Chemistry 2720 Fall 2002 Final Examination

Write all answers in the booklets provided.
Time: 3 h
Total marks: 107
Aids allowed: $8\frac{1}{2} \times 11$-inch information sheet, calculator.
Read the instructions for each section carefully. If you are asked to answer only a limited number of questions, make sure to make it clear (by crossing out any aborted work which you don't want marked) which question(s) I should mark. Otherwise, I will mark the first answer(s) I see. **I will not mark more than the required number of questions from any given section.**
A periodic table is attached to the back of this exam.
Useful information:

$c = 2.997\,924\,58 \times 10^{8}\,\text{m/s}$
$e = 1.602\,176\,46 \times 10^{-19}\,\text{C}$
$\varepsilon_0 = 8.854\,187\,817 \times 10^{-12}\,\text{C}^2\text{J}^{-1}\text{m}^{-1}$
$h = 6.626\,068\,8 \times 10^{-34}\,\text{J/Hz}$
$\hbar = 1.054\,572 \times 10^{-34}\,\text{J s}$
$m_e = 9.109\,381\,9 \times 10^{-31}\,\text{kg}$
$N_A = 6.022\,142\,0 \times 10^{23}\,\text{mol}^{-1}$
$R = 8.314\,472\,\text{J K}^{-1}\text{mol}^{-1}$
$R_H = 2.179\,871\,90 \times 10^{-18}\,\text{J}$
$1\,\text{bar} = 100\,000\,\text{Pa}$
$1\,\text{m}^3 = 1000\,\text{L}$

To convert degrees Celsius to Kelvin, add 273.15.

Isotopic Masses	
Isotope	Mass (amu)
^{12}C	12
^{32}S	31.972 070 69
^{34}S	33.967 866 83

Bohr model:

$$r_n = \frac{n^2 h^2 \varepsilon_0}{\pi Z e^2 m_e}$$

$$v_n^2 = \frac{Ze^2}{4\pi\varepsilon_0 m_e r_n}$$

Electromagnetic Spectrum	
Region	Wavelengths (m)
radio	over 1
microwave	10^{-3}–1
infrared	7.1×10^{-7}–10^{-3}
red	5.8×10^{-7}–7.1×10^{-7}
yellow	5.4×10^{-7}–5.8×10^{-7}
green	4.8×10^{-7}–5.4×10^{-7}
blue	3.9×10^{-7}–4.8×10^{-7}
ultraviolet	10^{-8}–3.9×10^{-7}
X rays	10^{-11}–10^{-8}
γ rays	under 10^{-11}

Standard Thermodynamic Properties at 25°C and 1 bar			
Species	$\Delta\overline{H}_f^\circ$ (kJ/mol)	$\Delta\overline{G}_f^\circ$ (kJ/mol)	$\overline{C}_p$ ($\mathrm{J\,K^{-1}mol^{-1}}$)
$Cl_{(g)}$	121.301	105.305	21.84
$H_{(g)}$	217.998	203.276	20.786
$HCl_{(g)}$	−92.31	−95.30	29.1
$MnO_{2(s)}$	−520.0	−465.2	54.1
$Mn_2O_{3(s)}$	−959	−881	107.7
$Si_{(s)}$	0	0	20.1

1 Answer all questions in this section.

Value of this section: 75 marks

1. (a) A 350 g block of silicon is brought from 20°C to its melting point, 1693 K. How much heat does this require? [4 marks]

   (b) Do you expect the value calculated in part (a) to be reasonably accurate? Why or why not? If you wanted to do better, what data would you need? How would the calculation differ from that carried out in part (a)? [6 marks]

2. Helium boils at 4.20 K with an enthalpy of vaporization of 84 J/mol. What is the entropy of vaporization of helium at its boiling point? [3 marks]

3. Give the ground-state electronic configuration of an antimony (Sb) atom using spectroscopic notation. Briefly discuss the location of this element in the periodic table with reference to its electronic configuration. [6 marks]

4. A velocity selector is a device which removes all particles from a beam except those with a particular velocity. Suppose that you use an electron velocity selector tuned to $1200 \pm 2\,\mathrm{m/s}$. What is the minimum uncertainty in the positions of the electrons emerging from this device? [4 marks]

5. The professor-in-a-box problem: A 75 kg quantum mechanics professor has been locked into a short, narrow hallway of length 5 m. To pass the time, he decides to calculate the minimum kinetic energy which quantum mechanics requires him to have, assuming that he can treat himself as a particle in a one-dimensional box. What value should he get? Is this a large or a small kinetic energy? [4 marks]

6. The absorption lines in the rotational spectra of $^{12}C^{32}S$ and of $^{12}C^{34}S$ are spaced by 49 168.6140 and 48 380.1866 MHz, respectively.[1] Do these two isotopic variants of CS have the same bond length? [16 marks]

7. (a) Calculate the dissociation enthalpy of gaseous HCl at 298.15 K. [3 marks]

   (b) Calculate the dissociation enthalpy of gaseous HCl at 900 K. [8 marks]

   (c) Calculate the dissociation *energy* of HCl at 298.15 K. [4 marks]

   (d) What is the maximum wavelength of a photon with sufficient energy to cause the dissociation of an average HCl molecule at 298.15 K.[2] In what spectral region would such a photon fall? [5 marks]

   (e) Estimate the temperature at which gaseous HCl at an initial pressure of 0.4 bar be 50% dissociated into its atoms. [12 marks]

2 Answer *one* question from this section.

Value of this section: 8 marks

Extra answers will not be marked.

1. In the Bohr model, how long would it take for an electron in the ground state of a hydrogen atom to complete one orbit? [8 marks]

2. Does the emission spectrum of the hydrogen atom contain any lines in the X-ray range of the electromagnetic spectrum? If so, give an example (initial and final values of the principal quantum number). Otherwise, what is the minimum atomic number required for a hydrogenic atom to emit X rays? [8 marks]

[1] V. Ahrens and G. Winnewisser, Z. Naturforsch. A **54**, 131 (1999).

[2] Quantities calculated from thermodynamics are averages rather than values appropriate to all the molecules.

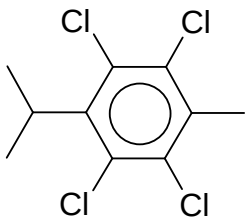
3 Answer *two* questions from this section.

Value of this section: 24 marks

Extra answers will not be marked.

1. During the reversible adiabatic expansion of an ideal gas, the pressure and volume are related by $PV^\gamma = a$ where $\gamma = \bar{C}_P/\bar{C}_V$, and a is a constant determined by the initial pressure and volume. For gases, $\bar{C}_V \approx \bar{C}_P - R$, so γ can easily be calculated from the constant-pressure heat capacity. Calculate the work done during a reversible adiabatic expansion of 1.85 mol of nitrogen gas ($\bar{C}_P = 29.12\,\mathrm{J\,K^{-1}mol^{-1}}$) from an initial pressure and temperature of 0.94 bar and 225°C, to a final pressure of 18 mbar. Treat nitrogen as an ideal gas. [12 marks]

2. The octanol-water partition coefficient of a compound is the equilibrium constant for the process $\mathrm{A}_{(\mathrm{aq})} \rightleftharpoons \mathrm{A}_{(\mathrm{sol,octanol})}$. (Octanol is less dense than water, and octanol and water don't mix, so imagine a layer of octanol floating on water with the solute being free to move between the two phases.) This partition coefficient correlates reasonably well with the tendency of a substance to enter cell membranes and thus to bioaccumulate. Bleaching pulp for the production of paper produces a number of environmentally undesirable compounds, including chlorinated cymenes. Tetrachloro-p-cymene (TCPC)



   has a molar mass of 274.1 g/mol, a solubility in water of $0.15\,\mathrm{g/m^3}$, and an octanol-water partition coefficient of 6.8×10^6 at 25°C.[3]

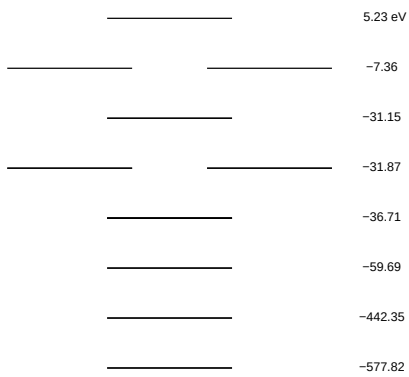
   The high solubility of TCPC in hydrophobic phases such as octanol and cell membranes poses a serious toxicological problem, but it also presents opportunities for removal of this substance from aqueous waste. If $10.0\,\mathrm{m^3}$ of an aqueous solution containing 0.98 g of TCPC is put in contact with 2.0 L of octanol, what mass of TCPC remains in the aqueous phase once the system has come to equilibrium? [12 marks]

   Note: To get a reasonable answer for this problem, you'll have to keep a lot of digits (as many as possible) in intermediate steps of the calculation.

3. Is the conversion of MnO_2 to Mn_2O_3 spontaneous at 80°C under an oxygen pressure of 0.2 bar? [12 marks]

[3] R. Lun et al., J. Chem. Eng. Data **42**, 951 (1997).

4. Here is the orbital energy diagram of NO^+:

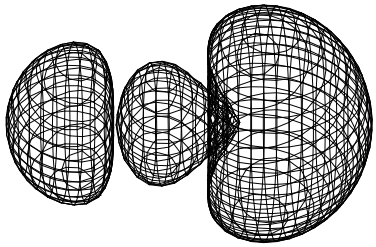


The diagram is not drawn to scale. The numbers on the right are the orbital energies in electron-volts.

(a) Reproduce the diagram in your exam booklet. Assume that a similar labeling system can be used for this molecule as for homonuclear diatomics, and label the orbitals. For example, the bottom two orbitals would be labeled σ_{1s} and σ^*_{1s}. [3 marks]

(b) Determine the bond order in NO^+. [5 marks]

(c) The orbital at $-31.15\,\text{eV}$ has the following shape:



Does the shape of this orbital agree with your label in part a of this question? Explain briefly. [4 marks]

Merry Christmas
and
Happy New Year!

1																	18
1 H 1.01	2											13	14	15	16	17	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	3	4	5	6	7	8	9	10	11	12	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