Exam 2: Bonding, Equilibria, and Kinetics

Chemistry 123	**Monday, November 25 3:30 pm – 6:00 pm**	**Fall Term 2002**
Final Exam	**4 Pages / 4 Problems SHOW YOUR WORK!**	**Instructor: R. Rossi**

Don't Panic!

Instructions:

- **Aaaaah! Stop Panicking!!! Remain calm.**
- **There are a total of four problems in this exam, one on each double-sided page. You need to answer the questions on *one* side of each page, and it's your choice which side that is. If you do both sides of the same page, I'll only grade the first one I come to. Your exam grade will be based on the four page sides that I grade, 25% of your total for each side.**
- **You may refer to the equations and conversion factors on the back of this sheet, your textbook, your notes [notes you or I wrote, but not copies of what someone else wrote], your returned homework and anything you have written on it, and your Ni lab notebook. If you have to look *everything* up, you won't finish this exam, but *do* use these references!**
- **You *MAY NOT USE COPIES OF MY SOLUTIONS TO ANYTHING,* including my assignment solutions and the sample exam solutions, but if you make notes and corrections on your own homework and sample exams, that's fine. Make sure you understand the mistakes you made on the homework! The same holds true of mistakes made in doing the labs!**
- **You may use a calculator, a computer, a periodic table, a ruler, and any other tools you OK with me in advance. *You may not use references or tools other than those listed in the paragraphs above. You may not use a computer except as a computational or writing aid.***
- **You can start working on this exam at 3:30 pm. You must hand in your exam when I ask you for it at 6:00 pm, if not before that time.**
- **SHOW YOUR WORK AND LOGIC UNLESS SPECIFIED OTHERWISE. If you don't offer a good explanation of how your answer came to be, you will get no credit!!!**
- **If you think there is an error in your exam, ask me about it! It's OK to ask me questions. (As we learned on the midterm, no matter how much I bust my hump, I do make mistakes.)**
- **You'll likely need more paper for some of your answers. Please get that from me.**

Restrictions:

- **You may not get any form of help from others in working this exam. It's all you.**

Results:

- **I will post the exam solution on the course web page as soon as practical after the exam**
- **I will send updated grade reports to your campus email address periodically, as I progress through grading the exams, popular science projects, and labs.**
- **If you want to have your Ni lab re-graded, leave it with me after the exam, or put it in the cubbies near my office. Your old score will be completely forgotten and replaced with the one I come up with. If you make changes to your Ni lab between getting it back and re-submitting it, those changes should be clearly dated and will not be considered in the re-grade, but it is fine for you to make them in preparation for the exam.**

Final Exam Equation Sheet (You can add information to this sheet if you like.)

Formulas and Equations

$E_{photon} = \frac{hc}{\lambda}$ | $c = \lambda\nu$ | $E_{photon} = h\nu$

$E_{Bohr\ Electron} = R_H\left(\frac{Z^2}{n^2}\right)$ | $E_{photon(Emission)} = R_H Z^2\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$ | $E_{photon} = |\Delta E_{electron}|$

$P_{tot} = \rho gh + P_o$ | $\rho = \frac{m}{V}$ | $PV = \eta RT$

$q = \eta\ \tilde{C}_p\ \Delta T = \eta\ \Delta\tilde{H}$ | $P_{gas} = k\ C_{gas}$ (Henry's Law) | $P_{solution} = \chi_{solvent}\ P^o_{solvent}$

$w_{system} = -P_{opposing}\ \Delta V_{system}$ | $\Delta E_{system} = q + w$ | $H \equiv E + PV$, $G \equiv H - TS$

$A = \varepsilon\ b\ C$ | $k = Ae^{\left(\frac{-\Delta G^{\ddagger}}{RT}\right)}$ | $K_\alpha = e^{\left(\frac{-\Delta G^o}{RT}\right)}$ = Equilibrium constant in terms of activities

Constants and Conversion Factors

$g = 9.8067\ \frac{m}{s^2}$ | $h = 6.626 \times 10^{-34}$ J·s $= 4.136 \times 10^{-15}$ eV·s | 273.15 K = 0 ºC

