

# An Exact and Simple Approach to log-log Plots for Defect and Ionic Equilibria

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An alternative approach to log-log plots for defect equilibria in the solid state and ionic equilibria in solution is presented. The method is based on the strictly monotone character of the functional dependence of an externally controlled thermodynamic variable (e.g. the oxygen partial pressure  $P(\text{O}_2)$  for the defect equilibria in a simple oxide, or a total concentration for the ionic equilibria in solution) on a chemically relevant compositional variable (such as the electron concentration  $n$  for defect equilibria, or  $[\text{H}_3\text{O}^+]$  or a free ligand concentration for solution equilibria). This functional dependency can be safely inverted. The concentration of all species and the externally controlled thermodynamic variable can be calculated as a function of the chemically relevant compositional variable. The appropriate plots are then obtained using naïvely a spreadsheet program. This method gives *exact* results in many more cases than the traditional approach.

**Key words:** Chemical equilibria, Point defects, log-log plots.

## 1. Introduction

Log-log plots play an important role in discussing different types of chemical equilibria, such as point defect equilibria in solids and ionic equilibria in solution. Here, the (logarithms of the) concentrations of various chemical species are plotted as a function of (the logarithm of) an appropriate independent variable  $x$ .

Drawing these plots is not always straightforward. Essentially, the difficulties are related to the choice of the  $x$  variable which is considered as the most appropriate *independent* variable of the particular case under discussion: because of this choice one frequently has to face a high-order polynomial equation, which is impossible to solve analytically.

Obvious solutions, then, are to resort to numerical methods, or to introduce various kinds of approximate treatments. It is well known, for instance, that it is sometimes possible to find a particular range of  $x$  where some concentrations can be neglected in a balance equation. The approximation then produces for each concentration [...] a power law solution: [...]  $\propto x^\alpha$ , where  $\alpha$  is a rational constant depending on the nature and charge of the species, and on the  $x$  range. These laws correspond to straight lines on the log-log plot. Analogous treatments are possibly made

for other ranges of  $x$ , and finally the various segments are smoothly connected to each other to complete the plot for each concentration.

Recently [1], it was shown that there is an alternative approach, which holds for a large class of problems and does not require different *ad hoc* treatments nor particular approximations. This approach essentially relies on a variable change from the *natural* independent variable ( $x$ ) (for instance, oxygen partial pressure for defects in oxides, or an overall acidic concentration for the equilibria of a polyprotic acid in water) to another one ( $y$ ), which is analytically more appropriate (the electron concentration or  $[\text{H}_3\text{O}^+]$ , respectively). The mathematical foundation of this approach has been discussed for point defect equilibria in crystalline solids [1] and is based on the monotone relation between  $x$  and  $y$ . The advantage of this approach is that an exact solution of the equilibrium equations can be worked out in many more cases than by the direct approach. Moreover, the difficulties due to the variable change can be easily managed by the now widespread familiarity with spreadsheet programs.

Aim of the present paper is to give a comprehensive account of this approach with emphasis on similarities between different types of chemical equilibria.

The treatment is organized as follows. The method is first illustrated through a discussion of the formation equilibrium of oxygen vacancies in a non-stoi-

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chiometric binary oxide. The next section gives a comprehensive account of defect equilibria in pure and doped oxides, being greatly indebted to a monography by Kofstad [2] and somehow reproducing with an exact but simple treatment this well known seminal work. The final section gives two examples concerning ionic equilibria in aqueous solution. While we do not try here to provide a general mathematical foundation for a so large field of applications, we hope that the examples will provide sufficient insights into the feasibility of the present approach, as well as into its features and its limitations.

For the sake of simplicity, the concentrations are identified with activities throughout and, for what concerns point defects, the regular structure elements are assigned unit concentration. The Kröger-Vink notation [3] of point defects is used.

## 2. Oxygen Vacancies in a Binary Oxide

As a first example, let us consider a simple oxide (a binary system) showing oxygen under-stoichiometry because of oxygen vacancies. Let us also assume that all kinds of vacancies are formed: neutral ( $V_O^x$ ), with a single charge ( $V_O^\bullet$ ), and with a double charge ( $V_O^{\bullet\bullet}$ ).

The equilibrium equations are



where  $n \equiv [e']$  and  $w \equiv [P(O_2)]^{1/2}$ .

The amounts of charged defects  $n$ ,  $[V_O^\bullet]$  and  $[V_O^{\bullet\bullet}]$  are related to each other by the charge balance

$$[V_O^\bullet] + 2[V_O^{\bullet\bullet}] = n, \quad (4)$$

so that, by combining (1–4),

$$n = n^{-1} K_{V_0} K_{V_1} w^{-1} \{1 + 2 K_{V_2} n^{-1}\}, \quad (5)$$

which shows that  $n(w)$  can be obtained by solving a third-degree equation.

The usual approach to this problem [2] is to separately discuss the cases

a)  $[V_O^\bullet] \gg 2[V_O^{\bullet\bullet}]$ , so that  $[V_O^\bullet] \sim n$  and

$$\begin{aligned} 2 K_2 &\ll n = [K_{V_0} K_{V_1}]^{1/2} w^{-1/2} \\ &= [K_{V_0} K_{V_1}]^{1/2} [P(O_2)]^{-1/4} \end{aligned} \quad (6)$$

b)  $2[V_O^{\bullet\bullet}] \gg [V_O^\bullet]$ , so that  $2[V_O^{\bullet\bullet}] \sim n$  and

$$\begin{aligned} 2 K_2 &\gg n = [2 K_{V_0} K_{V_1} K_{V_2}]^{1/3} w^{-1/3} \\ &= [2 K_{V_0} K_{V_1} K_{V_2}]^{1/3} [P(O_2)]^{-1/6}. \end{aligned} \quad (7)$$

Equation (6) and (7) give the well-known functional dependence of electron concentration on oxygen partial pressure. On a logarithmic plot, cases a) and b) give for  $n$  vs  $P(O_2)$  two lines with slopes  $-1/4$  and  $-1/6$ , respectively, which hold for different oxygen partial pressure ranges. In the same ranges, similar laws describe also the functional dependence of  $[V_O^\bullet]$  and  $[V_O^{\bullet\bullet}]$ , and can be easily obtained from (6) and (7).

However, this approach is not completely satisfactory. For instance, it is not immediately obvious how to calculate, from a given set of equilibrium constant values, the  $P(O_2)$  ranges where these conditions can be applied to within a prefixed approximation. Also, this approach does not provide the solution for the possibly most interesting range where neither kind of charged vacancy predominates. Finally, one is unavoidably brought to infer that solving defect equilibria means finding a particular trick, that no reasonably general approach can be found, and that numerical methods are needed for solving accurately even very simple defect systems.

In our opinion, a more satisfactory approach exists, and does not require changing much of the algebraic machinery. Let us start by recognizing that  $n$  is a monotonic function of  $w$  or, more precisely, a *strictly* monotonically *decreasing* function that can be safely inverted. Therefore, instead of solving (5) for  $n(w)$ , we can more easily solve it for  $w$  as a function of  $n$ :

$$w = w(n) = n^{-2} K_{V_0} K_{V_1} [1 + 2 K_{V_2} n^{-1}].$$

Now, by direct substitution, the other defect concentrations *and* the usual *independent variable*  $P(O_2)$  can be calculated as a function of the *new independent variable*  $n$ :

$$P(O_2) = w^2 = \{n^{-2} K_{V_0} K_{V_1} [1 + 2 K_{V_2} n^{-1}]\}^2, \quad (8)$$

$$[V_O^x] = K_{V_0} w^{-1}, \quad (9)$$

$$[V_O^\bullet] = K_{V_0} K_{V_1} w^{-1} n^{-1}, \quad (10)$$

$$[V_O^{\bullet\bullet}] = K_{V_0} K_{V_1} K_{V_2} w^{-1} n^{-2}. \quad (11)$$

The usual log-log plots are then obtained with a spreadsheet program using the following ‘recipe’:

- Start from a column of  $\log(n)$  values (in most cases, equally-spaced values work well: the range and

step can be easily found by trial or by inspection of the formulas).

- Using (8–11), calculate columns corresponding to each variable:  $P(\text{O}_2)$ ,  $[V_O^x]$ ,  $[V_O^+]$ ,  $[V_O^{++}]$ ;
- Make a plot for each defect concentration (including  $n$ ), assigning the abscissas axis to  $P(\text{O}_2)$ .

Figure 1 shows the results obtained with this procedure using  $K_0 = 10^{-12}$ ,  $K_1 = 10^{-6}$ ,  $K_2 = 10^{-8}$ . Here (and in the following) the evenly spaced values of the *new independent* variable used to make the plot are shown as dots. Note that, for this particular set of equilibrium constants and  $P(\text{O}_2)$  range, a large part of the plot corresponds to the transition region between the above cases a) and b), and is therefore out of reach of the traditional approach.

The case of metal interstitials can be discussed in a very similar way.

### 3. Other Defect Equilibria

#### 3.1. Oxygen Vacancies Coupled to Metal Interstitials

It is well known that, for this problem, different reference stoichiometries require more or less complex treatments, because the oxygen partial pressure can appear with different powers in the various equilibrium constants. Let us consider here an  $\text{MO}_2$  oxide. The pertinent equilibria are

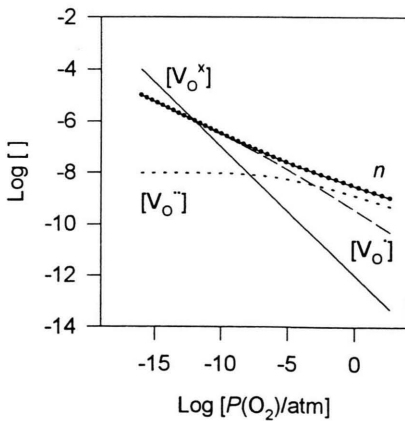
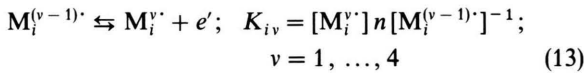
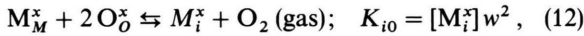


Fig. 1. Defect equilibria of a simple oxide with all kinds of oxygen vacancies.

in addition to the above vacancy equilibria (1–3). Two different powers of  $w \equiv [P(\text{O}_2)]^{1/2}$  now enter the equilibrium constants because the ratio of regular sites is 1:2. The charge balance is

$$n = \sum_{v=1}^4 v [M_i^{v+}] + \sum_{\mu=1}^2 \mu [V_O^{\mu-}] = \frac{A(n)}{w^2} + \frac{B(n)}{w}, \quad (14)$$

where  $A(n)$  and  $B(n)$  are defined as

$$A(n) = \sum_{v=1}^4 \frac{v \overline{K}_{iv}}{n^v}; \quad \overline{K}_{iv} \equiv \prod_j K_{ij},$$

$$B(n) = \sum_{\mu=1}^2 \frac{\mu \overline{K}_{v\mu}}{n^\mu}; \quad \overline{K}_{v\mu} \equiv \prod_j K_{vj},$$

( $\overline{K}_{iv}$  and  $\overline{K}_{v\mu}$  are the overall formation constant of the  $v$ -th charged interstitial, and  $\mu$ -th charged vacancy).

When solved of  $n$  as a function of  $w$ , (14) gives a fifth degree equation. Instead, it gives a second-degree equation if solved for  $w$  as a function of  $n$ :

$$n w^2 - b w - a = 0; \quad a \equiv A(n); \quad b \equiv B(n).$$

Now, the desired solution must be in agreement with the constraints:  $n > 0$ ,  $a > 0$ ,  $b > 0$ ,  $w > 0$ . Therefore, by considering only one sign in the standard formula for solving second degree equations, one obtains

$$w = \frac{b + \sqrt{b^2 + 4an}}{2n}.$$

Finally, the complete expressions for the various defect concentrations can easily be written by comparison with (9–11). Figure 2 shows the results for

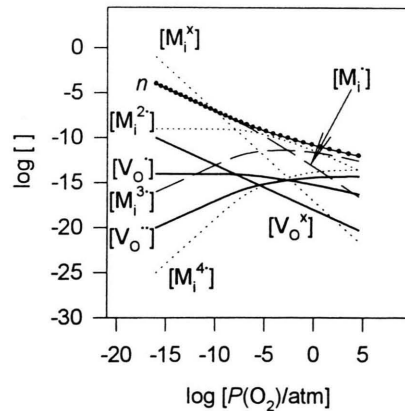


Fig. 2. Defect equilibria in an  $\text{MO}_2$  oxide with the full set of oxygen vacancies (full lines) and metal interstitials (dotted and dashed lines).

$$K_{V0} = 10^{-18}, K_{V1} = 10^{-8}, K_{V2} = 10^{-10}, K_{i0} = 10^{-17}, \\ K_{i1} = 10^{-7}, K_{i2} = 10^{-9}, K_{i3} = 10^{-11}, K_{i4} = 10^{-13}.$$

### 3.2. Vacancies and Interstitials of the Same Atomic Species

Let us consider a simple oxide that can be both oxygen – under- and over-stoichiometric because of vacancies on oxygen sites and excess oxygen atoms on interstitial sites. It is not difficult to discuss the most general problem where vacancies and interstitials can be neutral, partially, or fully ionized.

The equilibrium equations are (1–3) and

$$\frac{1}{2} \text{O}_2(\text{gas}) \rightleftharpoons \text{O}_i^x; \quad K_{i0} = [\text{O}_i^x] w^{-1}, \quad (15)$$

$$\text{O}_i^x \rightleftharpoons \text{O}_i' + h^*; \quad K_{i1} = [\text{O}_i'] p [\text{O}_i^x]^{-1}, \quad (16)$$

$$\text{O}_i' \rightleftharpoons \text{O}_i'' + h^*; \quad K_{i2} = [\text{O}_i''] p [\text{O}_i']^{-1}, \quad (17)$$

$$\text{nil} \rightleftharpoons h^* + e'; \quad K_e = n p, \quad (18)$$

where, again,  $n \equiv [e']$ ,  $p \equiv [h^*]$ ,  $w \equiv [P(\text{O}_2)]^{1/2}$ .

The charge balance is

$$2[\text{V}_O^{\bullet}] + [\text{V}_O'] + p = 2[\text{O}_i''] + [\text{O}_i'] + n. \quad (19)$$

Using (9–11) and

$$[\text{O}_i^x] = K_{i0} w; \quad [\text{O}_i'] = K_{i1} K_{i0} K_e^{-1} w \cdot n;$$

$$[\text{O}_i''] = K_{i2} K_{i1} K_{i0} K_e^{-2} w \cdot n^2,$$

the balance equation becomes

$$a w^2 + b w - c = 0,$$

where

$$a = K_{i1} K_e^{-1} n (2 + K_{i2} n K_e^{-1}) > 0, \quad (20)$$

$$b = n - p = n - K_e n^{-1}, \quad (21)$$

$$c = K_{V1} n^{-1} (2 + K_{V2} n^{-1}) > 0, \quad (22)$$

which gives a (unique) positive solution  $w = w(n)$ :

$$w = \frac{-b + \sqrt{b^2 + 4ac}}{2a} \quad (23)$$

because of the conditions  $a > 0$ ,  $c > 0$ ,  $w = \text{O}$ . Now, the variables  $P(\text{O}_2) = w^2$ ,  $[\text{V}_O^x]$ ,  $[\text{V}_O']$ ,  $[\text{V}_O^{\bullet}]$ ,  $[\text{O}_i^x]$ ,  $[\text{O}_i']$ ,  $[\text{O}_i'']$ , and  $p$  can be directly computed as a function of  $n$ .

### 3.3. Doping with Aliovalent Ions

The treatment of the previous sections can be extended to more than one external variable. Let us consider, for instance, the case of an  $\text{MO}_2$  oxide doped

with (small amounts of) a lower valence cation that enters the lattice as substitutional defect with a negative effective charge:  $\text{Mf}_M'$ , and let us indicate with  $z$  ( $z \ll 1$ ) the external variable corresponding to the site fraction occupied by this dopant. If the predominant defects of the phase are oxygen vacancies, the previous treatment can be applied, with appropriate modifications. It is well known [2] that in this case

- at low oxygen partial pressure (intrinsic region) the foreign cations do not affect the native equilibria, whereas
- at high oxygen partial pressure (extrinsic region) the concentrations of charged vacancies are buffered by the impurity content.

The treatment of the extrinsic behavior, however, can be made more complex [2] by the need of taking into account holes (in addition to electrons) in the high- $P(\text{O}_2)$  range.

With the present approach it is not difficult to solve the problem taking into account the whole set of defects:  $n$ ,  $p$ ,  $\text{V}_O^x$ ,  $\text{V}_O'$ , and  $\text{V}_O^{\bullet}$ , and without need of discussing separately the intrinsic and extrinsic regions. Moreover, let us consider a still more complex case, i.e. the case of a foreign impurity which can enter the cationic sites in two different charge states, for instance as neutral or negatively charged substitutional defect. A real example is Ce-doped zirconia, where equilibrium between  $\text{Ce}^{4+}$  (the neutral defect) and  $\text{Ce}^{3+}$  (the charged defect) occurs. Here, a further equilibrium describes ionization of the foreign impurity:

$$\text{Mf}_M^x + e' \rightleftharpoons \text{Mf}_M'; \quad K_f = [\text{Mf}_M'] n^{-1} [\text{Mf}_M^x]^{-1}. \quad (24)$$

Using the balance for foreign atoms

$$z = [\text{Mf}_M^x] + [\text{Mf}_M'], \quad (25)$$

the relative amounts of neutral and ionized substitutionals can be obtained as a function of  $n$ :

$$[\text{Mf}_M^x] = z [1 + K_f n]^{-1}, \quad [\text{Mf}_M'] = z K_f n [1 + K_f n]^{-1} \quad (26)$$

and placed into the charge balance

$$2[\text{V}_O^{\bullet}] + [\text{V}_O'] + p = n + [\text{Mf}_M'], \quad (27)$$

so that

$$n + z K_f n [1 + K_f n]^{-1} \\ = n^{-1} K_{V0} K_{V1} w^{-1} \{1 + 2 K_{V2} n^{-1}\} + K_e(n) \quad \text{or} \\ w = \frac{K_{V0} K_{V1} (n + 2 K_{V2})}{n^2 [n + z n K_f (1 + K_f n)^{-1} - K_e/n]}. \quad (28)$$



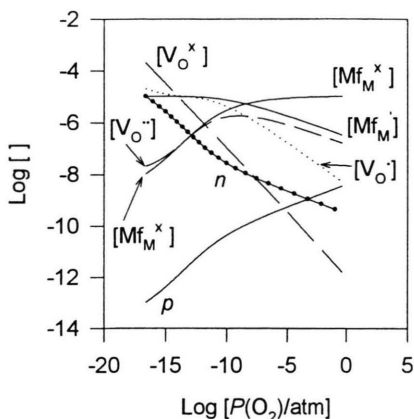


Fig. 3. Defect equilibria in a simple oxide with all kinds of oxygen vacancies (dotted and dashed lines) and doped with a fraction  $z_{\text{Mf}} = 10^{-5}$ . The substitutional defects (continuous lines) can be neutral or negatively charged. Electron holes (continuous lines) are also considered.

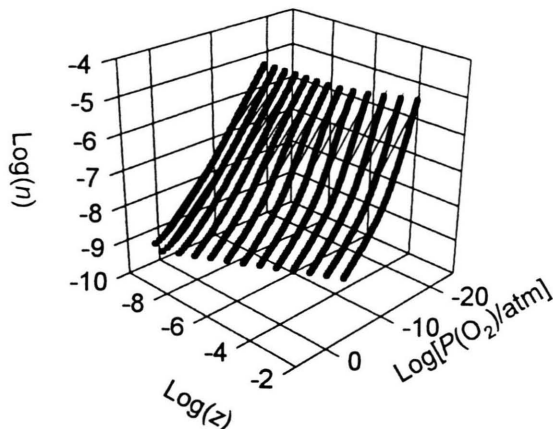


Fig. 4. Defect equilibria of the previous figures: tridimensional plot the electronic defect as a function of overall dopant content.

Now, the log-log plots can be built using (26, 28) in addition to the previous equations (9–11). Figure 3 shows the results obtained using  $z = 10^{-5}$ ,  $K_f = 10^{-10}$  and  $K_e = 10^{-18}$ , as well as the equilibrium constants ( $K_{V0}$ ,  $K_{V1}$ , and  $K_{V2}$ ) of the previous examples. It may be interesting to note the complex behavior of the various defect concentrations, in particular the electronic concentration. In the plotted range of oxygen pressure, the slope of this function is always negative but changes twice. These plots are important as a warning about the usual practice of inferring a particular defect equilibria situation from the slopes of the conductivity vs  $P(\text{O}_2)$  plots: as the figure shows, a more carefully analysis might be required when dopant ionization occurs.

Along the same lines, it is possible to obtain a tridimensional representation by plotting each defect concentration as a function of both  $z$  and  $P(\text{O}_2)$ , as in Fig. 4 where, for simplicity, only a single defect concentration ( $n$ ) is plotted.

### 3.4. General Remarks on Defect Equilibria

The approach shown in the previous sections can be summarized in the following steps.

1) From the pertinent equilibrium constants, the concentrations (site fractions) of the defects with effective charge  $v$  involving the atomic species  $A$  on site  $s$  (in the previous examples:  $A = \text{V}, \text{M}$  or  $\text{O}$ , and  $s = \text{M}$ ,

$\text{O}$ , or  $\text{i}$ ) can be written as

$$[A_s^v] = C_{A s v} n^{-v} w^{m(A,s)}; w = [P(\text{O}_2)]^{1/2},$$

where  $m(A, s)$  is an integer number that depends on the kind of defect [i.e. on the couple  $(A, s)$ ] and on the stoichiometry of the oxide but does not depend upon its charge ( $v$ ), and  $C_{A s v}$  is an equilibrium constant or a product of equilibrium constants.

2) The charge balance condition is

$$R(n, w) = n - K_e n^{-1} - \sum_{\mu(A,s)} w^{m(A,s)} F_{(A,s)} = 0;$$

$$F_{A s} \equiv \sum_v C_{A s v} v n^v,$$

where  $\mu(A, s)$  is the charge of the most ionized defect of kind  $(A, s)$ .

3) The condition  $R(n, w) = 0$  implicitly defines two functions:  $n = f(w)$  and  $w = f(n)$ . By working out (when possible) the explicit form of  $n = f(w)$ , one obtains the full solution set, i.e. all the defect concentrations as functions of the external variable  $w$ . This is the most generally known approach to the log/log plots of point defect equilibria. The alternative approach is based on the inverse function  $w = f(n)$ , which is more effective in producing the solution.

The correctness of the latter approach is related to the existence of the inverse function  $w = f(n)$ , which can be stated [1] either by considering that  $n = f(w)$  is a strictly monotonically decreasing function (and

therefore can be safely inverted), or by directly taking into account the implicit function theorem.

The actual possibilities of working out the explicit forms of the functions  $n = f(w)$  and  $w = f(n)$  are differently related to the number and type of involved equilibria. The point is that the implicit function  $R(n, w) = 0$  is a polynomial of degree  $m(A, s)$  in the variable  $w$ , but it is usually a higher degree polynomial in  $n$ , because the electron defect concentration is involved in many successive ionization equilibria of the same kind  $(A, s)$  of point defects. As a result, the explicit function  $w = f(n)$  can be obtained in many more cases than the other one. This is a clear *advantage* of the present approach. In particular, we have shown in the previous examples that

- $w = f(n)$  is obtained in a straightforward manner when the same power of  $w$  appears in  $R$ : ( $m_1 = m_2 = \dots$ ), in particular when one is considering a single kind of defects;
- in many other interesting cases, the implicit function  $R$  gives a second-degree polynomial in  $w$ , and the appropriate explicit solution can be obtained without much additional difficulty.

4) When one wants to consider as external variable(s) ( $z_k$ ) also the dopant content(s) corresponding to substantial defects with (fixed) effective charge(s)  $v_k$ , the charge balance is modified accordingly:

$$n = K_e n^{-1} + \sum_k v_k z_k + \sum_{(A, s)} w^{m(A, s)} F_{(A, s)}.$$

The case of interstitial dopants can be faced in a similar way.

5) The treatment can be applied with obvious changes also when the dopant species gives rise to differently charged defects, which are related to each other by appropriate equilibrium constants. Then, the concentrations of the defects produced by a particular dopant ( $k = \text{Mf}$ ) are given by

$$[\text{Mf}_S^v] = z_{\text{Mf}} \cdot g_v(K, n),$$

where  $z_{\text{Mf}}$  is the total amount of the dopant (the external variable) and the functions  $g_v(\cdot)$  contain  $n$  and the constants of the equilibria between these defects. Because of the analytic form of these functions, the cases 4) and 5) do not change the actual possibility of solving  $R(w, n, z_k) = 0$  to obtain  $w = f(n, z_k)$ , and the remarks of the previous point 3) are still valid.

## 4. Applications to Solution Chemistry

It is not difficult to show that the above treatment can easily be applied to other kinds of chemical equilibria, for instance to ionic equilibria in aqueous solution. The main difference now is the precise meaning of the external variable, which changes from a partial pressure (i.e. a chemical potential), to an overall concentration. Some algebraic details should be modified, without changing, however, the main lines of the argument.

### 4.1. Acid/Base Equilibria

As a first example, let us discuss the ionization equilibria of a triprotic acid  $\text{H}_3\text{A}$ , with equilibrium constants  $K_1$  to  $K_3$ . If we denote with  $C_a$  its total concentration, with  $\alpha_0, \dots, \alpha_3$  the ionic fractions of the different ionic species:

$$\alpha_0 \equiv \frac{[\text{H}_3\text{A}]}{C_a} = \frac{[\text{H}_3\text{O}^+]^3}{A}; \dots$$

$$\alpha_3 \equiv \frac{[\text{A}^{3-}]}{C_a} = \frac{K_1 \cdot K_2 \cdot K_3}{A},$$

and

$$A = [\text{H}_3\text{O}^+]^3 + K_1 [\text{H}_3\text{O}^+]^2 + K_1 K_2 [\text{H}_3\text{O}^+] + K_1 K_2 K_3,$$

the charge balance becomes

$$[\text{H}_3\text{O}^+] - \frac{K_w}{[\text{H}_3\text{O}^+]} = C_a [\alpha_1 + 2\alpha_2 + 3\alpha_3] = \frac{B}{A} C_a, \quad (29)$$

$$B = K_1 [\text{H}_3\text{O}^+]^2 + 2 K_1 K_2 [\text{H}_3\text{O}^+] + 3 K_1 K_2 K_3,$$

