

GENERAL CHEMISTRY

WITH EMPHASES ON THERMODYNAMICS
MOLECULAR ORBITALS AND QUANTUM MECHANICS

BY

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Preface

Chem 1A at UC Berkeley is not meant to be hard. What makes it hard for many is a glaring lack of practice problems (unless you take Chem 1A with Prof. Pete Marsden). I compiled these questions while I was taking the class with Prof. Martin Head-Gordon, and I learned a lot by working through them. I scored consistently in or near the top 10 on exams in a class of ~ 1100 and earned an A+ despite having minimal AP Chemistry experience from high school. My hope is that these practice questions can help other students too.

That being said, since I wrote these questions as a student, many of the solutions are quite terse, and the reader is often expected to finish the algebra. If this book is to be used effectively, familiarity with requisite formulas and symbols is necessary. This book will not guide you through the baby steps. It should serve as a supplement to the materials already given in lecture.

Feel free to reach out to me at [derek.wan11\[at\]berkeley.edu](mailto:derek.wan11[at]berkeley.edu) if you find any blatant mistakes or would like to offer any suggestions.

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Chapter 1

Basic Quantum Calculations

1.1 Plug and Chugs

1. How many photons are produced in a laser pulse of 0.807 J at 451 nm?
2. Calculate the emitted energy of a photon when an electron in hydrogen goes from $n = 6$ to $n = 1$.
3. Calculate the wavelength, in nanometers, of the spectral line produced when an electron in a hydrogen atom undergoes the transition from the energy level $n = 2$ to the level $n = 1$.
4. Name the series beginning at: $n=1, n=2, n=3, n=4, n=5, n=6$
5. A line in the Brackett series of hydrogen has a wavelength of 2166 nm. From what state did the electron originate?
6. In what region of the electromagnetic (EM) spectrum is the line in 5 located?
7. A ground state hydrogen atom absorbs a photon of light having a wavelength of 93.03 nm. It then gives off a photon having a wavelength of 2165 nm. What is the final state of the hydrogen atom?
8. Find the surface temperature of a star in which the maximum wavelength is 649 nm. Assume that stars are black bodies.
9. Find the kinetic energy of an electron ejected from a metal with a threshold frequency of 5.55×10^{14} Hz when a light of wavelength 255 nm is shined on it.
10. A rifle bullet has mass 5.97 g. Calculate its de Broglie wavelength as it travels at 1337 mph.
11. What is the uncertainty in position of an electron moving at $6 \times 10^6 \frac{m}{s}$ with uncertainty of 0.167%?
12. Consider a 2650 lb automobile clocked by law enforcement radar at a speed of 85.5 mph. If the position of the car is known to within 5.0 feet at the time of the measurement, what is the uncertainty in the velocity of the car?
13. Consider the hydrogen atom as a one-dimensional box with length 106 pm. Calculate the wavelength of radiation emitted when its electron transitions from $n=4$ to $n=3$.
14. Predict the wavelength of transition from $n=2$ to $n=1$ in He^+ .
15. In the hydrogen spectrum, a line is observed at 102.6 nm. Determine the values of n for the initial and final energy levels of the electron during the emission of energy that leads to this spectral line.
16. Calculate the wavelength of radiation generated by the transition from $n = 2$ to $n = 1$.
17. Lines in the Balmer series of H atom are observed at 656.3, 486.1, 434, and 410.2 nm. What is the wavelength of the next line in the series?

18. A bowling ball of mass 8kg is rolled down an alley at 5.00 m/s with uncertainty of 100%. What is the minimum uncertainty in its position?
19. What is the minimum uncertainty in the speed of an electron confined with an atom of 350 pm? Model the atom as a one-dimensional box.
20. What is the velocity of a neutron of wavelength 100 pm?
21. A baseball is 5.15 oz and thrown at 92 mph. Find its wavelength.
22. An astronomer discovers a new red star that emits light with max intensity at 632 nm. What is the temperature at the surface of the star?

1.2 Conceptual Questions

1. The energy levels of a particle of mass m in a 2D box of side L are given by $\frac{(n_1^2+n_2^2)h^2}{8mL^2}$. Do any of these levels have the same energy? If so, find the values of the quantum numbers n_1 and n_2 for the first three cases.
2. Evaluate the probability of finding an electron in a small region of hydrogen 1s orbital at $0.55a_0$ from the nucleus relative to finding it in the same small region located at the nucleus.
3. Explain how the electron distribution is spherically symmetrical for an atom in which an electron occupies each of the three p orbitals in a given shell.
4. What is meant by a node? How many radial nodes and angular nodal surfaces are there in 1s 2s 2p 3d? Predict the number of nodal planes expected for a 4f orbital?
5. How many orbitals are in subshells with l equal to 0, 2, 1, 3?
6.
 - a) How many values of the quantum number l are possible when $n = 7$?
 - b) How many values of m_l are allowed for an electron in a 6d subshell?
 - c) How many values of m_l are allowed for an electron in a 3p subshell?
 - d) How many subshells are there in the shell with $n = 4$?
7. Official names for n , l , m_l and m_s ?
8. How many orbitals can have the following quantum numbers in an atom?
 - a) $n = 2, l = 1$
 - b) $n = 4, l = 2, m_l = -2$
 - c) $n = 2$
 - d) $n = 3, l = 2, m_l = +1$
9. What is the order of magnitude of energy that the electrons require to show diffraction if the interatomic spacing is 10^{-10} m?
10. Helium beams also diffract. Which particle beam (electron or helium) would require more energy to show diffraction?
11. Why does a heated black body emit white light when it gets super hot?
12. What is the Bohr radius?

Chapter 2

Intro to MO Theory and IMFs

2.1 Conceptual Questions

1. Acceptable or not acceptable? $n = 4, l = 1, m = 2, m_s = -\frac{1}{2}$
2. Rank the third period's elements in order from smallest to highest ionization energy.
3. Internuclear C-C distance is 139 pm. A wave function extends over two adjacent carbon atoms.
 - a) If each atom in a linear chain of 10 carbon atoms contributes one electron, what is the minimum number of wave functions required to account for all the electrons?
 - b) Use PIB model for a linear chain of 10 carbon atoms with the same internuclear distance but in which the transition takes place from the uppermost filled level to the one above.
 - c) A certain carbon compound requires 696 nm to promote an electron from $n = 6$ to $n = 7$. How long is the chain of carbon atoms?
4. Why are s-block metals typically more reactive than p-block metals?
5. What are diagonal relationships? Classic example?
6. Why is the second ionization energy of sulfur significantly higher than that of phosphorus? Why are the first ionization energies almost identical?
7. Three types of exceptions to octet rule, and some classic examples?
8. Which atomic orbital (i.e. wavefunction) of the H atom do you expect to have more nodes? 3s, 3p or 3d?
9. Which **radial** wavefunction of the H atom should have more nodes? 3s, 3p, or 3d?
10. Which 1 e^- atom or ion has the lowest energy?
 - (a) $H(2p)$
 - (b) $He^+(3p)$
 - (c) $Li^{2+}(4p)$
11. Which atom has the lowest outer energy level?
 - (a) $H(2p)$
 - (b) $He(1s\ 3p)$
 - (c) $Li(1s_2\ 4p)$
12. Which species, in its ground state, can show $n = 1 \rightarrow 2$ absorption?
 - (a) F
 - (b) F^-
 - (c) Na

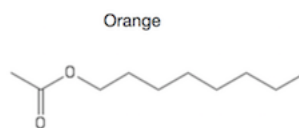
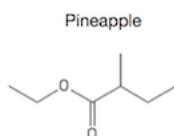
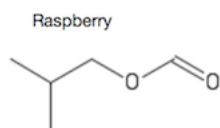
13. Which of the following has the highest ionization energy?
(a) Cl^-
(b) Ar
(c) K^+
14. Explain the critical distance in terms of numbers.
15. Which of the following factors affects the lattice energy of a material, MX?
(a) IE of M
(b) EA of X
(c) size of ions
16. Which of the following is the lattice energy of KCl, given that the other two are NaCl and LiCl?
(a) $-829 \frac{kJ}{mol}$
(b) $-769 \frac{kJ}{mol}$
(c) $-698 \frac{kJ}{mol}$
17. Describe the relationship between EA/IE and screening.

