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

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

P1. Mannitol, C₆H₁₄O₆, 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 LD₅₀ (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 is 457.43 g mol⁻¹. (PV)

a) How much amygdalin is present in a cherry seed whose mass is 1.49 grams?

b) Is eating a cherry seed likely to be lethal to a rat?

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 ¹²C scale?
CHAPTER 2: Cumulative Problems

P4. Theobromine (IUPAC name 3,7-Dimethyl-1H-purine-2,6-dione) is a compound found in cocoa beans that is toxic to dogs and cats. This compound has an LD<sub>50</sub> (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<sub>3</sub>, 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<sub>2</sub>H<sub>5</sub>NO<sub>2</sub> 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 NH₂ 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

*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 sulfur and carbon, 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\(_3\)C(O)O\(^-\).)

CHAPTER 4: Cumulative Problems

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, \(^{99m}\text{Tc}\), 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, \(^{99}\text{Tc}\) is formed. Most of the emitted photons have an energy of 140.5 keV, but there is an excited state of \(^{99m}\text{Tc}\) that is 2.1 eV higher in energy than \(^{99m}\text{Tc}\); this excited state of \(^{99m}\text{Tc}\) may also emit a photon and produce \(^{99}\text{Tc}\).

a) What is the wavelength of the emitted photon when \(^{90m}\text{Tc}\) decays by emitting a photon to produce \(^{99}\text{Tc}\)?

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

c) Are the emitted photons visible photons, ultraviolet photons, X-rays, or \(\gamma\)-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.)

P9. 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 \(\beta\)-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 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**

**P10.** 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.
P11. 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.

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

P12. 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 $\pi$-bonding molecular orbital (MO). Which three atomic orbitals combine constructively to make the $\pi$-bonding MO?

b) The benzyl group is also better represented in a delocalized $\pi$-bonding representation. The lowest energy $\pi$-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?

P13. 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 $\pi$ electrons are involved in the bonding in the ring and what is the contribution to the bond order in the ring due to the $\pi$ electrons alone? You may assume that each atom participates equally in the bonding.

e) 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

P14. 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 sp³ hybridized).

\[ \text{The} \ \pi \ \text{bonding MO in formamide. (PS)} \]

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

P15. 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 (4S,4aR,5S,5aR,6R,12aS)-4-(dimethylamino)-3,5,10,12,12a-pentahydroxy-6-methyl-1,11-dioxo-4,4a,5,5a,6,7,8,9-octahydrotetracene-2-carboxamide.

\[ \text{The structures of doxycycline and tetracycline.} \]

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?
P16. 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.
CHAPTER 8: Cumulative Problems

P17. 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).

![Heme structure](https://en.wikipedia.org/wiki/Heme)

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$_2^-$.

![Oxygen binding](https://en.wikipedia.org/wiki/Heme)

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

b) When oxygen binds to a heme unit, the iron reversibly oxidizes from Fe$^{2+}$ to Fe$^{3+}$. At the same time, O$_2$ temporarily turns into O$_2^-$. What is the oxidation state of each of the O atoms in the O–O depicted in red in the figure 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$. The acidity in the red blood cell results in the hemoglobin releasing more needed O$_2$ (the Bohr effect first described by Christian Bohr in 1904). Write the reaction of CO$_2$ with water that produces H$^+$. 

Write the reaction of CO$_2$ with water that produces H$^+$. 

$a + b + c + d$
CHAPTER 9, Section 9.2: Pressure and Temperature of Gases

P18. 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 H₂O (cm H₂O 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 H₂O 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 H₂O is a gauge pressure or an absolute pressure? Explain.

CHAPTER 9, Section 9.3: The Ideal Gas Law

P19. A patient can be kept unconscious during an operation by having them breathe a mixture of O₂ and isoflurane from an anesthesia machine. If the hospital does not have a central gas supply, the O₂ 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 20 °C.

a) How many liters of O₂ at atmospheric pressure can a full gas cylinder provide?

b) For a 75 kg patient, gas inhalant anesthesia starts initially with a high O₂ 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 O₂ cylinder is depleted?

c) If the hospital does have a central gas supply, the O₂ 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

P20. A patient can be kept unconscious during an operation by having them breathe a mixture of \( \text{O}_2 \) and isoflurane, where the mole fraction of isoflurane is 1.2 %. The total pressure is one atmosphere. What is the partial pressure of isoflurane in the mixture?

