Chemistry 2720 Fall 2005 Final Examination

Time: 3 h

Marks: 103

Aids permitted: calculator, one 8.5×11-inch formula sheet

Write all answers in the booklets provided.

Useful data is given at the end of this exam paper.

You have some choice in section 2. Only answer the required number of questions.

1 Answer all questions in this section.

Value of this section: 79

1. Give the ground-state electronic configuration of Tc and predict the ions it would form. [7 marks]

2. The photoelectron spectrum of neon obtained with X-rays of wavelength 1 nm contains three peaks at electron kinetic energies of 372, 1191 and 1218 eV. Use these data to sketch (approximately to scale and with appropriate labels) the energy level diagram of neon. [10 marks]

3. The line spacing in the rotational spectrum of $^{127}I^{79}Br$ is 3.422 488 GHz. What is the bond length? [10 marks]

4. A physical chemistry professor has set the following question on an exam:

   > Calculate the de Broglie wavelength of a neutron (mass = $1.674\,927\,16 \times 10^{-27}$ kg) moving at a speed of 1200 m/s.

   One of the students gives the following answer:

$$
\begin{aligned}
E &= hv = (6.626 \times 10^{-34})(1200) = 7.95 \times 10^{-31}\,\text{J}. \\
\lambda &= \frac{hc}{E} = \frac{(2.998 \times 10^{8})(6.626 \times 10^{-34})}{7.95 \times 10^{-31}} = 2.50 \times 10^{5}\,\text{m}.
\end{aligned}
$$

   What error(s) do you see in this solution? If you had to explain to this student where he or she went wrong, what would you tell them? [4 marks]

5. In an exothermic reaction, the energy released carries mass according to $E = mc^2$. This is the principle behind the huge release of energy in nuclear reactions, where part of the mass (which was in fact binding energy of the protons and neutrons) is converted to energy. In theory, this also applies to ordinary chemical reactions: The mass of the products of an exothermic reaction should be less than the mass of the reactants. Calculate the mass lost due to this effect when 100 L of liquid ethanol is burned in air at 25°C. The density of ethanol is 0.79 g/mL and its molar mass is 46.068 g/mol. Could you imagine measuring this mass difference? [14 marks]

   Hint: It's *energy* that matters here, not heat.

6. The harmonic oscillator energy levels seen in class are only an approximation to the vibrational energy levels of a diatomic molecule. The following is a more accurate equation:

$$E_n = h\nu_0\left(n + \frac{1}{2}\right) - \frac{(h\nu_0)^2}{4D_e}\left(n + \frac{1}{2}\right)^2,$$

   where ν_0 and D_e are constants specific to a molecule. For $^1H^{35}Cl$, $\nu_0 = 8.97 \times 10^{13}$ Hz and $D_e = 7.41 \times 10^{-19}$ J. Assuming that the molecules start out in the ground state, calculate the photon frequencies for the fundamental and first two overtones of the vibrational spectrum of $^1H^{35}Cl$. How do these compare to the values you would have calculated from the harmonic oscillator equations? [12 marks]

7. In basic solution, zinc (II) ions form a complex with hydroxide:

$$\mathrm{Zn^{2+}_{(aq)}} + 4\mathrm{OH^-_{(aq)}} \to \left[\mathrm{Zn(OH)_{4(aq)}}\right]^{2-}.$$

   This complexation reaction has an equilibrium constant of 2.9×10^{15} at 25°C.

   (a) Calculate the standard free energy of formation of the complex $\left[\mathrm{Zn(OH)_{4(aq)}}\right]^{2-}$. [6 marks]

   (b) The solubility product of $Zn(OH)_2$ at 25°C is quite small, about 3×10^{-17}. Calculate the solubility of zinc (II) hydroxide in a pH 12 buffer without taking the complexation reaction into account. $K_w = 10^{-14}$. [8 marks]

   (c) Calculate the solubility in a pH 12 buffer now taking the complexation reaction into account. [8 marks]

2 Answer any *four* questions in this section.

In the event that you answer more than four questions from this section, I will mark the first four answers I see. **Extra answers will not be marked.** It is therefore in your best interest to select the questions you want marked yourself. If you try more than four questions from this section, make sure to cross out the ones you don't want marked.

Value of this section: 24 marks

1. Describe (a) one success and (b) one failure of the Bohr theory of the atom. [6 marks]

2. Explain why it is not possible for a particle in a box to occupy the $n = 0$ energy level. [6 marks]

3. Explain how we can get both σ and π orbitals by adding p atomic orbitals in LCAO theory. [6 marks]

   Note: A mostly pictorial answer may be satisfactory.