Chapter 3

More MO Theory and IMFs

3.1 Plug and Chugs

- Ultra-high-molecular-weight polyethylene (UHMWPE) may have 300,000 monomers per molecule. What is its MW?
 - $\sim 1 \frac{Gg}{mol}$
 - $\sim 10 \frac{Mg}{mol}$
 - $\sim 100 \frac{kg}{mol}$
- Which has the most stable bond? Which has the most reactive bond?
 - Single bond
 - Double bond
 - Triple bond
- Which has a higher melting point?
 - HDPE (low branching)
 - LDPE (much branching)
- Order following esters from least to most pungent when mixed with water to form a solution:
 - raspberry < orange < pineapple
 - orange < raspberry < pineapple
 - raspberry < pineapple < orange



- Is the HXH angle larger in ammonia or water?
 - water
 - equal
 - ammonia
- Which of the following molecules has a non-zero dipole moment?
 - CS_2
 - SiF_4
 - O_3
 - none
- What types of attractions correspond to which $-\frac{1}{R^n}$ curves?

Chapter 4

Spectroscopy

4.1 Which Equation?

1. What are the 3 formulas for vibration? (potential energy, fundamental frequency, spacing of energy levels). What are the implications for evenly spaced energy levels?
2. What is the order of magnitude of a bond stretch?
3. Formula for $J \rightarrow J + 1$? General formula? Find bond length of HCl using formula, given that the spacing between peaks is 1.2×10^{12} J
4. Formula for column height pressure?
5. Boyle's Law? Charles' Law? Absolute zero?

4.2 Conceptual Questions

1. What are the selection rules for UV-vis? For photoelectric? For rotational energy? For vibrational?
2. Why is cyclobutadiene (square shaped carbon ring with two double bonds) anti-aromatic instead of non-aromatic?
3. Why is the interaction between Lewis acid (BH_3) and Lewis base (NH_3) not as strong as a chemical bond?
4. What does photoelectron spectroscopy do? What does it measure? What is it for?
5. What does UV-vis spectroscopy do? What does it measure? What is it for?
6. What does infrared spectroscopy do? What does it measure? What is it for?
7. What does microwave spectroscopy do? What does it measure? What is it for?
8. What are selection rules?
9. How to multiply dipoles? How to determine whether the product has a dipole?
10. Recalling that the $\pi \rightarrow \pi^*$ transition in ethene was 171 nm, which is the lowest $\pi \rightarrow \pi^*$ transition in butadiene? (Butadiene has 4 carbons and is conjugated)
 - (a) 120 nm
 - (b) 170 nm
 - (c) 220 nm
11. Is the $\pi_2 \rightarrow \pi_4^*$ transition allowed or forbidden in butadiene?

12. How many degrees of freedom in translation? In rotation? In vibration?
13. How does the energy level spacing of diatomic molecules actually change as n increases, as opposed to the quantum harmonic oscillator model?
14. Name the three vibrational modes of CO_2 . Which vibrational mode of CO_2 will be nearly invisible on an infrared spectrum?
15. What is Beer's Law? Explain each variable and specify units.
16. A vibration frequency with high wavenumber corresponds to a (strong or weak?) bond.
17. Compare the vibrational frequency of
 - a) molecule made up of light atoms joined by stiff bonds to
 - b) heavy atoms joined by loose bonds
18. How do you determine the strength of a bond using a potential energy graph?
19. Describe the spectroscopy graph for rotation.
20. Applications for microwave spectroscopy?
21. Has benzene been detected in space via microwave spectroscopy? (this is a science question, not a history question)
22. Why are microwaves (the kitchen appliance) so effective?
23. STP vs SATP?

Chapter 5

Kinetics and Electrochemistry

5.1 Which Equation?

1. Relate work to voltage.
2. Relate work to G.
3. Relate G to voltage.
4. Relate voltage to K.
5. Nernst equation for nonstandard conditions?
6. What is the calculus form of the rate law for $aA + bB \rightarrow cC + dD$?
7. Graphical equations for 0th, 1st, and 2nd order reactions?
8. Half-life equations for 1st and 2nd order reactions?

5.2 Plug and Chugs

1. What are 4 tricky oxidation/reduction rules?
2. Positive voltage—spontaneous or non-spontaneous?
3. A reduction potential that is way bigger than 0—strong oxidizer or strong reducer?
4. How to tell the order of a reaction given the linear plot? How to make the graphs linear? Slopes as related to k for each order?
5. How to make the Arrhenius equation linear?

5.3 Conceptual Questions

1. $C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 24H^+ + 24e^-$; is carbon reduced, oxidized, or no change?
2. Which of the following will occur if Zn is placed in Ag_2SO_4 solution? Standard Reduction for Zn is -0.76, Standard Reduction for Ag is 0.8
 - (a) reaction
 - (b) nothing
3. What happens if Cu is placed in $ZnSO_4$ solution? Standard reduction for Cu is 0.34.
4. What happens to voltage when $Q < K$?

5. Zn standard reduction has voltage < 0 . What about Zn at 0.1M?
6. What is the voltage of a copper cell with the following conditions:
Left: $Cu_{(s)} \rightarrow Cu^{2+}(0.1M)$ to right: $Cu^{2+}(1M)$ to $Cu_{(s)}$?
7. 2 examples of 0th order reaction?
8. Examples of 1st order reaction?
9. Example of 2nd order reaction?
10. How do you find the order of a reaction with respect to A given A and B?

Chapter 6

Gases

6.1 Which Equation?

1. Formula for pressure in 3 dimensions?
2. Formula for root-mean-square velocity?
3. Formula for kinetic energy?
4. Formula for kinetic energy per molecule?
5. Formula for collision frequency?
6. Effusion formula, Graham's Law?

6.2 Plug and Chugs

1. A rigid oxygen tank stored outside a building has a pressure of 20 atm when the temperature is 10°C . What will be the pressure in the tank when the temperature is 30°C ?
2. A sample of neon of volume 10 L at 300 Torr is allowed to expand isothermally into an evacuated tube with a volume of 20.0 L. What is the final pressure of the neon in the tube?
3. A helium balloon is filled at -20°C and a certain pressure to a volume of 2.5×10^4 L with 1.2×10^3 moles of He. What is the molar volume of helium under those conditions?
4. When the piston is pushed in, the volume inside the chamber is decreased from $100.\text{cm}^3$ to 20cm^3 before ignition. Suppose that the compression is isothermal. Estimate the final pressure of the compressed gas mixture, given an initial pressure of 1.00 atm
5. Sample of argon has volume 10 mL at 200 Torr. Gas expands isothermally into an evacuated tube with volume 0.2 L. What is the final pressure of argon in the tube?
6. Gas has volume 500 mL at 28°C , exerts pressure of 92 kPa. What pressure will it exert when it is compressed to 300 mL and cooled to -5°C ?
7. Gas has volume 1000 L at 20°C and 1 atm pressure. It rises up a mountain where pressure is 0.75 atm and -10°C . What is its new volume?
8. Evaluate the root-mean-square velocity of N_2 at room temperature.

6.3 Conceptual Questions

1. What is Avogadro's principle?
2. Limitations of the ideal gas law?
3. Our lungs work ideally at $P(O_2) = 0.2$ atm. For a dive of 10 meters, how do you change the mole fraction of O_2 ? Make it:
 - (a) 2x smaller
 - (b) 2x bigger
 - (c) same
4. 4 Assumptions about the kinetic theory of gases?
5. One mole of He gas is at STP. So is a separate sample of N_2 gas. What are their relative kinetic energies?
6. If we were in a helium atmosphere instead of a nitrogen atmosphere, what would the speed of sound be?
7. Implications for Maxwell distribution for heavy vs. light molecules? For high temperature vs. low temperature?
8. Explain the cylinder concept of a molecule set to crash with another.
9. What does it mean to have a compression factor > 1 ? < 1 ?
10. What does it mean when the potential energy graph starts going up?
11. How does the pressure of an ideal gas compare to the pressure of a real gas? Why? What is the relationship between real/ideal volume/pressure?
12. Deviations from ideal gas conditions? (pressure/temperature)
13. Describe the graph of ideal gas volume vs temperature in Celsius.
14. Describe comparing a gas at different temperatures on a graph of pressure/volume.
15. What is the critical temperature?
16. What is the critical temperature for water? Above $100^\circ C$, $100^\circ C$, or below $100^\circ C$.
17. What is the boiling temperature of water on Mt. Kilimanjaro ($\sim 6000m$)?
 - a) Below $100^\circ C$
 - b) $100^\circ C$
 - c) Above $100^\circ C$
18. Why does soap decrease the surface tension of water?
19. Describe critical point and superfluid.
20. What does water in a graduated cylinder look like compared to mercury? Why?
21. Describe molecular solids vs ionic solids vs metallic solids vs network solids
22. What happens to surface tension as temperature increases?
23. Colloid or solution for each of these?
 - a) Sugar water
 - b) Whipped cream
 - c) Fog
 - d) Butter
 - e) Oxygen in water
 - f) Gasoline

Chapter 7

Acid-Base Chemistry

*This was a not a big emphasis in Professor Head-Gordon's class. Your professor may ask you to do much more complicated problems than the ones presented here.

