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MODELLING OF ACIDS AND BASES REVISITED

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ABSTRACT. Models for dissociation and mixing of acids and bases are the main subject of many analytical chemistry textbooks. Preparing the solutions for any titration generally involves diluting acids and bases. The mathematics behind precise calculation of pH and pOH is treacherous even for monoprotic acids and bases, becoming mathematically complex when processes of chemical complexation are considered and one should consider any simplifying approximation when available.

Keywords: *dilution, acids, bases, 3D visualization, simulation software*

INTRODUCTION

Titration is a common laboratory method of quantitative chemical analysis to determine the concentration of an identified analyte.

Titrant (reagent) is generally prepared as a standard solution of known concentration. Then the titrant is mixed to react with a solution of analyte (titrand) to determine the analyte's concentration. The volume of titrant that reacted (until equivalence point) with the analyte is termed the titration volume.

There are several textbooks dedicated to the study of the titration process, and Hodisan's is one of them [1].

A titration curve is a curve in graph, the x-coordinate representing the volume of titrant added since the beginning of the titration, and the y-coordinate representing the concentration of the analyte at the corresponding stage of the titration.

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There are different types of titrations with different procedures and goals. However, the most common types of qualitative titration are acid–base and redox.

In an acid–base titration, the y-coordinate usually represents the pH of the solution, but electrical potential can also be used (p. 92 in [1]). There are two reference moments (points) in titration: the initial (before titration starts) and the equivalence (the moment when the consumption of the analyte by the reagent is identified). However, when an instrumental method of determination is involved, the process usually continues after the equivalence point and the exact position of it on the x-coordinate is determined later [2].

If one reagent is weak (acid or base) and the other is strong (base or acid), the titration curve is irregular and the measured (pH for instance) shifts less with small additions of titrant near the equivalence point. Titration curves for the titration between a weak acid and a strong base are depicted in [3], [4], and [5], between a weak base and a strong acid in [6], [7], and [8], between a weak acid and a weak base in [9], [2], [10], while some connections with buffer solutions are discussed in [11].

Measuring the pH of the solution during titration may have as alternative or accompanying a visual change in colour of the solution if an indicator is used. The next table (Table 1) lists some of those indicators.

It should be noted that each of those indicators are in fact weak acids or bases themselves, so adding them into the reaction flask changes a little the equilibrium point. This is the reason for which, when used, they are used in very small amounts, and one of their important qualities is that they produce the change in colour even if are much diluted.

Equivalence point in titration between a weak acid and a strong base is slightly shifted to the right relative to the pH of neutral water. Thus, for instance, when oxalic acid is titrated with sodium hydroxide, the expectation is to have the equivalence occurring at a pH between 8 and 10. One should notice that Phenolphthalein (entry 19 in Table 1) would be an appropriate visual indicator of the equivalence point. Following the same reasoning, a weak base and a strong acid equivalence point is slightly shifted to the left relative to the pH of neutral water; when ammonia solution is titrated with hydrochloric acid, the expectancy is to have the equivalence occurring at a pH between 4 and 6. One should notice that Methyl red (entry 11 in Table 1) would be an appropriate visual indicator of the equivalence point. Titrations between a weak acid and a weak base have titration curves which are irregular; because of this, no definite indicator may be appropriate and a pH meter is better suited to monitor the reaction. In an acid–base titration, one can see the titration curve representing the strength of the corresponding acid and base. For a strong acid and a strong base, the curve will be relatively smooth and very steep near the equivalence point. Near the equivalence point, a small change in titrant volume produces a large pH change, thus in this instance many indicators would be appropriate.

Table 1. Colour change based indicators (adapted and corrected from [12], p. 46)

No.	Name	pH range	λ_{max} [nm]	Colour change
1	Dihydroxyphthalophenone, Phenolphthalein	(-2.0, -1.0)	374,552	o/-
2	o-Cresolsulfonphthalein, Cresol red	(0.5, 2.5)	519	p/y
3	Trinitrophenol, Picric acid	(0.6, 1.3)	465	-/y
4	Thymolsulfonephthalein, Thymol blue	(1.2, 2.8)	594	r/y
5	m-Cresolsulfonephthalein, Metacresol purple	(1.2, 2.8)	434, 578	r/y
6	Dinitrophenol, α-Dinitrophenol	(2.4, 4.0)	360	-/y
7	Tetrabromofenolsulfonftalein, Bromophenol blue	(3.0, 4.6)	437, 592	y/b
8	Sodium diphenyldiazo-naphthylaminesulfonate, Congo red	(3.0, 5.0)	343, 496	b/r
9	Benzenesulfonic acid, Methyl orange	(3.1, 4.4)	464	r/o
10	Tetrabromo-m-cresolphthalein sulfone, Bromocresol green	(3.8, 5.4)	423	y/b
11	Dimethylaminoazobenzene-2-carboxylic acid, Methyl red	(4.4, 6.2)	435, 520	r/y
12	5,5'-Dibromo-o-cresolsulfonphthalein, Bromocresol purple	(5.2, 6.8)	419	y/p
13	Dibromothymolsulfonphthalein, Bromothymol blue	(6.0, 7.6)	431	y/b
14	o-Cresolsulfonphthalein, Cresol red	(6.5, 8.5)	573	y/p
15	Hydroxyphenylazo-vinylenebenzenesulphonate, Brilliant yellow	(6.6, 7.8)	400	y/o
16	Phenolsulfonphthalein, Phenol red	(6.8, 8.2)	415, 560	y/p
17	m-Cresolsulfonephthalein, Metacresol purple	(7.4, 9.0)	434, 578	y/p
18	Thymolsulfonephthalein, Thymol blue	(8.0, 9.6)	376	y/b
19	Dihydroxyphthalophenone, Phenolphthalein	(8.3,10)	374,552	-/p/-
20	Thymol phenolphthalein, Thymolphthalein	(9.3, 10.5)	595	-/b
21	5-(3-Nitrophenylazo)salicylic acid sodium salt, Alizarin yellow	(10.1, 12.0)	375	y/r
22	$C_{28}H_{19}N_5Na_2O_6S_4$, Clayton yellow	(12.2, 13.2)	403	y/r

λ_{max}: UV-Vis maximum absorption wavelength(s); Colours: **o**range, **p**urple, **y**ellow, **r**ed, **b**lue

The process of titration is a recurrent process - small amounts of reagent are consecutively added, and in general can be watched by permanent measurement of either a simple property such as pH [13], mass [14], current intensity [15], potential [16], volume [17], or a complex property such as adsorption [18], heat of reaction [19], which needs a complex evaluation.

Since the numerical solutions of nonlinear equations associated with chemical equilibriums are often stressing the computation capability of the numerical processor, as both pH and pOH often are around the value of 7, near the machine epsilon of single precision computations, this manuscript aims to investigate the numerical stability of some models for dilution of acids and bases.

MATHEMATICAL MODELLING

Let us use *a*, *b*, *c*, *w*, *g*, *h*, *u* and *v* as variables (Eq. (1), where № stands for "number of" moles) expressing corresponding quantities.

$$\begin{gathered} a = \text{№}(A^-),\ b = \text{№}(B^+),\ c = \text{№}(AB),\ w = \text{№}(H_2O), \\ g = \text{№}(HO^-),\ h = \text{№}(H^+),\ u = \text{№}(HA),\ v = \text{№}(BOH) \end{gathered} \tag{1}$$

It should be noted that Eq. (1) are more than simple notations; it is also assumed that the variables are common for all equations, which, in terms of chemistry is translated that all species may exist, in (a general) equilibrium, as a chemical system.

Let *d* be the (molar) fraction (mol/mol) of a HA solution (HA + H_2O); then *x* moles of HA + H_2O contain *xd* HA and *x*(1-*d*) H_2O.

Let *e* be the (molar) fraction (mol/mol) of BOH solution (BOH + H_2O); then *y* moles of BOH + H_2O contain *ye* BOH and *y*(1-*e*) H_2O.

Upon mixing these two solutions, Table 2 gives the balance for the mixture.

Table 2. HA + BOH + H_2O balance without complexation (see Eq. (1) and Eq. (13))

Mixture	$x \cdot d\text{HA} + x \cdot (1-d)\text{H}_2\text{O} + y \cdot e\text{BOH} + y \cdot (1-e)\text{H}_2\text{O}$	
Equilibrium	$a\text{A}^- + b\text{B}^+ + c\text{AB} + w\text{H}_2\text{O} + g\text{HO}^- + h\text{H}^+ + u\text{HA} + v\text{BOH}$	
Species total	z	$a + b + c + w + g + h + u + v$
Charges balance	$a + g$	$h + b$
A total	xd	$a + c + u$
B total	ye	$b + c + v$
HO total	$x(1-d) + ye + y(1-e)$	$w + g + v$
H total	$xd + x(1-d) + ye + y(1-e)$	$w + h + u$
acidity constant	$k_a uz$	ah
basicity constant	$k_b vz$	bg
salt dissociation constant	$k_d cz$	ab
water dissociation constant	$k_w wz$	gh

If *d* = 0 (instead of HA, the solution is only water), then the system defined in Table 2 simplifies to the one given in Table 3.

Table 3. BOH + H_2O balance without complexation (see Eq. (1) and Eq. (13))

Mixture ($d = 0$)	$x\text{H}_2\text{O} + y \cdot e\text{BOH} + y \cdot (1-e)\text{H}_2\text{O}$	
Equilibrium ($a = c = u = 0$)	$b\text{B}^+ + w\text{H}_2\text{O} + g\text{HO}^- + h\text{H}^+ + v\text{BOH}$	
Species total	z	$b + w + g + h + v$
Charges balance	g	$h + b$
B total	ye	$b + v$
HO total	$x + y$	$w + g + v$
H total	$x + y(1-e)$	$w + h$
basicity constant	$k_b vz$	bg
water dissociation constant	$k_w wz$	gh

Similarly, if $e = 0$ (instead of BOH, the solution is only water), then the system defined in Table 2 simplifies to the one given in Table 4.

Table 4. HA + H_2O balance without complexation (see Eq. (1) and Eq. (13))

Mixture ($e = 0$)	$x \cdot d\text{HA} + x \cdot (1-d)H_2O + yH_2O$	
Equilibrium ($b = c = v = 0$)	$a\text{A}^- + wH_2O + g\text{HO}^- + h\text{H}^+ + u\text{HA}$	
Species total	z	$a + w + g + h + u$
Charges balance	$a + g$	h
A total	xd	$a + u$
HO total	$x(1-d) + y$	$w + g$
H total	$x + y$	$w + h + u$
acidity constant	$k_a uz$	ah
water dissociation constant	$k_w wz$	gh

When complexation is considered (Eq. (14)), by applying the conservation of atoms numbers, the following equations are established (Eq. (2)).

$$\begin{gathered} a\text{A}^- + amH_2O = a(H_2O)_m\text{A}^-,\ b\text{B}^+ + bnH_2O = a(H_2O)_n\text{B}^+, \\ g\text{HO}^- + gpH_2O = g(H_2O)_p\text{HO}^-,\ h\text{H}^+ + hqH_2O = h(H_2O)_q\text{H}^+ \end{gathered} \tag{2}$$

When complexation is considered (Eq. (14)), part of the water molecules (exactly $a \cdot m + b \cdot n + g \cdot p + h \cdot q$ moles) is fixed into the clusters and the equilibrium is slightly changed. Thus, for the same x moles of HA + H_2O solution of d (molar) fraction (mol/mol) mixed with y moles of BOH + H_2O solution of e (molar) fraction (mol/mol), the new balance for the mixture is given in Table 5.

Table 5. HA + BOH + H_2O balance with complexation (see Eq. (1) and Eq. (14))

Mixture	$x \cdot d\text{HA} + x \cdot (1-d)H_2O + y \cdot e\text{BOH} + y \cdot (1-e)H_2O$	
Equilibrium	$a(H_2O)_m\text{A}^- + b(H_2O)_n\text{B}^+ + c\text{AB} + wH_2O + g(H_2O)_p\text{HO}^- + h(H_2O)_q\text{H}^+ + u\text{HA} + v\text{BOH}$	
Species total	z	$a + b + c + w + g + h + u + v$
Charges balance	$a + g$	$h + b$
A total	xd	$a + c + u$
B total	ye	$b + c + v$
HO total	$x(1-d) + y$	$w + g + v + am + bn + gp + hq$
H total	$x + y(1-e)$	$w + h + u + am + bn + gp + hq$
acidity constant	$k_a uzw^{m+q}$	ahz^{m+q}
basicity constant	$k_b vzw^{n+p}$	bgz^{n+p}
salt dissociation constant	$k_d czw^{n+q}$	abz^{n+q}
water dissociation constant	$k_w wzw^{p+q}$	ghz^{p+q}

If $d = 0$ (instead of HA, the solution is only water), then the system defined in Table 5 simplifies to the one given in Table 6.

Table 6. BOH + H_2O balance with complexation (see Eq. (1) and Eq. (14))

Mixture (d = 0)	$xH_2O + y\cdot eBOH + y\cdot(1-e)H_2O$	
Equilibrium (a = c = u = 0)	$b(H_2O)_nB^+ + wH_2O + g(H_2O)_pHO^- + h(H_2O)_qH^+ + vBOH$	
Species total	z	$b + w + g + h + v$
Charges balance	g	$h + b$
B total	ye	$b + v$
HO total	$x + y$	$w + g + v + bn + gp + hq$
H total	$x + y(1-e)$	$w + h + bn + gp + hq$
basicity constant	k_bvzw^{n+p}	bgz^{n+p}
water dissociation constant	k_wwzw^{p+q}	ghz^{p+q}

If e = 0 (instead of BOH, the solution is only water), then the system defined in Table 5 simplifies to the one given in Table 7.

Table 7. HA + H_2O balance with complexation (see Eq. (1) and Eq. (14))

Mixture (e = 0)	$x\cdot dHA + x\cdot(1-d)H_2O + yH_2O$	
Equilibrium (b = c = v = 0)	$a(H_2O)_mA^- + wH_2O + g(H_2O)_pHO^- + h(H_2O)_qH^+ + uHA$	
Species total	z	$a + w + g + h + u$
Charges balance	$a + g$	h
A total	xd	$a + u$
HO total	$x(1-d) + y$	$w + g + am + gp + hq$
H total	$x + y$	$w + h + u + am + gp + hq$
acidity constant	k_auzw^{m+q}	ahz^{m+q}
water dissociation constant	k_wwzw^{p+q}	ghz^{p+q}

RESULTS AND DISCUSSION

General considerations about the numerical simulation

Table 2 gives the general system of equations, characterizing the dissociation in water for the HA + BOH + H_2O (neutralization) system, without considering the ions complexation processes, while Table 5 gives the general system of equations, characterizing the dissociation in water for the HA + BOH + H_2O (neutralization) system and considering the ions complexation processes. However, to solve these equations analytically, no symbolic calculation software (including ptc MathCad and Wolfram Mathematica) is able to provide calculation formulas (not even for the simpler case, without complexation).

The formulation of the general problem is of non-negative least squares type (for typical uses see for instance [20]). One should notice that the simplex method (or algorithm) is not applicable, since the system also contains non-linear equations (last four equations in Tables 2 and 5). The solution for the general cases (Table 2 and Table 5) is not simple at all and requires a few mathematical tricks (cite [21-25]) which are out of scope in the discussion here.

Two limit cases were considered here: BOH dilution (Table 3 without complexation and Table 6 with complexation) and HA dilution (Table 4 without complexation and Table 7 with complexation). When referring to the experimental data regarding the acidity, basicity and dissociation constants, it cannot be said for sure that their values were patched to correct for the complexation effects so that the definitions of those constants were in perfectly valid agreement with their values. Since the complexation processes always exist (Eq. (14)), it is possible that their corresponding twins (Eq. (15)) are in fact usually determined. Here both scenarios are considered, and corresponding plots are given.

BOH + H_2O and HA + H_2O systems without complexation

The system of equations defined in Tables 3 and 4 may be conveniently processed to express the variables of interest. In Tables 3 and 4, one more equation than the number of unknown variables is given, but not all equations are independent. No matter how one may approach the system, exactly four out of the first five equations are independent. One may say that the system defined in Tables 3 and 4 admits only one unique solution (and this makes physical sense) but a mathematical solving of the system reveals the need to deal with more than one solution (in fact, the polynomial has three real roots but only one is positive) from which we need to select the solution which have physical sense. Specifically, any solution with non-positive (“ ≤ 0 “) values for any of the variables makes no physical sense.

The equation giving the quantity of H^+ (h) from the BOH + H_2O system (Table 3) is given as Eq. (3), in which the true value of h is the positive ($h > 0$) root of the equation.

$$\begin{gathered} f_3h^3 + f_2h^2 - f_1h - f_0 = 0, \\ f_3 = (1+k_\mathrm{b})(1+k_\mathrm{w}),\ f_2 = k_b(1-e+k_w)y+ek_wy+k_b(1+k_w)x, \\ f_1 = (x+y)(e(k_b-k_w)y+(1+k_b)k_w(x+y)),\ f_0 = k_bk_w(x+y)^3 \end{gathered} \tag{3}$$

The equation giving the quantity of HO^- (g) from the BOH + H_2O system (Table 3) is given as Eq. (4), in which the true value of g is the positive ($g > 0$) root of the equation.

$$\begin{gathered} f_3g^3 + f_2g^2 - f_1g - f_0 = 0, \\ f_3 = (k_b-k_w)(1+k_w),\ f_2 = e(k_b-k_w)(1+2k_w)y+k_w(1+k_w)(x+y), \\ f_1 = (k_b-k_w)k_w((x+y)^2-(ey)^2),\ f_0 = (x+y)(k_w(x+y-ey)^2 \end{gathered} \tag{4}$$

The equation giving the quantity of H^+ (h) from the HA + H_2O system (Table 4) is given as Eq. (5), in which the true value of h is the positive ($h > 0$) root of the equation.

$$\begin{gathered} f_3h^3 + f_2h^2 - f_1h - f_0 = 0, \\ f_3 = (k_a-k_w)(1+k_w),\ f_2 = d(k_a-k_w)(1+2k_w)x+k_w(1+k_w)(x+y), \\ f_1 = (k_a-k_w)k_w((x+y)^2-(dx)^2),\ f_0 = (x+y)(k_w(x+y-dx)^2 \end{gathered} \tag{5}$$

The equation giving the quantity of HO^- (g) from the HA + H_2O system (Table 4) is given as Eq. (6), in which the true value of g is the positive ($g > 0$) root of the equation.

$$\begin{gathered} f_3g^3 + f_2g^2 - f_1g - f_0 = 0, \\ f_3 = (1+k_a)(1+k_w),\ f_2 = k_a(1-d+k_w)x+dk_wx+k_a(1+k_w)y, \\ f_1 = (x+y)(d(k_a-k_w)x+(1+k_a)k_w(x+y)),\ f_0 = k_ak_w(x+y)^3 \end{gathered} \tag{6}$$

One should notice the symmetry in the equations (by symmetry Eq. (3) and (6) are paired; Eq. (4) and (5) are also paired). The presence of the symmetry stands as proof that the formulas have no typo errors.

BOH + H_2O and HA + H_2O systems with complexation

Moving to seek for solutions to the complexation problem (Tables 6 and 7), the problem is not simple anymore and also no analytical formula can be derived with the current symbolic calculation software. Thus, this case falls (again and) already in the numerical optimization. However, since it appears in an important theoretical and practical case - dilution of acids and bases with important impact into protonated systems [26] - it is further discussed and exemplified here.

In the case of BOH complexation in water (Table 6) one approach leading to a solution is expressing all others as functions of b (quantity of $(H_2O)_nB^+$) and g (quantity of $(H_2O)_pHO^-$), and Eq. (7) gives the result of this approach.

$$\begin{gathered} d = a = c = u = 0;\ v = ye - b - c;\ h = g + a - b; \\ w = x(1-d)+y-g-v-am-bn-gp-hq \text{ or } x+y(1-e)-h-u-am-bn-gp-hq; \\ z = a+b+c+g+h+u+v+w \\ 0 = k_bvzw^{p+n} - bgz^{p+n} \\ 0 = k_wwzw^{p+q} - ghz^{p+q} \end{gathered} \tag{7}$$

The last two equations in Eq. (7) can be solved by constrained optimization ($b, g, h, v, w, z > 0$; $b < ye$, $g < (x+y)/(p+1)$).

Similarly, in the case of HA complexation in water (Table 7) one approach leading to a solution is to express all others as functions of *a* (quantity of $(H_2O)_mA^-$) and *h* (quantity of $(H_2O)_qH^+$), and Eq. (8) gives the result of this approach.

$$
\begin{gathered}
e = b = c = v = 0;\ u = xd - a - c;\ g = h + b - a; \\
w = x(1\text{-}d)+y\text{-}g\text{-}v\text{-}am\text{-}bn\text{-}gp\text{-}hq \text{ or } x+y(1\text{-}e)\text{-}h\text{-}u\text{-}am\text{-}bn\text{-}gp\text{-}hq; \\
z = a+b+c+g+h+u+v+w \\
0 = k_a uzw^{m+q} - ahz^{m+q} \\
0 = k_w wzw^{p+q} - ghz^{p+q}
\end{gathered}
\tag{8}
$$

Once the values of *b* and *g* are obtained by solving the last two equations of Eq. (7), the value of the rest of the variables are to be found from the other equations part of the Eq. (7), and Eq. (8) is addressed in a similar manner. The value of the pH and of the pOH are simply expressed by Eq. (9).

$$
pH = \log_{10}h - \log_{10}z,\ pOH = \log_{10}g - \log_{10}z \tag{9}
$$

Numerical results and discussion

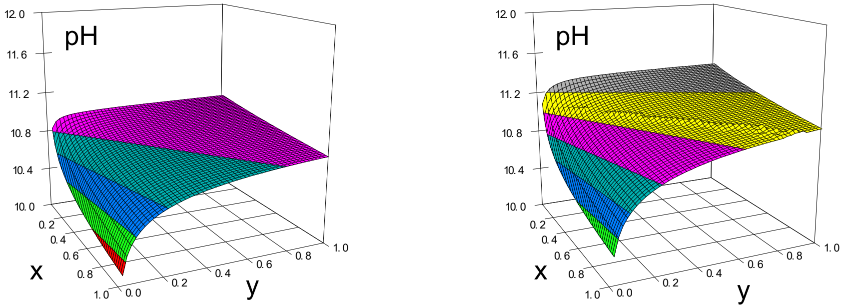
The numerical implementation of the models has shown that it is difficult to draw definite conclusions about the path followed by the process in the case of complexation, and this is a negative result. It seems that there exists at least another saddle point which prevents the global optimization to reach the global optimum. In the Table 8 such an example is given for the case of BOH + H_2O. As inspecting the values in Table 8 reveals, Case 1 is a typical case of near-total dissociation (the quantity of undissociated BOH is about 30000 times smaller than the quantity of B^+) while Case 2 is a case of partial dissociation (the quantity of undissociated BOH is about 2 times smaller than the quantity of B^+). Even so, the big difference is actually from the dissociation of water. As such, in Case 1 a significant amount of water molecules are dissociated when compared to Case 2, and this fact is visible through the quantity of hydrogen ions (h in Table R1; about $9\cdot10^{-4}$ moles in Case 1 vs. $2\cdot10^{-13}$ moles in Case 2) and from amount of free and undissociated water molecules (w in Table 8; about $1.4\cdot10^{-2}$ moles in Case 1 vs. $2.7\cdot10^{-2}$ moles in Case 2).

