

Analytical Chemistry Cumulative Exam
August 25, 2006

Potentially Useful Data

$$K_{a1}(\text{H}_2\text{CO}_3) = 4.45 \times 10^{-7}$$

$$K_{a2}(\text{H}_2\text{CO}_3) = 4.69 \times 10^{-11}$$

$$K_{sp}(\text{CaCO}_3) = 4.5 \times 10^{-9}$$

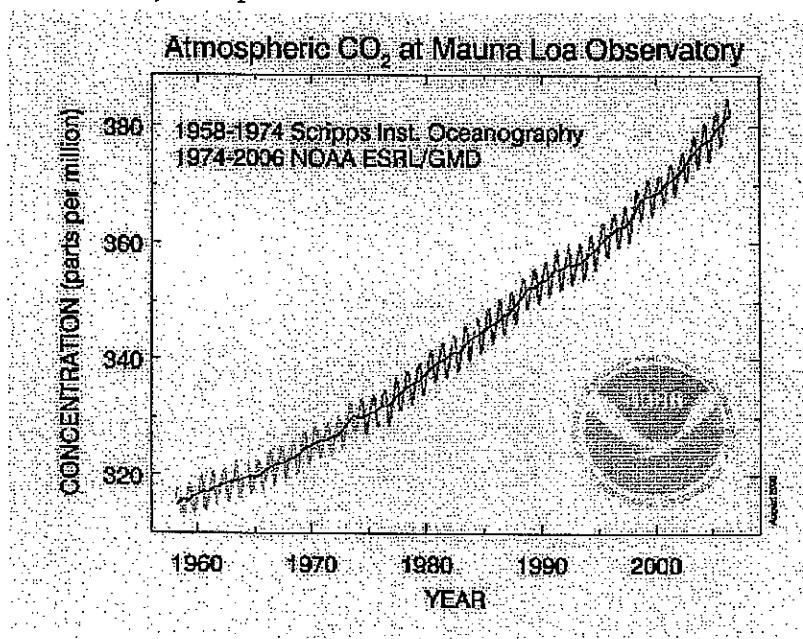
$$R = 8.314 \text{ J/K}\cdot\text{mole}$$

$$\Delta H_f^\circ(\text{CO}_2) = -393.51 \text{ kJ/mole}$$

$$\Delta H_f^\circ(\text{H}_2\text{O}) = -241.82 \text{ kJ/mole}$$

$$\Delta H_f^\circ(\text{C}_2\text{H}_5\text{OH}) = -235.31 \text{ kJ/mole}$$

[20] 1. Atmospheric carbon dioxide measurements have been made non-stop at Mauna Loa, Hawaii, since 1958. From the data in the Figure below (conc. in parts-per-million, i.e. $\mu\text{moles CO}_2/\text{mole air}$), estimate and discuss the requirements for both the accuracy and the precision of the measurement, in order to determine, from the first 10 years of the data record, that the slope of the annual average line is statistically significantly different from zero (in other words, that there is a trend). Be quantitative.



To determine whether or not there is a trend, there are not stringent requirements for accuracy. For example, if you had a systematic error of 50%, but this error was very consistent (e.g. a calculation error), so that your precision is very good, then you can identify that the trend is real. The requirements for precision are tough indeed. Over the first 10 years, CO₂ increased by ~ 7 ppm, or a relative change of $7/320 = \sim 2\%$. The seasonal variability in [CO₂] (from greater uptake in the Northern Hemisphere summer) is ~ 5 ppm. There is considerable information in the seasonal variability, so it would be better to have at least 1% precision. In fact, the precision of

the methods used to collect the data shown is $\sim 0.1/350$, i.e. $\pm 0.03\%$. This is difficult for any measurement!

[25] 2. If you wanted to design and build an instrument for quantitative determination of CO_2 based on the Beer-Lambert Law, what wavelength range would you use?

[5] IR. There is an envelope of bands around 2300cm^{-1} ($4.3\mu\text{m}$).

Describe as specifically as you can the nature of the molecular transitions involved in the measurement.

[5] When CO_2 absorbs at $4.3\mu\text{m}$, vibrational modes are excited. Since there has to be a change in the dipole moment, this has to be either an asymmetric stretch, or a bending mode.

Discuss what design characteristics would promote optimum sensitivity.

[5] Sensitivity is the slope of the cal. curve. For this you need a long path length. However, it is noteworthy that CO_2 is a strong IR absorber and there is a high conc. in the atmosphere, so adequate sensitivity isn't much of a challenge.

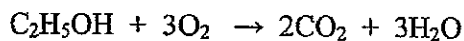
Discuss what design characteristics would promote low limits of detection.

[5] For good limits of detection you want low noise. For this you want a high quality detector and a stable source. Mechanical sources of vibration and noise (e.g. choppers) should be minimized.

Discuss what design characteristics would promote selectivity for CO_2 quantitation.

[5] For good selectivity, you want high resolution spectroscopy, e.g. resolution better than $\sim 1\text{cm}^{-1}$. Use of FTIR can achieve this. For gases like CO_2 , this has been achieved using a filter wheel, with a gas cell window containing CO_2 . This then removes all radiation that CO_2 absorbs, and thus any absorption in this mode is caused by all other potential interferences. Measurement through an open window in the wheel allows measurement of the absorption caused by all gases including CO_2 .

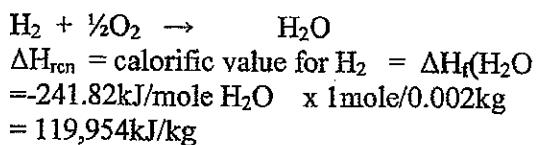
[20] 3. Because atmospheric CO_2 has increased by $\sim 35\%$ from human activities, many people are worried about the environmental impacts, which include a measurable change in pH of the world's oceans. A solution to this problem is to convert to fuels that are "Carbon-neutral", such as $\text{C}_2\text{H}_5\text{OH}$ and H_2 . Calculate the "calorific value" or "heat content" of these two fuels that is available from combustion, in units of kJ/kg.



$$\Delta H_{\text{rcn}} = \text{calorific value} = 3\Delta H_f(\text{H}_2\text{O}) + 2\Delta H_f(\text{CO}_2) - \Delta H_f(\text{C}_2\text{H}_5\text{OH})$$

$$= 1277.17\text{kJ/mole C}_2\text{H}_5\text{OH}$$

$$\times 1\text{mole}/0.04602\text{kg} = 27,752\text{kJ/kg}$$



[20] 4. Imagine you allow a beaker of absolutely pure water to equilibrate with the atmosphere (See Figure above for p_{CO_2}). Which indicator (in principle) from the table shown below would you best use to detect when it was fully equilibrated with CO_2 ? $\text{H}_{\text{CO}_2} = [\text{dissolved CO}_2]/(p_{\text{CO}_2} \text{ in atm}) = 0.034 \text{ M/atm}$. Discuss why in practice this experiment might be difficult.

Common pH indicators		
Common name	pK_a	Indicator range
Methyl yellow	3.3	2.9-4.0
Methyl orange	4.2	3.1-4.4
Methyl red	5.0	4.2-6.2
Chlorophenol red	6.0	4.8-6.4
Bromothymol blue	7.1	6.0-7.6
Cresol purple	8.3	7.4-9.0
Phenolphthalein	9.7	8.0-9.8
Thymolphthalein	9.9	9.3-10.5

$$\begin{aligned}
 [\text{CO}_2]_{\text{aq}} &= [\text{H}_2\text{CO}_3]_{\text{aq}} = P_{\text{CO}_2} \cdot \text{H}_{\text{CO}_2} = 380 \times 10^{-6} \text{ atm} \times 0.034 \text{ M/atm} \\
 &= 1.29 \times 10^{-5} \text{ M H}_2\text{CO}_3 \\
 \text{H}_2\text{CO}_3 + \text{H}_2\text{O} &\leftrightarrow \text{H}^+ + \text{HCO}_3^-
 \end{aligned}$$

To a first approximation, ignoring the 2nd acid dissociation constant,

$$\begin{aligned}
 4.45 \times 10^{-7} &= [\text{H}^+]^2 / 1.29 \times 10^{-5} \\
 [\text{H}^+] &= 2.39 \times 10^{-6} \text{ M} \\
 \text{pH} &= 5.6
 \end{aligned}$$

I would choose chlorophenol red, although I will accept methyl red.