**HH abbreviation means Henderson-Hasselbach

7.1 Plug and Chugs

1. pH of 0.010 M acid is 2.95. What is its K_a ?
2. High pK_a means this acid is strong or weak?

7.2 Practice

1. Find percent dissociation for 0.080 M acetic acid, given that its K_a is 1.8×10^{-5} .
2. A buffer has 0.08 M acetic acid, 0.04 M sodium acetate. We add 0.02 mol NaOH. The solution has 300 mL. What is the pH of the solution?
3. A buffer has the same conditions as the previous question, except that we add 0.01 moles of HCl. Solution has 500 mL. What is the pH?
4. Find pH at equivalence point for the titration of 25.00 mL of 0.010 M HClO with 0.020 KOH. K_b of ClO^- is 3.3×10^{-7} .
5. Find pH at equivalence point of 25 mL of 0.020 M NH_3 with 0.015 M HCl. K_a of NH_4^+ is 5.6×10^{-10}
6. Find pH of 0.1M HCOOH 25 mL after adding 10 mL of 0.15 M NaOH. K_a of HCOOH is 1.78×10^{-4}
7. Suppose that 25 mL of 0.1 M acetic acid is titrated with 0.1 M NaOH.
 - a) What is the initial pH?
 - b) What is the pH after the addition of 10 mL of NaOH?
 - c) What is the pH at the equivalence point? K_a of acetic acid is 1.8×10^{-5}

Chapter 8

Equilibrium

8.1 Which Equation?

1. How to find G when given G° and Q ?
2. How to find G° at equilibrium?
3. How to find G given Q and K ?
4. What is Henry's Law?
5. How to relate P_{vap} with H and T ?
6. How to find freezing/boiling point depression/elevation?
7. How to find osmotic pressure?
8. How to relate $\ln K$ to $\frac{1}{T}$?

8.2 Conceptual Questions

1. What is Raoult's Law? What are its limits?
2. Explain fractional distillation.
3. What do the $\ln(K)$ to $\frac{1}{T}$ graphs look like? (4 types)
4. What is the partition coefficient?
5. Does precipitate form when $Q > K_{sp}$ or $Q < K_{sp}$?

Chapter 9

Thermodynamics

9.1 Which Equation?

1. How do you find entropy of reversible isothermal expansions?
2. What is the general form of the equation for entropy at constant temperature?
3. How do you find the entropy of reversible isothermal expansions using pressure?
4. How do you find entropy provided that C is constant and the system is being heated?
5. How do you find work done in an irreversible reaction?
6. How do you find entropy at the boiling temperature?
7. How do you find entropy at the melting temperature?
8. How do you find entropy of the surroundings? What are the assumptions that validate this equation?
9. What is the mathematical definition for enthalpy?
10. What is the value of ΔS_{total} at equilibrium?
11. How to find reversible isothermal expansion work?
12. What are C_V and C_P for diatomic and monoatomic gases?
13. How do you relate entropy to the number of microstates?
14. How do you relate enthalpy to energy when the moles of gas in a reaction change?
15. How do you find the efficiency of a Carnot engine?
16. How do you find the number of microstates available to N particles?

9.2 Plug and Chugs

1. If you combine 390 mL of water at $25^\circ C$ and 140 mL of water at $95^\circ C$, what is the final temperature of the mixture?
2. Find the absorption/release of heat that corresponds to the formation of 74 g of Fe:
 $2Fe_2O_3 \rightarrow 4Fe + 3O_2$, where $\Delta H_{rxn} = 824.2$ kJ
3. MX_2 is an ionic compound. The enthalpy of formation of MX_2 is $\Delta H_f = -677 \frac{kJ}{mol}$. Enthalpy of sublimation is $111 \frac{kJ}{mol}$. First and second ionization energies of M are $767 \frac{kJ}{mol}$ and $1383 \frac{kJ}{mol}$. Electron affinity of X is $-343 \frac{kJ}{mol}$. Bond energy of X_2 is $167 \frac{kJ}{mol}$. Find the lattice energy.

4. Consider a process in which an ideal gas is compressed reversibly to $\frac{1}{2}$ its original volume at constant temperature. Calculate the entropy change per mole of gas.
5. C_V is $20.17 \frac{J}{Kmol}$. A 9 L flask contains carbon monoxide at a pressure of 5000 Pa at a temperature of $25^\circ C$. Assuming that C is constant over a temperature change, find ΔS when the gas is heated to $800^\circ C$.
6. A container holds 2.62 moles of neon gas. The volume can be increased and decreased. The volume changes from 7 L to 6L reversibly and the temperature is changed from 270K to 178K. C_V is $12.47 \frac{J}{molK}$ for neon. Assume this value will not change over the given temperature range. Find ΔS .
7. How do you find the enthalpy of ideal gases? What about the energy?

9.3 Conceptual Questions

1. How does one find work given ΔG ?
2. What's interesting about the heat transfer at phase transitions?
3. What does it mean if the ΔS of a substance is much higher than Trouton's Rule would predict?
4. Explain residual entropy.
5. Explain the pattern of standard molar entropies and compound size.
6. Name the classic state functions and path functions.
7. Compare adiabatic processes to isothermal processes.
8. What is the enthalpy change of the expanding gas of fire extinguisher? Assume change occurs instantly.
9. Which is bigger? C_V or C_P ? Why?
10. How do you find kinetic energy for diatomic molecules? For atomic molecules?
11. Explain what makes a good fuel in terms of enthalpy.
12. 4 common spontaneous tendencies?
13. Describe the amount of work that goes into reversible expansion/compression
14. Describe the Carnot cycle.
15. What are the three laws of thermodynamics?

Chapter 10

Solutions

10.1 Basic Quantum Calculations

10.1.1 Plug and Chugs

- $1.83 * 10^{18}$ electrons
Find energy of one photon with $E = hv$. Divide total energy by energy of one photon.
- $2.12 * 10^{-18}$ J
Use $R(\frac{1}{n^2} - \frac{1}{n'^2})$. $R = 3.29 * 10^{15}$, first n is 1 and the second n is 6. Multiply the whole thing by $6.626 * 10^{-34}$ for energy
- 121.6 nm
frequency = $R(\frac{1}{n^2} - \frac{1}{n'^2})$ first n is 1, second n is 2
 $c = f\lambda$
 $\lambda = \frac{c}{f}$
- Lyman series(1), Balmer(2), Paschen/Bohr(3), Brackett(4), Pfund(5), Humphreys(6)
(Life Bears Puppies Bringing Plenty Happiness)
- $n = 7$
 $\frac{c}{R(\frac{1}{16} - \frac{1}{n^2})} = 2166 * 10^{-9}$
Solve for n
- Infrared. Color is from 400 to 750 nm.
- $n_f = 4$
 $\frac{c}{\lambda} = R(\frac{1}{n^2} - \frac{1}{n'^2}) = \lambda = 93.03 * 10^{-9}$ m (solve for the second n (should be 7.1), first n is 1).
 $\frac{c}{\lambda} = R(\frac{1}{n^2} - \frac{1}{n'^2}) = \lambda = 2165$ nm (second n is answer from first part) first n should be 4.01, your answer
- 4468 K
 $T(\lambda) = \text{constant}$ (constant is 2.9 mm K)
 $T * 649 * 10^{-9}$ m = $2.9 * 10^{-3}$ m K
- $4.12 * 10^{-19}$
 $KE = h(\frac{c}{wavelength} - 5.55 * 10^{14})$
- $1.86 * 10^{-34}$
1 m = 3.28 ft
5280 ft in one mile
 $1337 \frac{\text{miles}}{\text{hour}} * (5280 \frac{\text{ft}}{\text{mile}}) * (1 \frac{\text{hr}}{3600\text{s}}) * (1 \frac{\text{m}}{3.28\text{ft}}) = 597.85 \frac{\text{m}}{\text{s}}$
 $\lambda = \frac{h}{5.97 * 10^{-3} * 597.85}$

