

Quick Guide to Energy Calculations

Thermochemistry – the relationship between molecular structure and energy

Equilibria. One of the simplest thermochemical questions we can ask about a chemical equation is, “is this reaction favorable as drawn?” As you know, this question has a quantitative answer. The favorability of a chemical reaction is related to its equilibrium constant, K_{eq} , and its standard free energy of reaction, ΔG° . These quantities are interchangeable because $K_{eq} = \exp(-\Delta G^\circ/RT)$ and $\Delta G^\circ = -RT \ln K_{eq}$

Favorable	$K_{eq} > 1$	$\Delta G^\circ < 0$
Unfavorable	$K_{eq} < 1$	$\Delta G^\circ > 0$

If we want to make sense of the relationship between structure and energy, it is helpful to break the free energy into two components, enthalpy and entropy. These are related by

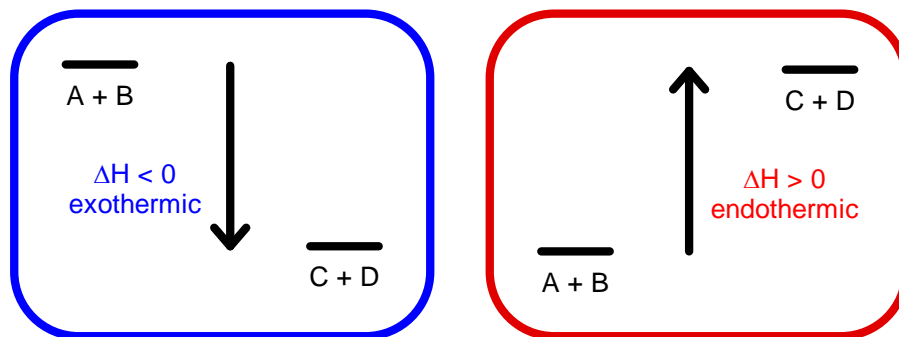
$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$$

From this, we see that a reaction might be favorable if it is exothermic ($\Delta H^\circ < 0$) or if the reaction leads to a large increase in entropy ($\Delta S^\circ > 0$). Sometimes these quantities work together, but not always. A bimolecular Diels-Alder reaction is exothermic, but it is accompanied by a large decrease in entropy ($\Delta S^\circ < 0$) because two reactant molecules must combine to form a single product molecule.

Enthalpy. The heat of reaction (or reaction enthalpy) is defined as the difference in the enthalpy of the products and the enthalpy of reactants. For example, if we have a reaction $A + B \rightarrow C + D$, the reaction enthalpy is given by:

$$\Delta H^\circ = (H_C + H_D) - (H_A + H_B)$$

Thus, an exothermic reaction is one in which the product enthalpy is lower than the reactant enthalpy. An endothermic reaction features the reverse relationship.



The relationship between enthalpy and structure is easy to understand. Strong bonds, resonance stabilization, low strain, low steric hindrance, and favorable electrostatic interactions, all lower a

molecule's enthalpy. Therefore, exothermic reactions tend to be those that replace weak bonds with stronger ones, increase resonance stabilization, reduce strain, and so on.

Entropy. The entropy of reaction is defined in a completely analogous way as the difference in the entropy of the products and the entropy of the reactants:

$$\Delta S^{\circ} = (S_C + S_D) - (S_A + S_B)$$

The relationship between entropy and structure is not so transparent, however. Entropy is fundamentally related to the number of ways a molecule can store energy. The more ways in which a molecule can store its energy, the higher its entropy.

Chemists find it helpful to divide entropy into three components: translational (S_{trans}), rotational (S_{rot}) and vibrational (S_{vib}). It is beyond the scope of this class to analyze the formulas for these components, but the formulas are derived in Chem 332, Statistical Thermodynamics. More important to us is the fact that molecular modeling programs like *Spartan* can calculate these entropies for us. We will look at some entropy values elsewhere.

Energy calculations. Molecular modeling programs contain a number of tools¹ for calculating molecular energies. Every tool employs approximations of some sort (that's why we call these *models!*) but a detailed explanation of these approximations would take us far off track, so I will just cover the high points.

