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General Equation of State of Acid-Base Balance in Solutions: Resolution of the Equation with Respect to Hydrogen ion Concentrations and Concerning the Amount of Added Base or Acid. Titration Curves.

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Abstract

Original Research Article

The paper considers the state of the system, which is an electrolyte solution containing an acid and a base in various ratios. The general equation of the state of the system is derived. Methods are proposed to solve the general equation for the concentration of hydrogen ions and for the base/acid introduced into the system. The theoretical dependencies are compared with experimental titration curves.

Keywords: Electrolyte solution, general equation of state, acid-base titration.

INTRODUCTION

An analytical chemist is faced almost daily with the task of determining or calculating the acidity of solutions. The methods of these determinations and calculations are well-known and customary (LibreTexts Chemistry 2023; General Chemistry 2023; pH at The Equivalence Point 2023; Titrations and pH Curves. 2020; Khan Academy 2023). But, some chemists, like us, are not satisfied that you must use a special formula in each case. So, for example, to calculate the titration curve of an acid with an alkali, one formula is used up to the equivalence point, another formula is used at the equivalence point, and a third after the equivalence point (Titrations and pH Curves. 2020). From a practical point of view, it would be much more convenient to have a general formula. From the point of view of theory, the general formula is the model of the state of the system. We are not the first to clearly recognize the problem and try to solve it. Charlot Gaston published a paper (Charlot, G.1947) in which he proposed the derivation of a formula for the special case of a solution of a weak acid and its salt formed with a strong base. Harvey D presented examples of programs for plotting titration curves based on the approach of Robert de Levie (Harvey D. 2016). The present work is devoted to the derivation of the general equation of state and its application in particular situations including, but not limited to titration process.

MATERIALS AND METHODS

For the calculations, the Microsoft EXCEL spreadsheet was used.

The experiment was performed on HI2221 Calibration check pH/ORP Meter "HANNA instrument" with glass electrode HI1131. The instrument was calibrated using 3 standard solutions: pHRed-4, pHYellow-7, and pHBlue-10 "Inorganic Ventures".

Reagents: Hydrochloric acid 1.0M standard solution "Lab Chem"; Acetic acid glacial "Sigma-Aldrich"; Phosphoric acid for HPLC 85% Sigma-Aldrich"; Sodium hydroxide solid "Sigma-Aldrich"; Water for HPLC "TEDIA". A secondary standard NaOH 0.9–1.1 M solution was prepared by dissolving 40 g of solid NaOH in water, followed by titration with a standard HCl solution to check the concentration. Solutions of acids with a concentration of about 0.001 M were prepared by dissolving aliquots of acids in 1L of water, followed by titration with standard NaOH solution to control the concentration.

Experimental titration curves were obtained by titrating 1 liter of 0.0009-0.0011 M acids with 1.0 M standard NaOH titrant. No volume adjustment was made. The solutions were open to atmospheric air.

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RESULTS AND DISCUSSION

Derivation of the Equation of State

The derivation of the equation of state consists of 7 stages: 1) The reaction scheme of the electrolytic dissociation of an acid and a base is written; 2) An equation is written for the degree of dissociation, this is an auxiliary variable; 3) An equation is written for the dissociation constant; 4) The degree of dissociation is expressed in terms of the dissociation constant; 5) The equation of electrical neutrality is written; 6) All members of the electrical neutrality equation are expressed in terms of known variables and coefficients; 7) The electrical neutrality equation thus obtained is converted into a normal polynomial.

We assume the system has a constant unit volume of 1L. For the convenience of deriving the equation, we introduce the following temporary abbreviations:

B^+ - a number of moles of cation (B^+) in solution

oh^- - a number of moles of hydroxide (OH^-) in solution equal to W/h.

Ah_n, $Ah^{-1}_{(n-1)}$, $Ah^{-2}_{(n-2)}$, and $Ah^{-3}_{(n-3)}$ - a number of moles of acid and dissociated acid, for example, if n=3: Ah_3 (not dissociated acid), Ah_3^{-1}, Ah_2^{-2}, and A^{-3} in particular: H_3PO_4, $H_2PO_4^{-1}$, HPO_4^{-2}, PO_4^{-3} phosphoric acid and products of its dissociation.