Table 8. $b(H_2O)_nB^+ + wH_2O + g(H_2O)_pHO^- + h(H_2O)_qH^+ + vBOH$ equilibrium: two numerical solutions to Eq. (7)

Parameters and Equations	*Case 1*	*Case 2*
$n = p = q = 4$; $d = a = c = u = 0$; $k_w = 10^{-14}$, $k_b = 10^{4.747}$ (dissociation constant of a very strong base; hypothetic value); $e = 0.1$, $x = y = 0.02$ moles		
b	$1.9999 \cdot 10^{-3}$	$1.3358 \cdot 10^{-3}$
g	$2.8920 \cdot 10^{-3}$	$1.3358 \cdot 10^{-3}$
h	$8.9205 \cdot 10^{-4}$	$2.1176 \cdot 10^{-13}$
v	$6.7571 \cdot 10^{-8}$	$6.6415 \cdot 10^{-4}$
w	$1.3972 \cdot 10^{-2}$	$2.7313 \cdot 10^{-2}$
z	$1.9756 \cdot 10^{-2}$	$3.0650 \cdot 10^{-2}$
$a+b+c+g+h+u+v+w-z$	$1.76 \cdot 10^{-8}$	$-1.25 \cdot 10^{-6}$
$a+g-h-b$	$5.00 \cdot 10^{-8}$	$-2.12 \cdot 10^{-13}$
$b+c+v-ye$	$-3.24 \cdot 10^{-8}$	$-5.00 \cdot 10^{-8}$
$w+g+v+am+bn+gp+hq-x(1-d)-y$	$-1.32 \cdot 10^{-7}$	$-6.50 \cdot 10^{-7}$
$w+h+u+am+bn+gp+hq-x-y(1-e)$	$-1.50 \cdot 10^{-7}$	$-6.00 \cdot 10^{-7}$
$k_bvzw^{p+n}-bgz^{p+n}$	$-2.59 \cdot 10^{-20}$	$3.52 \cdot 10^{-13}$
$k_wwzw^{p+q}-ghz^{p+q}$	$-5.99 \cdot 10^{-20}$	$-2.18 \cdot 10^{-28}$
total residual (unexplained) error*	$3.8 \cdot 10^{-7}$	$2.6 \cdot 10^{-6}$

Note: *as sum of absolute values (with the number of digits given in Table 8); with Float 64-bit precision the total residuals are $2.6 \cdot 10^{-18}$ (Case 1) and $3.5 \cdot 10^{-13}$ (Case 2) respectively.

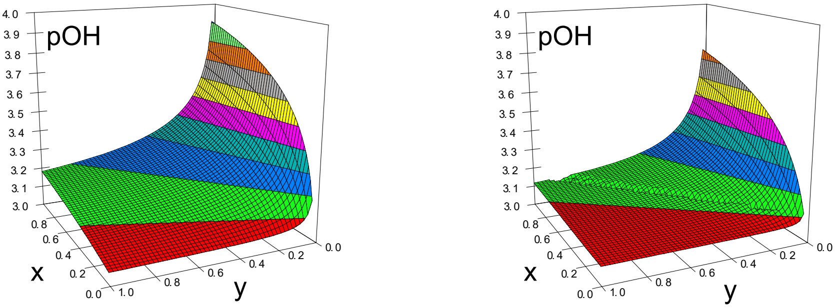
The following figures depict the change in pH and in pOH due to dilution for one base (NH_4OH, with $n = 4$, $p = 4$ and $q = 4$ [27] and $k_b = 10^{-4.747}$).



(a) Values obtained with Eq. (3)

(b) Values obtained with Eq. (7)

Figure 1. pH of *y* moles of 0.1 mol/mol $NH_3 + H_2O$ solution diluted with *x* moles H_2O - with (a) and without (b) assumption of complexation

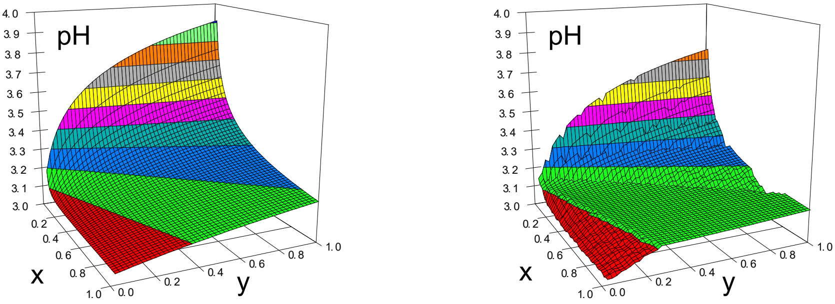


(a) Values obtained with Eq. (4)   (b) Values obtained with Eq. (7)

Figure 2. pOH of *y* moles of 0.1 mol/mol $NH_3 + H_2O$ solution diluted with *x* moles H_2O - with (a) and without (b) assumption of complexation

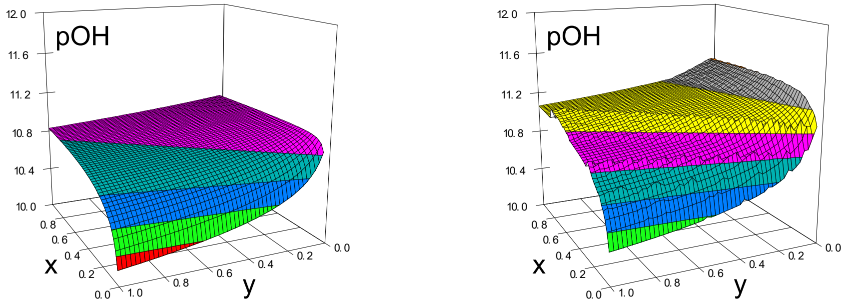
For small amounts of added water (*x*) under the assumption of complexation, there is a considerable amount of water required for complexation. For each NH_4OH dissociated molecule, 8 water molecules are required to construct $(H_2O)_4NH_4^+$ and $(H_2O)_4HO^-$ complexes ($p = 4$ and $n = 4$ in Eq. (5)). Similarly, for each H_2O dissociated molecule, another 8 water molecules are required to construct $(H_2O)_4H^+$ and $(H_2O)_4HO^-$ complexes ($p = 4$ and $q = 4$ in Eq. (5)). This is the most likely explanation for which the solution of Eq. (15) model jumps between two local minima like in Table R1 and visible in Fig. 1(b) and Fig. 2(b) as vertical surfaces. The relative change in pH and pOH is still small (no more than 0.1 log units) and is larger for small amounts of water and large amounts of ammonium hydroxide.

The following figures depict the change in pH and in pOH due to dilution for one acid (CH_3COOH, with $p = 4$, $q = 4$ and $m = 6$ [28] and $k_a = 10^{-4.754}$).



(a) Values obtained with Eq. (5)   (b) Values obtained with Eq. (8)

Figure 3. pH of x moles of 0.1 mol/mol $CH_3COOH + H_2O$ solution diluted with *y* moles H_2O - with (a) and without (b) assumption of complexation



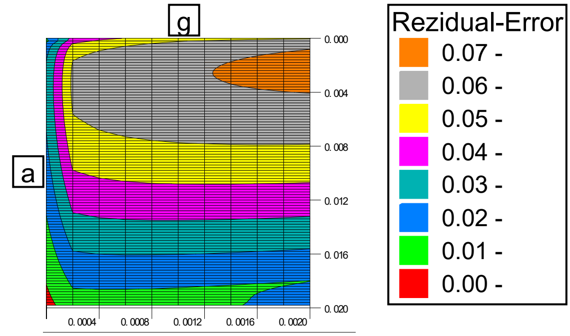
(a) Values obtained with Eq. (6)

(b) Values obtained with Eq. (8)

Figure 4. pH of *x* moles of 0.1 mol/mol $CH_3COOH + H_2O$ solution diluted with *y* moles H_2O - with (a) and without (b) assumption of complexation

Equations as given in Tables 2 and 5 support further generalization. Let's assume that we have the equilibrium constants as function of temperature (for instance as in [29] p. 137). In that case, at any arbitrary temperature in the applicability domain of the defined functions of temperature, the standard values of the constants are simply replaced by the new values, at the new temperature.

The main difficulty encountered in obtaining the global minima defining the equilibrium in the solution for which the complexation phenomena are considered into the model were due to the shape of the residual error. Considering the case of the acetic acid diluted with water for which pH and pOH are represented in Figures 3 and 4 for *x* and *y* ranging from 0.02 mol to 1 mol while Figure 5 represents the residual error (Rezidual-Error(*a*, *g*) from Figure 5) for initial guess values of a and g ranging from 0.00 to 0.02 mol.



$$\text{Rezidual-Error}(a, g) = (k_a uzw^{m+q} - ahz^{m+q})^{1/8} + (k_w wzw^{p+q} - ghz^{p+q})^{1/8}$$

Figure 5. Residual error in finding of the quantities of chemical species for x = 0.2 mol of $CH_3COOH + H_2O$ 0.1 mol/mol diluted with 0.02 mol of H_2O: a region containing the global minima (near a = 0 and g = 0) and another valley region (near a = 0.02 and g = 0)

Figure 5 reveals that the choice of initial values is determinant in finding of the global minima. A good initial guess for the case depicted in Figure 5 lies in the upper part of the representation (for instance a = 0.002 mol, g = 0.0002 mol) - and this choice leads to the global minima being in the right side of the ridge (orange spot in Figure 5) while a poor initial guess lies in the lower part of the representation (for instance a = 0.016 mol, a = 0.0002 mol) - and this choice leads to a local minima being in the wrong side of the ridge (see Figure 6).

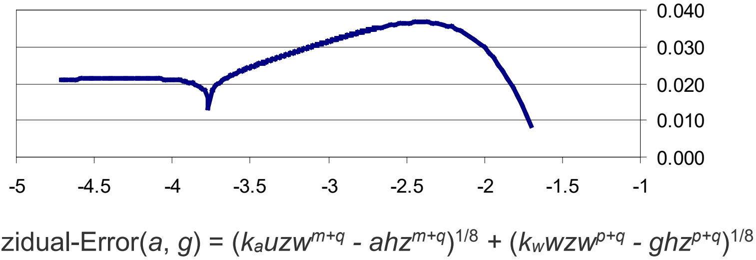


Figure 6. Residual error for x = 0.2 mol of $CH_3COOH + H_2O$ 0.1 mol/mol diluted with 0.02 mol of H_2O when g = $5\cdot10^{-10}$ as function of a (in logarithmic scale)

The main trouble in the optimization actually resides in the fact that the global minima is located in a steep ravine (see Figure 6) which is not visible in a regular grid search (like the one used in Figure 5). For this reason a successful optimization must either start from a very good starting point or use heuristics capable of identifying the global minima.

CONCLUSIONS

The study aimed to investigate the differences which may appear in dissociation by using pH and pOH as indicators of dissociation when complexation of the dissociated ions is accounted. The models for acids and bases mixing and dilution were derived. Analytic solutions were derived for solving without complexation and a numeric approach was used for solving with complexation. Stability of the numeric approach was found questionable and some local minima may be responsible for the failure of the global minimum search. When the models with and without complexation were compared, small differences in the values of pH were obtained for solutions of CH_3COOH and NH_4OH. The proposed approach can be applied for dilution and mixing of any acid and base as long as the acidity, basicity and dissociation constants are known.

Starting from general equilibrium equations (Tables 2 and 5) numerical solutions for acid-base titrations can be derived as well.

EXPERIMENTAL SECTION

Chemical activity (*a* in Eq. (10)) measures effective concentration of a species (*Sp* in Eq. (10)) in a mixture, in the sense that the species' chemical potential (μ in Eq. (10)) depends on the activity of a real solution in the same way that it would depend on concentration for an ideal solution [30,31] (Eq. (1)).

$$a(Sp) = \exp\left(\frac{\mu(Sp) - \mu^{o}(Sp)}{RT}\right) \tag{10}$$

where R is the constant of gases (R = 8.31446261815324 J/mol·K), T the temperature and $\mu(Sp)$ and $\mu^{o}(Sp)$ are the chemical potential and its standard value which depends on the choice of the standard state. Activity depends on temperature, pressure and composition of the mixture.

For a solvent in the liquid state (such as for H_2O) the standard state is that of the pure substance in the liquid or solid phase at the standard pressure p^{o} (of 10^5 Pa = 1 bar). For a solute (such as a salt AB) in liquid solution it is the (hypothetical) state of solute at the standard molality m^{o} (of 1 mol/kg) or standard concentration c^{o} (of 1 mol/dm^3) and exhibiting infinitely dilute solution behaviour.

Equilibrium constants (K) are strictly thermodynamically defined [32] in terms of (relative) activities. For a general chemical reaction involving R_1, R_2, …, R_r as reactants, S_1, S_2, …, S_s as products, and α_1, α_2, …, α_r, β_1, β_2, …, β_s as stoichiometric coefficients, the equilibrium constant is defined as in (Eq. (11)).

$$K(\alpha_1 R_1 + \ldots + \alpha_r R_r \rightleftharpoons \beta_1 S_1 + \ldots + \beta_s S_s) \overset{def.}{=} \prod_{i=1}^{s}(a(S_i))^{\beta_i} \Big/ \prod_{j=1}^{r}(a(R_j))^{\alpha_j} \tag{11}$$

The activity for each species is defined in terms of some measurable quantity, e.g., a concentration, a partial pressure, a mole fraction, so that the activity approaches this quantity as the system approaches a certain limiting state.

Standard free energy change (ΔG^{o}) is related to the equilibrium constant (K) via Eq. (12).

$$-RT\ln K(\Sigma_i\alpha_i R_i \rightleftharpoons \Sigma_j\beta_j S_j) = \Delta G^o(\Sigma_i\alpha_i R_i \rightleftharpoons \Sigma_j\beta_j S_j) \tag{12}$$

When relating the dissociation in water with known quantities, the definition formulas for acidity constant (K_a), basicity constant (K_b), dissociation constant (K_D) and ionic product of water (K_W) should be used. In Eq. (13), the volume of the solution was noted with z for convenience, and ΔG^o is the standard free enthalpy of the reaction.

$$\begin{gathered} K(AB \rightleftharpoons A^- + B^+) = K_D = a(A^-)a(B^+)/a(AB) \\ K(H_2O \rightleftharpoons HO^- + H^+) = K_W = a(HO^-)a(H^+)/a(H_2O) \\ K(HA \rightleftharpoons A^- + H^+) = K_a = a(A^-)a(H^+)/a(HA) \\ K(BOH \rightleftharpoons HO^- + B^+) = K_b = a(HO^-)a(B^+)/a(BOH) \end{gathered} \tag{13}$$

When one express ionic product of water $K_w = a(H^+)a(HO^-)$ it actually omits the activity of water, $a(H_2O)$, which means that the value of K_w differs from the value of K_W from Eq. (4). Table 2 gives some values for comparison ($K_W = K_w \cdot M(H_2O)/\rho(H_2O)$, where M the molar mass [g/mol] and ρ the density [g/l]).

Table 9. Constant of dissociation and ionic product of water at some temperatures

t (°C)	K_W [l/mol]	K_w	pK_w [33]
0	$2.02\cdot10^{-17}$	$1.12\cdot10^{-15}$	14.95
25	$1.84\cdot10^{-16}$	$1.02\cdot10^{-14}$	13.99
50	$9.89\cdot10^{-16}$	$5.49\cdot10^{-14}$	13.26
75	$3.59\cdot10^{-15}$	$2.00\cdot10^{-13}$	12.70
100	$1.01\cdot10^{-14}$	$5.62\cdot10^{-13}$	12.25

One usually writes a dissociation (in water) process as $HA \rightleftharpoons H^+ + A^-$ (for acids), $BOH \rightleftharpoons B^+ + HO^-$ (for bases), $H_2O \rightleftharpoons H^+ + HO^-$ (for water) and $AB \rightleftharpoons B^+ + A^-$ (for salts), but those scholastic equations do not quite describe the process accurately, and definitely may lead to errors when involved as they are into calculations. When discussing about water alone, H^+ is actually trapped by a variable number (q) of water molecules ($H^+ + qH_2O \rightleftharpoons (H_2O)_qH^+$), and different protonated species actually exist ($(H_2O)_qH^+$) containing 3 to 12 (q = 3, 4, …, 12) water molecules, the most likely being: $(H_2O)_4H^+$ (Eigen cation, [29] p. 103). Moving forward to ions dissolved in water (anions, A^- and cations B^+), the number (m, n) of surrounding water molecules (forming $(H_2O)_mA^-$ and $(H_2O)_nB^+$ clusters) varies from 4 to 6 for certain strong anions and cations (see [27]). The corresponding equations of the chemical equilibriums are then formally expressed by Eq. (14).

$$\begin{gathered}\text{For AB in } H_2O\text{: AB} + (m+n)H_2O \rightleftharpoons (H_2O)_mA^- + (H_2O)_nB^+ \\ \text{For } H_2O \text{ in } H_2O\text{: } H_2O + (p+q)H_2O \rightleftharpoons (H_2O)_pHO^- + (H_2O)_qH^+ \\ \text{For HA in } H_2O\text{: HA} + (m+q)H_2O \rightleftharpoons (H_2O)_mA^- + (H_2O)_qH^+ \\ \text{For BOH in } H_2O\text{: BOH} + (p+n)H_2O \rightleftharpoons (H_2O)_pHO^- + (H_2O)_\mathrm{n}B^+\end{gathered} \qquad (14)$$

If K_{DW}, K_{WW}, K_{aW} amd K_{bW} are the equilibrium constants for the processes from Eq. (14), then their relations with the Eq. (13) constants are the ones from Eq. (15), in which the activities of clustered species were (formally) considered to be equal with the corresponding free species: $a(A^-) = a((H_2O)_mA^-)$, $a(B^+) = a((H_2O)_nB^+)$, $a(HO^-) = a((H_2O)_pHO^-)$, and $a(H^+) = a((H_2O)_qH^+)$.

$$\begin{gathered}K_{DW} = K_D/(a(H_2O))^{m+n} \\ K_{WW} = K_W/(a(H_2O))^{p+q} \\ K_{aW} = K_a/(a(H_2O))^{m+q} \\ K_{bW} = K_b/(a(H_2O))^{p+n}\end{gathered} \qquad (15)$$

