Chemistry 2720 Fall 2003 Final Examination

Aids allowed: Calculator, one $8\frac{1}{2} \times 11$-inch sheet of notes

Time: 3 hours.

Total marks: 104

Useful data is given at the end of this paper.

1. Suppose that U is a state function, and consider the following process:

$$\begin{array}{ccc} (P_1, V_1) & \xrightarrow{\Delta U_1 = -1.41\,\mathrm{u}} & (P_1, V_2) \\ {\scriptstyle \Delta U_4}\uparrow & & \downarrow{\scriptstyle \Delta U_2 = 2.25\,\mathrm{u}} \\ (P_3, V_1) & \xleftarrow{\Delta U_3 = -3.09\,\mathrm{u}} & (P_3, V_2) \end{array}$$

   What is ΔU_4? (Note that 'u' represents the units of U, whatever they are.) [3 marks]

2. Indicate whether each of the following equations applies to photons only, to ordinary particles only, or to both. [1 mark each]

   (a) $\lambda = h/p$

   (b) $E = hc/\lambda$

3. When cyanide ions (CN^-) react with permanganate (MnO_4^-) in basic solution, the products are manganese (II) oxide ($MnO_{2(s)}$) and cyanate ions (OCN^-). Balance the reaction. [6 marks]

4. An experiment to measure the speed of a neutral π meson (a particle produced in certain high-energy processes) is accurate to $\pm 3\,\mathrm{m/s}$. Is it possible to simultaneously know the position of this meson to $\pm 1\,\mathrm{nm}$? The mass of the neutral π meson is $2.4059 \times 10^{-28}\,\mathrm{kg}$. [7 marks]

5. (a) According to the simple MO theory studied in class, would the molecular ion Ne_2^+ be stable? If the molecular ion is stable, give the bond order. Otherwise, explain how you concluded that this is an unstable species. [7 marks]

   (b) A theoretical calculation predicts that the fundamental vibrational transition in $^{20}Ne_2^+$ occurs at a wavelength of $19.6\,\mu\mathrm{m}$. What is the force constant for this bond? [8 marks]

6. When sodium metal reacts with water, sodium and hydroxide ions are produced, as well as hydrogen gas. Suppose that 1.12 g of sodium metal is put in a **rigid**, insulated container with 120 g of water initially at 22°C. The container is rapidly sealed with a rigid lid.

   (a) Calculate the final temperature. [13 marks]

   (b) Name one *justifiable* approximation about the thermodynamics of this process made in your calculation. [2 marks]

7. Differences in free energies for reactions are fixed by experimental data, but our decision to assign the free energies of formation of certain substances to be zero is purely arbitrary. Suppose that we had decided instead that the free energies of formation of the elements and of the aqueous hydrogen ion should each be 13 kJ/mol. What would the free energy of formation of the hydroxide ion then have to be? [5 marks]

8. It has recently been proposed that there are two different forms of the nitrate ion in aqueous solution, which have tentatively been named α-nitrate and β-nitrate.[1] The equilibrium constant for the interconversion

$$\alpha\text{-}NO_{3(aq)}^{-} \rightleftharpoons \beta\text{-}NO_{3(aq)}^{-}$$

   has been measured at several temperatures over the range 10–70°C. In particular, $K = 0.122$ in dilute sodium nitrate solution at 25°C, and $K = 0.132$ at 30°C. In the discussion section of their paper, Simeon and coworkers argue that the reaction shown above involves the breaking of a hydrogen bond between nitrate and water, i.e. that the reaction is something along the lines of

$$[NO_3(H_2O)_{n+1}]^- \rightleftharpoons [NO_3(H_2O)_n]^- + H_2O.$$

   Calculate the standard entropy change for the reaction. Is the result consistent with the breaking of a hydrogen bond as suggested by Simeon and coworkers? [8 marks]

9. Metals are sometimes described using a very simple free electron model in which the valence electrons are assumed to be completely free to move within the metal, acting as a "box". Suppose that we have an 35 cm long sodium wire with a diameter of 1 mm. Because this wire is much narrower than it is long, it can be treated in some calculations as a one-dimensional system.

   (a) How many valence electrons are contained in the bar? The density of sodium metal is $0.97\,\mathrm{g/cm^3}$. [5 marks]

   (b) What is the highest occupied energy level? Don't forget to take the Pauli exclusion principle into account. [2 marks]

   (c) What is the difference in energy between the highest occupied and lowest unoccupied energy level? It may be helpful to derive an equation for this difference in energy before attempting to plug in any numbers. This energy difference is critical in the theory of metals. In good electric conductors, this difference is small compared to $\frac{1}{2}k_BT$, the

[1] V. Simeon et al., Phys. Chem. Chem. Phys. **5**, 2015 (2003).

