# Molecules Have Potential Energy
Chemical Potential is the Propensity of a Molecule to Undergo Change

The energies of the staggered and eclipsed forms are not equal. Before describing how the energies of these two conformations differ, it will be worthwhile to have a discussion about the potential energy of molecular objects.

The relationship between potential energy and stability are understood by analogy to potential energy of a purely mechanical system. It will thus be useful to compare a mechanical system such as a ball on a platform to a chemical structure whose potential energy is represented on an energy scale. Regardless of the specific energy units we use, the main point to keep in mind is this: *the lower the potential energy, the less able the structure is to change, and the greater is its stability*. The reason the ball on a platform is a good analogy to our chemical system is because the height of the ball is directly proportional to its gravitational potential energy. The higher the platform, the less stable the ball. Similarly, for a chemical structure placed on an energy scale, the higher its chemical potential, the less stable it will be; the higher the chemical potential, the more energy that can be released through chemical change.
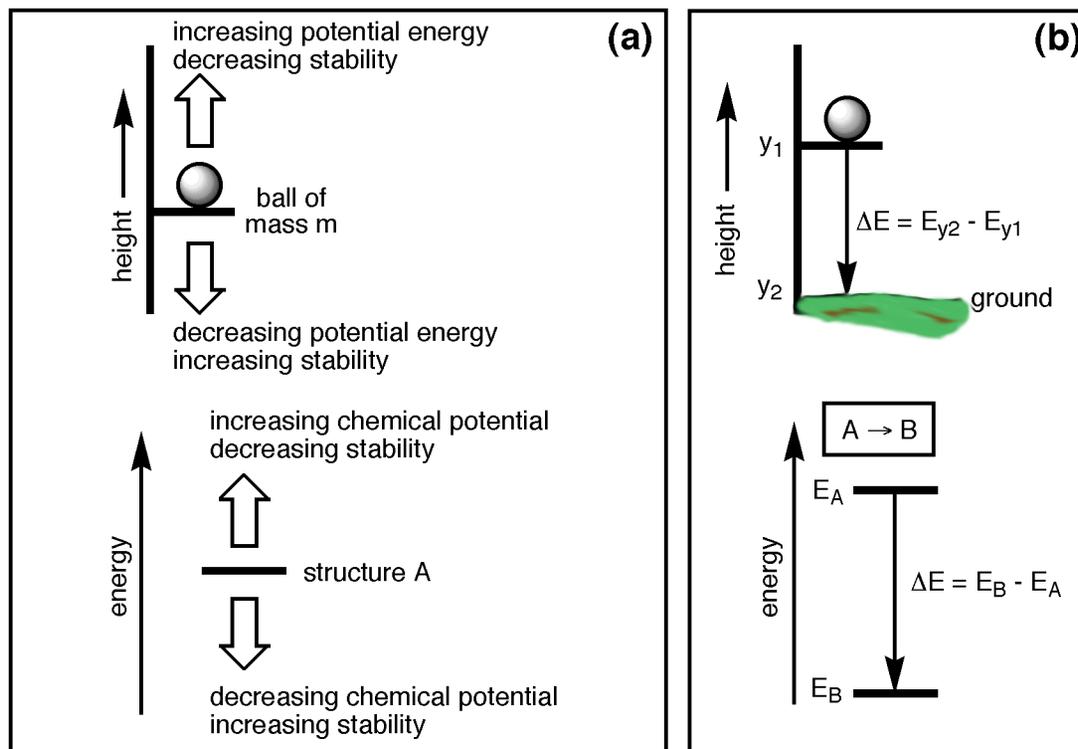

(a) Comparison of a ball on a platform to a chemical structure on an energy scale. (b) A meaningful description of potential energy requires a reference point such as the position of the ground or the energy of the products of a chemical reaction.

Conformation and Energy

The energy of ethylbromide depends on the **dihedral** angle. The figure shows the continuous variation in potential energy (i.e., the y-axis) as a function of dihedral angle, θ (i.e., the x-axis). In this plot, the dihedral angle of θ=0° corresponds to the eclipsed conformation.

