Problem Set 6

Chemistry 448
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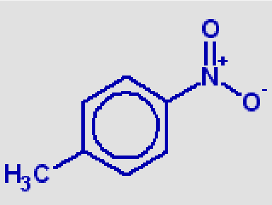
1. Consider a large number of diatomic molecules with electric dipole moment placed in an electric field.

(a) Consider diatomic molecules with electric dipole moment μWhen placed in an electric field of strength F, its potential energy will equal $-\mu F$ if the dipole is lined up with the field and $+\mu F$ if the dipole opposes the field. Suppose the molecules in the field are capable of exhibiting only two orientations, in the direction of the applied field and opposed thereto. At temperature T, what fraction of the molecules will exhibit each kind of orientation, and what will be the average potential energy?

(b) The dipole moment of HCl is equal to 1.03x10^{-18} esu cm. If some hydrogen chloride gas at 300 K were placed in an electric field of 100,000 V cm^{-1}, what fraction of the molecules would be oriented in each direction? What would be the average energy?

(c) How strong a field would be necessary to cause 55% of the hydrogen chloride molecules to line up with the field at 300 K? What does this suggest as to the practical possibility of lining up a large fraction of molecular electrical dipoles?

An application in which the answers to these questions were used is the following: NMR spectroscopy using DC electric field for alignment was proposed and observed by David Buckingham, for the explicit purpose of determining the then experimentally unknown absolute sign of a spin-spin coupling constant in a polar molecule. [A. D. Buckingham and K. A. McLauchlan, The absolute sign of the spin-spin coupling constant. *Proc. Chem. Soc.*, 144 (1963); A. D. Buckingham and E. G. Lovering, Effects of a strong electric field on NMR spectra. The absolute sign of the spin coupling constant, *Trans. Faraday Soc.,* 58, 2077 (1962).]. If isotropic averaging occurs over all orientations of the molecule with respect to the external magnetic field of the spectrometer, then the direct dipolar coupling (magnetic dipole of nucleus A and magnetic dipole of nucleus B) averages to zero and does not contribute to the observed NMR spectrum; thereby, only the isotropic value of the indirect (through electrons in the bonds) spin-spin coupling of the nuclei A and B is observed as splitting(s) in the spectrum. On the other hand, any partial alignment permits contributions from the direct-dipolar coupling to be observed. The latter contribution is positive, dependent only on the direct distance between the two nuclei in the molecule, whereas the indirect coupling can be positive or negative. Whereas only the isotropic part of the indirect coupling is observed at zero electric fields, in gases or solutions at sufficiently high electric field strengths, direct dipolar interactions may modify the NMR spectrum sufficiently that the sum of the two couplings which is observed in the presence of the DC electric field can distinguish whether the indirect coupling is adding or subtracting from the direct dipolar contribution.
The absolute sign of $^{3}J(^{1}H,^{1}H)^{iso}$ for *p*-nitrotoluene was obtained in this way.



The following involve mixtures of isotopes.

2. In calculating the entropy for a monatomic gas consisting of a mixture of isotopes, one can to a good approximation, use the average atomic weight. This does not, of course, take care of the entropy of mixing.

(a) Derive an expression for the difference between the sum of the calculated entropies of two isotopes, of mole fractions x_1 and x_2, and the entropy calculated for the material assumed to have the average molecular weight

(b) Assuming neon to consist of 90% isotope 20 and 10% isotope 22, calculate the above-defined differences in cal deg^{-1} mol^{-1}.

3. Consider the isotopes of chlorine.

(a) Assuming that 75% (actually the natural abundance of this isotope is 75.78%) of the atoms of chlorine have mass 35 and 25% have mass number 37 (actually 24.22%), what fraction of the molecules of chlorine will have masses 70, 72, and 74, if pairs of atoms are taken at random? Actually the masses are 34.968852721 (69) and 36.96590262 (11) amu, so the possible molecular weights are actually 69.937705442, 71.934755341 and 73.93180524 amu, but let us stick to the simpler 2-digit values for the purpose of this problem.

(b) For a total of 1 mole of molecular chlorine, what is the entropy of mixing of the three kinds of molecules?

(c) How does the answer to part (b) differ from the entropy of mixing of the same total number (2 moles) of atoms if we assume that no diatomic molecules exist?

4. In the problem above, it was shown that the entropy of mixing of isotopic chlorine atoms is not the same as the entropy of mixing of the equivalent number of atoms in their molecular forms. Show that the difference, $2x_1x_2R\ln 2$ for 2 moles of atoms, arises from the difference between the symmetry numbers of $^{35}Cl^{37}Cl$ and $^{35}Cl_2$ and $^{37}Cl_2$. Hence, observe how the indistinguishability of atoms must be taken into account in connection with rotation of the molecule.