TIGP727200 Physical Chemistry (II)

Homework 2 Due date: 1 May 2012

**1. Conjugated polymers: why the absorption wavelength increases with chain length.**

Polyenes are linear double-bonded polymer molecules $(C{=}C{-}C)_N$, where $N$ is the number of C=C−C monomers. Model a polyene chain as a box in which $\pi$-electrons are particlesthat can move freely. If there are $2N$ carbon atoms each separated by bond length $d$ = 1.4A, and if the ends of the box are a distance $d$ past the end C atoms, then the length of the box is $L = (2N + 1)d$. An energy level, representing the two electrons in each bond, is occupied by two paired electrons. Suppose the $N$ lowest levels are occupied by electrons, so the wavelength absorption of interest involves the excitation from level $N$ to level $N + 1$. Compute the absorption energy $\Delta\varepsilon = \varepsilon_{N+1} - \varepsilon_N = hc/\lambda$, where $c$ is the speed of light and $\lambda$ is the wavelength of absorbed radiation, using the particle-in-a-box model.

**2.** Although expressions like $\langle\varepsilon\rangle = -\mathrm{d}\ln q/\mathrm{d}\beta$ are useful for formal manipulations in statistical thermodynamics, and for expressing thermodynamic functions in neat formulas, they are sometimes more trouble than they are worth in practical applications. When presented with a table of energy levels, it is often much more convenient to evaluate the following sums directly:

$$q = \sum_j \mathrm{e}^{-\beta\varepsilon_j} \quad \dot{q} = \sum_j \beta\varepsilon_j \mathrm{e}^{-\beta\varepsilon_j} \quad \ddot{q} = \sum_j \left(\beta\varepsilon_j\right)^2 \mathrm{e}^{-\beta\varepsilon_j}$$

(a) Derive expressions for the internal energy, heat capacity, and entropy in terms of these three functions. (b) Apply the technique to the calculation of the electronic contribution to the constant-volume molar heat capacity of magnesium vapour at 5000 K using the following data:

| Term | $^1S$ | $^3P_0$ | $^3P_1$ | $^3P_2$ | $^1P_1$ | $^3S_1$ |
|---|---|---|---|---|---|---|
| Degeneracy | 1 | 1 | 3 | 5 | 3 | 3 |
| $\tilde{\nu}/\mathrm{cm}^{-1}$ | 0 | 21 850 | 21 870 | 21 911 | 35 051 | 41 197 |

**3.** In a spectroscopic study of buckminsterfullerene $C_{60}$, F. Negri, G. Orlandi, and F. Zerbetto (*J. Phys. Chem.* **100**, 10849 (1996)) reviewed the wavenumbers of all the vibrational modes of the molecule. The wavenumber for the single $A_u$ mode is 976 $\mathrm{cm}^{-1}$; wavenumbers for the four threefold degenerate $T_{1u}$ modes are 525, 578, 1180, and 1430 $\mathrm{cm}^{-1}$; wavenumbers for the five threefold degenerate $T_{2u}$ modes are 354, 715, 1037, 1190, and 1540 $\mathrm{cm}^{-1}$; wavenumbers for the six fourfold degenerate $G_u$ modes are 345, 757, 776, 963, 1315, and 1410 $\mathrm{cm}^{-1}$; and wavenumbers for the seven fivefold degenerate $H_u$ modes are 403, 525, 667, 738, 1215, 1342, and 1566 $\mathrm{cm}^{-1}$. How many modes have a vibrational temperature $\theta_V$ below 1000 K? Estimate the molar constant-volume heat capacity of $C_{60}$ at 1000 K, counting as active all modes with $\theta_V$ below this temperature.