4.2: Background

As was discussed in the lecture portion of the course, substituted cyclohexane rings exist as chair structures that can place the substituent in either the axial or equatorial position. As shown in Figure 1, the equilibrium generally favors the conformer that places the substituent in the equatorial position over the one that places the substituent in the axial position. One measure of how much a substituent causes the equatorial conformer to be favored is known as an A value. An A value measures the difference in energy (ΔG°) in kcal/mol for a monosubstituted cyclohexane ring in the equilibrium as written in Figure 1. The bigger in magnitude an A value is, the greater the substituent will cause the equilibrium to favor the equatorial conformer.
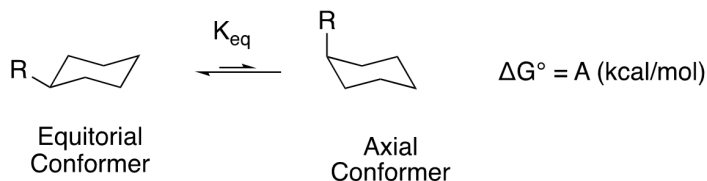

Figure 1. Equilibrium of monosubstituted cyclohexane chair conformers.

The difference in energy between conformers can also be related to the equilibrium constant (K_{eq}) by equation $4.2.1$. R represents the ideal gas constant [1.987 cal/(mol*K)] and T represents the temperature in Kelvin, and ln is the natural logarithm. This means if we can calculate the change in energy between two cyclohexane conformers, it will be possible to estimate the equilibrium constant of the process. By extension you can then estimate the proportion of each conformer (axial and equatorial) at equilibrium.

$$G_{ax} - G_{eq} = \Delta G^\circ = -R\,T\ln(K_{eq}) \tag{4.2.1}$$