Chemistry 2000 Fall 2017 Final Examination

Time: 3 hours

Total marks: 105

Aids permitted: calculator (wireless communication capabilities OFF), molecular model kit.

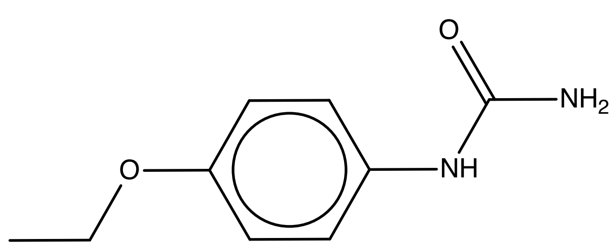
Significant figures: I will specifically ask when I want you to track your significant figures. Otherwise, just give me a sensible number of digits in your answer given the precision of the data.

All answers are to be written in the exam booklets provided. Answers need not appear in the exam booklet in the order asked, but all answers need to be **clearly labeled** with the section and question number.

1 A mixed bag of questions

Value of this section: 45 marks

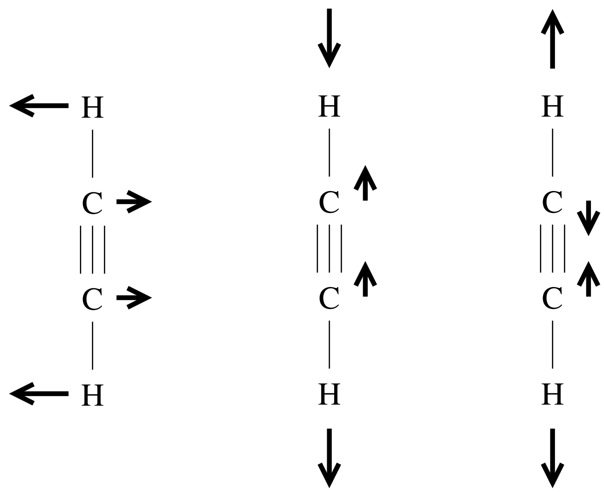
1. MO theory and the band theory of solids use different language to describe similar concepts. Give the term used in band theory that corresponds to each of the following terms from MO theory: [2 marks]
   (a) molecular orbital
   (b) HOMO
2. Explain, with the help of a diagram, what a p-type semiconductor is. [5 marks]
3. Dulcin is an artificial sweetener invented in the 19th century that went out of use in the mid-20th century due to suspected carcinogenicity and to toxicity when taken in large quantities. The structure of dulcin is the following:



   Redraw the molecule in your exam booklet, and identify all the functional groups in this molecule. [4 marks]

4. Explain why a carboxylic acid is a much stronger acid than an alcohol. One or two Lewis diagrams might be useful for answering this question. [5 marks]

5. Three of the normal modes of ethyne are illustrated below:



(a) (b) (c)

Which of these modes are IR active? [3 marks]

6. Develop the π MO diagram of CO_2. Determine the carbon-oxygen π bond order. [10 marks]

7. Nickel-hydrogen batteries have been used extensively in satellites, including for example the Hubble space telescope. The cathode and anode half-reactions, respectively, are the following:

$$\mathrm{NiO(OH)_{(s)} + H_2O_{(l)} + e^- \rightarrow Ni(OH)_{2(s)} + OH^-_{(aq)}} \qquad E^\circ = 0.49\,\mathrm{V}$$
$$\mathrm{H_{2(g)} + 2OH^-_{(aq)} \rightarrow 2H_2O_{(l)} + 2e^-} \qquad E^\circ = 0.828\,31\,\mathrm{V}$$

Note that the half-cell potentials given above are for the half-reactions **as written**, with half-cell potentials given at 25 °C.

Nickel-hydrogen batteries are built inside a high-pressure containment vessel and operate at very high hydrogen pressures.

(a) A nickel-hydrogen cell operates at a pressure of 80 bar of hydrogen. Calculate the emf of the cell at 25 °C. [5 marks]

(b) As the cell operates, hydrogen is consumed so the hydrogen pressure decreases. What effect does this have on the emf? [1 mark]

8. Calculate the pH of a 1.43×10^{-3} mol/L solution of trimethylamine [$(CH_3)_3N$] at 25 °C. The pK_b of trimethylamine at this temperature is 4.19. [10 marks]

2 Questions on formic acid

Value of this section: 14 marks

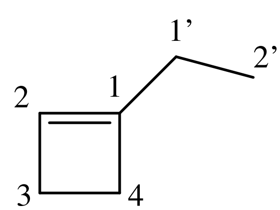
Formic acid is the simplest possible carboxylic acid, with the chemical formula HCOOH.