1. Approximations are introduced to make calculations more convenient. "Convenient" means the calculations can be done more rapidly, or on smaller less expensive computers, or both. Generally speaking, more convenience requires more approximations.
2. It is convenient to separate the motions of nuclei from the motions of electrons. This approximation normally does not cause significant problems because nuclear masses are thousands of times greater than the electron mass and nuclei move correspondingly slowly. However, separating these motions means you must 1) choose a geometry, i.e., position the nuclei in space, and then 2) calculate how the electrons move around those nuclei. This raises two questions: Which geometry is best? And, if the nuclei are frozen in place, how do we calculate their kinetic energy? Both questions are answered below.
3. It is convenient to partition the molecule's energy into the following components:
 - a. **Electronic energy, E_{elec} .** This is the sum of the electron kinetic energies and potential energies. The former are due to electron motions. The latter are due to electrostatic interactions between charged particles, electrons with electrons and electrons with nuclei. $E_{\text{elec}} = 0$ corresponds to a set of motionless electrons that are

¹ "Tool" is a good word, but it is not the one that chemists use routinely. Computational chemists refer to an energy-calculating tool instead as a *method*, a *level of theory*, or a *model*. The last term is unfortunate because we also refer to the molecular systems that we build as *models*. This leads to confusing discussions in which we talk about different "models" (energies, wave functions) of a "model" (molecular system).

separated from each other by an infinite distance. $E_{\text{elec}} \ll 0$ for any atom, ion, or molecule.

- b. **Total energy, E_{tot} .** This is the sum of the electronic energy (see above) and the potential energy of the nuclei that is due to electrostatic interactions between nuclei. The latter are fixed by the molecular geometry, so we can associate a particular total energy with each geometry. $E_{\text{tot}} = 0$ corresponds to a set of motionless electrons and nuclei that are separated from each other by an infinite distance. $E_{\text{tot}} \ll 0$ for any atom, ion, or molecule.
- c. **$E(0 \text{ K})$.** This is the sum of E_{tot} and the “zero-point energy” (ZPE). The latter is the kinetic energy of the nuclei at 0 K and is due to molecular vibrations.
- d. **$E(298 \text{ K})$.** This is the sum of $E(0 \text{ K})$ and additional contributions to the kinetic energy of the nuclei. As we warm a molecule from 0 K to 298 K, the nuclei, and the entire molecule, begin to move around (translate, rotate, vibrate) more and increase the molecule’s energy.
- e. **$H(298 \text{ K})$.** This is the sum of $E(298 \text{ K})$ and PV (work done by moving gas phase molecules). For one mole of an ideal gas, $PV = RT$ so we usually write $H(298 \text{ K}) = E(298 \text{ K}) + RT = E(298 \text{ K}) + 0.6 \text{ kcal/mol}$.
- f. The magnitude of these different contributions to the molecular energy can be seen in the following chart.

E_{elec}	-53619.36 kcal/mol
+ PE_{nn}	5756.97
E_{tot}	-47862.39
+ ZPE	13.60
$E(0 \text{ K})$	-47848.79
+ $E(0 \rightarrow 298)_{\text{trans}}$	0.89
+ $E(0 \rightarrow 298)_{\text{rot}}$	0.89
+ $E(0 \rightarrow 298)_{\text{vib}}$	<0.01
$E(298 \text{ K})$	-47847.01
+ RT	0.59
$H(298 \text{ K})$	-47846.42 kcal/mol

The electronic and total energy (E_{elec} & E_{tot}) are exquisitely sensitive to molecular geometry. The zero-point energy (ZPE) is much less sensitive, and the other terms hardly respond to geometry at all. Since the calculation of ZPE is very time-consuming, *casual* modeling exercises tend to ignore everything beyond E_{tot} .

4. Although I cannot easily explain *how* the electronic energy (E_{elec}) is calculated, it is helpful to explain a few concepts that are related to its calculation (going from E_{elec} to E_{tot} involves only a trivial application of Coulomb’s Law).

