalations and exhalations the fraction of helium in the tank is measured to be 7.4% at the smallest lung volume during a normal expiration and stays roughly constant after that. Assuming the total number of moles of helium in the tank and the sister's lungs is constant (i.e. He has not entered the bloodstream), that the temperature of the tank of gas is constant at the patient's body temperature, and that the helium has distributed itself uniformly in the tank and the sister's lungs, what is the sister's functional residual capacity? The total pressure of gas in the sister's lungs (and in the tank open to her lungs) at the lowest lung volume during exhalation is 1 atm also (since CO_2 and H_2O may enter the lungs from the bloodstream and lung tissue respectively and O_2 may also transfer between lungs and blood to equalize pressures.)

CHAPTER 10, Section 10.2: Intermolecular Forces: Origins in Molecular Structure and Section 10.3: Intermolecular Forces in Liquids

P25. Morphine is a potent pain-killer. When protonated, it binds to μ-opiod receptors (abbreviated MORs in medical literature). Crystal structures of morphine bound to the μ-opiod receptor shows that two amino acid residues in the binding site of the receptor are particularly important in binding morphine, Asp147 (where Asp stands for aspartic acid) and Tyr148 (where Try stands for tyrosine). At physiological pH a proton from the COOH group has transferred to the NH_2; the figure to the right depicts these structures.



Asp



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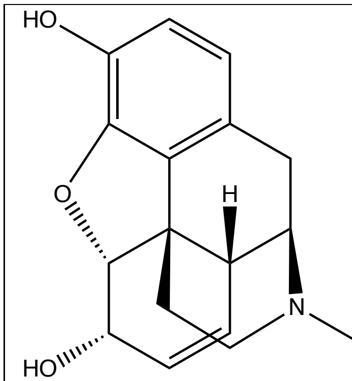


Morphine

a) The binding energy of morphine to the μ-opiod receptor binding site is 44 kcal/mol. What is the most likely intermolecular force responsible for the binding, ion-ion, dipole-dipole or hydrogen bonding? Explain.

b) If you are administering morphine to a patient under anesthesia and their blood pressure drops dangerously low, one action you can take is to "reverse" the morphine. This may be done by administering a drug that competitively binds at the μ-opiod receptor binding site. Naloxone and naltrexone are two such reversal agents. Do you expect their binding energy is lower or higher than morphine? Explain.

c) Buprenorphine is also an opioid that binds to μ-opiod receptors. It does not stimulate euphoria in awake patients as strongly as morphine does, so is sometimes prescribed to persons addicted to morphine. However naloxone does not effectively reverse the effects of buprenorphine. Order the three molecules by their binding energy to the μ-opiod receptors, with the strongest bonding molecule first and the weakest last.

d) If you define the potential energy as 0 when morphine is far from the μ-opiod receptor, what is the potential energy when they are bound together? You may use the information in part a.

P26. Choose and describe the most important intermolecular interaction (ion-ion, dipole-dipole, ion-dipole, Van der Waals, charge induced dipole, London dispersion (van der Waals, hydrogen bonding) for the following:

a) In a patient suffering from alkylosis (a blood pH of 7.45 or higher), the binding of calcium to albumin. (This can reduce the free Ca^{2+} in the blood to dangerously low levels.)
b) The binding of one strand in DNA's double helix to the other.

c) In KCl solutions used for intravenous supplementation of potassium ions, the attraction between the K^+ and Cl^- ions.

d) In the alveoli of your lungs, the forces by which a liquid-like monolayer of phospholipids (a phospholipid is a molecule with a negatively charged head group, with an appropriate counter ion nearby, attached to a long non-polar chain of CH_2 groups) lowers the surface tension and prevent your alveoli from collapsing. Give a complete answer here, as there is a competition between forces between water molecules, the forces between water molecules and phospholipids, and the forces between the long chains of the phospholipids in the monolayer. Order the strength of the attractive forces described.

CHAPTER 11, Sections 11.1/11.2: Composition of Solutions/Nature of Dissolved Species

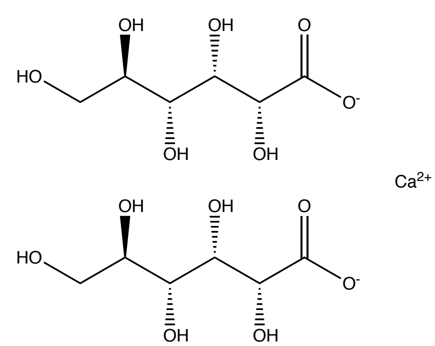
P27. Patients being treated for prolonged vomiting are often dehydrated and hypokalemic. Hypokalemia refers to a level of K^+ in the blood which is too low; normal is 3.5 to 5 mEq/L. For solutions of electrolytes in medicine, the concentration is often expressed in milliequivalents per liter (abbreviated mEq/L); a K^+ concentration of 1 mmol/L is also 1 mEq/L but a Ca^{2+} concentration of 1 mmol/L is 2 mEq/L.

a) If a patient's potassium is less than 3.2 mEq/L, a standard protocol for supplementing potassium is to administer six 100 mL doses of a dilute solution, 10 mEq/100 mL, of KCl intravenously. Each infusion may be done over 1 hour. If you wish to prepare the solution for these six doses using stock KCl provided at a concentration of 2 mEq/mL, how much of the stock solution would you combine with a sterile normal saline solution to make the 600 mL of solution needed?

b) A common fluid used to rehydrate patients intravenously is Plasma-Lyte, which contains 5 mEq/L of potassium. Why might you neglect the potassium content of Plasma-Lyte if you are simply adding the needed potassium supplement to the fluid used to rehydrate the patient? You may answer this qualitatively.

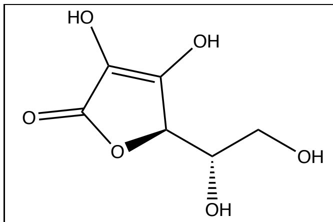
c) The normal concentration range for total serum calcium is 4.4 to 5.2 mEq/L. What is this range in mg/dL?

d) Hypocalcemia (low serum calcium levels) may cause tetany (involuntary twitching of muscles in hands or feet) and may progress to tetanic seizures. Early on, mild hypocalcemia may be treated with an intravenous injection of 2 g of calcium gluconate (see structure on the right). How many mmol and how many mEq of Ca^{2+} is this?

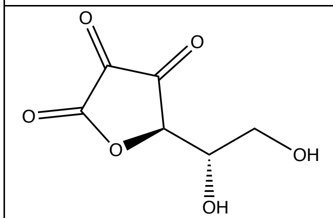


CHAPTER 11, Section 11.4: Reaction Stoichiometry in Solutions: Oxidation-Reduction Titrations

P28. Ascorbic acid (the L-enantiomer), $C_6H_8O_6$, also known as vitamin C, is shown in the top frame of the figure. It is an important antioxidant in redox biochemistry. By reacting with oxidizers, it tends to inhibit harmful oxidation of cellular components. Let's investigate this claim. For this problem, you may assume that the oxidation half-reaction of ascorbic acid is $C_6H_8O_6 \rightarrow C_6H_6O_6 + 2H^+ + 2e^-$. (The product $C_6H_6O_6$ is called dehydroascorbic acid; it is shown in the lower frame of the figure.) **(PS)**



Ascorbic acid



Dehydroascorbic acid

a) H_2O_2 is a toxic oxidizer; we expect an antioxidant to convert it to a safer product. Its two-electron reduction half-reaction (unbalanced) is $H_2O_2 + 2e^- \rightarrow H_2O$. Using this information, complete and balance a chemical equation for the reaction of H_2O_2 oxidizing ascorbic acid.

b) Vitamin C also readily reduces other chemical species, like converting Fe^{3+} to Fe^{2+}. Complete and balance a chemical equation for this reaction.

c) H_2O_2 can also be reduced via the one-electron half-reaction $H_2O_2 + 1e^- \rightarrow OH + OH^-$. The OH species is a free radical that, like H_2O_2, is highly reactive and harmful to cells. Complete and balance a chemical equation for the reaction of H_2O_2 oxidizing Fe^{2+} to Fe^{3+}.

d) Suppose a solution contains a small amount of ascorbic acid and H_2O_2, and a large excess of Fe^{3+}. From your answers above, you know that there will be a chain reaction in this solution as the ascorbic acid reduces Fe^{3+} to Fe^{2+}, then the resulting Fe^{2+} reduces H_2O_2 to $OH + OH^-$. Combine your answers from parts b) and c) into a net equation for this chain reaction. Is vitamin C acting like an antioxidant in this solution?

e) Hemochromatosis is an anomalous accumulation of iron in the body. (Its causes include blood transfusions and genetic disorders.) Why might vitamin C, vitamin E, and other "healthy" antioxidants be dangerous if consumed by a person with hemochromatosis?

