Chemistry 2720 Fall 2001 Final Examination

Write all your answers in the booklets provided. Read the instructions carefully. In some sections, you have some choice. DO NOT answer more than the required number of questions in these sections. Extra answers WILL NOT be marked.

Formulas and data are given at the end of this paper.

Aids allowed: calculator. Periodic tables and other printed aids are strictly forbidden.

Pages: 6. Time: 3 h.

1 Answer all questions in this section.

Value of this section: 69

1. Calculate the ionization energy of a Be^{3+} ion. [2 marks]

2. Show the orbital occupancy (using an orbital box diagram) in the ground state of an iridium atom. [5 marks]

3. In an ordinary incandescent light bulb, approximately 35% of the energy used is converted to photons. The rest is lost in the form of heat.

   (a) Assuming that the average photon has a wavelength of 580 nm (about the middle of the optical range), roughly how many photons are produced per hour by a 100 W light bulb? Express your answer in moles. [6 marks]

   (b) Suppose that the heat from a light bulb were captured in 1 kg of water initially at 20°C. How long would it take for the water to come to a boil? The specific heat capacity of water is $4.184\,\mathrm{J\,K^{-1}g^{-1}}$. [5 marks]

4. The entropy of vaporization of most substances at their boiling point is usually between 85 and $95\,\mathrm{J\,K^{-1}mol^{-1}}$. This observation is known as Trouton's rule. There are exceptions to Trouton's rule. Water for instance has a very high entropy of vaporization at its boiling point: $108.951\,\mathrm{J\,K^{-1}mol^{-1}}$. Why? [4 marks]

5. Explain, using a fundamental quantum mechanical principle, why the regular orbits which are central to the Bohr theory of the atom are impossible. [4 marks]

6. CODATA, the Committee on Data for Science and Technology, produces a table which gives generally accepted values of thermodynamic properties for a broad range of substances. Their table is a little different from the one in most textbooks. Here is an excerpt from that table, with notations adjusted to match the ones used in this course:

Substance	State	$\Delta\bar{H}_f^\circ$ (298.15 K) kJ/mol	$\bar{S}^\circ$ (298.15 K)[1] $\mathrm{J\,K^{-1}mol^{-1}}$	$\bar{H}^\circ(298.15\,\mathrm{K}) - \bar{H}^\circ(0\,\mathrm{K})$ kJ/mol
Al	s	0	28.30	4.540
Al^{3+}	aq	−538.4	−325	
H^+	aq	0	0	
H_2	g	0	130.680	8.468

(a) Calculate the standard free energy of formation of $Al^{3+}_{(aq)}$. [6 marks]

(b) To which thermodynamic property of a substance is the last column of the table related? Give the precise mathematical relationship. [4 marks]

7. A common dry cell ("battery"), also known as a Leclanché cell, has the following overall reaction:

$$\mathrm{Zn_{(s)} + 2NH^+_{4(aq)} + 2MnO_{2(s)} \rightarrow Zn^{2+}_{(aq)} + 2NH_{3(aq)} + H_2O_{(l)} + Mn_2O_{3(s)}}.$$

Suppose that a dry cell operating at 25°C starts off with the following concentrations: $[\mathrm{NH_4^+}] = 1.5\,\mathrm{mol/L}$, $[\mathrm{Zn^{2+}}] = 0.03\,\mathrm{mol/L}$ and $[\mathrm{NH_{3(aq)}}] = 0.12\,\mathrm{mol/L}$. The solid reactants zinc and manganese (IV) oxide are present in excess. The water exists in a concentrated paste rather than as a free solution (hence the name "dry cell"). For the sake of argument, assume that $a_{\mathrm{H_2O}}$ is constant and has the value 0.5. Calculate the maximum work which can be performed by this cell per mole of zinc consumed

(a) initially, and [5 marks]

(b) when half the ammonium ion available has reacted. [5 marks]

8. (a) Derive an equation for the *frequencies* of photons involved in the rotational absorption spectroscopy of a linear molecule. [4 marks]

(b) Metal fluorides are generally fairly easy to make due to the very high electronegativity of fluorine. However, gold (I) fluoride has only been made very recently by a group at the University of British Columbia.[2] They were able to make $^{197}\mathrm{Au}^{19}\mathrm{F}$ in the gas phase and to study its rotational spectrum by microwave spectroscopy. The spacing between the rotational lines is 15 849.667 MHz. The masses of ^{19}F and of ^{197}Au are, respectively, 18.998 403 20 and 196.966 552 amu. Calculate the bond length in AuF. [9 marks]

[1] Defining absolute entropies for solvated ions poses practical problems which are resolved by presenting values relative to the aqueous hydrogen ion.

[2] C.J. Evans and M.C.L. Gerry, J. Am. Chem. Soc. **122**, 1560 (2000).

9. The carbon-atom ring in benzene is a regular hexagon of side 0.139 nm. Assuming that the π electrons of benzene exist in orbitals which follow this hexagonal ring and that there is no potential energy (not a particularly good assumption), develop an equation for the orbital energies. There are six π electrons in benzene. What is the wavelength of the lowest-energy electronic transition according to this model, i.e. the wavelength associated with moving a single electron from the highest occupied molecular orbital to the lowest unoccupied orbital? [10 marks]

2 Answer exactly *two* questions from this section.

Do not answer more than the required number of questions in this section. Extra answers will not be marked.