$c = 2.998 \times 10^8\ \frac{m}{s}$ | $\rho_{H_2O} = 1.00\ \frac{g}{m\ell}$ | $R = 8.3145\frac{J}{mol \cdot K} = 0.08206\frac{\ell \cdot atm}{mol \cdot K}$

1 m = 10^9 nm = 10^{10} Å | 1 m = 3.2808 feet | 1 m = 100 cm = 10^3 mm = 10^6 μm

1 eV = 1.602×10^{-19} Joules | R_H = 13.6 eV = 2.18×10^{-18} J | 10^{-3} kg = 1 g = 10^3 mg = 10^6 μg

$1\ \text{Newton} \equiv 1\ \frac{kg \cdot m}{s^2}$ | $1\ \text{Joule} \equiv 1\ \frac{kg \cdot m^2}{s^2}$ | $1\ \text{Pascal} \equiv 1\ \frac{kg}{m \cdot s^2}$

1.00000 atm = 760.000 Torr = 101325 Pa | 1 mole = 6.022×10^{23} | 1 m^3 = 1000 ℓ = 264.17 gallons

The table at right is from Daniel C. Harris, *Quantitative Chemical Analysis*, 2nd ed., New York: W. H. Freeman (1987).
A complete electromagnetic spectrum chart appears in Figure 7.2 on p. 293 of your textbook, and a detailed color spectrum can be found in Figure 20.23 on p. 994.

Common unit conversions: See Appendix 6 in your book, p. A-28

Complete electromagnetic spectrum: in your book on p. 293

Thermodynamic Data: See Appendix 4 in your book, pp. A21-A24

Table of Bond Energies: in your book on p. 373

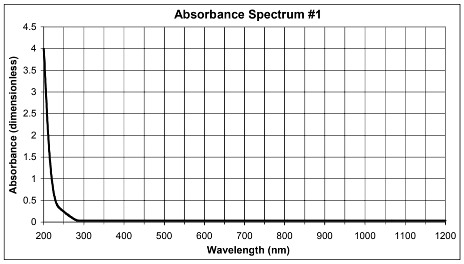
Pauling Electronegativities: Figure 8.3, p. 354 of your book

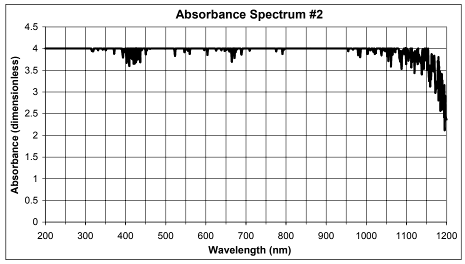
Table 20-1
Colors of visible light

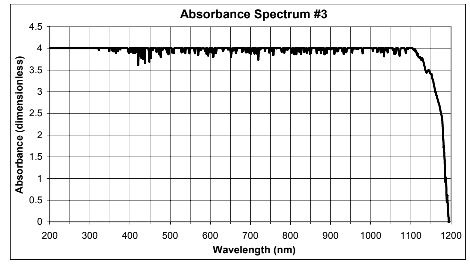
Wavelength of maximum absorption (nm)	Color absorbed	Color observed
380–420	Violet	Green-yellow
420–440	Violet-blue	Yellow
440–470	Blue	Orange
470–500	Blue-green	Red
500–520	Green	Purple
520–550	Yellow-green	Violet
550–580	Yellow	Violet-blue
580–620	Orange	Blue
620–680	Red	Blue-green
680–780	Purple	Green

Problem 1: Properties of Atoms, Intermolecular Forces, and Condensed Phases

A. Shown below are the UV/Vis spectra of three familiar solids, as if taken with our lab spectrophotometers:







Match up these spectra with the correct solid, given that each corresponds to a different one of the following:

- Diamond (a network solid insulator with a 5.5 eV bandbap)
- Silicon (a network solid semiconductor with a 1.1 eV bandgap)
- Alumin(i)um (a metal)

You need not explain your work, but if you do you can garner partial credit. The information in parentheses can be quantitatively helpful, but isn't truly needed in arriving at the correct answer to this question.