CHAPTER 11, Section 11.5.4: Osmotic Pressure

P29. Blood serum proteins include albumin, globulin and fibrinogen. The normal concentration range of albumin and globulin in human blood are 3.4-5.4 g/dL and 2.6-3.5 g/dL respectively. Albumin proteins are typically lower molecular weight proteins than globulins; they typically range from 65 to 70 kilodaltons (kD) or 65-70 kg/mol, with an average of 69 kD.

a) The balance between intravascular water and extravascular water is maintained to a large degree by the albumin proteins in your blood. What is the oncotic (osmotic) pressure from a concentration of 5 g/dL albumin in your blood? Your body temperature is 98 ^{o}F.

b) Albumin is made in the liver, so liver failure can result in very low levels of albumin in your blood. Would water then leak out of your blood into your tissues (causing edema) or the reverse? Why?

CHAPTER 12: Cumulative Problems for Thermodynamic Processes and Thermochemistry

P30. In introductory biology texts, the term anabolism, or "building up", refers to reactions that construct molecules from smaller units; the texts explain that these reactions require energy. The term catabolism, or "breaking down", is used for reactions that break down molecules into smaller units. The introductory biology texts claim this releases energy. One might (erroneously) conclude that breaking a peptide-peptide bond in a protein releases the energy stored in the bond.

a) Now that you have learned some thermodynamics, lets critique the statements above. First, calculate whether energy is released or consumed when you break a mole of O_2 into two moles of O atoms under a constant pressure of 1 atm and 25^{o}C.

b) What is the change in enthalpy for the system and the change in energy of the system in the above process?

c) Did the system go down in energy, and thus release energy to the surroundings? You should have found the answer is no, so this bond-breaking reaction certainly does not release energy!

d) You have learned that the simple breaking of bonds typically requires energy, it does not release energy. So now you can investigate the real reason why catabolism in biological systems releases energy. Calculate the standard enthalpy change when glucose is broken down using the net reaction $C_6H_{12}O_6 + 6\ O_2\ (g) \rightarrow 6\ CO_2\ (g) + 6\ H_2O\ (l)$. The standard enthalpy of formation of glucose is −1273.3 kJ/mol. You will see it is exothermic (and exoergic), but it is not the breaking of the bonds in glucose that makes it so; it is the formation of the very stable (low energy) CO_2 molecules. Higher level biology texts describe this as oxidation (of the intermediates in the metabolic mechanism) – the oxidation state of each O atom in O_2 is 0 while the oxidation state of each of the O atoms in CO_2 is −2.

P31. Striated muscle fibers contain actin and myosin filaments. When a muscle contracts to allow you to lift an object, say a five-pound weight you are holding in your hand, the energy to do so is provided by adenosine triphosphate (ATP) molecules in your striated muscle cells. In the net reaction ATP is hydrolyzed to ADP (adenosine biphosphate) plus a phosphate molecule PO_4^{3-} . The net charges on the ATP and ADP depend on the acidity of the mixture.

a) If the enthalpy change of the ATP + H_2O →ADP + phosphate is -100×10^{-21} J per molecule of ATP hydrolyzed, what is the minimum number of ATP molecules that must be hydrolyzed to lift a 5 lb mass a distance of 1 meter?

b) You know from experience that your body gets warmer when you lift weights. If the system is your muscle fibers containing the reactants and products of the hydrolysis of ATP, and the surroundings is the rest of your body and the mass you are holding, what is the sign of ΔU for the system? What are the signs of q and w for the **surroundings**?

c) Explain why we asked for the "minimum" number in part a).