C1, C2, and C3.- dissociation degree of the first, second, and third stages of dissociation, respectively. It is the fraction of original solute molecules that have dissociated.

Now let's write down the equations that will be needed to derive the general equation of state:

$B \to B^+ + oh^-$ a base dissociation.

Let's write 3 equations of acid dissociation:

$Ah_n \to Ah^{-1}_{(n-1)} + h^+$,

$Ah^{-1}_{(n-1)} \to Ah^{-2}_{(n-2)} + h^+$,

$Ah^{-2}_{(n-2)} \to Ah^{-3}_{(n-3)} + h^+$

Here we use an auxiliary variable, the degree of dissociation (C):

$Ah^{-1}_{(n-1)} = C1*Ah_n$, $Ah^{-2}_{(n-2)} = C2*Ah^{-1}_{(n-1)}$, $Ah^{-3}_{(n-3)} = C3*Ah^{-2}_{(n-2)}$

Let's make a chain of transformations linking dissociation constants K, degrees of dissociation C, and acid concentrations:

$K1 = Ah^{-1}_{(n-1)}*h/(Ah_n - Ah^{-1}_{(n-1)})$

$Ah^{-1}_{(n-1)} = C1*Ah_n$,

$K1=C1*h/(1-C1)$, and $C1 = K1/(K1+h)$, then

$Ah^{-1}_{(n-1)} = K1*Ah_n/(K1+h)$.

$K2 = Ah^{-2}_{(n-2)}*h/(Ah^{-1}_{(n-1)} - Ah^{-2}_{(n-2)})$

$Ah^{-2}_{(n-2)} = C2*Ah^{-1}_{(n-1)}$

$K2=C2*h/(1-C2)$

$C2 = K2/(K2+h)$

$Ah^{-2}_{(n-2)} = K2*Ah^{-1}_{(n-1)}/(K2+h) = K1*K2*Ah_n/[(K1+h)*(K2+h)]$

$K3 = Ah^{-3}_{(n-3)}*h/(Ah^{-2}_{(n-2)} - Ah^{-3}_{(n-3)})$,

$Ah^{-3}_{(n-3)} = C3*Ah^{-2}_{(n-2)}$

$K3=C3*h/(1-C3)$

$C3 = K3/(K3+h)$

$Ah^{-3}_{(n-3)} = K3*Ah^{-2}_{(n-2)}/(K3+h) = K1*K2*K3*Ah_n/[(K1+h)*(K2+h)*(K3+h)]$

Now we write the equation of electrical neutrality. On the left, we place negatively charged particles, and on the right, positively charged particles:

$Ah^{-1}_{(n-1)} + Ah^{-2}_{(n-2)} + Ah^{-3}_{(n-3)} + W/h = B + h$ (l)

To simplify the equation, let us denote the amount of acid added to the solution by one letter "A" and rewrite the equation:

$A*K1/(K1 + h) + A*K1*K2/(K2 + h)/(K1+h) + A*K1*K2*K3/(K3 + h)/(K2 + h)/(K1+h) + W/h = B + h$. [**].

This is the equation of state of the system, it includes only known or given variables and constants: A - the number of moles of acid added to the solution, B - the number of moles of alkali added to the solution, W - the Water Ionization Constant, K - the dissociation constant, h - the number of moles of hydrogen ions in the solution. We limited ourselves to the triprotic acids, but you can similarly write an equation for n-protic acids (n>3). Now let's convert the fractional notation [**] to a linear one and group the terms:

$h^5 + a*h^4 + b*h^3 + c*h^2 + d*h + e = 0$ [***]. This is the normal form of the equation of state for an aqueous solution of a mixture of a triprotic acid and a strong base. The coefficients (a, b, c, d) are presented in Table 1.

It is easy to show, that if we put K3=0, then from the equation [***] we get the equation for a diprotic acid, and if K3=0 and K2=0, then we get the equation for a monoprotic acid, Table 1.

A Mixture of Several Acids

The equation of state for a mixture of acids is derived in the same way as in the previous case. The equation contains the amount of each of the acids (A1, A2, ... An), dissociation constants (K), and the amount of added strong base (B). Let us derive the equation of state for a mixture of two acids, diprotic (A1, K1, K2) and monoprotic (A2, K3). Passing all 7 steps of the derivation we take the equation of state:

$h^5 + a*h^4 + b*h^3 + c*h^2 + d*h + e = 0$, The coefficients a, b, c, d, and e are in Table 1.

***Note 1**: The equation of state for an aqueous solution of a weak base and a strong acid is symmetrical to this one [***]. The acid dissociation constants are replaced by the base dissociation constants, A is replaced by B, B is replaced by A, and h is the number of moles of hydroxide ions in the solution.*

Using this method, one can derive the equations of state for many systems and use them for model experiments.

Table 1: Polynomial coefficients of the general equation of state, weak or strong acid, and strong base

Max. degree.	Mix of diprotic acid A1(K1, K2) and monoprotic acid. A2(K3). $h^5 + a*h^4 + b*h^3 + c*h^2 + d*h + e = 0$	triprotic acid. (AH_3) $h^5 + a*h^4 + b*h^3 + c*h^2 + d*h + e = 0$	diprotic acid. (AH_2) $h^4 + a*h^3 + b*h^2 + c*h + d = 0$	monoprotic acid. (AH) $h^3 + a*h^2 + b*h + c = 0$	Strong acid. $h^2 + a*h + b = 0$
h^5	1	1	0	0	0
h^4	B + K1+K2+K3	B + K1+K2+K3	1	0	0
h^3	K1*K2 + K1*K3 + K2*K3 + B*(K1 + K2 + K3) – W – A1*K1-A2*K3	K1*K2 + K1*K3 + K2*K3 + B*(K1 + K2 + K3) – W – A*K1	B + K1 + K2	1	0
h^2	K1*K2*K3 + B*(K1*K2 + K1*K3 + K2*K3) – W*(K1 + K2 + K3) – A1*(2*K1*K2 + K1*K3) - A2*(K1*K3 + K2*K3)	K1*K2*K3 + B*(K1*K2 + K1*K3 + K2*K3) – W*(K1 + K2 + K3) – A*(2*K1*K2 + K1*K3)	B*(K1 + K2) + K1*K2 - W – A*K1	B + K1	1
h	B*K1*K2*K3 – W*(K1*K2 + K1*K3 + K2*K3) – 2*A1*K1*K2*K3 – A2*K1*K2*K3	B*K1*K2*K3 – W*(K1*K2 + K1*K3 + K2*K3) – 3*A*K1*K2*K3	B*K1*K2 – W*(K1 + K2) -2*A*K1*K2	B*K1 – W – A*K1	B - A
h^0 (const.)	-W*K1*K2*K3	-W*K1*K2*K3	-W*K1*K2	-W*K1	-W

Let us add two important cases to our consideration.

Weak Base and Weak Acid

Let us compose the equation of state for an aqueous solution of a mixture of a weak base and a weak acid. The equation will contain both the acid dissociation constant Ka and the base dissociation constant Kb. The derivation of the equation is like the one above:

Ka=K1, Kb=K2

Ca= K1/(K1 + h)

Cb= K2/(K2 + OH^-) = K2*h/(K2*h + W)

A*Ca + W/h = h + B*Cb (equation of electrical neutrality)

A*K1/(K1 + h) + W/h = h + B*Kb*h/(K2*h + W). After transformations, we get the equation of state in normal form: $h^4 + a*h^3 + b*h^2 + c*h + d = 0$, where:

a = B + K1 + W/K2

b = B*K1 + W*K1/K2 – W – A*K1

c = -(W*K1 + A*W*K1/K2 + W^2/K2)

d = -K1*W^2/K2

A Special Case Used in Chemical Practice

Consider an aqueous solution prepared by dissolving S moles of a weak acid salt and a strong base (sodium acetate for example) to which ΔA moles of this weak acid are added. The state of this system can also be reached by adding S moles of a strong base to an aqueous solution of S moles of acid (we will get S moles of salt) and another ΔA moles of acid, in total (S + ΔA) moles of acid. Let's apply our equation of state for a weak monoprotic acid and a strong base: $h^3 + (B + K1)*h^2 + (B*K1 - W - A*K1)*h - W*K1 = 0$. Having made a change of variables, B = S, A= S+ΔA we get: $h^3 + (S + K1)*h^2 + (K1*(S - S - \Delta A) - W)*h - W*K1 = 0$ or $h^3 + (S + K1)*h^2 - (K1*\Delta A + W)*h - W*K1 = 0$. The last equation is the Charlot equation (Charlot equation 2023) in our notation. Note 1 is also valid for the last two cases.

Connection to the formula of Robert de Levie

Let's show how to derive the equation of state at the constant volume from the De Levie formula for titration: Vb= Va*(Ca*&-D)/(Cb+D) (Harvey D. 2016), where &=K/(h+K), D=h-oh, Va – the volume of acid, Vb – the volume of base (titrant), Ca – molarity of acid, Cb – molarity of base.

Vb*Cb + Vb*D = Va*Ca*& -Va*D, where Vb*Cb = B (mol), and Va*Ca=A (mol)

B + D*(Vb+Va) = A*&.

Let us make a single, but reasonable, simplification. We will assume that the total volume is unit and constant Vb+Va=1. In practice, this is easy to implement, for example, dissolve 0.001 mol of analyte in 1 liter of water and titrate by 1.0 M titrant. The volume change is negligible. Then, B + D = A*&. → B+(h-oh)=A*K/(h+K) → B+ h - W/h=A*K/(h+K) → B*(h+K) + h*(h+K)-W*(h+K)/h = A*K → B*h+B*K+h^2+h*K-W*h+W*K)/h=A*K → B*h^2 + B*K*h + h^3+ h^2*K -W*h-W*K – A*K*h= h3 + h2*(B+K) + h*(B*K-A*K-W)-W*K=0. So, it is exactly the normal form of the equation of state for weak monoprotic acid, Table 1.

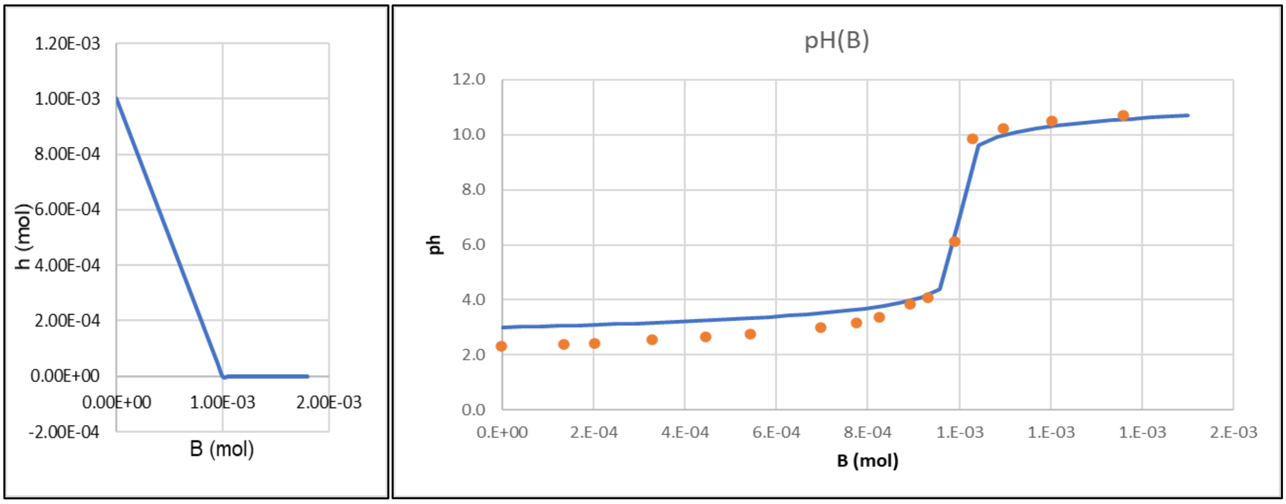
Solution of the Equations of State in Radicals (Утешев А. 2022)

The next task is to solve the derived equations of state, that is, to find their roots. Solving equations in radicals will give us a formula with which we can plot the dependence of the concentration of hydrogen ions on the coefficient of the equation - B or A (the amount of base or acid added to the solution). In other words, we will get the formula of the Titration Curve. Thanks to the work of Omar Khayyam (1048–1131), Niccolo Tartaglia (1500–1557), Gerolamo Cardano (1501–1576), Lodovico Ferrari (1522–1565), and other great mathematicians, we know how to find the roots of polynomials 2nd, 3rd, and 4th degree.

Each equation of state has as many roots as its degree, but we are only interested in one real, positive root, and as we will show below, such a root exists.

Let's formulate the Chemist's Theorem: The equation of state presented as a normal polynomial of the n-th degree with real coefficients ($h^n + a_1h^{(n-1)} + \ldots + a_{(n-1)}h + a_n = 0$) has at least one real positive root if the free term of the polynomial is negative ($a_n < 0$). If the value of the polynomial at h=0 is positive ($a_n > 0$), then a positive root may or may not exist. This can be verified by moving the graph, for example, of a cubic polynomial ($P=h^3 + a*h^2 +b* h + c$), along the P-0-h coordinate plane. In Table 1, the bottom row shows the free terms of the polynomials, all of which are negative, so the real positive root exists.

Strong acid and strong base. $h^2 +(B - A)* h - W = 0$
$h=(A-B)/2 + sqrt(D)$ (&), where $D = (A-B)^2/4 + W$ is discriminant of this quadratic equation.
$ph = - \log_{10}((A-B)/2 + sqrt((A-B)^2/4 + W))$ (&&)
The pH at the equivalence point according to the visual assessment is 7 (Figure 1 b). This is quite the expected result.



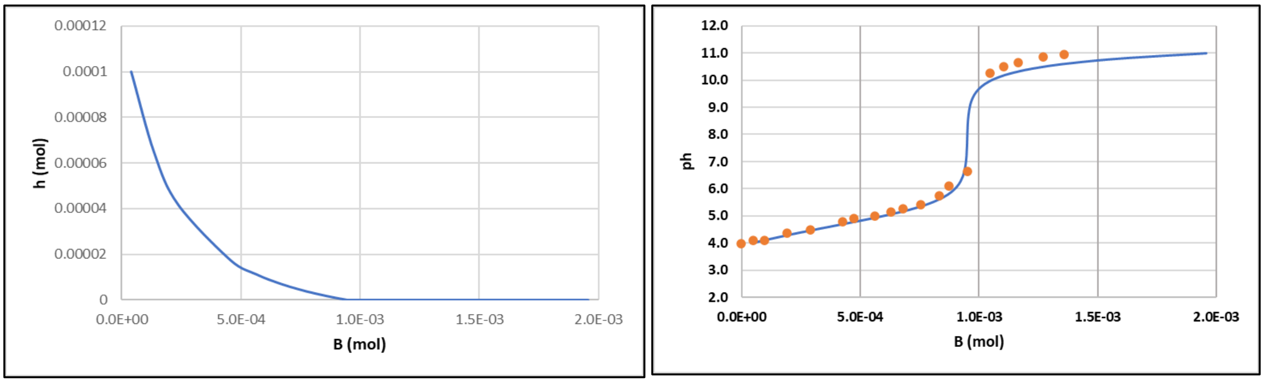
a b

Figure 1 (a, b): A – 10^{-3} mol, a- function (&), b – function (&&). The line is the calculation, and the markers are the experimental points

Week monoprotic acid and strong base. $h^3 + a*h^2 +b* h + c = 0$. The root is given by the equation:
$h = y - a/3$, where
$y = 2*sqrt(-p/3)*\cos(\varphi/3)$
$\varphi = \arccos(3*q*sqrt(-3/p)/(2*p))$
$p = b – a^2/3$,
$q = 2*a^3/27 – a*b/3 + c$

For details see appendix#1. Based on the found root of the polynomial (h), a theoretical titration curve is constructed, with the dependence of ph on the amount of titrant (B) and polynomial coefficients. The theoretical curve and experimental points are presented in Figure 2. The ph at the equivalence point according to the visual assessment is 7.9 (Figure 2 b).