B. One Monday morning you wake up feeling a little strange, but can not figure out why. Sitting in class, you suddenly realize that while some things are vaguely familiar, certain key rules governing the properties of matter have changed! Somehow you are in a parallel universe! Looking at the periodic table, it looks very different. In this universe there are different rules governing the allowed values for quantum numbers:

- The principal and angular momentum quantum numbers (n and ℓ) follow the same rules as in our universe.
- The magnetic quantum number(m_ℓ) now ranges from -2ℓ to $+2\ell$; there's more degeneracy for each $n\ell$ orbital.
- The only allowed value for m_s is 0; electrons no longer have spin, so each orbital can only hold one electron!
- However, electrons still fill atomic orbitals in the order same order as they do in our universe.

The periodic table in this alternate universe has only one element in the first row, the first ideal gas. The second row is also short, consisting of only six elements; it contains the second noble gas, which has an atomic number of 7. The novel periodic table reflects the modified electronic configurations that electrons in atoms are allowed to have in this universe. Please answer the following questions:

a. Prepare a sketch of the **first 5 rows** of this universe's periodic table, akin to ours as shown in Figure 7.26 on p. 323 of Zumdahl. (You don't need to come up with new "Group" labels, but do label everything else.) Briefly explain your logic if you want to be eligible for partial credit, but don't go into great detail.

b. Explain why, in this universe, element 28 might have about the same atomic radius as does element 9.

Remember that you only have to answer the questions on *one* side of this page, it's your choice which one!

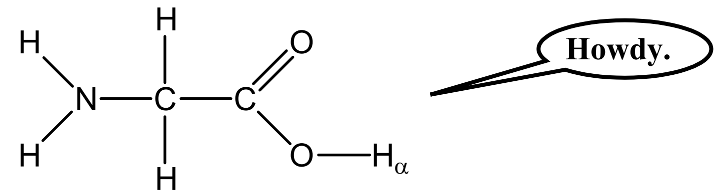
C. This term we compared the atomic emission spectrum of low-pressure hydrogen gas against that of low-pressure deuterium gas (deuterium is a heavier isotope of hydrogen, with a neutron in the nucleus), and found them to be exactly the same. Why do H and D have identical electronic emission spectra?

D. Explain in detail why the Bohr model can not be used to predict the electronic structure of the Li^+ ion.

E. Proteins are long molecular chains essential to life here on earth. A large part of their utility stems from their ability to "fold" into pre-programmed shapes as a result of their chemical composition: they hydrogen bond to themselves, and work to maximize other forms of intermolecular attraction, by twisting back on themselves to touch themselves in as many appropriate places as possible. (Get your mind out of the gutter!) All proteins undergo a process called "denaturation" when they are heated: they unfold from their natural, programmed shape into a random, floppy chain. (This is what happens when you cook a protein.) It turns out that you can accomplish denaturation in many other ways as well, including adding them to water containing a lot of acid, base, or surfactant. Choose any one of these four means of denaturation and explain how it acts to break up the intermolecular forces (especially the strong ones) and thereby "unfold" a protein.

Problem 2: Properties of Molecules

A. Amino acids are the "links" that make up molecular chains called proteins, essential to life here on earth. There are lots of different amino acids, but they each have a good deal in common, and we can learn a lot about them by getting to know the simplest amino acid of them all, glycine. Hey glycine, c'mon out here!



a) Amino acids are actually ***amphoteric***, which means that they can act as both acids and bases. In fact, under typical biological conditions, the H_α proton on glycine (and most amino acids) moves to the N atom, leaving its home on the O atom. The resulting molecular ion has both a positive and a negative end, and is called a "***zwitterion***." Draw the complete Lewis structure of the resulting $(H_3N)(CH_2)(CO_2)$ zwitterion.

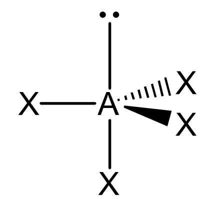
b) Clearly draw the three-dimensional shape of the glycine zwitterion, as predicted by VSEPR.

B. Draw the complete Lewis structure of the $[O_2P\text{–}NO_2]^{2-}$ molecular ion, which contains no O–O bonds. (The shorthand used here indicates that P is bonded to N, but not necessarily by a single bond.)

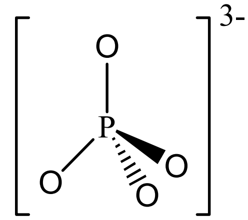
C. Based on Lewis structures and VSEPR, would you expect ozone (O_3) to be IR active, in other words, a greenhouse gas? Back up your answer with Lewis structures and a careful explanation of your logic.

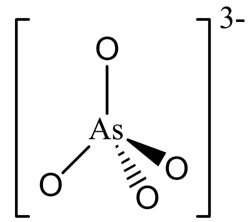
Remember that you only have to answer the questions on *one* side of this page, it's your choice which one!

D. Why is the molecular structure shown at right never observed in nature? Explain fully.

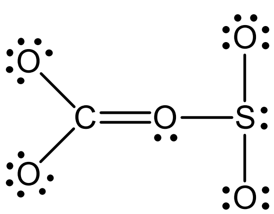


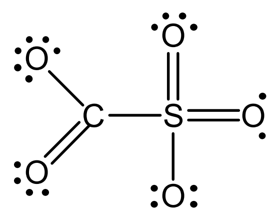
E. Shown at right are the VSEPR-predicted shapes of the phosphate (PO_4^{3-}) and arsenate (AsO_4^{3-}) ions, which are important constituents in many rocks and minerals. The equivalent nitrogen-centered ion, NO_4^{3-}, is so unstable that it is not found in nature. Explain why, basing your justification on the Lewis structures of these ions. (Note that this does *not* mean you have to draw out all the Lewis structures for all of these ions!)

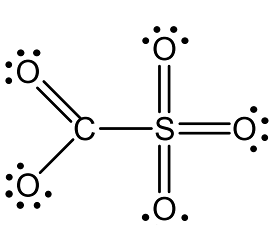


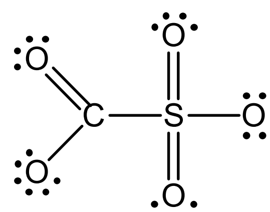


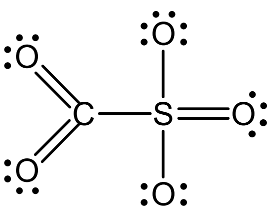
F. Shown below are three valid and three invalid resonance structures for the $[O_2C–SO_3]^{2-}$ molecular ion. Rank the valid resonance structures from best to worst, explaining your rationale. Cross out the three structures that can't possibly be resonance contributors, briefly stating what makes each of them completely ineligible.

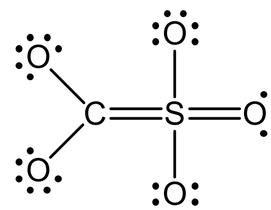












Problem 3: Kinetics and Equilibria

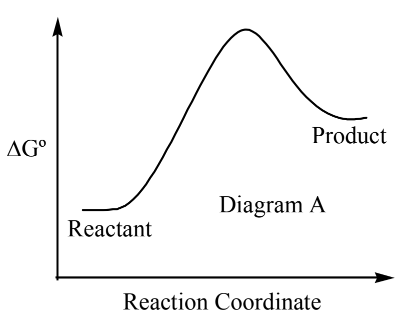
A. Silver chloride (AgCl) is a pretty darn insoluble solid: it has a K_{sp} of 1.5×10^{-16} M^2 at 25ºC. It does dissolve a little, though, via the reaction $AgCl_{(s)} \rightarrow Ag^{+}_{(aq)} + Cl^{-}_{(aq)}$. Suppose you have a huge tank containing 1000. liters of pure water, in a room at 25ºC, and you add 12.04 milligrams of solid silver chloride to it.