This might be difficult because the concentration of H_2CO_3 at equilibrium will be very low. So, you would need to use a very low concentration of indicator, otherwise the acid will be consumed in reaction with the indicator.

- [15] 5. About 30% of all the CO_2 emitted through fossil fuel combustion has ended up in the oceans, where some of it is "sequestered" as calcite, i.e. $\text{CaCO}_3(\text{s})$ (e.g. "coral"). The average concentration of Ca^{2+} in the oceans is .0105M. Calculate the concentration of CO_3^{2-} in ocean water, assuming it is in equilibrium with calcite.

$$K_{\text{sp}}(\text{CaCO}_3) = 4.5 \times 10^{-9} = [\text{Ca}^{2+}][\text{CO}_3^{2-}]$$

Since $[\text{Ca}^{2+}] = 0.0105\text{M}$, then $[\text{CO}_3^{2-}] = 4.3 \times 10^{-7}\text{M}$

No Biochemistry Crib available

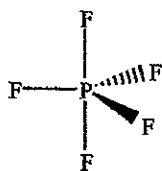
8-26-06

Written by Dr. Hrycyna

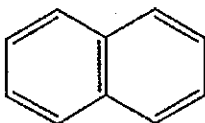
Inorganic Cumulative Exam

August 26, 2006

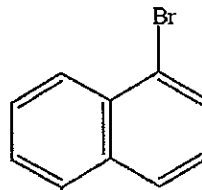
1. (25 pt) Identify point symmetry group for each of the following molecules/ions. Use the diagram on p.3 if necessary.



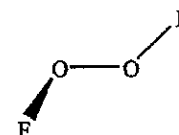
(a, 3pt)
D_{3h}



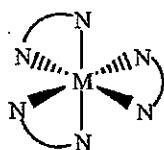
(b, 3pt)
D_{2h}



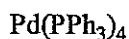
(c, 3pt)
C_{2h}



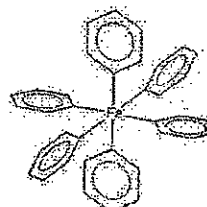
(d, 3pt)
C₂



(e, 3pt)
D_{3h}



(f, 5pt)
T_d



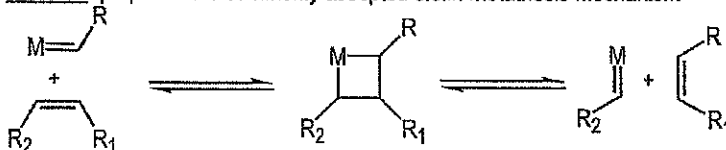
(g, 5pt)
T_d

Note: Pd(PPh₃)₄ is tetrahedral because Pd⁰ is d¹⁰

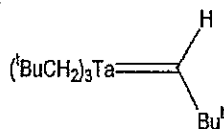
2. (24 pt) Name three 2005 Nobel Laureates (last name only, 2 pt each), and describe the Nobel winning contribution of each laureate using reaction equations/catalytic schemes/structures or whatever deemed necessary (6 pt for each).

2005 Nobel prize was awarded "for the development of the metathesis method in organic synthesis" see link below for more details http://nobelprize.org/nobel_prizes/chemistry/laureates/2005/index.html

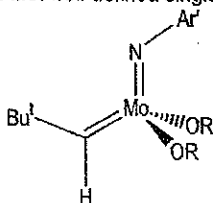
Chauvin: proposed the commonly accepted olefin metathesis mechanism



Schrock: synthesis of the first metal-alkylidene (Schrock carbene); Schrock type carbenes are the initiators in the Chauvin mechanism; Developed the first well-defined single site homogeneous catalyst for olefin metathesis (Mo).