11. 6 nm

$$p * x \geq \frac{h}{4\pi}$$

$$(9.1 * 10^{-31})(0.00167 * 6 * 10^6)(x) \geq \frac{h}{4\pi}$$

Solve for x

12. $6.42 * 10^{-38} \frac{m}{s}$

$$mvx \geq \frac{h}{4\pi}$$

$$2650lb * \frac{1kg}{2.2lb} * (5ft) \left(\frac{1m}{3.28ft} * v \geq \frac{h}{4\pi} \right)$$

$$v \geq 2.87 * 10^{-38} \frac{m}{s}$$

*Not sure where I got $6.42 * 10^{-38}$ when I originally wrote these solutions in Pages. Left it here in case I'm forgetting some conversion factor, but otherwise it should be $2.87 * 10^{-38} \frac{m}{s}$

13. 5 nm

$$\frac{hc}{\lambda} = \frac{n^2 h^2}{8mL^2}$$

$$\frac{hc}{\lambda} = \frac{(2n+1)(h^2)}{8mL^2}$$

$$\frac{c}{\lambda} = \frac{(2n+1)(h)}{8mL^2}$$

$$\lambda = 5 \text{ nm}$$

14. 30.4 nm

$$E = Z^2 R \left(\frac{1}{n^2} - \frac{1}{n'^2} \right) \text{ first } n \text{ is } 1, \text{ second } n \text{ is } 2. R \text{ is } 13.6 \text{ eV} * 1.602 * 10^{-19} J$$

$$\frac{hc}{\lambda} = E, \text{ solve for } \lambda$$

15. n = 3

Assume that it's falling to ground state. If ground state doesn't work, solve for $n_f = 2$

$$\frac{c}{102.6 * 10^{-19}} = R \left(\frac{1}{n^2} - \frac{1}{n'^2} \right), \text{ where } R = 3.29 * 10^{15}$$

Second n is 3

16. 122 nm

$$\frac{c}{\lambda} = R \left(1 - \frac{1}{4} \right)$$

17. 397 nm

$$\frac{c}{\lambda} = R \left(\frac{1}{n^2} - \frac{1}{n'^2} \right)$$

Set first n = 2

18. $1.32 * 10^{-36} \text{ m}$

$$(8)(5)(x) \geq \frac{h}{4\pi}$$

19. $1.66 * 10^5 \frac{m}{s}$

$$(mv)(x) \geq \frac{h}{4\pi}$$

$$(9.1 * 10^{-31})(v)(350 * 10^{-12}) \geq \frac{h}{4\pi}$$

20. $3.96 * 10^3 \frac{m}{s}$

$$\lambda = \frac{h}{mv}$$

$$100 * 10^{12} = \frac{h}{(1.675 * 10^{-27})v}$$

21. $1.11 * 10^{-34} \text{ m}$

1 oz is 28.3 g. 3.28 ft = 1 m
Convert and plug into de Broglie's formula

22. 4590 K

Total intensity emitted over all wavelengths = $5.67 * 10^{-8} * T^4$
 $T(\lambda_{max \text{ intensity}}) = 2.9mK$
 Solve for T

10.1.2 Conceptual Questions

1. 1 and 2, 1 and 3, 2 and 3

n_1 is the x axis and n_2 is the y axis. Two quantum numbers give a semicircle shape. 1 and 2 is the same as 2 and 1. 1 and 3 is the same as 3 and 1. 2 and 3 is the same as 3 and 2. The sum of squares is 5, 10, 13. They are the smallest sum of squares.

2. 33.3%

Wave function equation is $\sqrt{\frac{1}{\pi a^3}} * e^{-\frac{r}{a}}$

a is the Bohr radius 52.9 pm

Square the wave function and compare the values. The first term cancels out because it's a constant, and the e term becomes $e^{-\frac{2r}{a}}$. Usually you're asked to compare relative to $r = 0$, so really you only have one term to evaluate (usually).

3. A p-orbital on x y and z axes makes a symmetrical distribution no matter which axis you make your x or y or z.

4. A node is somewhere where the wave function passes through 0, so somewhere where the probability density is 0.

There are 0 radial nodes for the most basic n for that l. For example, 0 for 1s 2p and 3d because those are the lowest energy orbitals for their respective letters. Increase the number of nodes by 1 for each $n + 1$. Angular nodal surfaces also increase with l, but they start with 0 for s, 1 for p, 2 for d, 3 for f. s has 0 nodes.

2s has 0 angular nodal surfaces but 1 radial node.

2p has one angular nodal surface and 0 radial nodes.

3d has 2 angular nodal and 0 radial nodes.

5. 1, 5, 3, 7

6. a) 7 (0 to n-1)
b) 5 (5 orientations)
c) 3 (3 orientations)
d) 4 (0 to n-1)

7. Principle quantum number, orbital angular momentum/number, magnetic number, spin magnetic number.

8. a) 3
b) 1
c) 4
d) 1

9. 10^{-17} J

$$\lambda = \frac{h}{\sqrt{2mE}} \text{ where } m = 10^{-30}$$

Solve for E

10. Electrons

$$\sqrt{2mE} * \lambda = h$$

$$\sqrt{2mE} = \frac{h}{\lambda}$$

$$2mE = \left(\frac{h}{\lambda}\right)^2$$

$$E = \frac{\left(\frac{h}{\lambda}\right)^2}{2m}$$

Increasing the denominator will decrease the energy required.

11. Black body curve is shifted upward, meaning it starts to emit light at all wavelengths in intensities that we can see.
12. Bohr radius is the most probable distance of an electron from the nucleus.

10.2 Intro to MO Theory and IMFs

10.2.1 Conceptual Questions

- Not acceptable because l is a p-orbital, and m can only be -1, 0, or 1.
- Na, Mg, Si, Al, S, P, Cl, Ar
- 9 wave functions
 - 4.25×10^{-19} J; 13 carbon atoms, 9 C-C bonds, so 9 wave functions. There are 40 electrons total, so they will occupy up to 5s and 4d. Highest level is 5, upping it to 6. Use PIB again, with $L = 139 \times 10^{-12} \times 9$. Should be 11 as coefficient before the h^2 factor in the PIB equation.
 - Use PIB, use coefficient 13 before h-squared term. Set equation equal to $\frac{hc}{\lambda}$ and solve for L. Add one to number of bonds to get number of carbon atoms.

***Note:** Frankly, this question is pretty crazy, and as I write this one year after finishing Chem 1A, I don't exactly remember all the equations that were needed to solve this question. This question is likely way beyond the scope of Chem1A (actually most of the MO questions are beyond the scope of the course), so don't worry if you didn't understand this solution.
- s-block metals have nearly complete screening, but p-block metals typically experience very little screening. s-metals therefore lose electrons easier (more reactive = easier to ionize)
- Similarity between an element and the one below it and one to the right. Arises because trends "cancel" out. Electronegativity increases to the right and up, so moving down and right can be thought of as an increase in electronegativity (right) and then a decrease in electronegativity (down), resulting in a "cancelling" effect.
 Li^+ and Mg^{2+} are examples
- S^+ has a half-filled p shell, which is more stable than P^+ because P^+ has $2p^2$. Sulfur has one orbital in which the electrons repel each other, so this offsets increasing electronegativity for the first ionization energy. Another way to think about the first part: as soon as that electron-electron repulsion is removed, the higher electronegativity of sulfur kicks in, raising the IE.
- Radicals, electron deficiency, hypervalence
Radicals: O_3 , OH
Electron deficiency: Be, B
Hypervalence: XeF_6 , PCl_5 , SF_6 , ClF_3
- All equal because H only has one electron, so all levels have the same energy and thus the same number of nodes.
- $3s > 3p > 3d$
- C
 $-\frac{Z^2R}{n^2}$ reveals that Li^{2+} has the most negative energy (most negative, so least energy)
- A
The same formula as the previous question. H has greatest magnitude, taking into account $Z_{effective}$ instead of just Z
- Only F. A jump from $n = 1$ to $n = 2$ means there must be a vacancy somewhere in the 2 shell. Only F has a vacancy.
- K^+ has the highest ionization energy because they all have the same number of electrons, but K has the greatest nuclear charge.
- Critical distance is where (Coulombic attraction) $>$ (ionization energy) - (electron affinity)

