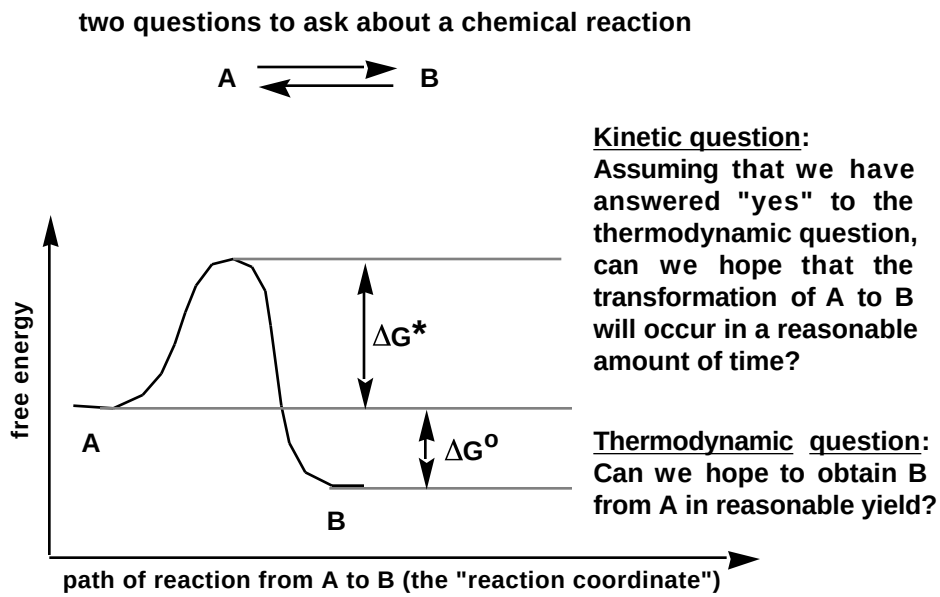
Text Related to Segment 9.01 ©2002 Claude E. Wintner

In preparing to deal with our central concern — a consideration of the chemical transformations undergone by organic molecules — we must develop a framework that allows discussion of chemical reactions in terms of energy. For an equilibrium involving molecules A (reactant) and B (product) we are interested in answering two central questions:

1. Given reactant A, does its free energy, relative to that of product B, allow us to hope that the transformation A $\rightarrow$ B will take place in a reasonable yield? This generally is referred to as a question of *thermodynamics,* framed in terms of the standard free energy of reaction function ΔG°.
2. If the answer to question 1 is "yes," then: Is the activation energy barrier separating A and B low enough to allow us to hope that the transformation A $\rightarrow$ B will take place within a reasonable amount of time? This generally is referred to as a question of *kinetics,* framed in terms of the free energy of activation function ΔG^{*}.

While these are extremely complex multidimensional problems, chemists are nonetheless accustomed to sum them up in simple two-dimensional diagrams:



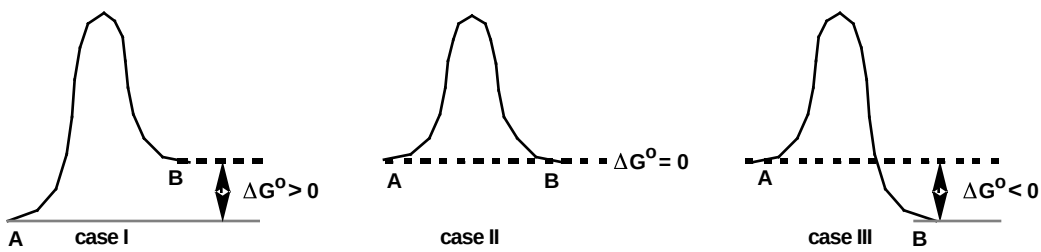
In answering the first question we take as our point of departure the fundamental relationship between the standard free energy of reaction ΔG° and the equilibrium constant K_{eq}, modifying the equation to suit our present needs, as in the next figure, so that it is expressed in the form: $\Delta G^\circ = -1.4 \log K_{eq}$ kcal/mole at room temperature. The three general cases shown for the relative positions of the free energies of product B and reactant A are the familiar ones of reactions that are unfavorable, or going "uphill" in free energy (case I, ΔG° is positive); reactions where the reactant and the product have the same energy, that is, are identical (case II, $\Delta G^\circ = 0$); and reactions that are favorable, or going "downhill" in free energy (case III, ΔG° is negative). We then construct a chart to relate the percent yield of the reaction at room temperature to ΔG°. From left to right the chart moves from a few heuristically chosen cases for the free energy change of the reaction, to the logarithms of the corresponding equilibrium constants as calculated from the equation, to the equilibrium constants themselves, and finally — remembering that $K_{eq} = ([B]/[A])$ at equilibrium — to the percent yield of product at room temperature.

$$\Delta G^o = - RT \ln K_{eq}$$

At room temperature:

$$\Delta G^o = \frac{-2 \text{ cal}}{\cancel{\text{degree}} \text{ mole}} \times 300 \cancel{\text{degree}} \times 2.3 \log K_{eq}$$

$$\Delta G^o = -1.4 \log K_{eq} \text{ kcal/mole}$$



	ΔG^o kcal/mole	log K_{eq}	K_{eq}	$\left(\frac{[B]}{[A]}\right)_{eq}$	% yield B at room temp
case I	+4.2	-3	0.001	$\frac{1}{1,000}$	0.1
	+2.8	-2	0.01	$\frac{1}{100}$	1
	+1.4	-1	0.1	$\frac{1}{10}$	9
case II	0	0	1	$\frac{1}{1}$	50
case III	-1.4	+1	10	$\frac{10}{1}$	91
	-2.8	+2	100	$\frac{100}{1}$	99
	-4.2	+3	1000	$\frac{1000}{1}$	99.9

relationship between ΔG^o and yield of reaction

The quantitative conclusion perhaps is less familiar than are the qualitative concepts of unfavorable and favorable, or "uphill" and "downhill" reactions: it is immediately clear from the chart that we are, in fact, at the mercy of some relatively small numbers when we consider ΔG° in the critical region around $\Delta G^\circ = 0$. We can be thrown from a 99% yield to a 1% yield by an alteration of just 5.6 kcal/mole in

ΔG°. By the same token, in other circumstances the same 5.6 kcal/mole will change a theoretical yield from 99.9999% to 99%, hardly a matter of concern when isolation techniques may be inadequate to isolate, say, more than 98% of the product in any case, or from 1% to 0.0001%, again probably a situation of little practical significance. In particular, it should be remembered that a quantity such as 5.6 kcal/mole is minuscule in the arena of the hundreds of kcal/mole of total bond energy in an organic molecule with many bonds. Small wonder, then, that a question of the sort: "Why does a reaction give X and not Y?" may be, in practice, *extremely* difficult to answer, depending as it may on very small differences among very large numbers.