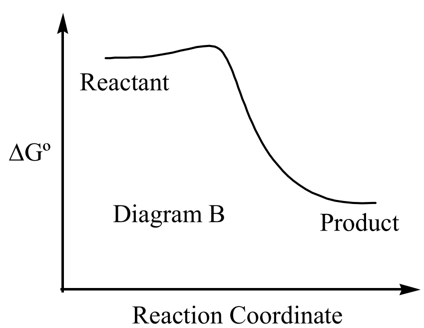
a) How much solid silver chloride will be left at the bottom of the tank once equilibrium is attained?

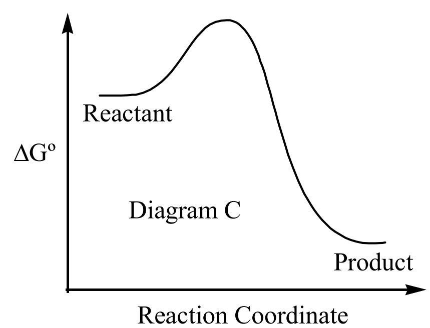
b) What would happen to the amount of solid AgCl in the tank if you were to dump in a bunch of (very soluble) table salt (NaCl), which dissolves completely to give $Na^{+}_{(aq)}$ and $Cl^{-}_{(aq)}$? Why?

B. Shown below are three reaction coordinate diagrams, each representing one of the following reactions. Match up each diagram with the reaction it represents, explaining your logic.

1) The detonation of ammonium nitrate, a common fertilizer: $NH_4NO_{3(s)} \rightarrow N_{2(g)} + 2\ H_2O_{(g)} + \frac{1}{2}\ O_{2(g)}$ Ammonium nitrate is extremely stable and safe in routine handling; it requires incredible heat and pressure to cause it to detonate. (But it is an explosive commonly used by terrorists - it ***is*** very powerful.)
2) The detonation of nitrogen triiodide, an extremely touchy explosive powder: $2\ NI_{3(s)} \rightarrow N_{2(g)} + 3\ I_{2(g)}$ Nitrogen triiodide can be caused to detonate by merely touching it with a feather. It detonates ***very*** fast.
3) The formation of glucose from carbon dioxide and water, performed by plants during photosynthesis: $6\ CO_{2(g)} + 6\ H_2O_{(\ell)} \rightarrow C_6H_{12}O_{6(aq)} + 6\ O_{2(g)}$ This reaction is ***not spontaneous*** (in the least!) under either standard or atmospheric conditions, which is why plants have to capture photons to make it happen.







Remember that you only have to answer the questions on *one* side of this page, it's your choice which one!

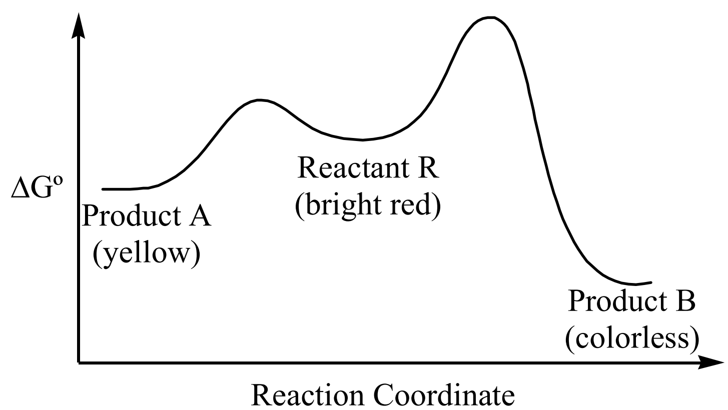
C. Does it make sense to store an activated lightstick (Assignment 6, problem 6) in a cool place when you go to bed, if you hope to have it glow for you when you wake up again the next morning? Explain carefully.

