Chemistry 2000 Fall 2013 Final Examination

NAME: ________________________________ Student number: ______________

Time: 3 hours

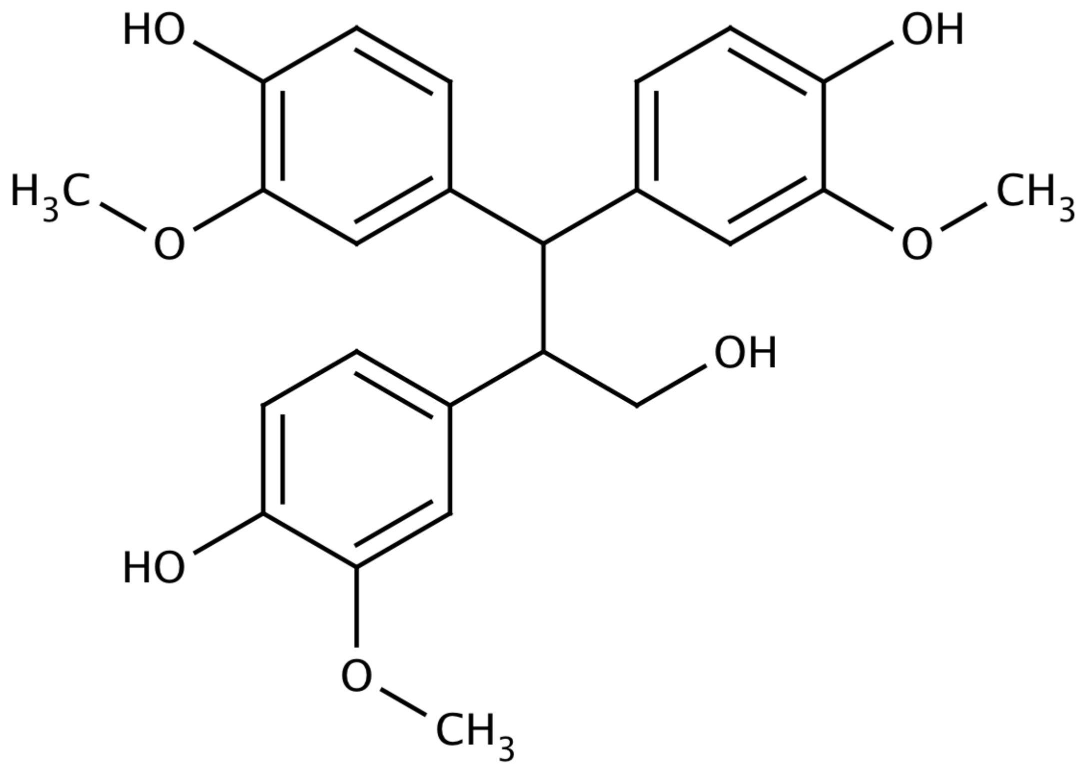
Aids permitted: calculator, molecular model kit

Overflow space: There is overflow space at the bottom of page 13, as well as on the reverse of that page. If you do need extra space for a question, make sure to give me a clear indication of where I can find the rest of your answer, and label any answers continued in the overflow space with the question number.

Question	Mark
1	/8
2	/4
3	/2
4	/3
5	/13
6	/10
7	/13
8	/13
9	/21
10	/18
Total:	/105

NAME:______________________________________

/8 1. The following compound, which has been dubbed "Quebecol" by its discovers at the University of Rhode Island, has recently been isolated from maple syrup. (I am not making this up.[1])



(a) Circle each functional group and name it. There are pieces of this molecule that are identical copies of each other. You need only label the functional groups in one of these copies. /3

(b) Identify (on the drawing) an sp^3 carbon. /1

(c) Identify (on the drawing) an sp^2 carbon. /1

(d) How many chiral centres does this molecule have? Identify any chiral centres you find on the drawing.

Number of chiral centres:_____ /2

(e) Is this molecule an acid, a base, or neither? If it's an acid or a base, point out (on the drawing) what part of the molecule is acidic or basic. Again, if the acidic or basic part is in a repeated piece of the molecule, you need only do this once. Note that only sites that are expected to have significant acidity or basicity (i.e. a stronger acid or base than water) are of interest. /1

[1] L. Li and N. P. Seeram, *J. Funct. Foods* **3**, 125–128, (2011).

NAME:____________________________________

/4 2. Thermodynamic tables contain absolute entropies. What is the reference point with respect to which absolute entropies are defined? On what law of thermodynamics is the existence of this reference point based? Explain briefly.

/2 3. Suppose that you wanted to make an n-type extrinsic semi-conductor using silicon as the host material. What dopant could you use? Explain your choice briefly.

/3 4. Calculate the average kinetic energy of the molecules in the air at 15 °C.

NAME:____

/13 5. Aldehydes can be made from alcohols by chemical oxidation. For example, ethanal, CH_3CHO, can be made by oxidizing ethanol, CH_3CH_2OH.