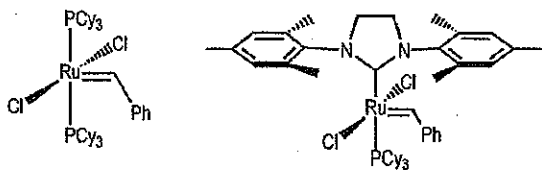


Schrock carbene



Schrock's catalyst
(other variations w/ Mo and W also possible)

Grubbs: developed the Ru-based catalysts that are functional groups tolerant, which renders olefin metathesis one of the most practiced reactions by inorganic, organic, materials and medicinal chemists.



Two of commonly used Grubbs' catalysts

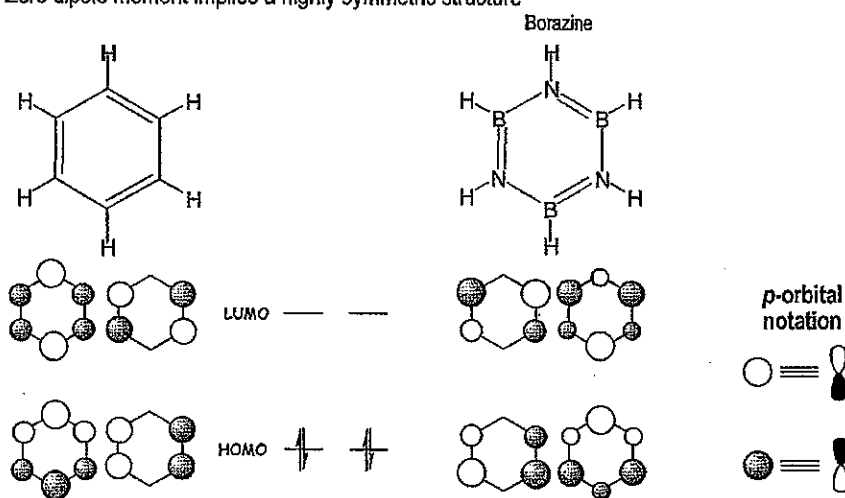
All three Nobel lectures can be found in Y. Chauvin, *Angew. Chem. Int. Ed.*, 2006, 45, 3740; R. R. Schrock, *ibid*, 2006, 45, 3748; R. H. Grubbs, *ibid*, 2006, 45, 3760.

3. (20 pt)

Borazine has an empirical formula of BNH_2 , a formula weight of 80.50, and a dipole moment of zero. Please (i) derive its molecular formula (5pt); (ii) sketch its structure (5pt); (iii) draw both the HOMO and LUMO and rationalize your drawing (10 pt).

$\text{FW}(\text{BNH}_2) = 26.83 \Rightarrow$ Molecular formula: $(\text{BNH}_2)_3$ or $\text{B}_3\text{N}_3\text{H}_6$.

Zero dipole moment implies a highly symmetric structure



Borazine is very similar to benzene in structure and hence the frontier orbitals of borazine can be derived from those of benzene (on the left; you get full credit for drawing benzene MOs correctly): nitrogen (contributing 5 valence electrons, and hence the donor) dominant in HOMO; boron (contributing three valence electrons, and the acceptor) dominant in LUMO.

4. (12 pt)