1. Draw a complete Lewis diagram of formic acid. [2 marks]
2. The pK_a of formic acid is 3.75. Sketch the distribution curves of the acid and its conjugate base. [4 marks]
3. Using your distribution curves, explain why a very dilute solution of formic acid (for example, one with a concentration of formic acid of 10^{-6} mol/L or less) would behave like a strong acid, i.e. essentially all of the acid would be dissociated. [2 marks]
4. Formic acid melts at 8.3 °C with an enthalpy of fusion of 12.68 kJ mol^{-1}. Use an argument based on entropy to show that solid formic acid will melt in a room at 20.0 °C. [6 marks]

3 Questions on 1-ethylcyclobutene

Value of this section: 15 marks

All of the questions below refer to 1-ethylcyclobutene:



The numbers indicate how the carbon atoms are numbered in this compound according to the IUPAC convention. You will be able to use these numbers to identify particular carbon atoms in your answers below.

1. Give the molecular formula of this compound. [1 mark]
2. Draw one structural isomer of 1-ethylcyclobutene. [1 mark]
3. Give the hybridization of each carbon atom in 1-ethylcyclobutene. [3 marks]
4. Predict the product when 1-ethylcyclobutene reacts with HCl. For full credit, you must show the details of the reaction, and correctly carry out the electron pushing. [8 marks]

5. Does your product have stereoisomers (geometrical isomers or enantiomers)? If so, what kind of isomers does it have? If not, explain why not (briefly). [2 marks]

4 NO: Marc's (current) favorite small molecule

Value of this section: 31 marks

In my research, I am interested in a bacterial enzyme that catalyzes (speeds up) the redox reaction of nitric oxide (NO) with molecular oxygen to make the nitrate ion (NO_3^-). In the cell, all of these components are in aqueous solution.

1. The inside of a bacterial cell is nearly neutral (pH $\sim$ 7.5). Balance the reaction as it occurs inside a cell. States of matter must be clearly indicated. [6 marks]

2. The equilibrium constant for dissolving NO in water, i.e. for

$$NO_{(g)} \rightleftharpoons NO_{(aq)},$$

   is 0.00192 at 25 °C.[1] What is the standard free energy of formation of aqueous NO? Carry out this calculation to the correct number of significant figures. [6 marks]

3. Assume that the concentrations in a bacterial cell at 25 °C are as follows: [NO] = $50\,\mu\text{mol}\,\text{L}^{-1}$, [$O_2$] = $16\,\mu\text{mol}\,\text{L}^{-1}$, [$NO_3^-$] = $5\,\text{mmol}\,\text{L}^{-1}$, and pH = 7.5. These are concentrations that a cell might encounter in the lower gastrointestinal tract. (The temperature is, of course, too low, but we will leave this factor aside in this problem.) For the sake of argument, suppose that the activity of water inside the cell is the same as the activity of pure water. Is the reaction of NO with oxygen you balanced in question 1 thermodynamically allowed under these conditions? [6 marks]

4. (a) Develop the molecular-orbital diagram for NO. Predict the bond order from the MO diagram. [10 marks]

   (b) NO is a radical. In what orbital is the unpaired electron located? Does this tell us anything about which end of the molecule is likely to be more reactive? Explain briefly. [3 marks]

Merry Christmas!

[1] Calculated from the Henry's law data in Shaw and Vosper, *J. Chem. Soc., Faraday Trans. 1*, **73**, 1239 (1977).

Data

Constants and conversion factors

$0\,\mathrm{K} = -273.15\,^\circ\mathrm{C}$
$F = 96\,485.3329\,\mathrm{C\,mol^{-1}}$
$R = 8.314\,460\,\mathrm{J\,K^{-1}mol^{-1}}$
$K_w = 1.01 \times 10^{-14}$ at $25\,^\circ\mathrm{C}$

Orbital energies

Atom	Orbital	ϵ/Ry
N	2s	−1.88
	2p	−0.95
O	2s	−2.38
	2p	−1.17

Standard thermodynamic data

Species	$\frac{\Delta_f G^\circ}{\mathrm{kJ\,mol^{-1}}}$
$H_2O_{(l)}$	−237.192
$NO_{(g)}$	86.60
$NO^-_{3(aq)}$	−111.4
$O_{2(aq)}$	16.35
$OH^-_{(aq)}$	−157.220

Formulas

$$\Delta S = \frac{q_{\mathrm{rev}}}{T}$$

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta_r G_m = \Delta_r G_m^\circ + RT \ln Q$$

$$\Delta_r G_m^\circ = -RT \ln K$$

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta_r H_m^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\mathrm{pH} = -\log_{10} a_{\mathrm{H^+}}$$

$$\mathrm{p}K_a = -\log_{10} K_a$$

$$\mathrm{p}K_b = -\log_{10} K_b$$

$$K_w = K_a K_b$$

$$\Delta_r G = -\nu_e F E$$

$$E = E_0 - \frac{RT}{\nu_e F} \ln Q$$

Activities

State	**Activity (a)**
Solid	1
Pure liquid	1
Ideal solvent	X
Ideal solute	c/c°
Ideal gas	p/p°

Quadratic equation: For the equation $ax^2 + bx + c = 0$,

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}.$$

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H 1.01																	2 He 4.00
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.41	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57 La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.21	76 Os 190.2	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg							

58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm	62 Sm 150.36	63 Eu 151.97	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr