Computational Chemistry I

Text book Cramer: Essentials of Quantum Chemistry, Wiley (2 ed.)

Chapter 5. Entropy and Free Energy (Cramer: chapter 10)

Entropy

As mentioned earlier to be able to compute the free energy we need the entropy, **G=H-TS.** The entropy can be computed using **statistical mechanics.** In the following a very brief introductions of stat. mech. is given. More details can be found from any physical chemistry text book.

The statistical mechanics starts from the **partition function.** A single particle partition functions is a simple sum

$$q = \sum_n \exp(-\beta E_n)$$

In this form the β is 1/kT, where k is Boltzman constant and E_n is the energy of the quantum state n. To get the quantum states we can use simple model potentials, like particle in a box, rotating molecule and **harmonic approximation.** This approach is valid in gas phase. In liquid or in solid the molecular interactions are strong and we cannot use free molecule models. In solid it is possible to model the entropy by using only vibrations but I will postpone that part to the next course. In liquids so called thermodynamical integration methods can be used. These might be discussed in the second part of the course (MAYBE).

Particle in a box

The energy levels of a particle of mass m in 1-D box of length L is

$E_n = \frac{h^2 n^2}{8mL^2} = \varepsilon n^2, n = 1,2,...$ Here the h is the Planck constant. The exact calculation of q is not possible, but for macroscopic box (> 100 nm !) the energy states are very close to each other and we can replace the sum with integral. The (Gaussian) integral can be solved.

$$q^T = \sum_{n=1}^{\infty} \exp(-\beta\varepsilon n^2) = \int_0^{\infty} \exp(-\beta\varepsilon n^2) dn = \frac{1}{2}\sqrt{\frac{\pi}{\beta\varepsilon}}$$

We can define the thermal wave length $\Lambda = \sqrt{\frac{4\beta\varepsilon L^2}{\pi}} = \sqrt{\frac{\beta h^2}{2\pi m}}$ with this we can simplify the partition function.

$$q = \frac{L}{\Lambda}$$

The example above is 1-D but it is easy to generalize to 3-D because the quantum states do not interact and thus the 3-D partition function is a product of the 1-D partition functions.

$$q_{3D} = \sum_{n=1}^{\infty} \exp(-\beta\varepsilon n^2) \sum_{m=1}^{\infty} \exp(-\beta\varepsilon m^2) \sum_{k=1}^{\infty} \exp(-\beta\varepsilon k^2) = \frac{L_x}{\Lambda}\frac{L_y}{\Lambda}\frac{L_z}{\Lambda} = \frac{V}{\Lambda^3}$$

Note that the Λ is very small. For Ar at room temperature, m=6.63*10-26 kg and β=1/kT= 2.41*10^{20} 1/J then Λ=1.60*10^{-11} m.

Rotating molecule

The energy level of a diatomic molecule are $E_J = BhcJ(J+1), J = 0,1,2,...$ where B is the rotational constant B=h/(8π^2cI), and I = μr^2, μ=m1m2/(m1+m2) where m1 and m2 are the masses of the atoms. The states are degenerate as 2J+1. Again the direct sum

$q^R = \sum_J (2J+1)\exp(-\beta hcBJ(J+1))$ cannot be computed but also here the sum can be approximated with integral

$$q^R = \int_0^\infty (2J+1)\exp(-\beta hcBJ(J+1))dJ = \frac{1}{\beta hcB} = \frac{kT}{hcB} = \frac{T}{\theta}$$

Here it is more convenient to use the rotational temperature θ. For HCl the rotational temperature is 15.24 K so at room temperature the rotational partition function is 19.63. (The exact value from the summation is 19.969.)

Again most of the molecules are non-linear and we need to 3-D rotational partition function

$$q^R = \frac{1}{\sigma}\left(\frac{\pi kT}{hcB_A}\frac{kT}{hcB_B}\frac{kT}{hcB_C}\right)^{1/2} = \frac{1}{\sigma}\left(\frac{\pi T^3}{\theta_A\theta_B\theta_C}\right)^{1/2}$$

Example. ONCl, B_A = 2.84 cm^{-1}, B_B = 0.191 cm^{-1} , B_C = 0.179 cm^{-1}. The symmetry number = 1, T=298 K, q^R = 16 940.

Molecular vibration

For single molecular vibration the energy levels are ħω(n+1/2). Now the sum is easy to compute (Note that we ignore the zero point energy).

$$q^V = \frac{1}{1-\exp(-\beta\hbar\omega)}$$

This equation is valid for every vibration (there is not coupling between the vibrations) so we can compute the vibrational partition function for molecule that have several vibrations,

$$q^V = q_1^V q_2^V \ldots q_{3N-6}^V = \prod_n \frac{1}{1-\exp(-\beta\hbar\omega_n)}$$

Now we have all the components of the general molecules partition function.

$$q_{molek} = q^T q^R q^V = \frac{V}{\Lambda^3}\frac{1}{\sigma}\left(\frac{\pi T^3}{\theta_A\theta_B\theta_C}\right)^{1/2}\prod_n \frac{1}{1-\exp(-\beta\hbar\omega_n)}$$

The partition function above is for single molecule but we would like to study several molecules. In the ideal gas approximations the molecules do not interact so the many molecule partition functions is

$$Q = \prod_I q_{molek} = (q_{molek})^N$$

We need to take into account that in quantum mechanics the molecules cannot be distinguished so we can number them in any order. This modifies the partition function

$$Q = \frac{(q_{molek})^N}{N!}$$

If the system contain several gases the partition functions is

$$Q = \frac{(q_{molek-1})^{N_1}}{N_1!}\frac{(q_{molek-2})^{N_2}}{N_2!}$$

From the partition function we can compute the finite temperature internal energy and entropy

Energy

The energy is rather easy to compute

$$E = \sum_{i=0}^{M} \varepsilon_i n_i$$

From this one can derive a formula for energy that depend on the partition function

$$\boxed{U = \left(\frac{-d\ln Q}{d\beta}\right)_V = -\frac{Nd\ln q}{d\beta} = \frac{Ndq}{qd\beta}}$$

Entropy

Entropy is more complex but also it can be computer from the partition function. The final expression is

$$S = k\ln W = \frac{E}{T} + k\ln q^N = \frac{U}{T} + k\ln Q$$

This can be applied to each partition function part. For the translation part:

$$S = kN\ln(\frac{e^{5/2}kT}{p\Lambda^3}) = nR\ln(\frac{e^{5/2}RT}{pN_A\Lambda^3})$$

Rotational part, linear molecule

$$S = \frac{U}{T} + k\ln Q = 5nR/2 + nR\ln(\frac{V}{\Lambda^3} - \ln N + 1 + \frac{T}{\sigma\Theta}) = nR(\frac{7}{2} + \ln\frac{TV}{N\Lambda^3\sigma\Theta}) = nR\ln(\frac{e^{7/2}V}{N\Lambda^3}\frac{T}{\sigma\Theta})$$

And non-linear molecule

$$S = \frac{U}{T} + k\ln Q = nR\ln\left(\frac{e^3 V}{N\Lambda^3}\frac{1}{\sigma}\left(\frac{\pi T^3}{\Theta_A\Theta_B\Theta_C}\right)^{1/2}\right)$$

And last we need the vibrational entropy. The internal energy U is

$U^V = \sum_n \frac{N\hbar\omega_n}{\exp(\beta\hbar\omega_n) - 1}$ and ln Q is $-kN\sum_n \ln(1 - \exp(-\beta\hbar\omega_n))$

$$S^V = \sum_n \left\{\frac{N\hbar\omega_n}{T\exp(\beta\hbar\omega_n) - 1} - kN\ln(1 - \exp(\beta\hbar\omega_n))\right\}$$

Note: is the frequencies are very low the second term above will diverge like -ln(ħω/kT) (the first term will approach to nRT). So the low frequency modes need to be ignored and some cut-off is used. One rational cut-off is ħω/kT = 1. At room temperature this means frequency of ca. 210 cm^{-1}.

Now we have the full molecular entropy in **gas phase.** We have ignored the intramolecular interactions and this need to bear in mind when this model is used. This approach should be used only in gas phase reactions and reaction in apolar solvents. On the other hand the approach is easy. All we need is the molecules mass, geometry (for rotational part) and harmonic frequencies.

Note that this approach can be used in solids provided that the vibrations can be handled correctly. The polar liquids are dangerous and only qualitatively accurate results can be obtained.