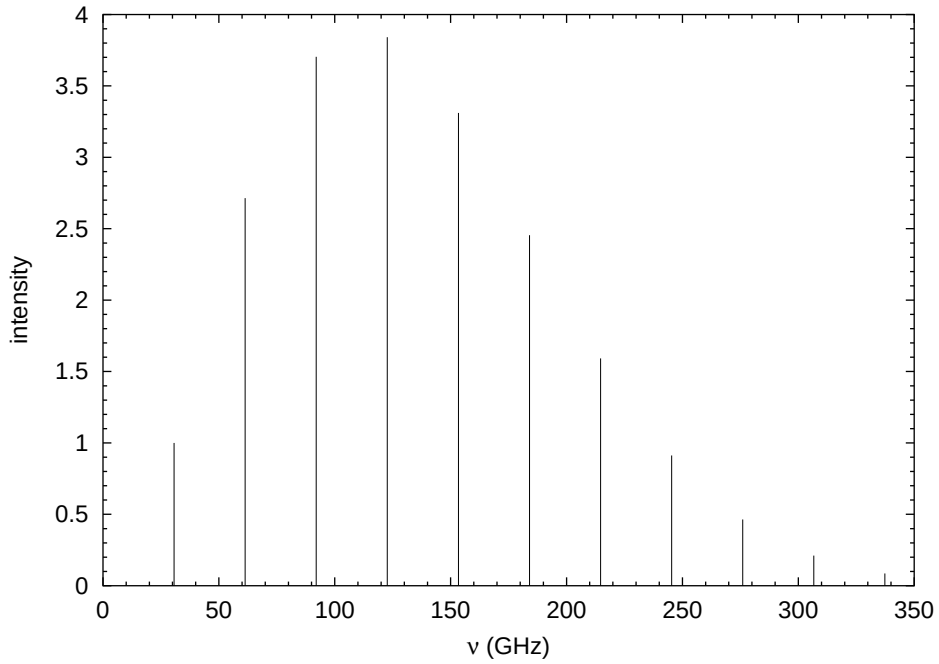

Figure 1: Rotational absorption spectrum of $^{35}Cl^{19}F$.

mean thermal energy for motion in one dimension. Would you predict that sodium is a good conductor based on this calculation? [9 marks]

10. Figure 1 shows the rotational absorption spectrum of $^{35}Cl^{19}F$.

    (a) Calculate the bond length in $^{35}Cl^{19}F$. [11 marks]

    (b) While it is possible to obtain isotopically pure $^{35}Cl^{19}F$, experiments are normally carried out with natural ClF, which contains a mixture of $^{35}Cl^{19}F$ and of $^{37}Cl^{19}F$. What would the spectrum of the mixture look like? The natural abundance of ^{35}Cl is about 76%. [6 marks]

11. A professor has asked the following question in an exam:

> Is the production of $Cl_2O_{(g)}$ from ClO spontaneous at 25°C when $P_{O_2} = 20\,\text{kPa}$, $P_{ClO} = 75\,\text{kPa}$, and $P_{Cl_2O} = 55\,\text{kPa}$?

One student's solution runs as follows:

$$2\text{ClO} \rightarrow \text{Cl}_2\text{O}.$$

$$\begin{aligned} K &= \frac{55}{75^2} = 0.0098. \\ \Delta G^\circ &= -RT\ln K = -(8.314472)(25)\ln(0.0098) = 961. \\ \Delta G &= \Delta G^\circ + RT\ln Q \\ &= 961 + (8.314472)(25)\ln\left(\frac{1}{2}\right) = 817\,\text{kJ/mol}. \end{aligned}$$

Since this is positive, the reaction is not spontaneous.

Find all the errors in this solution. Explain in a few words (no sentences necessary) the nature of each error. Note that I am **not** asking you to solve the problem. Rather, I'm asking you to pretend that you're the marker trying to explain to the student what is wrong with his or her thinking. [10 marks]

Useful data

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

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

$\hbar = 1.05457168 \times 10^{-34}\,\text{Js}$

$k_B = 1.3806503 \times 10^{-23}\,\text{J/K}$

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

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

$R = 8.314472\,\text{JK}^{-1}\text{mol}^{-1}$

$1\,\text{amu} = 1\,\text{g/mol}$

$1\,\text{bar} = 100\,\text{kPa}$

$1\,\text{eV} = 1.60217646 \times 10^{-19}\,\text{J}$

The specific heat capacity of liquid water is $4.184\,\text{JK}^{-1}\text{g}^{-1}$.

To convert degrees Celsius to Kelvin, add 273.15.

Standard thermodynamic properties at 25°C

Species	$\Delta\bar{H}_f^\circ$ (kJ/mol)	$\Delta\bar{G}_f^\circ$ (kJ/mol)	$\bar{C}_P$ ($\text{JK}^{-1}\text{mol}^{-1}$)
$ClO_{(g)}$	101.22	97.48	31.54
$Cl_2O_{(g)}$	87.88	105.10	47.50
$H_2O_{(l)}$	−285.830	−237.140	75.40
$Na^+_{(aq)}$	−240.34	−261.95	
$OH^-_{(aq)}$	−230.015	−157.220	

Isotopic Masses	
Isotope	Mass (amu)
^{19}F	18.998 403 20
^{20}Ne	19.992 440 175 9
^{35}Cl	34.968 852 71
^{37}Cl	36.965 902 60

Periodic Table of the Elements with Molar Masses

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