4. Isoelectronic species (species which have the same number of electrons) tend to have very similar molecular orbital diagrams. Based on this observation, would you expect CO to be paramagnetic or diamagnetic? [6 marks]

5. Ferredoxin (Fd) is an iron-containing protein which undergoes the following half-reaction:
$$\mathrm{Fd[Fe(III)]} + \mathrm{e}^- \rightarrow \mathrm{Fd[Fe(II)]}.$$
   Balance the equation for the reaction of *reduced* ferredoxin with acetaldehyde (CH_3CHO) in neutral medium. The products are oxidized ferredoxin and ethanol (CH_3CH_2OH). [6 marks]

6. X rays are produced by bombarding a piece of metal with high-energy electrons. Collisions between the high-energy electrons and those of the metal push the latter into highly excited states. On returning to the ground state, they release most of their energy in the form of X rays. The resulting X-ray emission spectra generally contain some sharp, intense lines against a broad background emission of lower intensity. In copper, two such lines occur very close together, at wavelengths of 154.433 and 154.051 pm. If you used a graphite crystal (interplanar distance = 335 pm) to monochromate these X-rays, at what angles would these two lines have their first-order reflections? Do you think they could be separated in this way for use in (e.g.) an X-ray diffraction experiment? [6 marks]

Useful data

Fundamental constants and conversion factors

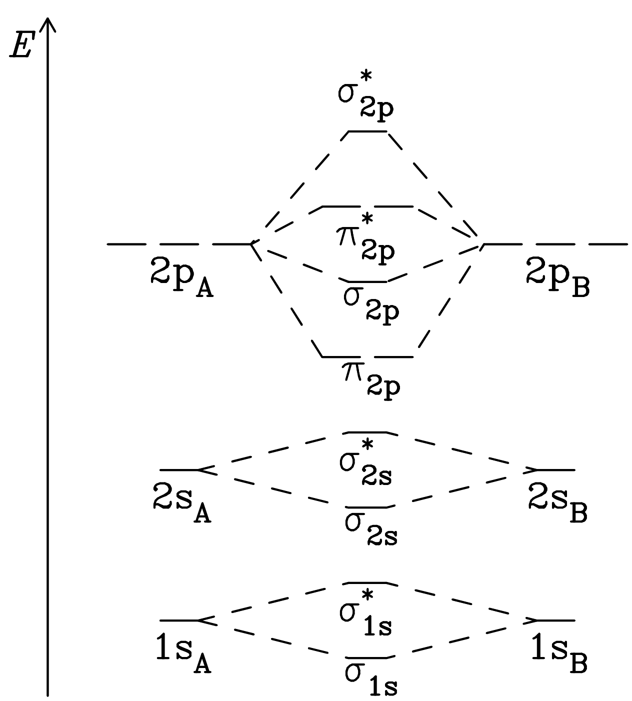
$$
\begin{aligned}
c &= 2.997\,924\,58 \times 10^{8}\,\mathrm{m/s} \\
h &= 6.626\,068\,8 \times 10^{-34}\,\mathrm{J/Hz} \\
\hbar &= 1.054\,571\,68 \times 10^{-34}\,\mathrm{J\,s} \\
N_A &= 6.022\,142\,0 \times 10^{23}\,\mathrm{mol}^{-1} \\
R &= 8.314\,472\,\mathrm{J\,K^{-1}mol^{-1}} \\
1\,\mathrm{eV} &= 1.602\,176\,46 \times 10^{-19}\,\mathrm{J}
\end{aligned}
$$

To convert degrees Celsius to Kelvin, add 273.15.

Isotopic masses

Isotope	Mass (amu)
^{127}I	126.904 473
^{79}Br	78.918 336

Molecular orbitals of homonuclear diatomic molecules:



Standard thermodynamic data

Species	$\Delta \bar{H}_f^\circ$ (kJ/mol)	$\Delta \bar{G}_f^\circ$ (kJ/mol)	$\bar{C}_P$ ($\mathrm{J\,K^{-1}mol^{-1}}$)
$C_2H_5OH_{(l)}$	-277.69	-174.78	111.5
$CO_{2(g)}$	-393.51	-394.37	37.1
$H_2O_{(l)}$	-285.830	-237.140	75.40
$OH^-_{(aq)}$	-230.015	-157.220	
$Zn^{2+}_{(aq)}$	-153.39	-111.62	

Periodic table

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	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