CHAPTER 13: Cumulative Problems in Spontaneous Processes and Thermodynamic Equilibrium

P32. Transport of substances across a cell membrane or across the wall of a blood vessel may be either passive or active. Typically, active transport requires energy and involves the participation of proteins on or in the membrane. Passive transport, on the other hand, does not require energy and, if the solvent is the same on both sides of the barrier, its direction is determined by the concentration gradient. Molecules may passively move from regions in which they are at high concentration to regions at which they are at low concentration. Give a thermodynamic analysis of passive transport, perhaps formulating the change in entropy for the solute molecules. Consider the change in entropy calculated from the change in the number of positional microstates available to the solute molecules, and assuming the transport occurs at constant temperature and pressure.

CHAPTER 14, Section 14.7.3: Temperature Dependence of Equilibrium Constants and Section 14.7.4: Temperature Dependence of Vapor Pressure

P33. To maintain an unconscious state for patients during an operation, one can have the patient breath a 1 atm gaseous mixture of oxygen and isoflurane in which the partial pressure of isoflurane is 9.12 torr. The vaporizer achieves this mixture by routing some of the O_2 gas past the vaporizer and some through the vaporizer to pick up the equilibrium vapor pressure of isoflurane at room temperature (20 °C).

a) The standard enthalpy change for the vaporization of isoflurane at 298 K is 31.93 kJ/mol and its normal boiling point is 48.5 °C. What is its equilibrium vapor pressure at 20 °C?

b) What fraction of the gas flow should be routed to pick up that equilibrium vapor pressure of isoflurane and what fraction should bypass the isoflurane to obtain the desired mixture of 9.12 torr of isoflurane in oxygen?

P34. Patients under respiratory distress may be prescribed medication to be administered with a nebulizer. A nebulizer typically contains an aqueous solution of a drug to be administered (in the case of asthma, perhaps albuterol) and when actuated, the nebulizer generates micron-sized droplets of the solution which the patient inhales. Let's consider the simple case of a patient in respiratory distress because they are dehydrated and they have been outside, breathing cold air.

a) The tidal volume, or volume of air that a person displaces in their lungs between inhalation and exhalation is about 7 mL per kg of body mass. What is the tidal volume for an 80 kg person?

b) At a body temperature of 98°F, what is the equilibrium vapor pressure of water? Do not consult a table; instead consider the temperature dependence of equilibrium constants and the normal boiling point of water.

c) On a cold day of 20°F, what is the equilibrium vapor pressure of water?

d) If an 80 kg person takes one breath of this cold air, how much water must the tissues of their lungs provide to bring the air in their lungs back into equilibrium?

e) Given your answer to part d, one might conclude that if the patient is dehydrated, the lung tissue might become further dehydrated if delivery of water to the tissues from the bloodstream does not keep up with the demands of rehydrating the air in the lungs. How then does a simple water nebulizer help this situation?

P35. The normal H_3O^+ concentration in your blood is between 3.55×10^{-8} and 4.47×10^{-8} moles/L. Use Le Chatelier's principle for each of the equilibria below to argue whether this concentration should increase or decrease for a patient who is hyperventilating. Hyperventilating reduces the partial pressure of CO_2 in your lungs. Relevant equilibria are:

$CO_2(g) \rightleftharpoons CO_2$ (*aq*, lung tissue) $\quad$ CO_2 (*aq*, lung tissue) $\rightleftharpoons CO_2$ (*aq*, blood)

HCO_3^- (*aq*, blood) + H_3O^+ (aq, blood) $\rightleftharpoons CO_2$ (*aq*, blood) + 2 H_2O (*l*)

(Note: we use *aq* loosely here to mean dissolved CO_2, then add a word after the comma to indicate where it is dissolved. Normally *aq* means dissolved in water.)

CHAPTER 15, Section 15.2: Properties of Acids and Bases in Aqueous Solutions: The Brønsted-Lowry Scheme

P36. Gastric acid is comprised mainly of hydrochloric acid HCl, which is produced by parietal cells in the stomach. The pH range of normal human gastric acid is 1.5 to 3.5. However, if a patient undergoes major stomach resection where approximately 60% of the stomach is removed, then the pH range is 5.7 to 6.8. Calculate the range (high and low limits) of the concentrations of H_3O^+ for both normal human gastric acid and the gastric acid of a patient whose has undergone the resection surgery described. **(PV)**

CHAPTER 15: Cumulative Problems for Acid-Base Equilibria

P37. The normal pH of human blood is about 7.40. This is largely maintained by the carbonic acid equilibrium H_2CO_3 (aq, blood) + H_2O (l) $\Leftrightarrow$ HCO_3^- (*aq*, blood) + H_3O^+ (*aq*, blood).

For this problem assume the pK_a of carbonic acid in blood is 6.1 (as compared to 6.37 in aqueous solution). The concentration of H_2CO_3 is related to the partial pressure of dissolved CO_2, p_{CO_2}, in the blood via the relation $[H_2CO_3] = k\, p_{CO_2}$ where k is approximately 0.03×10^{-3} (mol/L)/mmHg.

a) If the normal partial pressure of CO_2 in the blood is 40 mmHg, what is the normal concentration of bicarbonate ion, HCO_3^-, in the blood assuming the pH is 7.40?

b) Kidneys filter your blood, returning the good molecules you need, like bicarbonate ion, back to your bloodstream (this is called reabsorption), and excreting waste products in your urine. The filtration rate is large, about 180 L/day! Assuming all of the filtered bicarbonate is returned to your blood, how many mmol of bicarbonate ion is returned to your blood per day if the concentration of bicarbonate entering the kidney is the normal concentration you calculated in part a?

c) Patients with chronic kidney disease lose bicarbonate in their urine as the kidney is unable to return it to the bloodstream. Do you expect the pH of the blood of a patient with chronic kidney disease to be more basic or more acidic than 7.4? Explain the effect of a reduction of bicarbonate on the H_2CO_3 (aq, blood) + H_2O (l) $\Leftrightarrow$ HCO_3^- (*aq*, blood) + H_3O^+ (*aq*, blood) equilibrium. As the equilibrium shifts to counter the stress, does it increase or decrease H_3O^+ in a Le Chatelier picture?

d) When a change in pH of the blood is due to organ failure, the medical terms for this are metabolic acidosis and metabolic alkylosis. Which do you expect for a patient with chronic kidney disease?

P38. Tooth enamel consists mainly of hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, $K_{sp} = 6.8 \times 10^{-37}$). It is the hardest substance in the body. Cavities in teeth are caused by the dissolution of hydroxyapatite in the presence of an acid through the reaction

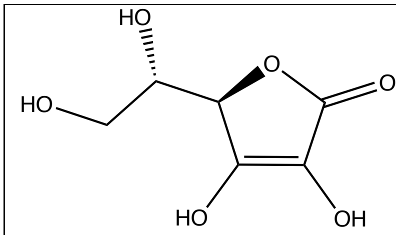
$$Ca_{10}(PO_4)_6(OH)_2\,(s) + 8\,H_3O^+(aq) \rightleftharpoons 10\,Ca^{2+}(aq) + 6\,HPO_4^{2-}\,(aq) + 10\,H_2O\,(l)$$

To combat tooth decay, fluoride treatment (even at low concentrations) is quite effective. In the presence of fluoride, the hydroxyapatite converts to fluoroapatite, $Ca_{10}(PO_4)_6F_2$. Feel free to use data from a table of acid K_a's, Table 15.2 in Oxtoby's textbook. **(GE)**

a) Is the ΔG of the reaction converting hydroxyapatite to fluoroapatite positive or negative? Explain your logic in a sentence.

b) Calculate the equilibrium constant for the reaction listed above at 25°C.

P39. Ascorbic acid (the L- enantiomer of which is vitamin C), is shown in the figure. Consider the number of resonance structures of the conjugate base to explain which of the four hydrogens shown is the most acidic. To do this, count the number of resonance structures for each conjugate base. Show in a diagram which atom has a negative charge in each of the resonance structures for the conjugate base resulting from the loss of the most acidic proton.



Ascorbic acid

CHAPTER 17, Section 17.1: Electrochemical cells

P40. The anaerobic catabolism of glucose in cell mitochondria occurs via a reaction of glucose with $C_{21}H_{26}N_7O_{14}P_2^-$ (one of two forms of nicotinic adenine dinucleotide (NAD)). The overall reaction is written as:

$$C_6H_{12}O_6 + 2\ C_{21}H_{26}N_7O_{14}P_2^- \rightarrow 2\ C_3H_4O_3 + 2\ C_{21}H_{27}N_7O_{14}P_2^{2-} + 2\ H^+ \qquad \textbf{(PV)}$$

a) Write the half-reactions. Which compounds are oxidized, and which are reduced?

b) Consulting Wikipedia or another online source, which of the molecules above is given the abbreviation NAD^+ and which is given the abbreviation NADH? Give your source and note that neither molecule has a +1 charge as the abbreviation NAD^+ might suggest!

CHAPTER 18, Section 18.8: Catalysis

P41. Enzymes are ubiquitous in biochemical reactions – they are often named with a root specifying their substrate, followed by -ase. (A notable exception is a polymerase, named by the polymer product of the reaction, not the substrate.) Match enzyme to substrate to function in the table below.

Enzyme	Substrate	Function
a. amylase	1.fatty acids (lipids)	i. speeds cleavage of peptide bonds
b. lipase	2. ribonucleic acid (RNA)	ii. facilitates energy storage in muscles by speeding the reversible conversion of ATP + creatine to ADP + phosphocreatine
c. ribonuclease	3. proteins	iii. fights HIV (a retrovirus, one of many RNA viruses)
d. lactase	4. acetylcholine	iv. speeds fat digestion
e. creatine kinase	5. starch	v. speeds breakdown of lactose, so deficient in lactose intolerant people
f. protease	6. lactose	vi. speeds hydrolysis of starch (Latin amylum) into sugars
g. acetylcholinesterase	7. creatine	vii. blocks neurotransmission at synapses of the cholinergic type.

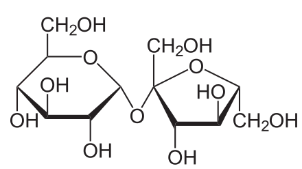
P42. Alcohol dehydrogenase is an enzyme that facilitates the conversion of alcohols to aldehydes or ketones. In the case of humans, alcohol dehydrogenase converts ethanol into acetaldehyde following the consumption of ethanol. The K_m for the $\beta_1\beta_1$ isozyme is 0.05 mM, and the V_{max} is 1.60 mM per hour. **(PV)**

a) What is the turnover frequency (sometimes called the turnover number), k_2, in s^{-1} if the $\beta_1\beta_1$ isozyme of alcohol dehydrogenase concentration (the sum of free enzyme and enzyme bound to ethanol) is 6.0×10^{-7} M under saturation conditions?

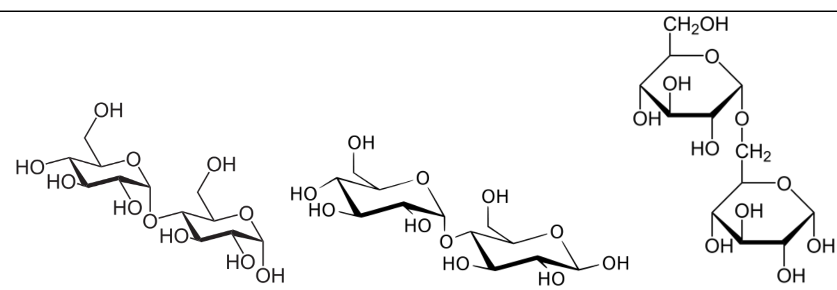
b) Drinking methanol is dangerous because alcohol dehydrogenase converts the methanol to a highly toxic substance. Comparing the structure of methanol to ethanol, what do you think this toxic substance is? Why might a person who has ingested methanol be treated with an intravenous injection of a 10% ethanol solution?

CHAPTER 23, Section 23.4: Natural Polymers

P43. The starch in food is one example of a polysaccharide. These polysaccharides are hydrolyzed to monosaccharides (simple sugars: glucose, fructose, and galactose) in your body with the assistance of various enzymes. An enzyme found in the microvilli of your intestine, sucrase-isomaltase, has two active sites. One active site catalyzes the hydrolysis of sucrose, a disaccharide, while the other active site catalyzes the hydrolysis of maltose. These disaccharides are shown in the figure below. **(LJB+PS)**



Sucrose



α- and β-maltose and isomaltose

a. Write a net reaction for the hydrolysis of sucrose and make a sketch to show where the H_2O adds to sucrose. What simple sugars result from this hydrolysis?

b. Write a net reaction for the hydrolysis of maltose and make a sketch to show where the H_2O adds to maltose. What simple sugars result from this hydrolysis?