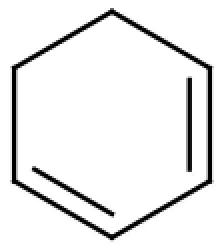
(a) Determine the oxidation numbers of the carbon atoms in the two compounds. Use these oxidation numbers to confirm that the conversion of ethanol to ethanal is an oxidation process. /7

(b) The oxidation of ethanol can be carried out by the dichromate ion ($Cr_2O_7^{2-}$) in acidic solution. In addition to ethanal, chromium(III) ions are formed. Balance the reaction. /6

NAME:____________________________________

/10

6. Predict the product of the reaction of 1,3-cyclohexadiene, pictured below, with one equivalent of HCl (i.e. enough to react with only one of the two double bonds). Show a complete mechanism using the curved arrow formalism.



NAME:____

/13 7. Answer the following questions using molecular orbital theory. Answers using other theoretical frameworks will receive no credit. Full explanations (typically including an MO diagram) are required for full credit.

(a) Why is there no such thing as He_2? /5

(b) What is the bond order in N_2? /8

NAME:_______________________________________

/13 8. The cyclopentadienyl anion, $C_5H_5^-$, abbreviated Cp^-, is a good nucleophile.

(a) Draw a Lewis diagram of Cp^-. If Cp^- has resonance structures, draw at least one resonance structure. Count the number of π electrons in this species. /6

Number of π electrons: _____

(b) Sketch the π MO diagram of this anion, and populate it with the appropriate number of electrons. /4

(c) The frontier orbitals (HOMO and LUMO) in Cp^- are π MOs. Which of these orbital pairs (HOMO or LUMO) is relevant to the nucleophilic property of Cp^-? Point out this orbital pair on your MO diagram and explain why this orbital is related to the nucleophilic property. /3

NAME:____

/21 9. The pK_a of pyruvic acid, $CH_3COCOOH$, is 2.50 at 25 °C.

(a) Draw a complete Lewis diagram of pyruvic acid. /2

(b) Many physiological processes (which occur near pH 7) produce the conjugate base of pyruvic acid, pyruvate. Why is pyruvate produced rather than pyruvic acid? /2

(c) Calculate the pH of a $0.034\,\mathrm{mol\,L^{-1}}$ solution of pyruvic acid at 25 °C. /13

NAME:____

(d) Calculate the standard free energy of formation of pyruvic acid. /4

NAME:______________________________________

/18 10. (a) Calculate the vapor pressure of mercury at $25\,^\circ\mathrm{C}$. /9

NAME:____

(b) The triple point of mercury is at $T = 234.316\,\text{K}$ and $p = 1.65 \times 10^{-9}\,\text{bar}$. The normal freezing point is $234.321\,\text{K}$, and the normal boiling point is at $629.8\,\text{K}$.

Sketch the phase diagram of mercury. Your phase diagram need not be drawn to scale, but it should maintain the correct order among the various temperatures and pressures. Label the special points of the phase diagram given above as well as the point representing the vapor pressure at $25\,^\circ\text{C}$ calculated in part a. /6

(c) Does the freezing point of mercury increase or decrease with increased pressure? Briefly explain your reasoning. /3

Have a great Christmas holiday!

NAME:________________________________

Constants and conversion factors

Atomic mass unit (u)	$1.6605 \times 10^{-27}\,\mathrm{kg}$	$0\,\mathrm{K} = -273.15\,°\mathrm{C}$
Avogadro's number (N_A)	$6.0221 \times 10^{23}\,\mathrm{mol^{-1}}$	$1\,\mathrm{bar} = 100\,\mathrm{kPa}$
Boltzmann's constant (k_B)	$1.3806 \times 10^{-23}\,\mathrm{J\,K^{-1}}$	$1\,\mathrm{atm} = 1.013\,25\,\mathrm{bar}$
Faraday's constant (F)	$96\,485\,\mathrm{C\,mol^{-1}}$	
Ideal gas constant (R)	$8.3145\,\mathrm{J\,K^{-1}mol^{-1}}$	

Standard thermodynamic data

Species	$\frac{\Delta_f G^\circ}{\mathrm{kJ\,mol^{-1}}}$
$CH_3COCOO^-_{(aq)}$ (pyruvate)	−474.22
$Hg_{(g)}$	31.84

At 25 °C, $K_w = 10^{-14}$.

Electronegativities

Element	χ
H	2.1
C	2.5
O	3.5

Formulas

$$pV = nRT \qquad \left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

$$\overline{K} = \tfrac{1}{2}m\overline{v^2} = \tfrac{3}{2}k_B T \qquad \overline{K}_m = \tfrac{3}{2}RT \qquad v_{\mathrm{rms}} = \sqrt{\overline{v^2}} = \sqrt{\frac{3RT}{M}}$$

$$S = k_B \ln \Omega \qquad \Delta S = \frac{q_{\mathrm{rev}}}{T}$$

$$\Delta G = \Delta H - T\Delta S \qquad \Delta_r G_m = \Delta_r G_m^\circ + RT\ln Q \qquad \Delta_r G_m^\circ = -RT\ln K$$

$$\Delta_r G = -\nu_e F E \qquad E = E^\circ - \frac{RT}{\nu_e F}\ln Q$$

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

$$X = \frac{n}{\sum n} \qquad p_A = X_A p_A^\bullet \qquad [\mathrm{A}] = k_H p_A$$

$$\mathrm{pH} = -\log_{10}(a_{\mathrm{H^+}}) \qquad pK_{\{a,b\}} = -\log_{10} K_{\{a,b\}} \qquad K_w = K_a K_b$$

Quadratic equation: $x = \dfrac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

NAME:____

Activities

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

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