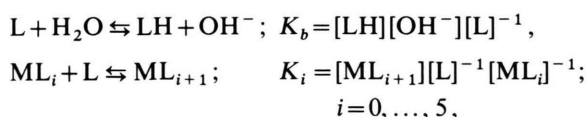
and  $C_a$  can be directly obtained as a function of the *new independent* variable ( $[\text{H}_3\text{O}^+]$ ). Then, the concentration of the various ionic species can be obtained using the definition of  $\alpha_0, \dots, \alpha_3$ .

Figure 5 shows the plot can be obtained using  $K_1 = 10^{-3.13}$ ,  $K_2 = 10^{-4.76}$ ,  $K_3 = 10^{-6.4}$ , and  $K_w = 10^{-14}$  (the constants are roughly those of the citric acid).

### 4.2. Complex Formation

As a second example, let us discuss the case of a metal ion in presence of a ligand (L) which is both a Lewis and a Brönstead basis. Its global amount ( $C_L$ ) is the pertinent external variable. The equilibria and

mass balances are



$$K_w = [H_3O^+][OH^-],$$

$$C_M = [M] + [ML] + [ML_2] + [ML_3] + [ML_4] + [ML_5] + [ML_6]$$

( $C_M$  is the overall amount of metal ion), and

$$C_L = [L] + [LH] + [ML] + 2[ML_2] + 3[ML_3] + 4[ML_4] + 5[ML_5] + 6[ML_6].$$

Then, let us define:

$$\bar{K}_j \equiv \prod_{i=0}^j K_i; \quad i, j = 0, \dots, 5,$$

$$D \equiv 1 + \bar{K}_0[L] + \bar{K}_1[L]^2 + \bar{K}_2[L]^3 + \bar{K}_3[L]^4,$$

$$\beta_j \equiv \frac{[ML_j]}{C_M}; \quad j = 0, \dots, 6,$$

so that

$$\beta_0 \equiv D^{-1}; \quad \beta_{i+1} \equiv \bar{K}_i[L]^{i+1} D^{-1}; \quad i = 0, \dots, 5,$$

which shows that  $\beta_0 \dots \beta_6$  depend on  $[L]$  only, while all  $[ML_j]$  depend on  $[L]$  and  $C_M$ .

Let us consider the example of  $Cr^{3+}$  with  $L \equiv CNS^-$ , here introduced as sodium salt. Then, the charge balance is

$$[H_3O^+] + 3[Cr^{3+}] + 2[CrCNS^{2+}] + [Cr(CNS)_2^+] + C_L = [OH^-] + 3C_M + [Cr(CNS)_4^-] + 2[Cr(CNS)_5^{2-}] + 3[Cr(CNS)_6^{3-}] + [CNS^-],$$

which gives, using  $C_M$  and  $C_L$

$$[H_3O^+] + [HCNS] = [OH^-] \text{ and therefore } [OH^-]^{-1} \{K_w + [L]K_b\} = [OH^-],$$

so that

$$[OH^-] = \sqrt{K_w + K_b \cdot [L]}.$$

Using the last equation, all concentrations and  $C_L$  can be obtained as functions of the variable  $[L]$  and the fixed parameter  $C_M$ . The results (using  $K_b = 10^{-1.84}$ ,  $K_1 = 10^{3.08}$ ,  $K_2 = 10^{1.8}$ ,  $K_3 = 10^{1.0}$ ,  $K_4 = 10^{0.3}$ ,  $K_5 = 10^{-0.7}$ ,  $K_6 = 10^{-1.6}$ , and  $C_M = 10^{-1}$ ) are shown in Figure 6.

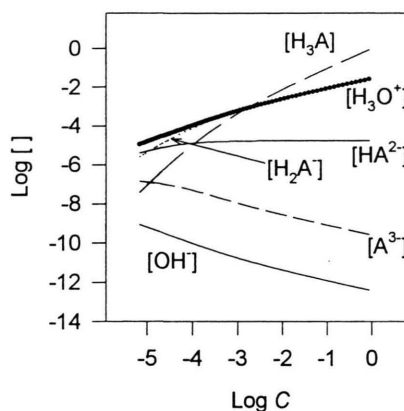


Fig. 5. Ionic equilibria of a triprotic acid ( $H_3A$ ).

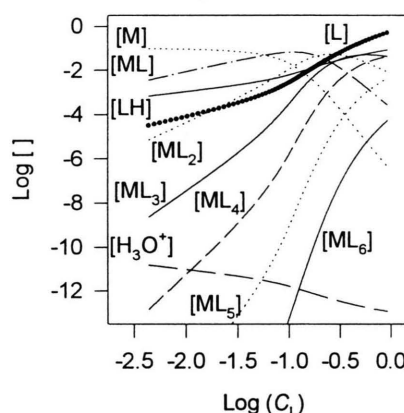


Fig. 6. Ionic equilibria of  $Cr^{3+}$  (M) with  $CNS^-$  (L).

Plots having  $[H_3O^+]$  or the concentration of free ligand  $[L]$  as abscissae are frequently used to discuss these kinds of chemical equilibria. The advantage of the present method relies on the fact that the abscissae axis now directly gives the quantity that is varied externally.

## 5. Final Comments

The method here presented is based on the possibility of finding a state variable (in the thermodynamic sense) that simplifies the algebraic machinery. If it is not possible to solve exactly a system of algebraic equations when the most natural variable  $x$  (an overall concentration, in the last examples) is used as state

variable, the problem can still be solved exactly if it is possible to find an auxiliary variable (let us say:  $y$ ) such that:

- $y$  is a thermodynamic variable that can safely replace  $x$  as independent variable, and
- the concentration of the various chemical species (and  $x$ ) can be computed exactly from  $y$  (for instance: by solving at most a second-degree equation).

While condition b) can be frequently suggested by the traditional approaches, condition a) deserves a few comments. The possibility of using  $y$  as independent thermodynamic variable in place of  $x$  relies on the existence of a one-to-one correspondence between  $x$  and  $y$ , and this correspondence must be checked carefully. In the examples above, it is immediately obvious that  $[H_3O^+]$  monotonously increases as  $C_a$  increases, or that  $n$  monotonously increases as  $P(O_2)$  decreases: then, the correctness of the present approach can be taken for granted on the basis of 'chemical intuition'. If one wants a formal proof, the first step is to write a condition  $R(x, y/\gamma) = 0$ , which summarizes the equilibrium and balance equations and is most naturally written by placing all other constraints into the charge balance equation. The set of fixed parameters ( $\gamma$ ) includes the appropriate equilibrium constants and possibly also includes other independent thermodynamic variables that are kept constant in the discussion. Then, two different procedures can be followed:

- if it is possible to rearrange  $R(x, y) = 0$  into an explicit function  $y = y(x)$ , a proof of the possibility of using  $y$  in place of  $x$  can be obtained by discussing the *strictly monotonous behavior* of  $y = y(x)$ , i.e. by discussing the sign of its derivative;
- alternatively, one can look at the derivative

$$\left. \frac{\partial R(x, y)}{\partial x} \right|_y$$

if it is non zero in the whole  $(x, y)$  field of interest, the property implicitly defines a function  $x = x(y)$ , and  $y$  can be taken as an independent thermodynamic variable which correctly replaces  $x$ , without need of discussing the details of the transformation.

The second procedure is usually simpler and is more easily extended to higher dimensional cases, when one wants to change more than one independent thermodynamic variable.

For instance, in the example about triprotic acid, the form

$$R([H_3O^+], C_a/K_1, K_2, K_3, K_w) = [H_3O^+] - \frac{K_w}{[H_3O^+]} - \frac{B([H_3O^+], K_1, K_2, K_3)}{A([H_3O^+], K_1, K_2, K_3)} C_a = 0$$

implicitly defines a function  $C_a = f([H_3O^+])$ . The derivative

$$\left. \frac{\partial R}{\partial C_a} \right|_{[H_3O^+]} = - \frac{B([H_3O^+], K_1, K_2, K_3)}{A([H_3O^+], K_1, K_2, K_3)}$$

is always non zero (it is the ratio of two quantities that never go to zero), and the explicit function  $C_a = f([H_3O^+])$  can be easily written (see (29)); both statements prove that  $[H_3O^+]$  can safely replace  $C_a$  as the thermodynamic variable.

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