D. Enzymes are proteins (often incorporating metal atoms into their structure) absolutely essential to our daily internal chemical operations. They act to speed up and direct chemical reactions that would otherwise be very slow (kinetically disfavored) or would lead to unwanted (often dangerous) side products. Cyanide ion (CN^-) is a powerful poison because it binds tightly to an enzyme critical to your body's use of stored energy, cytochrome oxidase:

$$\begin{array}{c}\text{Hydrogen itching to be pulled out of someplace} \\ \text{+ oxygen attached to hemoglobin}\end{array} \xrightarrow[\text{cytochrome oxidase}]{} \text{liquid water} \quad (\Delta G^{o}_{rxn} < 0)$$

If too much CN^- gets into your system, you will quickly die. In terms of either a reaction coordinate diagram or the terminology we have learned for kinetics, describe the role of cytochrome oxidase and cyanide ion in the reaction above. [Terminologically, liquid water is the *product* of the above reaction, while two hydrogen atoms and an oxygen atom are *reactants* in the above reaction. What are cytochrome oxidase and CN^-?]

E. At right is the reaction coordinate diagram for a system in which an unstable solid reactant can decompose to yield two possible solid products, A and B. (You'll see a lot of diagrams like these if you take organic chemistry!) Suppose that the reactant is bright red, product A is yellow, and product B is colorless.

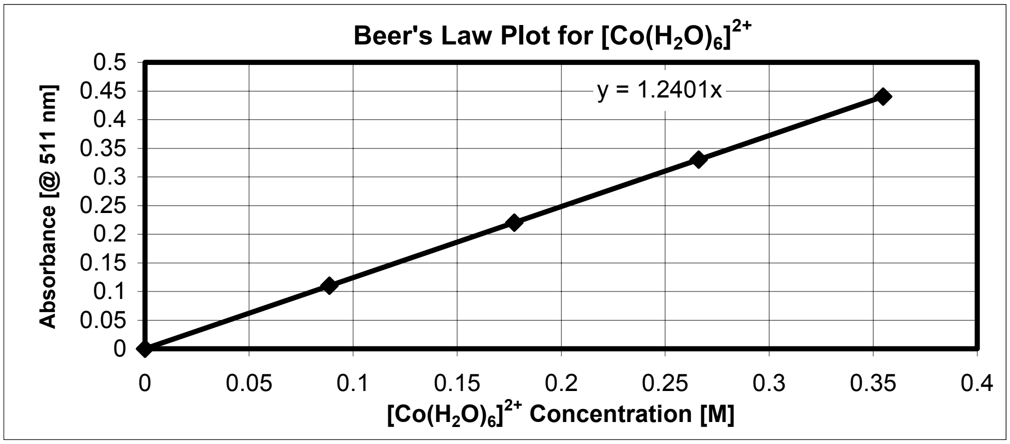


a) If you observe a dry sample of pure reactant over a long period of time, what color changes will you observe, and why?

b) Suppose the reactant and both products are highly soluble in water, but none of them react with water. In fact, in aqueous solution the reaction coordinate diagram looks qualitatively identical to the one above. If you observe an aqueous solution of the reactant over time, what color changes will you observe, and why?