- Quantum mechanics-based tools obtain E_{elec} by treating the electrons as if they move like waves and then constructing a model wave function to describe all of the electrons that are present. The “shape” of this model wave function, which depends on molecular geometry, charge, and number of unpaired electrons, determines E_{elec} .
- Model wave functions can be constructed in many ways. A model is essentially a set of mathematical constraints on electron (wave) motion that make the energy calculations convenient. The constraints say to the electrons, in effect, “you must limit your behavior to such-and-such so that I can calculate your energy easily.” We regard the result as a model because, in fact, no such limitations actually exist and actual electron behavior may be slightly, or even substantially, different from the constrained version that appears in our model.
- The number of constraints that might be imposed is highly flexible. One chemist might impose a large number of constraints in order to calculate E_{elec} rapidly, while another might impose only a few constraints so that the results are more realistic. The following chart shows some options.

Tool	Examples	Degree of Approximation	E_{elec} or ΔH_f
<i>ab initio</i>	correlated methods or post-HF (MP2, DFT, CCSD)	no drastic constraints, but basis set handicap	E_{elec}
	Hartree-Fock (HF)	one drastic constraint & basis set handicap	E_{elec}
semi-empirical	AM1, PM3, RM1	many constraints, all drastic	ΔH_f

“Low level” semi-empirical tools impose such incredibly drastic constraints that it is pointless (and needlessly time-consuming) to calculate E_{elec} . Therefore, these tools employ clever empirical formulas to convert the model “wave function” directly into a model “heat of formation” (ΔH_f). Since ΔH_f is a kind of enthalpy, it already contains contributions from nuclear kinetic energy and no further corrections are needed.

“High level” *ab initio* tools do not use empirical tricks to correct E_{elec} (*ab initio* means “from scratch”). However, different approximations can be employed within the *ab initio* category. Hartree-Fock (HF) models impose at least one drastic constraint on electron behavior. Post-HF do not. Also, the performance of *ab initio* models always depends on the number and nature of basis set² functions used to construct the model.

² A *basis set* is a set of mathematical functions or “building blocks” that get combined to make a model wave function. You can think of the size of the basis set as an extra handicap that is imposed on the basic model. If the

- d. Ultimately, it isn't so important which tool you use as long as the tool produces similar errors for all molecules. A meaningful reaction enthalpy can be obtained if errors in the product energies are *matched* by errors in the reactant energies, i.e., if the errors “cancel.”
 - e. Error cancellation is possible only when one uses the same tool for all of the molecules. (In the case of *ab initio* tools, we must also use the same basis set for all of the molecules.)
5. Because E_{elec} (and ΔH_f) depend on molecular geometry, it is important to choose the correct geometry for each molecule. The rules are these:
- a. Build a separate model of each molecule, reactant or product. Do not build a “complex” containing two or more molecules.
 - b. Perform an *equilibrium geometry* calculation on each model. Use the energy of the *equilibrium geometry* (a.k.a, optimized geometry, minimum-energy geometry) model for reaction enthalpy calculations (see above).³
 - c. Start your *equilibrium geometry* calculation from the lowest energy conformation. Equilibrium geometry calculations perform a trial-and-error search through different geometries and give a result that we call a “local” minimum, i.e., the minimum-energy geometry closest to your starting point. If you want the very best final geometry (and you do!), you must make sure the starting point is not too far off from your desired target. I recommend that you always clean up your model geometry by pressing the **Minimize** icon *before* commencing the *equilibrium geometry* calculation.
 - d. An *equilibrium geometry* calculation may occasionally fail by “running out of cycles”. This is a fail-safe mechanism written into *Spartan* by the computer programmers to end a geometry search after a certain number of steps. It protects the computer (and the chemist) from getting involved in an endless loop of trial-and-error. If your search ends with a “ran out of cycles” error, look at the result. If it looks reasonable, re-submit the calculation and keep searching. If it doesn't look reasonable, something went wrong and you can thank the computer for telling you about it sooner rather than later.

basis set is small (few building blocks), the handicaps will be more severe and the model won't perform as well as it might. A larger basis set allows a model to fulfill its potential, but a larger basis set cannot erase any fundamental constraints imposed by the model. Computational chemists learn from experience which basis sets might be suitable for a given calculation, much like a bench chemist learns which solvent might be suitable for a given reaction.

³ This energy will be displayed in the Molecular Properties window (select **Display: Properties**) and at the end of the equilibrium geometry output (select **Display: Output** and scroll down).