Minima on potential energy plots correspond to stable states. The "states" in this particular case are conformational isomers. The maxima correspond to barriers – in this particular case to barriers of rotation. The energy valleys are the regions of conformational movement in which the molecule tends to reside. Occasionally, the molecule will acquire enough thermal energy that it will jump a barrier and enter into an adjacent valley. To understand the meaning of this statement, think back to the molecular dynamics simulation (you may even want to re-run the simulation). The energy profile that governs the oscillatory, pendulum-like motion of the $-CH_3$ group is what this plot shows.
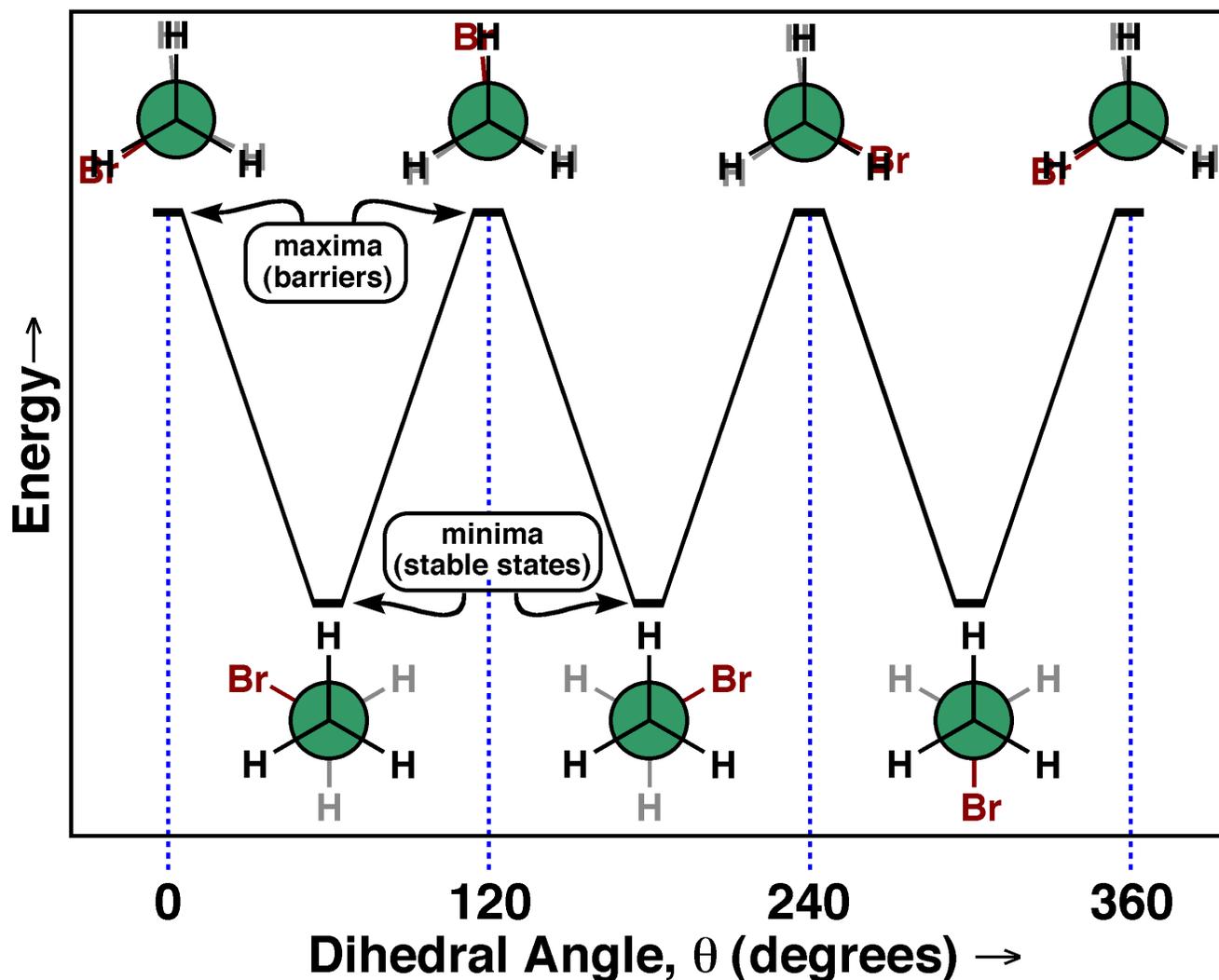
Barrier Height Determines Residence Time in an Energy Valley

The rate or frequency with which a molecule passes over a potential barrier, exiting one energy valley and entering the next, is determined by the **barrier height**. The barrier height is defined as the energy difference from minimum to maximum as seen in this Figure. The larger the barrier height, the longer the molecule will reside in its current valley, and the more infrequently will the molecule pass over the barrier.

The barrier height determines how often a molecule will pass from one state to another, illustrated here for the passage from one conformational state to another. The barrier height is an energy difference, often written as $\Delta G^{\ddagger}$.
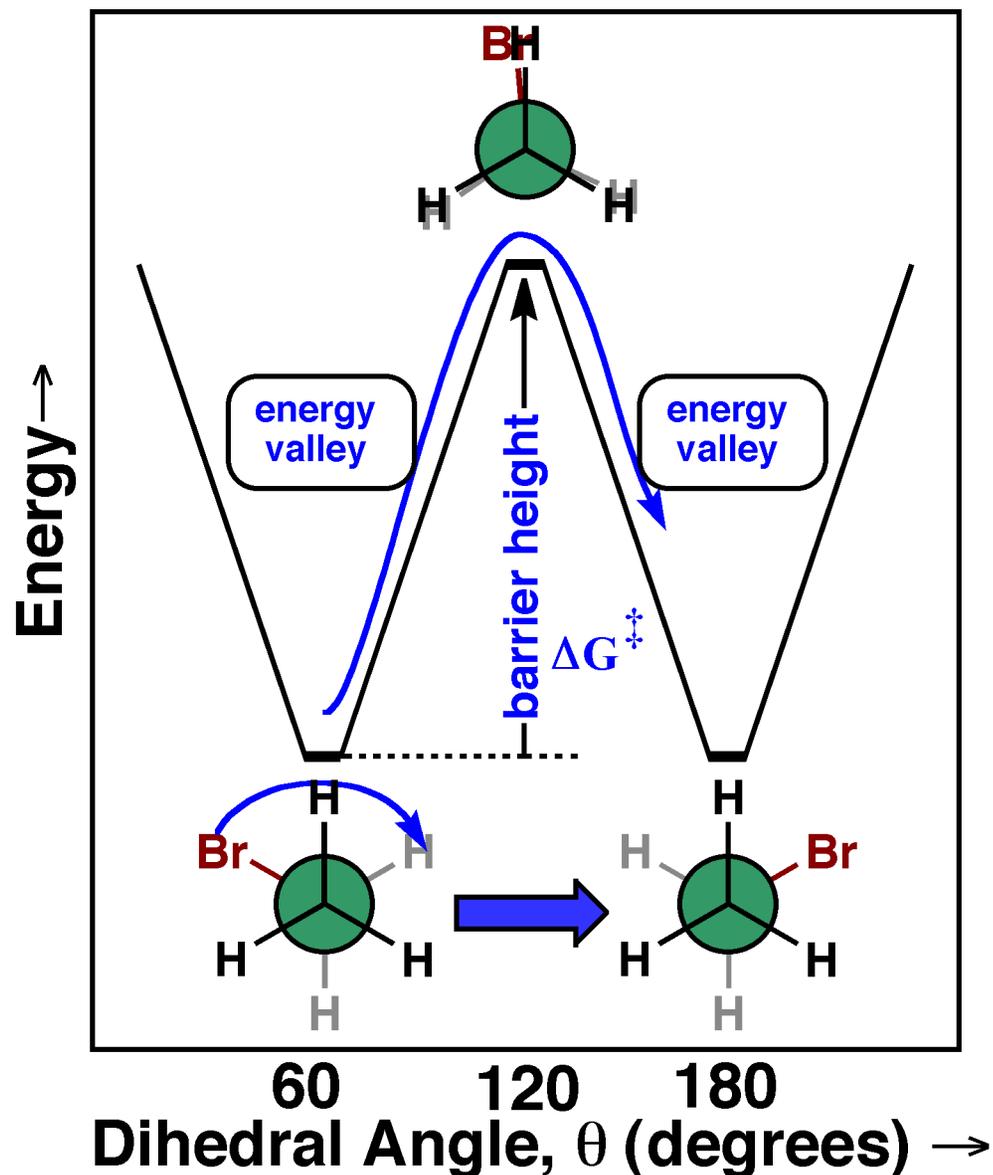
Barrier Height and Half-Life

The rate coefficient, k, describes how fast a molecule passes from one energy valley to the next. The rate coefficient is proportional to the number of times per second that a molecule crosses the barrier. Half-life, $\tau_{1/2}$, is the time it takes 50% of an initial population to escape from an energy valley. There is a quantitative relationship between barrier height, $\Delta G^{\neq}$, the rate coefficient, k, and half-life. The details of the formula are less important than an intuitive understanding of the relationships: **a larger rate coefficient means a faster process, a smaller barrier, and a shorter half-life**. The table provides some actual numbers for a process that takes place at room temperature (25 °C). The last column is the most important. It gives an approximate time scale associated with a particular barrier height. For instance, a barrier of 20 kcal/mol results in a residence time of seconds. There's an enormous span of time scales for barriers that differ only by a few kcal/mol. Barriers in the range from 5 to 30 kcal/mol govern all processes of physiological significance.

$$k = 2.084 \times 10^{10} \cdot T \cdot e^{-(\Delta G^{\neq}/1.986T)}$$

Convention: use small k for rate constants (and capital K for equilibrium constants)

Barrier in cal·mol^{-1}

Temperature in Kelvin

A barrier ($\Delta G^{\neq}$) of 20 kcal·mol^{-1} corresponds to an interconversion rate (k) of 1.3×10^{-2} s^{-1} at 25 °C (i.e., a half-life of ca. 1 min.).

Relationship between barrier height, rate coefficient and half life at 25 °C.

Barrier Height $\Delta G^{\neq}$ (kcal/mol)	Rate Coefficient, k (sec^{-1})	Half-life, $\tau_{1/2}$ (sec)	Time scale
5	1.3×10^{9}	5.2×10^{-10}	nanoseconds
10	2.8×10^{5}	2.4×10^{-6}	microseconds
20	1.3×10^{-2}	53	seconds
30	6.0×10^{-10}	1.1×10^{9}	years

Half-life $\tau_{1/2}$: the time it takes for 50% of the molecules to cross the barrier
$$\tau_{1/2} = \ln 2 / k$$