15. C
We have already "paid off" the IE/EA debt (lattice energy is defined as the energy released in bringing a gas to the solid phase, so the only thing that matters after ionization is ion size)
16. C
K is biggest and its bond will be biggest so it has the weakest bond = the least energy loss = greatest lattice energy
17. High EA means incomplete screening; low EA means nearly complete screening.
High IE means incomplete screening, low IE means complete screening—hence, if you have low IE, you will have low EA and vice versa
Note: IE = ionization energy, EA = electron affinity

10.3 More MO Theory and IMFs

10.3.1 Plug and Chugs

1. B
MW of C_2H_4 is about $28 \frac{g}{mol}$, which is about $30 \frac{g}{mol}$. Multiply by 300,000 and we get 9,000,000, which is about $1 \frac{Gg}{mol}$.
2. C has the most stable bond. C has the most reactive bond.
The second bond is weaker than the first, and the third bond is weaker than the second. So it's easier to break off bond 3 for polymerization than it is to break off a single bond. (the third bond is a pi bond but the first bond is a sigma).
3. HDPE because it has more LDF per unit volume.
4. raspberry < pineapple < orange
Least pungent is the one that has the weakest attraction to water. Orange is mostly LDF so it is the most pungent (highest VP). It is harder for water to H-bond with pineapple's oxygen atoms than with raspberry's because the atoms around oxygen in pineapple will repel water molecules and block them physically.
5. Larger in ammonia because ammonia only has one lone pair pushing the bond together.
6. Ozone has a non-zero dipole moment because it has a bent structure. Even though the polarity vectors appear to cancel, there is still a net vector pointing toward the side of the two base oxygen atoms.
7. $-\frac{1}{R}$ corresponds to Coulombic attractions
 $-\frac{1}{R^2}$ corresponds to ion-dp
 $-\frac{1}{R^3}$ corresponds to dp/dp and H-bonding
 $-\frac{1}{R^6}$ corresponds to rotating polar gas molecules, LDF, and dipole-induced-dipole
8. C
Li has a higher bond order, so it's stronger
9. B
Both have a bond order of $\frac{1}{2}$
10. A
Look at the notation. It's asking for sigma, not sigma* (so we're looking at the lower energy bonding orbital).

11. C
Look at the notation. It's asking for sigma* (higher energy anti bonding orbital).
12. C
C is the only bonding orbital. A is a pi antibond and B is a sigma antibond
13. Yes
Bond order increases when you ionize it.
14. Helium because helium has a higher $Z_{effective}$ (lower energy)
15. Polarized toward oxygen because fluorine is more electronegative: therefore, the bonding electrons will resemble fluorine more. Also, fluorine has higher $Z_{effective}$ so it has lower energy and is thus lower on the MO diagram.
16. There are 2. One on each carbon atom
17. Easier to ionize from ethene because it has a pi bond which is higher in energy.
18. $4n+2$ means aromatic; $4n$ means anti aromatic
19. D
Adding the orbitals together means the orientations of both p orbitals are both the same. Therefore, we must subtract the p orbitals to get a bonding orbital.
*Note: Adding the orbitals together would result in an antibond. If they are added, the two orbitals are pointing in the same direction. This can be visualized as $(-/+)$ + $(-/+)$, where the signs enclosed in parentheses are p-orbitals. You can see that adding these would result in the 'positive' wave function of one orbital destructively interfering with the 'negative' wave function of the other orbital. Subtracting the orbitals negates all the signs in the orbital, resulting in the bonding MO.

10.4 Spectroscopy

10.4.1 Which Equation?

1. $PE = 0.5 * kx^2$
Fundamental Frequency: $\frac{1}{2\pi} * \sqrt{\frac{k}{\mu}}$, where μ is $\frac{m_1 m_2}{m_1 + m_2}$
Spacing of E levels: $(0.5 + n)(h\nu)$, where n is the energy level.
Implication is that there is a discrete spectrum of absorption because light is absorbed in specific quanta.
2. 10^{-11}m
3. $\frac{h^2}{4\pi^2 \mu R^2} * (J + 1) = \Delta E$
General: $\frac{h^2}{8\pi^2 \mu R^2} * J(J + 1) = E$ (allowed energy levels)
Only for diatomic molecules. Don't forget to convert reduced mass to kg (multiply by $1.67 * 10^{-27}$). 1 angstrom is 10^{-10}m
4. Density * 9.8 * height = pressure
5. Boyles' Law: V is inversely proportional to P (think pressure cooker, which lowers "boyle"-ing temperature)
Charles: Volume is proportional to temperature at low pressure.
Extrapolate the volume/temperature line and you'll see that 0 volume occurs at -273 Celsius.

10.4.2 Conceptual Questions

1. **Photoelectric:** No selection rules, you're just ejecting electrons
UV-vis: Can only promote one electron at a time (but possible to go multiple levels), the promoted electron must have the same spin, and product of the two orbitals must be a dipole.
Rotational Energy (microwave): Can only jump a single level at a time, must have a non-zero molecular dipole. ***MUST BE EXACTLY 0 FOR A FORBIDDEN TRANSITION. Small polarity values that we might normally ignore are still non-zero and may allow for energy level jumping.
Vibrational (infrared): Can only jump a single level at a time; must create a dipole in its excited state, or have a permanent molecular dipole (i.e., HF has only symmetric stretching but it has an allowed transition because it is inherently polar)
2. The square molecule satisfies all rules for aromaticity except it has $4n$ electrons.
3. The energy difference between the HOMO of NH_3 and LUMO of BH_3 is not very small, so there is unequal mixing of orbitals. However, the MO diagram tells us that the net energy will still be lower, so the interaction still occurs.
4. PE spectroscopy ionizes electrons and measures the electron's KE. This is used to learn about the energies of occupied MOs.
5. UV-vis spectroscopy excites electrons from the HOMO to the LUMO. It measures the number of photons absorbed. This is used for a lot of things, but most especially molecular properties, analysis
6. Infrared excites molecules from $n=0$ vibrational state to the $n=1$ vibrational state. It measures the transmittance of photons (really measuring the absorbance, but we just look at fingerprint regions that have super low transmittance, meaning high absorption, meaning it's been excited to the next n state). This allows us to characterize unknown molecules because functional groups have characteristic vibrational frequencies. Also allows us to find the strength of bonds.
7. Microwave excites molecules from the $J=0$ to $J=1$ rotational state. It also measures transmission, the same way as infrared does (Note: x-axis is decreasing wavenumber, (typically measured cm^{-1} meaning increasing wavelength). Allows us to determine structure and characterize molecules.
8. Selection rules determine the intensity of a transition. Strongly allowed means strong intensity; forbidden means 0 intensity.
9. You multiply the magnitudes of the boundary surfaces. Nodal areas in the MO with more nodes can be considered as 0's (which give the product the same number of nodes as the MO with more nodes). Odd wave functions indicate a dipolar molecule ; even wave functions indicate a nonpolar molecule. Odd wave functions are exactly the same as odd functions ($y = x^3$), which flip their sign when you reflect over the axis coming out of the paper.
10. C
 Butadiene has a larger "box" because its conjugated system is bigger. The delocalized pi electrons can be considered as particles in a box, so the difference in energy between HOMO and LUMO is smaller than that of ethene. Therefore, it takes less energy to excite the electron, meaning longer wavelength.
11. Forbidden. The product of the dipoles is something that is not dipolar.
12. Translation: 3 degrees of freedom (x, y, z)
 Rotation: 2 if linear, 3 otherwise
 Vibration: $3A - 5$ if linear, $3A - 6$ otherwise
 A = Number of atoms
13. The spacing decreases as potential energy increases. As we excite electrons in a real molecule, we get closer to 0 PE (meaning the molecule no longer exists). However, the allowed energy levels exist only for $PE < 0$ (while the molecule exists; otherwise the atoms aren't a molecule anymore). Therefore, as PE approaches 0, the spacing will get infinitely smaller as the molecule attempts to stay together while its electrons get more and more excited.

