

7.2: Background

A powerful piece of information for understanding what will happen during a chemical reaction is the standard Gibbs free energy change of reaction (ΔG°). This single quantity dictates the extent to which a reaction will proceed starting from pure reactants and no products. For example, a negative value of ΔG° indicates a spontaneous reaction will convert a majority of starting reactants into products (we say this reaction favors the products). Conversely, a positive value of ΔG° indicates that the reaction will favor the reactants and will result in a final mixture which contains more reactants than products. A change in Standard Gibbs free energy close to zero indicates that a reaction that doesn't favor reactants or products; starting this reaction with pure reactants will end up with a 50/50 mixture of products and reactants.

Table 1. The relationship between reaction spontaneity and ΔG°

ΔG°	Reaction Favors
Positive	Reactants, Nonspontaneous
Negative	Products, Spontaneous
Zero	Neither Reactants nor Products

The change in Gibbs free energy (ΔG°) is related to both the change in enthalpy (ΔH°), which measures heat given off in a reaction at constant pressure, and the change in entropy of the reaction (ΔS°) which measures a change in order (Equation 7.2.1).

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (7.2.1)$$

To estimate the change in Gibbs free energy of a reaction we need information about both the ΔH° and ΔS° of the reaction. ΔH° is in large part determined by breaking or forming of bonds or intermolecular forces. Since intermolecular forces tend to be weaker than bonds, it's typical to ignore them (unless a phase change occurs!). The enthalpy from breaking or forming bonds can be estimated by subtracting the sum of the bond dissociation enthalpy (BDE) values of bonds formed from the sum of the bonds broken (Equation 7.2.2). Generic BDE's are published tabular form in a variety of sources.⁴

$$\Delta H^\circ \approx (\text{Sum of BDE of Bonds Broken}) - (\text{Sum of BDE of Bonds Formed}) \quad (7.2.2)$$

The value for the change in entropy, ΔS° , of a reaction is more difficult to estimate. A useful approximation is that, for a gas phase reaction, the change in entropy is determined by the change in the number of gas particles. If a reactant has the same number of moles of gas on both sides of the reaction, $\Delta S^\circ \approx 0$. From this, you may directly estimate the ΔG° of a reaction, $\Delta G^\circ \approx \Delta H^\circ$. All of our computations today will be performed for gas phase reactions, so every separate particle must be counted to determine if the entropy change is zero.

A.	B.
Change in Particles	ΔS°
More in Products	Positive
More in Reactants	Negative
None	Zero
	$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$
	$\Delta G^\circ \approx \Delta H^\circ - T \cdot 0$
	$\Delta G^\circ \approx \Delta H^\circ$

Figure 1. A. The relationship between the change in the number of particles and the ΔS° of the reaction. B. In the special case where the ΔS° of a reaction ≈ 0 the $\Delta G^\circ \approx \Delta H^\circ$

The proportion of products and reactants at equilibrium is determined by the ΔG° for a reaction, but this value has no bearing on how quickly a reaction progresses. Instead, the energy which influences the rate at which a reaction goes forward is called the energy barrier. The energy barrier associated with going from reactants to the transition state is referred to as ΔG^\ddagger (read as delta G double dagger). ΔG^\ddagger can be thought of as the free energy difference between the reactants and the transition state. The transition state of a reaction corresponds to a point during the reaction with the highest free energy. A transition state typically has a structure where bonds being made or broken during the reaction step are partially formed. Note that the transition state is the same arrangement of atoms whether the reaction is going forward or backwards, but the energy is different because it is always measured

with respect to the starting point for a given direction. Thus, if the products are downhill in energy from the reactants, there is a larger ΔG^\ddagger for the reverse reaction than there was for the forward reaction.

The energy of the transition state, when compared to the starting materials and products (or intermediates), can tell us valuable information about its structure. Specifically, Hammond's postulate states that the transition state of a reaction resembles the structure of the reactant, or product to which it is closer in energy. This means that if a reaction step is endergonic ($\Delta G^\circ > 0$) the transition state will look like the products more than the reactants. Conversely, if a reaction step is exergonic ($\Delta G^\circ < 0$), the transition state will more closely resemble the structure of the starting materials. When plotted versus reaction progress, the energies of starting materials, transition state(s), intermediate(s), and products are known as a reaction coordinate diagram.

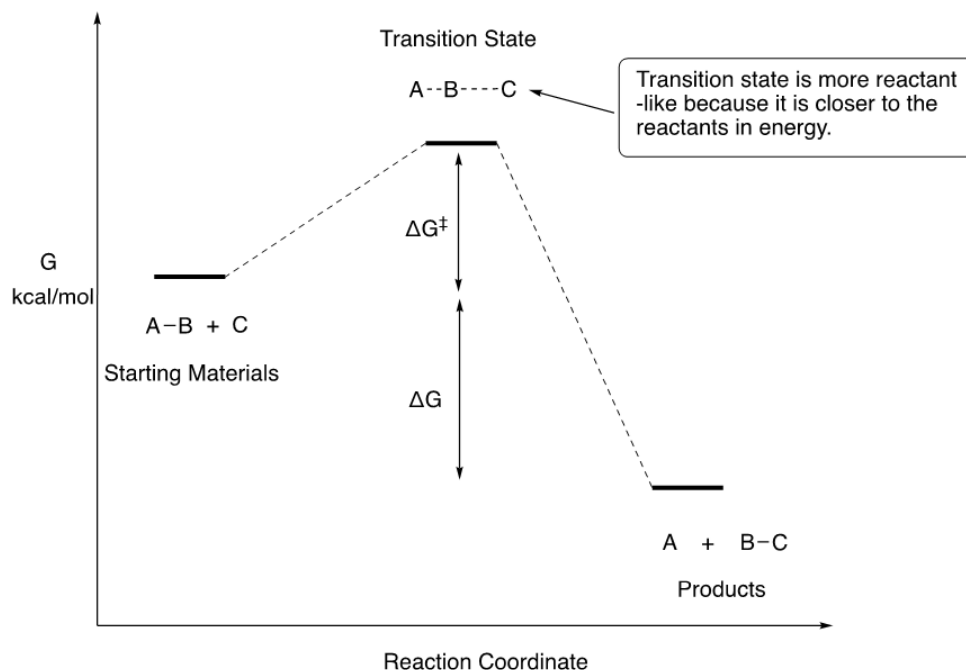


Figure 2. Example reaction coordinate diagram of a generic concerted substitution reaction. The value of ΔG° informs us as to the position of the equilibrium between the reactants and the products while the value of ΔG^\ddagger indicates how quickly the reaction will reach equilibrium.

In the computational exercise that follows you will learn to use Orca to calculate both the thermodynamic (ΔG° , ΔH° , ΔS°) and kinetic (ΔG^\ddagger) values of a simple substitution reaction.

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