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

P21. Morphine is a potent pain-killer. It binds to \( \mu \)-opioid receptors (abbreviated MORs in medical literature). Crystal structures of morphine bound to the \( \mu \)-opioid 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.

a) The binding energy of morphine to the \( \mu \)-opioid receptor binding site is 44 kcal/mol. What are the most likely intermolecular forces responsible for the binding, 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 \( \mu \)-opioid 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 \( \mu \)-opioid 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 \( \mu \)-opioid 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 \( \mu \)-opioid receptor, what is the potential energy when they are bound together? You may use the information in part a.
CHAPTER 11, Sections 11.1/11.2: Composition of Solutions/Nature of Dissolved Species

P22. 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 11.5.4: Osmotic Pressure

P23. 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 °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

P24.  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\textsubscript{2} into two moles of O atoms under a constant pressure of 1 atm and 25\degree 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 enthalpy change when glucose is broken down using the net reaction \( \text{C}_6\text{H}_{12}\text{O}_6 + 6 \text{ O}_2 \rightarrow 6 \text{ CO}_2 + 6 \text{ H}_2\text{O} \). You will see it is 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\textsubscript{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\textsubscript{2} is 0 while the oxidation state of each of the O atoms in CO\textsubscript{2} is −2.

CHAPTER 13: Cumulative Problems

P25.  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

P26. To maintain an unconscious state for patients during an operation, one can have the patient breathe 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?

P27. 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?

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

d) If a 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?

P28. The normal H$_3$O$^+$ concentration in your blood is between $3.55 \times 10^{-8}$ and $4.47 \times 10^{-8}$ 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:

\[
\text{CO}_2(g) \rightleftharpoons \text{CO}_2(aq, \text{lung tissue}) \quad \text{CO}_2(aq, \text{lung tissue}) \rightleftharpoons \text{CO}_2(aq, \text{blood})
\]

\[
\text{HCO}_3^-(aq, \text{blood}) + \text{H}_3\text{O}^+(aq, \text{blood}) \rightleftharpoons \text{CO}_2(aq, \text{blood}) + 2 \text{H}_2\text{O}
\]
CHAPTER 15: Cumulative Problems

P29. 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:

\[
\text{Ca}_{10}\text{(PO}_{4}\text{)}_{6}\text{(OH)}_{2}(s) + 8 \text{H}^{+}(aq) \rightleftharpoons 10 \text{Ca}^{2+}(aq) + 6 \text{HPO}_{4}^{2-}(aq) + 10 \text{H}_{2}\text{O}(l)
\]

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})_{6}F_{2}. (GE)

a) Is the \Delta G 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.

c) Estimate the equilibrium constant for the dissolution of fluoroapatite in water at 25°C. State any assumptions.

d) Explain why fluoride is a worse Lewis base than hydroxide. (Your explanation should consist of more than simply stating $K_b$.)

CHAPTER 17, Section 17.1: Electrochemical cells

P30. The anaerobic catabolism of glucose in cell mitochondria occurs via a reaction of glucose with C_{21}H_{26}N_{7}O_{14}P_{2} (one of two forms of nicotinic adenine dinucleotide (NAD)). The overall reaction is written as:

\[
\text{C}_{6}\text{H}_{12}\text{O}_{6} + 2 \text{C}_{21}\text{H}_{26}\text{N}_{7}\text{O}_{14}\text{P}_{2}^{-} \rightarrow 2 \text{C}_{3}\text{H}_{4}\text{O}_{3} + 2 \text{C}_{21}\text{H}_{27}\text{N}_{7}\text{O}_{14}\text{P}_{2}^{2-} + 2 \text{H}^{+}
\]  (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

P31. 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.

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

P32. 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 mmol 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 $6 \times 10^{-7}$ 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?