14. The symmetric stretch, asymmetric stretch, and bend. Asymmetric and bend are nearly invisible on the infrared spectrum (absorption will only appear for molecules that get excited to vibrational states that have dipoles)
15. Absorbance = Molar Absorptivity ($M^{-1}cm^{-1}$) * path length of cell (cm) * sample concentration (Molarity)
No units for absorbance
16. High wavenumber means high frequency means strong bond. Strong bonds tend to bounce back to original position faster, while weak bonds bounce slowly (hence, low wavenumber). Strong bonds absorb at higher wave number.
17. Stiff bonds have higher vibrational frequency than loose bonds. Stiff bonds will have high k values, which, according to the fundamental frequency equation, will increase the frequency and thus energy.
18. Strength of a bond is measured by how steeply the PE graph rises as the bond is stretched or compressed. Basically we're examining the rate at which the the PE changes with respect to displacement. If the rate of PE change is big, that means the bond is really strong and doesn't tolerate much displacement. If the steepness is minimal, that means the bond never really had any bonding effect anyway from the start.
19. Evenly spaced peaks (transitions). This is because equation for rotation increases linearly with respect to J+1.
20. a) Determining the rotational constants (B) yields the bond length and other structural information.
b) Finding molecules in space by comparing with lab spectra
21. No-benzene does not have a molecular dipole.
22. Water has a strong dipole, so it absorbs microwaves well and heats up food.
23. SATP means 298 K, and 1 mol has volume 24.8 L. STP means 273 K and 1 mol has volume 22.4 L. Both are at 1 atm

10.5 Kinetics and Electrochemistry

10.5.1 Which Equation?

1. work = voltage * charge (work of moving a charge through given voltage)
2. G is the maximum amount of work a system can do.
3. $G = work_{max} = \text{voltage} * \text{charge} = -nFV$
4. $nFV^o = RT \ln(K)$
5. $V = V^o - \left(\frac{RT}{nF} * \ln Q\right) = -\frac{RT}{nF} * \ln\left(\frac{Q}{K}\right)$
R is 8.314 because voltage has units $\frac{J}{C}$. F has units $\frac{C}{mole}$
6. $-\frac{1}{a}\left(\frac{\Delta A}{\Delta t}\right) = -\frac{1}{b}\left(\frac{\Delta B}{\Delta t}\right) = \frac{1}{c}\left(\frac{\Delta C}{\Delta t}\right) = \frac{1}{d}\left(\frac{\Delta D}{\Delta t}\right)$
7. 0: $[A_t] = [A_o] - k\Delta t$
1: $[A_t] = [A_o]e^{-kt}$
2: $\frac{1}{A_t} - \frac{1}{A_o} = kt$
8. 1st: $T_{\frac{1}{2}} = \frac{\ln(2)}{k}$
2nd: $T_{\frac{1}{2}} = \frac{1}{k[A_o]}$

10.5.2 Plug and Chugs

1. Fluorine has oxidation number of -1 always. Other halogens are -1 unless bonded with oxygen or a lighter halogen. H is +1 with nonmetals and -1 with metals. O is -2 unless it's in a peroxide or bound to F.
2. Spontaneous
3. Strong oxidizer—it is highly favored to take electrons, so it's a strong oxidizer
4. 0th: $[A_t]$ with respect to time: Slope = -k
1st: $\ln[A_t]$ with respect to time: Slope = -k
2nd: $\frac{1}{[A_t]}$ with respect to time: Slope = k
5. Plot $\ln(K)$ against $\frac{1}{T}$

10.5.3 Conceptual Questions

1. C goes from 0 to +4, so it is oxidized.
2. Reaction. Zn has 0.76 V for being oxidized, and Ag has positive voltage for being reduced. Therefore, it is favorable for Zinc to lose its electrons to silver. $0.76 + 0.8 > 0$
3. Nothing. Cu would have to be oxidized and Zn would have to be reduced for there to be a reaction. Cu oxidation: -0.34 V. Zn reduction: -0.76 V. Add those together, and the result is less than 0.
4. $Voltage > 0$
5. Slightly more negative because $Q > K$. Q is $\frac{1}{0.1}$ and K is $\frac{1}{1}$.
6. Positive voltage because the two sides want to reach equilibrium. This means that the ions on the left side will increase (so more electrons moving down the wire) and the ions on the right side will decrease (accepting electrons and becoming solid).
7. When you have so much reactant that its concentration barely changes over time. Or when the reaction is limited by the amount of catalyst, so it doesn't matter how much reactant you have.
8. Radioactive decay, or any kind of decay of a radioactive molecule. Or multistep reaction whose slow step is 1st order.
9. Reaction with one (elementary) step between two molecules (like $2N_2O$)
10. Method of isolation: Add a huge excess of B and then the rate becomes $\sim k[A]^m$ because the reaction doesn't depend on B anymore.
Rate comparison: $r_1 = [A]^m$
Therefore, $\frac{r_1}{r_2} = \frac{[A_1]^m}{[A_2]^m} \ln\left(\frac{r_1}{r_2}\right) = m * \ln\left(\frac{A_1}{A_2}\right)$
Solve for m

10.6 Gases

10.6.1 Which Equation?

1. $PV = \frac{1}{3} * Nmv^2$ where v is room-mean-squared velocity, N is the number of molecules, m is molecular mass (so the number listed on the periodic table multiplied by $1.66 * 10^{-27} \frac{kg}{amu}$)
2. average velocity = $\sqrt{\frac{3RT}{M}}$ where R = 8.314, T is in Kelvin, M is molar mass in kg
3. $0.5 * (molar\ mass)(average\ velocity)^2 = 1.5 * RT$ where R is 8.314 and M is in kg

- Same as the previous question but divide by 6.02×10^{23}
- $Z = \sqrt{2} \frac{N}{V} \pi d^2 \bar{v}$ where Z is the collision frequency, d is the molecular diameter, \bar{v} is the average speed, N is the number of molecules, and V is the volume of the container
- $\frac{rate_A}{rate_B} = \sqrt{\frac{M_B}{M_A}}$ where M is the molar mass of the compound
 **Head GSI and professor argued about this one. The final formula we used included a mole factor but I'm not sure if that works in all cases for effusion

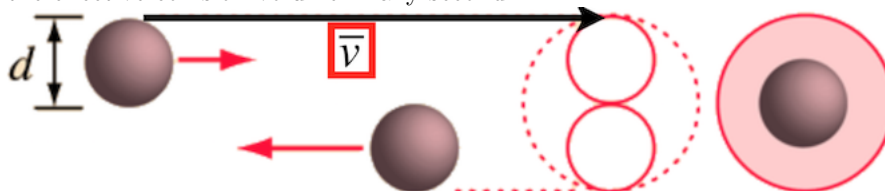
10.6.2 Plug and Chugs

- 21.4 atm
Use $\frac{P}{T} = \frac{P}{T}$ ratio, using Kelvin for temperature.
- 150 Torr
Use PV = PV ratio, just plugging in units
- $20.83 \frac{L}{mol}$
Take total volume and divide by total moles
- P = 5 atm
 $\frac{P}{V} = \frac{P}{V}$
 $100cm^3 = 100mL = 0.1L$
 $20cm^3 = 20mL = 0.02L$
 $\frac{1}{0.1} = \frac{P}{0.02}$
 P = 5 atm
- 10 Torr
Use PV = PV relationship. $0.01(200) = (0.2)x$
x = 10 Torr
- Use $\frac{PV}{nT} = \frac{PV}{nT}$
 $\frac{92(0.5)}{(28+273)} = \frac{x(0.3)}{268}$
 x = 136 kPa
- $\frac{PV}{T} = \frac{PV}{T}$
 $\frac{1(1000)}{293} = \frac{0.75V}{263}$
 V = 1196.8 L
- $515 \frac{m}{s}$
Remember to use kg for molar mass. T in Kelvin, R is 8.314

10.6.3 Conceptual Questions

- Under the same conditions of temperature and pressure, a given number of gas molecules occupy the same volume regardless of their chemical identity. Molar volume = $22.4 \frac{L}{mole}$ at STP.
- Only works reliably at atmospheric pressures. (more accurate as P approaches 0)
- A, 2x smaller
10 m water is about 1 atm. So that is equivalent to twice the number of moles of O_2 , so there is 0.4 atm $P(O_2)$ at this depth. Cut that in half to get 0.2 atm.
- Gas is made of identical separated particles
 - Elastic collisions (total KE is conserved)
 - Random directions with speed distribution
 - Move in straight lines with no IMFs

5. They are the same. KE of all gases at the same pressure/volume/temperature are the same. (however, velocity is different because KE formula depends on mass)
6. Speed would be greater. The speed of sound depends on how quickly the molecules are moving. Helium moves faster. To confirm your intuition, check the formulas in section 1 of this chapter.
7. Heavy molecules have many molecules traveling close to their average values. Light molecules have **higher average speed** but also a **wider range of speeds**. Lower temperature means many molecules at average speed; higher temperature means many molecules that are NOT at average speed.
8. For any given second, a molecule will travel (velocity)(1 s) meters. This is the “height” of our cylinder. Put the given molecule in the “center” of the cylinder. Above and below the molecule, there can be at most $\frac{1}{2}$ a molecule just barely brushing by the molecule. This is the closest that any given molecule can get to another without bumping into it. Therefore, the diameter of the “cylinder” is $d + \frac{d}{2} + \frac{d}{2} = 2d$. Volume of this theoretical cylinder is therefore $\pi d^2 * (\text{average speed} * 1s)$. Can also be thought of as the effective collision volume in any second.



