

- *Учебно съдържание, планове и програми* •
- *Curriculum Matters* •

# THE INFLUENCE OF THE VALUE OF EQUILIBRIUM CONSTANT ON THE CONCENTRATION DISTRIBUTION OF REACTING SPECIES IN REVERSIBLE REACTIONS

Nicolay V. TSAREVSKY,  
Carnegie Mellon University, Pittsburgh, PA

---

**Abstract.** The way to derive simple mathematical relations showing of the extent of reversible chemical reactions upon the value of the equilibrium constant and the initial concentrations of the reagents is presented. Both dilution-independent (such as the substitution  $AB + C = AC + B$ ) and dilution-dependent (exemplified by single- and multi-step association/dissociation) equilibria are examined. The graphical representation of the mathematical dependences is shown for all studied cases. The influence that the different parameters in the equations have on the concentration distributions is illustrated by these parameters' systematic variation.

---

## Introduction

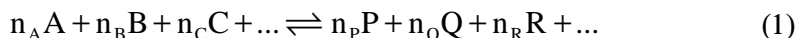
The vast majority of chemical reactions are reversible, with values of the equilibrium constant ranging broadly from less than  $10^{-6}$ , in which case it is usually said that no reaction takes place, to more than  $10^6$ , in which case the reaction is termed “practically irreversible”. The reasons for this “scientific slang” terminology will become apparent from the following text. Due to the impor-

tance of the chemical equilibria, mathematical problems related to them are essentially always included in competitions, Olympiads or other chemistry exams. Most of these problems require the calculation of equilibrium constants at given (not necessarily explicitly) equilibrium concentrations of the reacting species, or of the concentration(s) of certain compound(s) of interest. It is our impression, however, that most students cannot "feel" the impact that the equilibrium constant has on the distribution of the various species in a given reaction system. It has been suggested [1] that derivation of mathematical relations and especially their graphical representation are very important for the clear understanding of various phenomena included in chemistry textbooks.

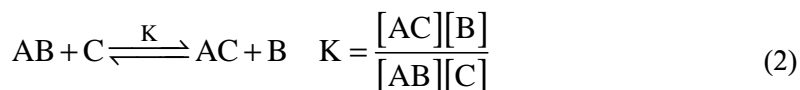
It is the purpose of this work to present in a simple and lucid way some unsophisticated mathematical dependencies related to reversible reactions. For educational purposes the numeric values in the examples illustrating the mathematical formulas are given in several different formats (e.g., a concentration of certain compound can variably be expressed as 0.05 M,  $5 \times 10^{-2}$  M, or 50 mM) — a simple but useful "brain exercise" for the students [2]. Numerous additional interesting examples are provided by Butler [3] in his thorough monograph.

### Dilution- or concentration-independent equilibria

The concentration distribution of reactants in a reversible reaction always depends upon the value of the equilibrium constant and the initial molar ratio of the reacting species. In some cases, which will be presented in the next section, the distribution depends also upon the total concentration of the reagents and can change upon mere dilution (or concentration by, say, solvent evaporation) of the system. If the sum  $n_A + n_B + n_C + \dots$  equals the sum  $n_P + n_Q + n_R + \dots$ , the equilibrium (1) is dilution- or total concentration-independent.



In this first section, attention is paid to the simplest case of concentration-independent equilibria. The substitution equilibrium (2) is firstly examined. The equilibrium concentrations of reacting species (AB, C, AC, and B) do not depend upon dilution (as will be demonstrated) which makes the description of such systems very simple.



The purpose is to determine the fraction of reacted compound C as a function of the concentration of the reagent AB. In other words, if  $n$  equivalents of AB are added to a solution of C, we need to know how much of C will be transformed to compound AC. This fraction should depend on the value of the

equilibrium constant  $K$ , which in turn changes with temperature, reaction medium, etc. Assume  $C$  (initial concentration  $[C]_0$ ) and  $AB$  (initial concentration  $[AB]_0 = n[C]_0$  with  $n$  being the number of equivalents) are mixed. In this text, the case of  $n \geq 1$  will be considered (i.e.,  $AB$  is present in excess compared to  $C$ ). Initially, no  $AC$  and  $B$  are present in the system. After the equilibrium (2) is established, the new values of the concentrations will be  $[AC] = [B] = x$ ,  $[C] = [C]_0 - x$ , and  $[AB] = [AB]_0 - x = n[C]_0 - x$ . The unknown concentration  $x$  can be found by inserting the equilibrium concentrations of the reactants into the expression for the equilibrium constant (2) and solving the quadratic equation thus obtained.

$$K = \frac{x^2}{(n[C]_0 - x)([C]_0 - x)} = \frac{x^2}{x^2 - (n+1)[C]_0 x + n[C]_0^2} \quad (3)$$

$$(K-1)x^2 - K(n+1)[C]_0 x + Kn[C]_0^2 = 0 \quad (4)$$

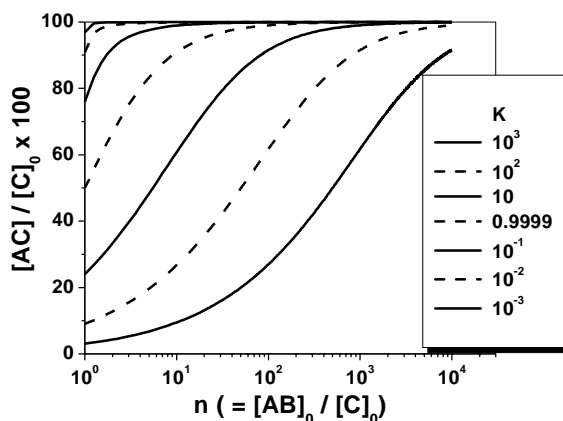
$$x_{1,2} = \frac{K(n+1)[C]_0 \pm [C]_0 \sqrt{K^2(n+1)^2 - 4(K-1)Kn}}{2(K-1)} \quad (5)$$

The root with a “plus” sign in the numerator has no physical meaning since the value of  $x$  (that is,  $[AC]$  or  $[B]$ ) can never be higher than  $[C]_0$  (recall that the reagent  $AB$  is taken in excess to  $C$ , and thus, even if compound  $C$  is completely consumed in the process, the concentrations of the products  $AC$  and  $B$  will be equal to  $[C]_0$ ). The fraction (or percent) of reacted  $C$  is given by (6).

$$\begin{aligned} \frac{[AC]}{[C]_0} (\times 100) &= \frac{[B]}{[C]_0} (\times 100) = \frac{x}{[C]_0} (\times 100) = \\ &= \frac{K(n+1) - \sqrt{K^2(n+1)^2 - 4(K-1)Kn}}{2(K-1)} (\times 100) \end{aligned} \quad (6)$$

Note that this fraction is independent of the exact concentrations of the reacting species  $AB$  and  $C$  but only depends upon the ratio in which they were mixed. This ratio ( $n = [AB]_0 / [C]_0$ ) remains constant when the reaction mixture is diluted. The dependence (6) is shown in Figure 1 for values of the equilibrium constant  $K$  covering a range of six orders of magnitude and differing from each other by a factor of 10. In real systems,  $n$  can be a number in the range from 1 to  $10^4$  or so (the initial concentration of  $AB$  can hardly be higher than 5 M and if the starting solution is relatively diluted with respect to  $C$ , for example  $[C]_0 = 0.5$  mM, the highest possible value of  $n$  is obtained as  $10^4$ ).

According to one’s intuition as well as to Figure 1, the larger the value of



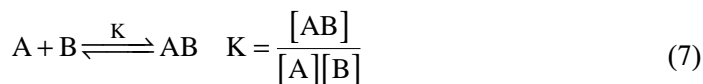
**Figure 1.** Fraction of reacted C in the equilibrium (2) as a function of the excess of the other reagent, AB, added to the reaction mixture for various values of the equilibrium constant K.

K, the easier (the lower the necessary excess of the reagent AB to C) it is to form AC. For values of K larger than 100, the addition of only 1 equivalent of AB is sufficient to “consume” more than 90% of C. On the other hand, if K is equal to about 0.01, more than 800 equivalents of AB should be added to reach the same degree of conversion of C to AC.

### **Equilibria in which equilibrium concentrations depend upon dilution or concentration of the reaction mixture**

#### *The simplest case: 1:1 stoichiometry*

The next reaction to be studied is the association / dissociation equilibrium (7) in which the substances A and B reversibly combine to form AB. Equilibria of this kind are very important and well-known examples include the formation of coordination compounds and the dissociation of weak acids.



The aim is to find the dependence of the extent of reaction upon the concentrations of the reagents A and B, and the equilibrium constant K. Assume, compounds A (initial concentration before reaction  $[A]_0$ ) and B (initial concentration  $[B]_0$ ) are mixed. After the equilibrium (7) is established, the compound AB is present in the system at a concentration, say,  $[AB] = x$ . The equilibrium concentrations of unreacted A and B will therefore be  $[A] = [A]_0 - x$  and  $[B] = [B]_0 - x$ . Let us assume that B had been added in excess to A. The extent of reaction can now be defined as the fraction or percent of reacted (i.e., bound in the form AB) compound A. In other words, the function of interest is

$[AB] / [A]_0 = x / [A]_0$  (multiplied by 100 to express the fraction in percent if needed). To determine  $x$ , one has to insert the equilibrium concentrations of all reaction mixture components into the expression for the equilibrium constant (7) and solve the obtained quadratic equation.

$$K = \frac{x}{([A]_0 - x)([B]_0 - x)} = \frac{x}{x^2 - ([A]_0 + [B]_0)x + [A]_0[B]_0} \quad (8)$$

$$Kx^2 - (K([A]_0 + [B]_0) + 1)x + K[A]_0[B]_0 = 0 \quad (9)$$

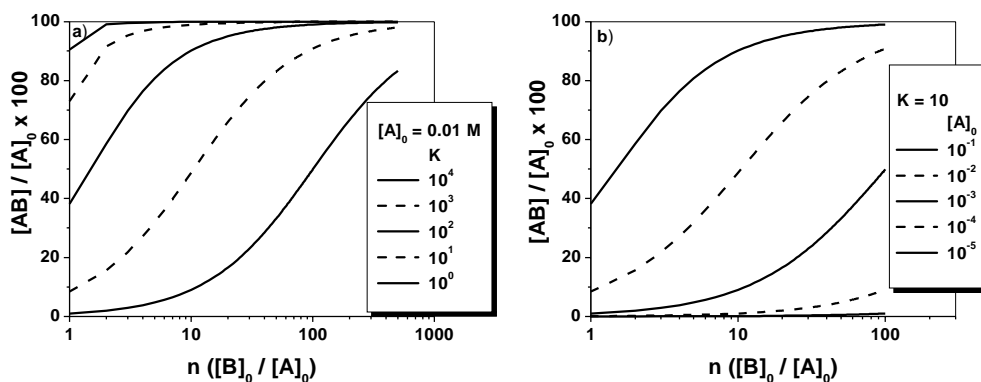
$$x_{1,2} = \frac{K([A]_0 + [B]_0) + 1 \pm \sqrt{(K([A]_0 + [B]_0) + 1)^2 - 4K^2[A]_0[B]_0}}{2K} \quad (10)$$

In equation (10), only the root with a “minus” sign in the numerator has a physical meaning, since  $x$  cannot be larger than  $[A]_0$  (recall the assumption that B is taken at concentration equal to or larger than this of A). The root with a “plus” sign is however larger than  $[A]_0$  and hence should be omitted. (In order to quickly check the validity of what was just stated, one can use  $[B]_0 = [A]_0$  and prove that the obtained  $\{2K[A]_0 + 1 + (4K[A]_0 + 1)^{1/2}\} / 2K$  is always larger than  $[A]_0$  since  $1 + (4K[A]_0 + 1)^{1/2}$  is a positive number.) Once an expression for  $x$  is available, one obtains the looked-for dependence of  $x / [A]_0$  on the concentrations of the reagents and the equilibrium constant. Often, it is convenient to use the excess of B versus A or in other terms the number of equivalents  $n$  of B relative to A in equations like (10). Using this number ( $n = [B]_0 / [A]_0$ ), and taking the meaningful root of equation (9), one obtains for the extent of reaction the following relation.

$$\begin{aligned} \frac{[AB]}{[A]_0} (\times 100) &= \frac{x}{[A]_0} (\times 100) = \\ &= \frac{K(1+n)[A]_0 + 1 - \sqrt{(K(1+n)[A]_0 + 1)^2 - 4K^2n[A]_0^2}}{2K[A]_0} (\times 100) \end{aligned} \quad (11)$$

It is important to note that the extent of the reaction depends on the concentration of the reacting compounds. Consequently, the amount of consumed compound A will change upon dilution of the reaction mixture. The dependence (11) is presented in Figure 2. In Figure 2a, the initial concentration of A is fixed at 0.01 M while the initial concentration of the other reactant, B, is being varied; the cases for equilibrium constant changing from 1 to  $10^4$  (by steps of 10) are shown. In principle (i.e., from a mathematical point of view),

the values of  $n$  can change from unity to very large numbers but it has to be born in mind that  $[B]_0$  cannot be larger than approximately 5 M, which in the case of  $[A]_0 = 0.01$  M corresponds to  $n = 500$ . Thus, in Figure 2a,  $n$  varies from 1 to 500. In Figure 2b, the equilibrium constant is kept at  $K = 10$ , and the starting concentration of A changes from  $10^{-5}$  to 0.1 M. Obviously, the realistic values of  $n$  for all presented cases range between 1 and about 100 (already a little high for  $[A]_0 = 0.1$ , since  $n = 100$  means that  $[B]_0 = 10$  M, which is high but still "acceptable").



**Figure 2.** Dependence of the extent of reaction, expressed as the fraction, in percent, of reacted A, upon the excess of added B for a) different values of  $K$  at fixed  $[A]_0 = 0.01$  M and b) variable initial concentrations of A at fixed  $K = 10$ .

It was already mentioned that often the equilibrium (7) is looked at as a reversible dissociation rather than combination reaction (in discussions concerning acidity, for instance). Therefore, it would be interesting to determine the degree of dissociation of a compound AB as a function of both its initial concentration  $[AB]_0$  and the value of the equilibrium constant  $K$ . For simplicity, the equilibrium constant will not be redefined, but it has to be remembered that the usual dissociation constants (such as  $K_a$  of acids) which can be found in handbooks equal actually  $1/K$ , if  $K$  is defined as in (7). Assume that the starting point is the dissolution of AB. The equilibrium (7) is established and the concentration of AB changes to  $[AB] = [AB]_0 - x$ . The concentrations of the newly formed components of the system A and B will be  $[A] = [B] = x$ . The degree of dissociation of AB, which has to be determined, is in fact the fraction (which again can be expressed as a percent) of dissociated AB, i.e.,  $([AB]_0 - [AB]) / [AB]_0 = x / [AB]_0$ . The concentration  $x$  can be determined in a manner similar to the one described above. The equilibrium concentrations of AB, A, and B are inserted into the expression for  $K$  (equation (7)) and a quadratic equation is then solved for the unknown  $x$ .

$$K = \frac{[AB]_0 - x}{x^2} \quad (12)$$

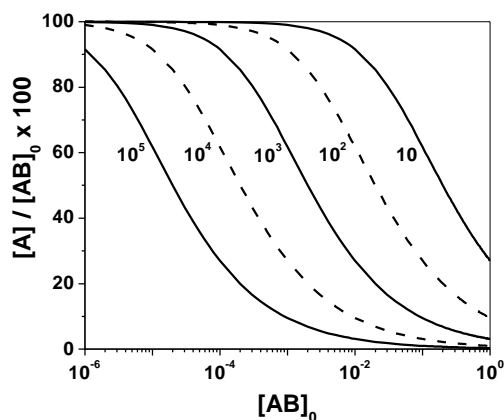
$$Kx^2 + x - [AB]_0 = 0 \quad (13)$$

$$x_{1,2} = \frac{-1 \pm \sqrt{1 + 4K[AB]_0}}{2K} \quad (14)$$

Clearly, only the root with a “plus” sign in the numerator has a physical meaning ( $x$  is a concentration and cannot be a negative number). Equation (14) yields the needed relationship between the degree of dissociation and the initial concentration of AB, and  $K$ .

$$\begin{aligned} \frac{[A]}{[AB]_0} (\times 100) &= \frac{[B]}{[AB]_0} (\times 100) = \\ &= \frac{x}{[AB]_0} (\times 100) = \frac{-1 + \sqrt{1 + 4K[AB]_0}}{2K[AB]_0} (\times 100) \end{aligned} \quad (15)$$

It is essential to remind that  $K$  is the formation, stability, or association equilibrium constant and not the instability or dissociation constant (which is equal to  $1/K$ ). The dependence (16) is shown in Figure 3 for different values of  $K$ .



**Figure 3.** Dependence of the degree of dissociation (in percent) of AB on its initial concentration  $[AB]_0$  for different values of the association equilibrium constant  $K$ , shown at each curve.

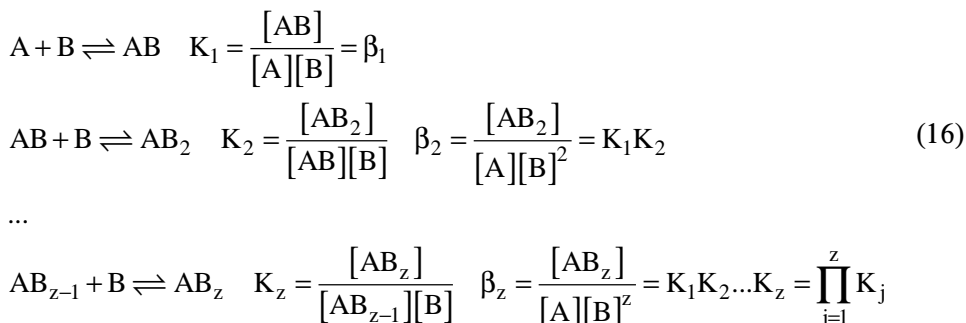
It is well known that for example weak electrolytes dissociate increasingly upon dilution. As seen from Figure 3, if the dissociation constant of such a compound is  $10^{-5}$  (corresponding to association constant of A and B equal to  $K = 1 / 10^{-5} = 10^5$ ), only around 1% is dissociated in 0.1 M solution, slightly

more than 3% at a concentration of 0.01 M, and more than 60% if the solution is diluted to  $10^{-5}$  M. Obviously, for stronger electrolytes (higher dissociation constant, meaning lower value of the association constant  $K$ ), the same degrees of dissociation can be reached in more concentrated solutions of AB. For example, if the dissociation constant is 100-fold higher than in the previous example ( $K = 10^3$ ), a little more than 60% of the compound AB will be dissociated at concentration  $[AB]_0 = 1$  mM.

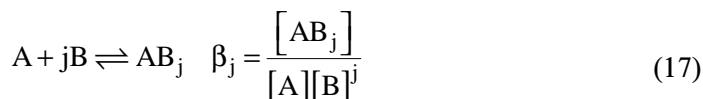
### *Stepwise processes*

Up to this point, the simplest cases were considered in which the reagents react with stoichiometric coefficients equal to one. However, a great number of more complex reactions are of interest to chemists. For example, the dissociation of weak polyprotic acids or other electrolytes, or the formation of metal complexes of the type  $AB_z$ , involve stepwise, consecutive, equilibria. The following section of this paper is dedicated to their description. Such equilibria and their graphical representation are described in many review papers and monographs [4-8].

Let us take the situation in which compound A (initial concentration  $[A]_0$ ) is mixed with B (initial concentration  $[B]_0$ ). The equilibria (16) are now established which can be characterized by two different types or sets of equilibrium constants: the stepwise or consecutive constants  $K_j$  ( $j = 1, 2, \dots, z$ ) and the overall (also known as cumulative or gross) constants  $\beta_j$  ( $j = 1, 2, \dots, z$ ), which are both defined in (16).



The overall constants  $\beta_j$  in fact define the equilibrium (17), which does not necessarily have to take place as such in the real system (where step processes occur characterized by the constants  $K_j$ ) but can rather be regarded a useful mathematical model. The two types of constants are related as shown in (16) but in some equations it is more convenient to use one or the other.



Employing equations (16) one can calculate the concentrations of the various species containing A (including that of free A) at a given starting concentration of B. The symbol  $\chi_i$  ( $i = 0, 1, 2, \dots, z$ ) is chosen to designate the fraction of A-containing compound with  $i$  attached atoms or groups of type B, i.e. the ratio of  $[AB_i]$  to the total concentration of A.

$$\chi_i = \frac{[AB_i]}{[A]_0} = \frac{[AB_i]}{[A] + [AB] + [AB_2] + \dots + [AB_z]} = \frac{[AB_i]}{[A] + \sum_{j=1}^z [AB_j]} \quad (18)$$

Since from (17)  $[AB_j]$  can be conveniently expressed as the product  $\beta_j[A][B]^j$ , (18) can be rewritten in the form (19).

$$\chi_0 = \frac{[A]}{[A]_0} = \frac{[A]}{[A] + \sum_{j=1}^z \beta_j [A][B]^j} = \frac{1}{1 + \sum_{j=1}^z \beta_j [B]^j}$$

$$\chi_1 = \frac{[AB]}{[A]_0} = \frac{[AB]}{[A] + \sum_{j=1}^z \beta_j [A][B]^j} = \frac{[AB]}{[A]} \frac{1}{1 + \sum_{j=1}^z \beta_j [B]^j} = \beta_1 [B] \frac{1}{1 + \sum_{j=1}^z \beta_j [B]^j} = \beta_1 [B] \chi_0 \quad (19)$$

...

$$\chi_z = \frac{[AB_z]}{[A]_0} = \frac{[AB_z]}{[A]} \frac{1}{1 + \sum_{j=1}^z \beta_j [B]^j} = \beta_z [B]^z \frac{1}{1 + \sum_{j=1}^z \beta_j [B]^j} = \beta_z [B]^z \chi_0$$

The fraction of A present in the form of the species  $AB_i$  ( $i = 0, 1, 2, \dots, z$ ) depends only on  $[B]$ . Note that  $[B]$  is the concentration of *free* B present in the system and *not* the total concentration of B which is given by (20).

$$[B]_{\text{tot}} = [B]_0 = [B] + [AB] + 2[AB_2] + \dots + z[AB_z] = [B] + \sum_{j=1}^z j [AB_j] \quad (20)$$

The concentration distribution of the various species present in the system can be presented graphically in two different ways. The first is based on plotting  $\chi_i$  vs. the free concentration of B (or typically, the negative logarithm of this concentration  $pB = -\log[B]$ ). Such a plot is presented in Figure 4a. Alternatively, plots of the sums of the fractions  $\chi_i$  against  $[B]$  or  $pB$ , termed cumulative distributions, can be constructed as shown in Figure 4b. In the Figure, the case of coexistence of four A-containing species is depicted: free A, and three compounds containing B, namely AB,  $AB_2$ , and  $AB_3$ . The two types of distribution graphs give basically the same information but sometimes one is more convenient to use than the other. The fractions of the different species present in the system can be easily calculated as shown in Figure 4b1 for case 1 in which

$\beta_1 = 10^2$ ,  $\beta_2 = 10^4$ , and  $\beta_3 = 10^6$  at a concentration of free ligand equal to 0.03 M ( $\text{pB} = 1.5$ ). For the same case, at  $\text{pB} = 2$  ( $[\text{B}] = 10 \text{ mM}$ ), all species — A, AB,  $\text{AB}_2$ , and  $\text{AB}_3$  — are present in the system at equal amounts (25%). Observe the importance of the value of the equilibrium constant on the shape and position of the distribution curves. In cases 1 and 2, presented in Figure 4, only the value of  $\beta_2$  is changed from  $10^4$  to  $10^5$ , while keeping the values of  $\beta_1$  and  $\beta_3$  unaltered. This change significantly influences the distribution. In case 1 (with the less stable complex  $\text{AB}_2$ , i.e., the lower value of  $\beta_2$ ), the maximum fraction of AB is 28% which is reached at  $\text{pB} = 2.2$ . Increasing the value of  $\beta_2$  by a factor of 10 leads to quite dramatic change: the maximum fraction of AB is about twice lower (13% reached at  $\text{pB} = 2.5$ ), although the stability of AB is the same as in the first case ( $\beta_1$  is kept constant).

One can vary the values of the overall formation constants in equations (19) and examine the changes, which this causes to the shape of the concentration distribution curves. Of course, either simpler or more complicated equilibria than the presented case with four A-based species can be considered.

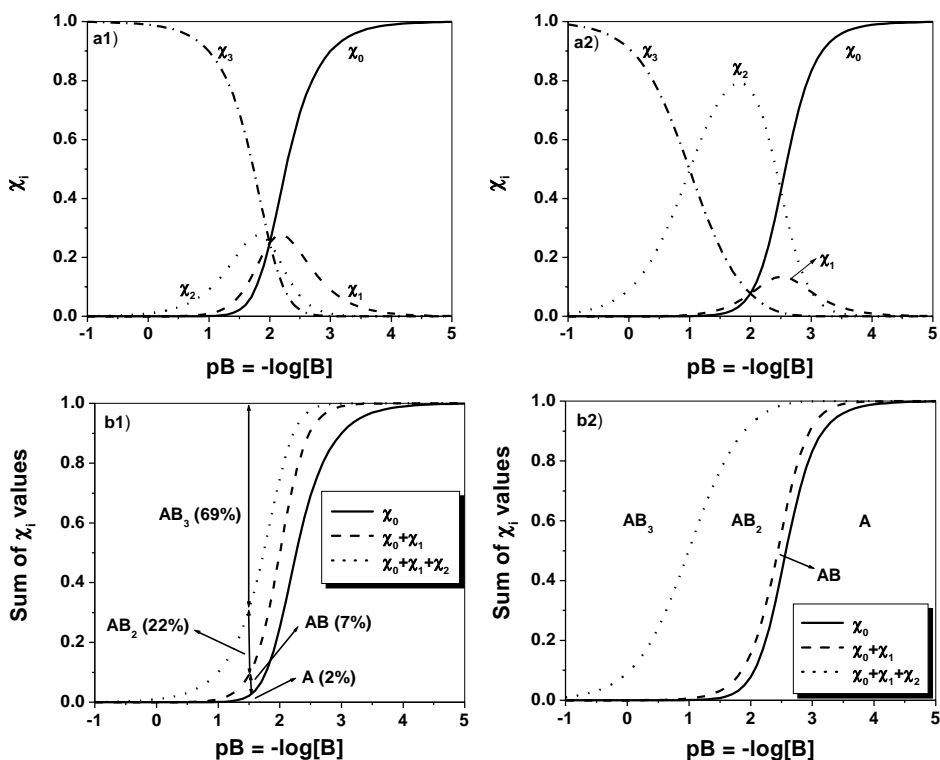


Figure 4. Distribution of the various A-containing species as a function of the concentration

