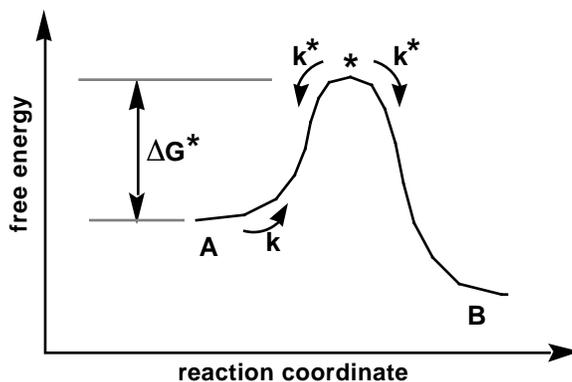


Text Related to Segment 9.02 ©2002 Claude E. Wintner

Turning now to the second, kinetic, question we assume that, in moving along the reaction coordinate to establish equilibrium between A and B, a transition state (*) lying at an energy higher than either A or B, and at energy G^* higher than A, must be traversed. Furthermore, we assume that there is an equilibrium between A and * (and between B and *):



The rate constant for molecules of A being transformed to * is k . In thinking about the reverse direction, the important postulate is made that (at a given temperature) molecules are leaving the transition state in all directions with a single universal rate constant k^* . It will be apparent from the figure that a reaction going from * in any direction has a zero activation energy barrier. Thus, we might expect intuitively, and we shall see the intuition confirmed below, that k^* should be the greatest rate constant physically possible. (The foregoing statement needs to be amplified to be strictly correct: k^* should be the greatest rate constant possible for a "normal" reaction occurring in the aggregate, such as in solution. For example, reactions carried out using molecular beams at low pressure in the gas phase do not fall under this theoretical treatment.) Less intuitively, and not justified here (except from the point of view of the units, which are consistent), theory evaluates k^*

quantitatively as the product of Boltzmann's constant and the absolute temperature, divided by Planck's constant, so that $k^* = 6 \times 10^{12} \text{ sec}^{-1}$:

$$k^* = \frac{k_{\text{Boltzmann}} T}{h_{\text{Planck}}}$$

At room temperature:

$$k^* = \frac{1.4 \times 10^{-16} \text{ erg degree}^{-1} \times 300 \text{ degree}}{6.6 \times 10^{-27} \text{ erg sec}}$$

$$k^* = 6 \times 10^{12} \text{ sec}^{-1}$$

At steady state: $k [A] = k^* [*]$

We now relate G^* to K^* , defined as $K^* = \frac{[*]}{[A]}$. We use the fact that as a result of the assumption of equilibrium between A and * we can say that $k [A] = k^* [*]$, and we end with an equation of the form: $G^* = -1.4 \log k + 18 \text{ kcal/mole}$ at room temperature:

$$\Delta G^* = -RT \ln K^* = -RT \ln \frac{[*]}{[A]} = -RT \ln \frac{k}{k^*}$$

$$\Delta G^* = -RT \ln k + RT \ln k^*$$

At room temperature:

$$\Delta G^* = -1.4 \log k + 1.4 \log (6 \times 10^{12}) \text{ kcal/mole}$$

$$\Delta G^* = -1.4 \log k + 18 \text{ kcal/mole}$$

relationship between ΔG^* and rate of reaction

From this relationship it is clear that as the activation energy barrier G^* increases, the rate constant must decrease (slower reaction), and that as G^* decreases, the rate constant must increase (faster reaction). Because of the logarithmic relationship, for each decrease of 1.4 kcal/mole in G^* the rate increases by a factor of 10. Furthermore, since $G^* = -RT \ln k + RT \ln k^*$, it must be true that

when G^* decreases to zero (no activation energy barrier), then $k = k^*$, so that our intuition that k^* should be the greatest rate constant possible (for "normal" reactions) is confirmed. Indeed, rate constants of the order of 10^{12} sec^{-1} are the fastest that have been observed experimentally for reactions obeying the assumptions made in the development of this equation.

Again, from a practical point of view we wish to relate the derived equation to what we want to know — in this case, how long we must expect to have to wait before equilibrium between A and B will be established, starting with pure A. To avoid dealing with an equivalent of one of Zeno's paradoxes, in which a body in motion never can reach its goal because it gets only half-way, and then only half-way, and so on, ad infinitum, we can avoid the entire issue of when a reaction is "complete" by considering the half-life of the (first-order) reaction, $t_{1/2} = (\ln 2)/k = 0.693/k$, which is the time needed for the reaction to be half completed. In the following brief analysis it is quite sufficient to make the simplifying approximation $0.693 \approx 1$, so that $t_{1/2} \approx 1/k$. Suppose we are interested in a reaction that will have a half-life of the order of a day ($\approx 10^5 \text{ sec}$) at room temperature. Then $k \approx 10^{-5} \text{ sec}^{-1}$. Plugging this value into our equation gives an activation energy barrier $G^* \approx 25 \text{ kcal/mole}$, a value which conforms well with general experience for reactions having this half-life:

If $k = 10^{-5} \text{ sec}^{-1}$ (half-life ≈ 1 day):

$$\Delta G^* = -1.4(-5) + 18 = 25 \text{ kcal/mole}$$

On the other hand, if the half-life is, for example, of the order of 10^{-5} sec , then $k \approx 10^5 \text{ sec}^{-1}$, and $G^* \approx 11 \text{ kcal/mole}$; in fact, the barriers for many conformational changes are found in this general region:

If $k = 10^5 \text{ sec}^{-1}$ (half-life $\approx 10^5 \text{ sec}$):

$$\Delta G^* = -1.4 (5) + 18 = 11 \text{ kcal/mole}$$

As in our discussion of G° , we can discern that it may be difficult to estimate G^* — once again likely to be a relatively small number among much larger ones — for any given reaction without direct experimental evidence. Furthermore, as already has been mentioned, small changes in G^* will lead to changes in rate that can have profound practical consequences. Barring any change in the temperature of a reaction, a change of just 4.2 (3×1.4) kcal/mole in G^* will change its rate by a factor of 10^3 . We can wait a day, but not necessarily a thousand days, for a result. Finally, the difference between a waiting time of a hundred days and one of 10^{12} days (of the order of the age of the earth) could be a matter of just 14 kcal/mole!

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