(Image courtesy of Martin Head-Gordon)

9. $Z = \frac{V_m}{V_{ideal}}$
 $Z < 1$: Attraction dominates
 $Z > 1$: Repulsion dominates
10. Molecules have come into direct contact (like pushing your finger into a ball).
11. Ideal pressure is higher than real pressure because real pressure has IMFs that slightly reduce its pressure against the container.
 $V_{ideal} = V - nb$
 $P_{ideal} = P + a(\frac{n}{V})^2$
 Real volume is greater than ideal volume; real pressure is less than ideal pressure.
12. Large pressure, low temperature leads to big deviations
13. y-axis volume, x-axis temperature, linear graph. However, at low temperature, there is a sudden vertical drop because the substance hits a phase change and volume drops drastically.
14. Increasing the temperature brings the curve closer to that of an ideal gas. Lowering the temperature eventually introduces a kink in the curve. Eventually at the critical temperature the curve just barely skims a parabola of liquid-vapor equilibrium. Lower temperatures will curve up to the edge of the parabola (vapor) (from right to left, pressure on y-axis and volume on x-axis), then straight horizontal line to the other edge of the parabola (liquid), then curve up again. Basically high pressure = low volume, low pressure = high volume and use vapor-or-liquid-state intuition.
15. Critical temperature is the lowest temperature at which only 1 phase is present (NOT the same as boiling temperature). (should be higher than the boiling temperature)
16. Above $100^\circ C$ because at $100^\circ C$ we hit equilibrium (meaning liquid and vapor exist). Need to keep going up to get only gas.
17. A
 Decreased pressure means gas can escape into vapor pressure easier. Therefore it takes less energy to send it all to the gas phase. (also, think pressure cookers)

18. The hydrophilic end of soap interacts with water, but the hydrophobic end will want to be on the surface interacting with air. The surface of water becomes soap, scattering hydrocarbons, which have lower surface tension than water.
19. Critical point is the point at which the superfluid exists; critical point is where density of liquid and gas are nearly indistinguishable from each other (high pressure and high temperature). Superfluid is a fluid with zero viscosity, and it rotates with zero loss of kinetic energy.
20. Water is concave down while mercury is concave up. Glass is made of SiO_2 , so there is some attraction between water and the edge of the glass. Therefore, water tends to spread out over the largest possible area in a cylinder. Mercury tries to stay compact and will have a bulgy top (like dew on a leaf).
21. a) Molecular solids: Low MP, crystalline or disordered (the "leftovers" category)
 b) Network solids: High MP, insoluble in water, atoms covalently bonded to each other in a network
 c) Ionic solids: High MP, brittle, hard, CANNOT CONDUCT ELECTRICITY because the ions are pretty stable with noble gas configurations
 d) Metallic: High MP, hard, conduct electricity. (Total MP order is $a < d < c = b$)
22. Surface tension decreases because thermal energy is overriding IMFs.
23. Sugar water, oxygen in water, gasoline are solutions.
 Butter, fog, and whipped cream are colloids.

10.7 Acid-Base Chemistry

10.7.1 Plug and Chugs

1. Find $[H^+]$, which is $10^{-2.95}$. Set up $\frac{[H^+]^2}{0.01 - [H^+]}$ and solve. Answer: $1.4 * 10^{-4}$
2. High pK_a means weak acid.

10.7.2 Practice

1. Set up $\frac{x^2}{0.08 - x} = 1.8 * 10^{-5}$. Solve for x and divide by 0.08 and then multiply by 100%. Answer: 1.5%
2. $CH_3COOH \rightarrow H^+ + CH_3COO^-$ Adding 0.02 moles of NaOH will cause 0.02 moles of acetic acid to dissociate to neutralize the base. Find the remaining moles: $(0.08)(0.3) - 0.02$. Then add 0.02 to $(0.04)(0.3)$ on the other side of the equation. Use Henderson-Hasselbach equation to find pH. pH = 5.65
3. Subtract 0.01 moles from $(0.5)(0.04)$ moles of the acetate anion. Add 0.01 moles to $(0.08)(0.5)$ moles of acid. Use HH equation to find pH. pH = 4.05
4. $(0.01M)(25mL) HClO = 0.02M (x mL) KOH$
 $x = 12.5 mL$
 So concentration of KOH is $(0.01M)(0.025 L)$ divided by $(0.025 + 0.0125 L \text{ total}) = 0.00666666666667$.
 $K_b = \frac{x^2}{0.00666666666667 - x}$ Find -log of x, and then subtract that value from 14. pH = 9.67
5. $(25)(0.02) = (0.015)(x)$
 $x = 33.33 mL$ of HCl needed to neutralize NH_3 . Residual NH_4^+ has concentration of $\frac{(0.025)(0.02)}{\frac{33.33+25}{1000}} \sim 0.0086$.
 $5.6 * 10^{-10} = \frac{x^2}{0.0086}$
 $-\log(x) = 5.66$
 pH = 5.66
6. Subtract $(0.01)(0.15)$ moles NaOH from $(0.1)(0.025)$ moles $HCOOH = 0.001$ moles of $HCOOH$ left. We've created $(0.01)(0.15)$ moles of $HCOO^-$ Divide both of these mole values by 35/1000 (volume), then plug them into Henderson-Hasselbach eqtn. pH = 3.92

7. **Part A:** Set $K_a = \frac{x^2}{0.1}$ and solve for x. Take negative log of that for initial pH 2.87
Part B: Subtract (0.1)(0.01) moles of NaOH from (0.025)(0.1) acetic acid. That number of moles of NaOH is the same number of moles of conjugate base that are formed. Use HH eqtn and pH = 4.57.
Part C: (0.025)(0.1) = 0.0025 moles of conjugate base formed. It took 25 mL of NaOH to get there. Therefore, $\frac{0.0025}{\frac{25+25}{1000}}$ is the concentration of the conjugate base (0.05M). Its K_b value is 10^{-14} divided by $1.8 * 10^{-5}$. Set that K value equal to $\frac{x^2}{0.05}$. Solve for x, take its negative log, and subtract that result from 14. pH = 8.72

10.8 Equilibrium

10.8.1 Which Equation?

- $G = G^\circ + RT \ln(Q)$
- $G^\circ = -RT \ln(K)$
- $G = RT \ln\left(\frac{Q}{K}\right)$
- $[X] = kPx$ where P is the partial pressure of X and k is a constant that is specific to each gas
- $\ln\left(\frac{P_2}{P_1}\right) = \left(-\frac{\Delta H_{vap}}{R}\right)\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$
 *This only works for comparing P_{vap}
- Freezing and boiling point depression and elevation = $ik * m = \Delta T$
 i is the number of particles per molecule formed when put in water
 k is a constant specific to each substance
 m is **molality** of solute
- Pressure = $iRTc$
 where i is the number of particles, R is 0.0821, T is temperature in Kelvins, c is the concentration of solute
- $G^\circ = -RT \ln(K)$
 $-\frac{G^\circ}{RT} = \ln K$
 $-\frac{(H^\circ - T\Delta S)}{RT} = \ln(K)$
 $-\frac{H}{RT} + \frac{S}{R} = \ln(K)$
 Slope of $\ln(K)$ vs $\frac{1}{T}$ would be $\frac{H}{R}$, and the y-intercept would be $\frac{S}{R}$
 Alternatively: $\ln(K_2) - \ln(K_1) = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

10.8.2 Conceptual Questions

- Partial pressure of substance = (mole fraction of substance) * (partial pressure of pure substance).
 This relationship only holds up to 0.1 M for nonelectrolyte solutions and up to 0.01 M for electrolyte solutions.
- Heat the solution to make some of the more volatile substance vaporizes. The gas is more benzene-pure than the liquid. However, the composition of this vapor still has some of the less volatile species. Let the vapor condensate. It will boil at a lower temperature than before because now it has a greater mole fraction of volatile species. Repeat until the gas is distilled to pure benzene.
- Increasing: Means H is negative (because that would make slope positive based on the equation)
 Decreasing: Means H is positive
 y-intercept is positive: Means S is positive
 y-intercept is negative: Means S is negative
 The trend of the line demonstrates whether the reaction progresses as temperature increases. If the graph slopes upward as T increases, that means the reaction is forward spontaneous (because high $\ln(K)$) at high T, and vice versa.