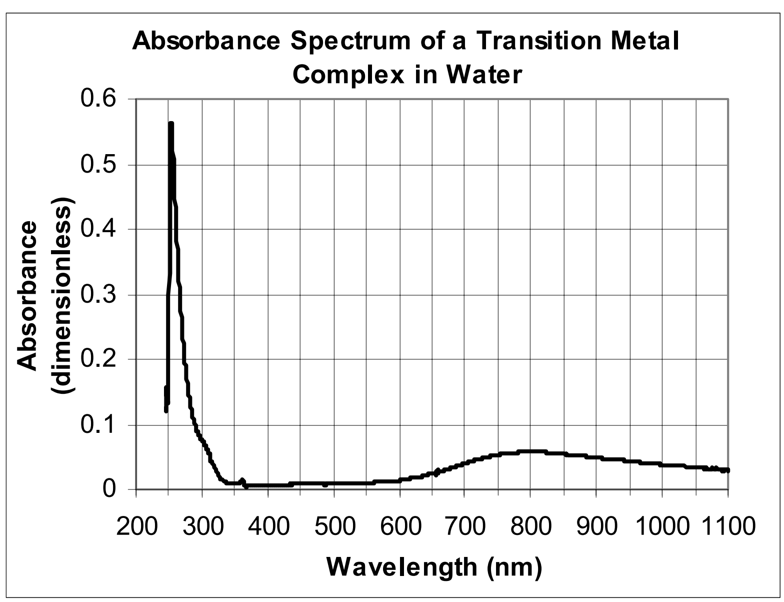
Problem 4: Goodies From Lab

A. Using a rather old, beat-up spectrometer and a 1.00 cm pathlength cuvette, you prepared a Beer's Law plot for a cobalt complex at 511 nm, its wavelength of maximum absorbance. It looked like this:



The spreadsheet you used to prepare the plot above performed a linear regression for you and calculated the optimum slope – but as a scientist, you know better than to trust a spreadsheet with significant figures! When you repeatedly measured the absorbance of your most concentrated standard, the machine spat out 0.44835, 0.45201, 0.44933. You prepared your standards from $Co(H_2O)_6Cl_2$ using the same equipment and techniques we employed in the Ni lab. Considering only ***relevant*** factors, and based on the sig. fig. method of error estimation, how many sig figs should the slope of this plot have, and why? Also, give the units of the slope.

B. Shown at right is the absorption spectrum of a dilute aqueous solution of a copper salt. What color would this solution appear to the human eye, and why? Be quantitative. Be careful!



Remember that you only have to answer the questions on *one* side of this page, it's your choice which one!

C. Megatron and his evil Decepticons (or possibly the boys of NSYNC, we aren't sure) are once again threatening the galaxy with their sinister plots - and this time the locus of their evil intent is focused right here in Minnesota! Using their powers of deception, they have secretly replaced the contents of a set of gas cylinders bound for the Mayo Clinic with gases other than those listed on the labels. They have done so in the knowledge that these cylinders are bound for an operating room in which the Saudi crown prince is undergoing an urgent, but otherwise routine, prostate operation involving anesthesia. With the gas substitutions the Decepticons have made, the crown prince will die in the hands of U.S. doctors, at a time when such an event could push an already unstable world over the edge. Optimus Prime (a.k.a. Paul Letendre) has discovered the evil plot and learned what he can about it, but he is too far from the Mayo Clinic to get there in time to remedy the situation. He calls upon you, his trusted lieutenant, to save the day.

The Mayo Clinic is set up with analytical equipment much like that we used in the mystery gas lab: an infrared spectrometer with a gas cell, a mass spectrometer, and an analytical balance are all readily available, as are vacuum pumps, gas bulbs, and some big balloons. There aren't any manometers around, though. Being a Transformer yourself, you can't taste or smell gases, and you don't have vocal chords. The gases are needed in the operating room immediately, so you can't afford to bring in new cylinders; you will have to very quickly identify gases that can be substituted for use in this critical operation. Most of the questions below have several possible answers, but some answers are better than others.

a) Optimus knows that the cylinder marked "oxygen" actually contains either argon (Ar) or Helium (He). What is the fastest and most reliable way you could determine which of these two it contains?

b) The cylinder marked "neon" actually contains either nitrogen monoxide (NO) gas, which is very unstable and breaks apart into N and O when ionized, or nitrogen (N_2) gas. What's the fastest and most reliable means by which you could discriminate between these two gases using the equipment available?

c) Optimus knows the cylinder marked "chlorine" actually contains a pure polyatomic molecular gas, but nothing more than that. Which one technique (gas density, mass spectrometer, or the IR spectrometer) would be the best tool for getting a good first guess as to what the mystery gas might be, and why?

d) The final cylinder is marked "acetylene," but Optimus believes it contains nitrous oxide (N_2O). It is absolutely critical that this gas actually be nitrous oxide, because the anesthesiologist is going to have to use it as her anesthetic. She has a small sample of pure nitrous oxide in a lecture bottle, but not enough for the surgery. How could you quickly and most reliably verify that the "acetylene" tank actually contains nitrous oxide, given a sample of pure nitrous oxide to compare it against? Explain.