of free B. In case 1 (distributions in graphs a1 and b1) the overall formation constants for AB, AB<sub>2</sub> and AB<sub>3</sub> are  $\beta_1 = 10^2$ ,  $\beta_2 = 10^4$ , and  $\beta_3 = 10^6$ , respectively, and in case 2 (distributions in graphs a2 and b2)  $\beta_2 = 10^5$  with  $\beta_1$  and  $\beta_3$  kept the same.

The derivation-of-equations-and-their-graphical-representation “games” as the ones presented herein, are undoubtedly very fruitful and can contribute largely to the better understanding of chemical equilibria. The study of the influence that the parameters in the equations have on the concentration distributions by their systematic variation is a crucial prerequisite to achieve this goal. Hopefully, such dependencies and calculation problems based on them will find place in the chemical educational literature.

### References and further reading

1. **Tsarevsky, N. V.**, *Chemistry: Bulg. J. Chem. Educ.*, 11(2), 139-52 (2002)
2. **Dimitrova, V., Tsarevsky, N., Manev, S.**, *Problems in Chemistry: Methods, Practice, Examples* (ISBN 954-680-162-3; in Bulgarian), Neofit Rilsky University Press, Blagoevgrad, 2000
3. **Butler, J. N.**, *Ionic Equilibrium: A Mathematical Approach*, Addison-Wesley, Reading, 1964
4. **Sillen, L. G.**, *Graphic Presentation of Equilibrium Data*, in *Treatise on Analytical Chemistry: Part I: Theory and Practice*, Vol. 1, 1<sup>st</sup> Ed., I. M. Kolthoff and P. J. Elving, Eds., Interscience Encyclopedia, New York, 1959, pp. 277-317
5. **Hoegfeldt, E.**, *Graphic Presentation of Equilibrium Data*, in *Treatise on Analytical Chemistry: Part I: Theory and Practice*, Vol. 2, 2<sup>nd</sup> Ed., I. M. Kolthoff and P. J. Elving, Eds., Wiley, New York, 1979, pp. 1-61
6. **Rossotti, F. J. C., Rossotti, H.**, *The Determination of Stability Constants*, McGraw-Hill, New York, 1961
7. **Ringbom, A.**, *Complexation in Analytical Chemistry*, Interscience, New York, 1963
8. **Beck, M. T.**, *Chemistry of Complex Equilibria*, Van Nostrand Reinhold, London, 1970

# **ВЛИЯНИЕ НА СТОЙНОСТТА НА РАВНОВЕСНАТА КОНСТАНТА ВЪРХУ РАЗПРЕДЕЛЕНИЕТО НА КОНЦЕНТРАЦИИТЕ НА РЕАГЕНТИТЕ В ОБРАТИМИ РЕАКЦИИ**

**Резюме.** Върху различни примери е изследвано влиянието на стойността на равновесната константа върху разпределението на концентрациите на реагентите в обратими реакции. Описани са прости математически процедури за анализ на този въпрос, свързан с приложението на закона за действие на масите в химията. Основните математически формули са илюстрирани с инструктивни графики.

✉ **Mr. Nicolay V. TSAREVSKY,**  
Department of Chemistry,  
Carnegie Mellon University,  
4400 Fifth Avenue,  
Pittsburgh, PA 15213, USA  
nvt@andrew.cmu.edu