Value of this section: 12 marks

1. The acid dissociation constant of phosphoric acid is 7.5×10^{-3} at 25°C. What is the standard free energy of formation of the aqueous H_3PO_4 molecule? [6 marks]

2. We established in class that He_2 is not expected to be a stable molecule based on a simple MO argument, a result which agrees with what we were all taught in high school about the chemistry of helium. Using a similar argument, determine whether or not the molecular ion He_2^+ should be stable. If it is stable, compute the bond order. Otherwise, discuss briefly whether your conclusion would extend to the other noble gases. [6 marks]

3. Draw (roughly) a simple square lattice in two dimensions. Add to your drawing an example of each of the following Miller-indexed planes: (10), (11) and (31). [6 marks]

3 Answer *one* question from this section.

Do not answer more than the required number of questions in this section. Extra answers will not be marked.

Value of this section: 20 marks

1. Carbonated drinks are made by forcing carbon dioxide into an aqueous solution under high pressure. Typical soft drinks are made at 4°C under a pressure of 120 kPa of carbon dioxide. Once the carbon dioxide is dissolved in the aqueous solution, it reacts with water to form carbonic acid. Carbonic acid has a relatively small pK_a, so it dissociates partly into a solvated proton and a hydrogen carbonate anion. Assuming there are no other acids present,[3] calculate the pH of the solution formed under the conditions given above. Clearly state any assumptions made in your calculations. [20 marks]

2. The distances between crystallographic planes in any cubic crystal can be calculated from the equation
$$d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}}.$$
However, the X-ray diffraction patterns of simple, face-centered and body-centered cubic crystals look quite different due to interference between the reflections from atoms in different lattice positions. In the simple cubic lattice, all possible reflections are observed. In the face-centered cubic (fcc) lattice, the only reflections seen are those for which all the Miller indices are either even or odd numbers. For instance, the pattern of an fcc crystal would have (111) (all odd) and (200) (all even) reflections, but no (100) reflection. In the body-centered cubic (bcc) lattice, reflections for which $h+k+l$ is an odd number are not observed. Thus, there is no (111) reflection from a bcc crystal because $1+1+1=3$.

   Almost all metals either crystallize in a hexagonal or a cubic structure. Among the cubic structures, the fcc and bcc lattices are most commonly observed. The simple cubic structure is rare, but not unknown. The diffraction pattern of a nickel single crystal was obtained using X rays of wavelength 1.785 Å. The following reflections were observed:
$$26.0, 30.4, 45.8, 57.1 \text{ and } 61.3^\circ.$$
   Analysis of these data has already eliminated the possibility that the structure is hexagonal. Determine the structure and lattice constant. [20 marks]

[3] Many soft drinks are further acidified with phosphoric or citric acid.

Formulas and data

$c = 2.99792458 \times 10^8\,\mathrm{m/s}$

$h = 6.6260688 \times 10^{-34}\,\mathrm{J/Hz}$

$\hbar = \dfrac{h}{2\pi} = 1.05457160 \times 10^{-34}\,\mathrm{J\,s}$

$m_e = 9.1093819 \times 10^{-31}\,\mathrm{kg}$

$N_A = 6.0221420 \times 10^{23}\,\mathrm{mol^{-1}}$

$R = 8.314472\,\mathrm{J\,K^{-1}mol^{-1}}$

$R_H = 2.17987190 \times 10^{-18}\,\mathrm{J}$

$P^\circ = 1\,\mathrm{bar} = 100\,\mathrm{kPa}$

$c^\circ = 1\,\mathrm{mol/L}$

1 W = 1 J/s

$1\,\mathrm{amu} = 1.66053873 \times 10^{-27}\,\mathrm{kg}$

To convert degrees Celsius to Kelvin, add 273.15.

$C_P = \left.\dfrac{\partial H}{\partial T}\right|_P$

$G = H - TS$

$\Delta\bar{G} = \Delta\bar{G}^\circ + RT\ln Q$

$\ln\left(\dfrac{K_1}{K_2}\right) = \dfrac{\Delta\bar{H}^\circ}{R}\left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right)$

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

$2d\sin\theta = n\lambda$

$p = mv$

$p = h/\lambda$

$E = h\nu$

$c = \lambda\nu$

$K = \frac{1}{2}mv^2$

$\Delta x\Delta p > \frac{1}{2}\hbar$

For hydrogenic atoms, $E_n = -Z^2R_H/n^2$.

For a rotating linear molecule, $E_J = \dfrac{J(J+1)\hbar^2}{2I}$.

For a diatomic molecule, $I = \mu R^2$ with $\mu = \left(\dfrac{1}{m_1} + \dfrac{1}{m_2}\right)^{-1}$.

The rotational absorption selection rule is $\Delta J = 1$.

Standard Thermodynamic Properties at 298 K and 1 bar			
Species	$\Delta\bar{H}_f^\circ$ (kJ/mol)	$\Delta\bar{G}_f^\circ$ (kJ/mol)	$\bar{C}_P$ ($\mathrm{J\,K^{-1}mol^{-1}}$)
$CO_{2(g)}$	−393.51	−394.37	37.1
$CO_{2(aq)}$	−413.26	−386.05	
$HCO^-_{3(aq)}$	−689.9	−586.8	
$H_2CO_{3(aq)}$	−699.7	−623.1	
$H_2O_{(l)}$	−285.830	−237.140	75.40
$H_2PO^-_{4(aq)}$	−1302.6	−1137.2	
$MnO_{2(s)}$	−520.0	−465.2	54.1
$Mn_2O_{3(s)}$	−959	−881	107.7
$NH_{3(aq)}$	−80.29	−26.50	
$NH^+_{4(aq)}$	−133.26	−81.19	
$Zn^{2+}_{(aq)}$	−153.39	−111.62	

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 65.39	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 226.03	89 Ac 227.03	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt									

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 237.05	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr