

Advanced Statistical Physics II – Problem Sheet 10

Problem 1 – Rate constant



The equilibrium rate constant K is defined as the ratio of the “backward” rate k' and the “forward” rate k , i.e. $K = k'/k$.

- a) (1P) Relate the ratio of the steady state concentrations c_A and c_B to the reaction rate constant.
- b) (2P) Consider a one-dimensional potential energy landscape, where states A and B correspond to local minima with energies U_A and U_B , respectively, and are separated by a barrier of height $U_{AB} > U_A, U_B$. Using Kramer’s formula, derive an expression for the forward and backward rates and for the equilibrium rate constant. Compare your result with the result derived in the lecture.

Problem 2 – Autocatalysis

Consider the autocatalytic reaction



of two chemical substances A and B . The chemical kinetics equation for this reaction is:

$$\dot{c}_B(t) = kc_A^2(t) - k'c_A(t)c_B(t) \quad (3)$$

Here, c_A and c_B are the concentrations of the two substances A and B , respectively.

- a) (2P) Assume, that no particles can enter or leave the system, such that the sum of the masses of both substances is conserved. Show that in this case, there are two stationary states, c_{B1} and c_{B2} , for the concentration of substance B.
- b) (3P) Solve equation (3) for the initial condition $c_B(t = t_0) = c_{B0}$. *Hint:* First show, that (3) can be written as

$$\int_{c_{B0}}^{c_B} \frac{d\tilde{y}}{(\tilde{y} - c_{B1})(\tilde{y} - c_{B2})} = (k' + k) \int_{t_0}^t d\tilde{t} \quad (4)$$

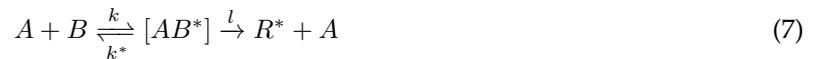
Result:

$$c_B(t) = c_{B2} + \frac{c_{B1} - c_{B2}}{1 - \frac{c_{B0} - c_{B1}}{c_{B0} - c_{B2}} e^{(t-t_0)(c_{B1} - c_{B2})(k' + k)}} \quad (5)$$

- c) (2P) Take the limit $t \rightarrow \infty$. Which initial values c_{B0} lead to the stationary state c_{B1} or c_{B2} ? How can this be interpreted?

Problem 3 – Kinetic proofreading

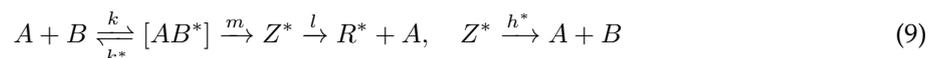
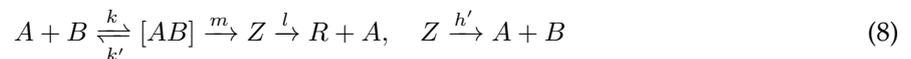
Consider the following two-step reactions



The first equation may model a process where an enzyme A recognizes a particular biomolecule B by binding to it. The intermediate product $[AB]$ then irreversibly reacts to the final product R . However a similar reaction may also occur which leads to the wrong final product R^* . This process is modelled by the second equation. Note that in the first step, the forward rates k are the same for both reactions, while the backward rates differ.

a) (5P) Assuming that the rate l is small compared to the other rates (and thus the concentrations of molecules A and B remain constant for the time period under consideration), calculate the error rate $f_0 := c_{R^*}/c_R$.

b) (5P) Now consider modified reactions in which an additional intermediate product Z (Z^*) is formed. It can again dissociate into the educts A and B however not into its precursor $[AB]$ ($[AB^*]$), thereby forming a “ratchet”.



Assuming that l and m are small compared to the other rates and $\frac{h'}{h^*} \approx \frac{k'}{k^*}$, calculate the error rate $f := c_{R^*}/c_R$ of the modified reaction: Show that $f = f_0^2$ and thus that the error is drastically reduced. This reduction is the main purpose of kinetic proofreading mechanism employed by nature for DNA replication and transcription [1].

References

- [1] J. J. Hopfield. Kinetic proofreading: A new mechanism for reducing errors in biosynthetic processes requiring high specificity. *Proceedings of the National Academy of Sciences*, 71(10):4135–4139, 1974.