- Partition coefficient is the ratio of concentrations of a substance in two different phases. i.e., $\frac{[X_{in\ water}]}{[X_{in\ hexane}]}$
- If $Q > K_{sp}$, that means there is too much dissolved substance. The reaction will go to the left (to the solid starting material) to reach equilibrium. Therefore, precipitate only forms when $Q > K$.

10.9 Thermodynamics

10.9.1 Which Equation?

- $\Delta S = nR \ln\left(\frac{V_f}{V_i}\right)$
- $\Delta S = -\frac{\Delta q^*R}{T}$
- $\Delta S = -nR \ln\left(\frac{P_i}{P_f}\right)$
- $\Delta S = nC \ln\left(\frac{T_f}{T_i}\right)$
- $Work = -P * \Delta V$ (note: 1 L*atm = 101.325 J)
- $\Delta S_{vap} = \frac{\Delta H_{vap}}{T_b}$
- $\Delta S_{fusion} = \frac{\Delta H_{fusion}}{T_{fusion}}$
- $\Delta S_{surr} = -\frac{\Delta H}{T}$
Temperature of surroundings is constant because surroundings are huge. Therefore, even a huge amount of heat transferred to surroundings will not affect temperature, and $\Delta S_{surr} = \frac{q_{surr, reversible}}{T}$
System is generally at a constant pressure, so $\Delta q = \Delta H$.
- $\Delta H = \Delta U + P\Delta V$
- $\Delta S_{total} = 0$
- $Work = -nRT \ln\left(\frac{V_f}{V_i}\right)$
- Atomic: $C_V = \frac{3}{2}nR$, $C_P = \frac{5}{2}nR$
Diatomic: $C_V = \frac{5}{2}nR$, $C_P = \frac{7}{2}nR$
- $S = k^* \ln(W)$ where W is the number of microstates and k is the Boltzmann's constant, which is $\frac{8.314}{(6.02 * 10^{23})}$
- $\Delta H \sim \Delta U + (\Delta n * RT)$
- $\frac{(T_H - T_C)}{T_H}$
- Number of micro states = CV^N

10.9.2 Plug and Chugs

- $m_1 c \Delta T_1 = m_2 c \Delta T_2$
 $(140)(95 - x)(4.184) = (390)(x - 25)(4.184)$
 $x = 43.5^\circ C$
- $\frac{74g}{55.845g} = 1.325$ moles However, H in this reaction is the molar H, so it's assuming each coefficient means 1 mole (i.e., 2 moles of reactant, 4 moles of Fe and 3 moles of O_2). So take 824.2 kJ and divide by (4/1.325) for the heat absorbed to make 1.325 moles of Fe.
Answer: 273 kJ

3. Lattice energy is the difference in energy from ionic gases to ionic solid. To break apart MX_2 into M and X_2 , put in 677 kJ. Then put in 167 kJ to break the X-X bond. Then make M a gas by putting in 111 kJ. Then ionize M with $767 + 1383$ kJ. Then let electrons bond with X, which is $2 * (-343 \frac{kJ}{mol})$. The “height” of the current energy hierarchy is the lattice energy. $\Delta H_{lattice} = 2419 \frac{kJ}{mol}$
4. $\Delta S = nR \ln(\frac{V_f}{V_i}) = (8.314) * \ln(0.5) = -5.76 \frac{J}{molK}$
5. $\Delta S = nC \ln(\frac{T_f}{T_i})$
 $n = PV/RT = (5000/101325)(9L)/(0.0821)(25 + 273) = .018mol$
 $\Delta S = (0.018)(20.17) * \ln(\frac{800+273}{25+273}) = 0.465 \frac{J}{K}$
6. $Cn * \ln(\frac{T_f}{T_i}) + nR * \ln(\frac{V_f}{V_i}) = -16.97 \frac{J}{K}$
7. Energy: $E = \frac{3}{2} * nRT$
 Enthalpy: $H = U + PV = (\frac{3}{2} * nRT) + nRT = \frac{5}{2} * nRT$

10.9.3 Conceptual Questions

1. The negative of the change in Gibbs free energy is equal to the maximum **non-expansion** work that the process can do at a constant temperature and pressure.
2. Transfer of heat is reversible at the temperature of a phase transition.
3. Trouton’s Rule says that the S vaporization value for many liquids is around $85 \frac{J}{mol}K$. If a liquid has a much greater value, that means that the molecule must have extremely strong IMFs. ΔS measures the change in disorder from a molecule’s liquid state to gas state, and since all gases have roughly the same amount of disorder, a larger ΔS value means the “starting” disorder in the liquid state was much lower than that of typical molecules. Hence, you can conclude that the molecule has unusually high IMFs (i.e., water).
4. Molecules that have a small dipole have residual entropy because the molecules at 0K will have random orientations. Molecules that have an electric dipole will have close to 0 residual entropy because they will tend to be arranged in an orderly crystal.
5. The greater the mass of a molecule, the closer together are the energy levels (larger “box” for the particle-in-a-box model). Larger species have larger molar entropies than simpler ones because larger molecules have more ways to jiggle around when they are excited. Molar entropies of gases > liquids > solids because it takes less energy to further disorder gases than liquids than solids.
6. State functions are energy, pressure, volume, temperature, moles, entropy, enthalpy (something that is associated with a particular thermodynamic state). Non-state functions are heat and work (system doesn’t “have” work or heat).
7. Adiabatic processes are FAST and INSULATED. They have 0 heat transfer, and $\Delta E = work$. Isothermal processes occur in NON-INSULATED systems and happen SLOWLY. They have $\Delta T = 0$ and $Q = -W$.
8. Enthalpy is 0. Remember that H is defined as exchange of HEAT at constant pressure. Adiabatic processes exchange 0 heat.
9. $C_P > C_V$ because if you don’t keep volume constant, injecting energy will cause the system to do expansion work, which will lower the temperature of the system. Therefore, it will take more energy to change the temperature of a system at constant pressure than a system at constant volume.
10. Diatomic molecules have 6 degrees of freedom, but at typical standard temperatures they only have 5 (vibrational spacing is too big). Therefore, based on equipartition theorem, there is $E = \frac{5}{2} * kT$. Atomic molecules have energy $E = \frac{3}{2} * kT$ because there are only three DOF.
 **In Physics, they say that diatomic molecules have 3 translational DOF and 3 rotational DOF. Think

of a diatomic molecule as a dumbbell: one of the rotational DOFs is along the axis of the bar. That rotation can be neglected because the contribution to the total kinetic energy of the molecule is tiny (small radius of rotation = negligible contribution to energy, something you will learn in more depth in Physics). I'm not entirely sure why Prof. Head-Gordon said that the negligible DOF is vibrational. ***DOF = degree of freedom, in case you were lost.

11. Good fuels have products whose bond enthalpies are higher. (i.e., put in 500 J to break the bonds, but then forming the products releases 1000 J. The opposite reaction would require input of 1000 J for a release of only 500 J).
12. Gas expands into larger volume, heat goes from hot to cold, miscible liquids mix into each other, soluble solids dissolve into each other.
13. Reversible expansion yields maximum work from the system. Reversible compression is the least amount of work required for compression
14. **Step 1:** Isothermal expansion: Work out, heat in (hot)
Step 2: Adiabatic expansion: Work out, system cools
Step 3: Isothermal compression: Work in, heat out (cold)
Step 4: Adiabatic compression: Work in, system heats
***** It takes less work to compress than to expand because it's easier to compress a cold gas** (less force required to push back on a cold gas, which exerts less force per unit area than a hot gas)
15. **First Law:** $U = Q + W$ (whether it's $Q + W$ or $Q - W$ depends on the convention that your professor/textbook uses).
Second Law: Energy is never created or destroyed in an isolated system
Third Law: ΔS is always positive in an isolated system. The number of micro states approaches zero as you approach absolute zero