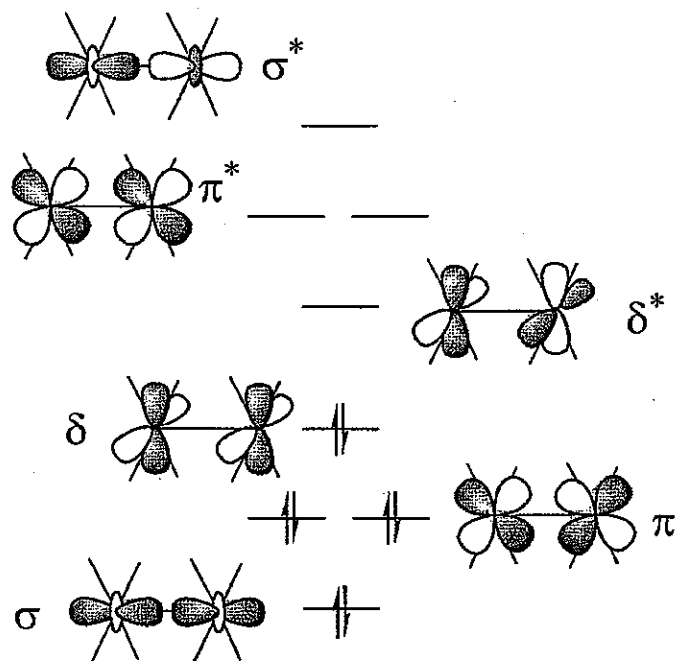
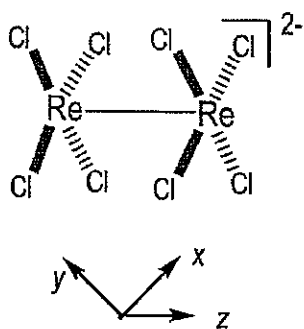
Oxyanions vanadate (VO_4^{3-}), chromate (CrO_4^{2-}) and permanganate (MnO_4^-) are colorless, yellow and dark purple, respectively. Please explain the color variation.

All three are tetrahedral and formally d^0 complexes, so the ligand field effect is not contributing. However, the gradual increase in oxidation state (V^{5+} , Cr^{6+} and Mn^{7+}) reduces the energy levels of empty d -orbitals and bring them closer to those of oxide lone pairs. The closeness in energy results in (i) lower energy LMCT band and (ii) better orbital overlap and thus intense absorptions.

5. (19 pt)

The recognition of the quadruple bond in octachlorodirhenate ($[\text{Re}_2\text{Cl}_8]^{2-}$) is a milestone in modern inorganic chemistry. Please (i) sketch $[\text{Re}_2\text{Cl}_8]^{2-}$ (6pt); (ii) draw a simple MO diagram that explains the quadruple bond (9 pt); (iii) name the Purdue faculty member (W. R. Robinson) who was a coauthor of the *Science* publication reporting the initial finding (4 pt).

(i) & (ii)



(ii) Continued: with the coordinates as shown, each Re^{3+} center (hence d^4) utilize dsp^2 (s, p_x, p_y and $d_{x^2-y^2}$) hybrid to form Re-Cl bonds; This leaves d_{zz} , $d_{xz,yz}$, and d_{xy} for Re-Re bonding, and the bonding and antibonding combinations are shown on right. Eight d electrons from two Re^{3+} centers fill four bonding orbitals.

Bonus Questions (10 pts)

These questions are based on recent Inorganic Seminars exclusively; Random guesses will be penalized with point deduction.

- B1. (2pt) Professor Kanatzidis presented a seminar in April 2006 on materials for
a) Photovoltaics b) Molecular Electronics c) Fuel cells
d) Catalytic Converters e) Thermoelectrics
- B2. (2pt) Professor Switzer also visited in April 2006, and mentioned RABITS during his talk. "RABITS" acronym stands for
a) tissue engineering test conducted on jack rabbits
b) biaxially textured copper substrate prepared by repeated rolling
c) random accessible binary image troughs
- B3. (3pt) Professor Bergman gave an ACS/Inorg/Org joint seminar in April 2006. Which transition metal center played the key role in the C-H activation chemistry described in his introduction?
a) Fe b) Ru c) Ir d) Re e) Rh
- B4. (3pt) Bergman's talk was focused on
a) Catalytic chemistry within a molecular cage
b) Catalytic chemistry of σ -bond metathesis
c) Catalytic aryl amination
d) Ta catalyzed olefination

No Organic Crib available

8-26-06

Written by Dr. Thompson

No Physical Crib available

8-26-06

Written by Dr. Szleifer