At infinite dilution $a(H_2O) \rightarrow 1$, and then $K_{DW} \rightarrow K_D/[H_2O]^{m+n}$, $K_{WW} \rightarrow K_W/[H_2O]^{p+q}$, $K_{aW} \rightarrow K_a/[H_2O]^{m+q}$, $\mathrm{K}_{Wb} \rightarrow K_b/[H_2O]^{p+n}$ (where [·] stands for molar concentration). One should notice in Eq. (15) that the constants of Eq. (14) do not have the same units as their corresponding standard versions from Eq. (13). At 273.15 K, $\rho(H_2O) \approx 999.84$ g/l and $a(H_2O) \rightarrow 55.5$ mol/l while at 298.15 K, $\rho(H_2O) \approx 997.05$ g/l and $a(H_2O) \rightarrow 55.34$ mol/l. In any instance, the units of the Eq. (13) and Eq. (14) equilibrium constants are scaled by the units of the corresponding water molecules (see the dimensional analysis from Eq. (16), and for further details see Table 7 at p. 12 in [34]).

$$\begin{gathered}\dim K_{DW} = \dim K_D\cdot(L^3/N)^{m+n} = (L^3/N)^{m+n-1} \\ \dim K_{WW} = \dim K_W\cdot(L^3/N)^{p+q} = (L^3/N)^{p+q-1} \\ \dim K_{aW} = \dim K_a\cdot(L^3/N)^{m+q} = (L^3/N)^{m+q-1} \\ \dim K_{bW} = \dim K_b\cdot(L^3/N)^{p+n} = (L^3/N)^{p+n-1}\end{gathered} \qquad (16)$$

All activities are, by convention, dimensionless quantities; thus, for numeric simulation purposes their quantities will be safely substituted with molar fractions and when ionic strength deviates significantly from 1, these formulas can be subject to revision.

In the vapour or gaseous state, water molecules are largely independent of one another and occur mostly as monomers ($(H_2O)_k$ with $k = 1$). Dissociation is expected to appear in gaseous state for the charged species as well (Eq. (17)).

$$\begin{array}{c} (H_2O)_mA^- \rightleftharpoons mH_2O + A^- \\ (H_2O)_nB^+ \rightleftharpoons nH_2O + B^+ \\ (H_2O)_pHO^- \rightleftharpoons pH_2O + HO^- \\ (H_2O)_qH^+ \rightleftharpoons qH_2O + H^+ \end{array} \qquad (17)$$

Eq. (17) processes can be considered part of the equilibrium in the gaseous state and are strongly dependent on the pressure (decreasing of the pressure such as in the mass spectrometer favours dissociation, [35]). As Eq. (17) reveals, each ionic species from Eq. (13) has a corresponding complex ion in Eq. (14).

Some acidity constants

A list of acidity constants for common inorganic acids has been collected from multiple sources and it is given as Table 10, and can be used to model the dilution.

Table 10. pKa values at standard ambient conditions (25°C, 1 bar, and zero ionic strength)

Acid	pKa	Ref
HF	3.19	[36]
H_2O_2	11.62	[37]
H_2S; HS^-	7.05; 19	[37]
HIO_3	0.78	[37]
$HClO_4$	$-11.55_{\pm0.75}$	[38]
HNO_2	3.25	[37]
H_3PO_4; $H_2PO_4^-$; HPO_4^{2-}	$2.16_{\pm0.02}$; 7.21; 12.32	[37, 39]
H_2SO_4; HSO_4^-	$-6.55_{\pm2.05}$; 1.99	[37,38]
H_2SO_3; HSO_3^-	$1.81_{\pm0.04}$; 7.2	[37, 40]
H_2O	13.995	[37]
HSCN	$-1.28_{\pm0.03}$	[41]
HCl	$-7.3_{\pm0.04}$	[42]
HBr	$-9.84_{\pm0.06}$	[42]
HI	$-10.29_{\pm0.08}$	[42]
HNO_3	$-1.37_{0.03}$	[43]
H_3O^+	0.0	[43]
NH_3	35	[43]
NH_4^+	9.25	[43]

Although K_A for HI is about $10^{7.5}$ times greater than K_A for HNO_3 ($pK_A(HI) - pK_A(HNO_3) \approx 7.51$ in Table 2), the reaction of either HI or HNO_3 with water gives an essentially stoichiometric solution of H_3O^+ and I^- or NO_3^-. A 0.1 M aqueous solution of any strong acid actually contains 0.1 M H_3O^+, regardless of the identity of the strong acid. This phenomenon is called the leveling effect [44]: any species that is a stronger acid than the conjugate acid of water (H_3O^+) is leveled to the strength of H_3O^+ in aqueous solution because H_3O^+ is the strongest acid that can exist in equilibrium with water (it is the manifestation of any species dissolved in water). Consequently, it is impossible to distinguish between the strengths of very strong acids such as HI and HNO_3 in aqueous solution, and usually alternative approaches are employed to determine their relative acid strengths.

Three definitions share the word base: Arrhenius bases, Brønsted bases, and Lewis bases. Even though all three definitions agree that bases are substances which react with acids to form salts, as originally proposed in 1754 by Rouelle [45], there are some differences which may cause difficulties in blunt application of Eq. (13.4), especially in the vicinity of the equilibrium. Thus, in 1886, Arrhenius proposed that a base is a substance which dissociates in aqueous solution to form HO^- [46]. According to the Brønsted–Lowry acid–base theory [47, 48], a base is a substance that can accept hydrogen cations (H^+)—otherwise known as protons. This does include aqueous hydroxides since OH^- does react with H^+ to form water, so that Arrhenius bases are a subset of Brønsted bases, but there are also other Brønsted bases which accept protons, such as NH_3, while the Lewis theory generalizes the Brønsted–Lowry model [49]. It should be noted that according to the Brønsted–Lowry acid–base theory, the constant of basicity defined by Eq. (13.4) should be rewritten as in Eq. (18):

$$B + H^+ \rightarrow BH^+,\ K_B = [BH]/[B][H^+] \qquad (18)$$

Some authors state that basicity constant does not require a separate definition, and can be defined through acidity (Eq. (19)).

$$B + H_2O \rightarrow HB^+ + HO^-,\ K_B = [HB^+][HO^-]/[B][H_2O] \qquad (19)$$

However, notable is the difference between Eq. (19) and Eq. (13.4) by the presence in the expression (of the chemical equation and of the associated mathematical equation) of the water. One should point out that the definitions are equivalent at infinite dilution but are significantly different in concentrate solutions and near the equilibrium.

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