The independent way to calculate the equivalence point of weak monoprotic (A) acids and a base (B). At this point, we have a solution of a salt formed by weak acid and a strong base. The pH is determined by the hydrolysis of this salt (Khan Academy. 2023, pH at The Equivalence Point 2023).
$A^- + H_2O$ <-> $AH + OH^-$ (hydrolysis equation)
$Kh = [AH]*[OH^-]/[A^-]$, (hydrolysis constant). At the equivalence point: $[AH]=[OH^-]$, and $[A^-]=[B]$, hence $Kh= [OH^-]^2/B = W^2/(h^2*B)$.
$Ka= [A^-]*[H^+]/[AH]$, (acid dissociation constant)
and $Kh*Ka=W= W^2*Ka/(h^2*B)$, hence: $h^2=W*K/B$. After taking the logarithm, we get the equation $ph=7 + (pK-pB)/2$ [$$] where p means the $-Log_{10}()$.
Calculation by the formula [$$] gives us the: $7+(pK-pB)/2=7+(4.76-3)/2=7.9$ The result is in good agreement with the estimation.



a b

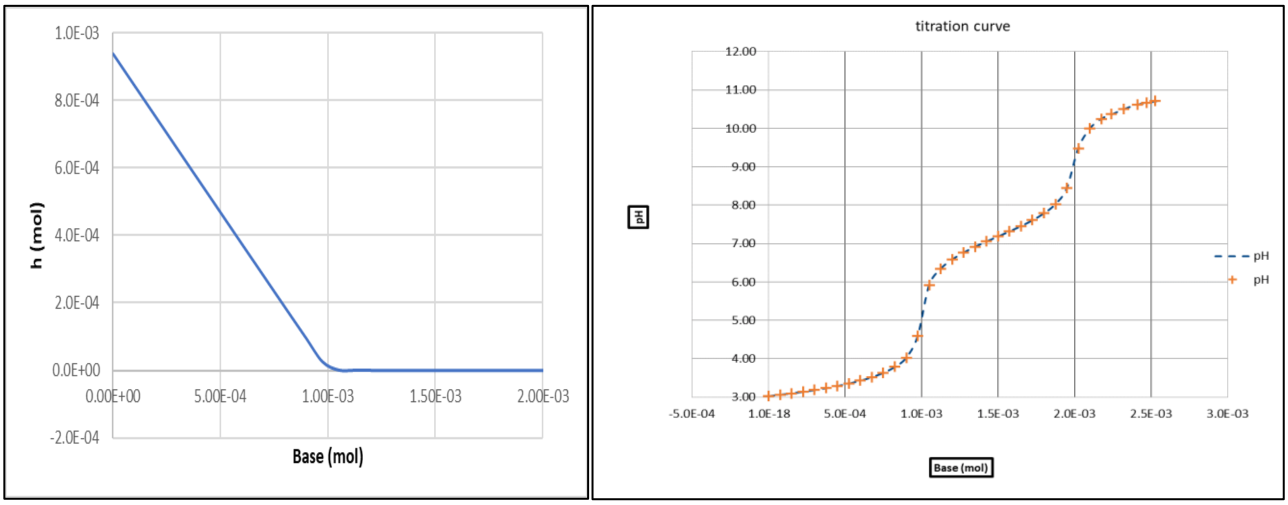
Figure 2 (a, b): A – acetic acid $0.95*10^{-3}$ mol $Ka=1.75*10^{-5}$. a- root of the cubic equation h=h(B), b – the root of the cubic equation pH=pH(B), the line is the calculation, and the markers are the experimental points

Diprotic acid (AH_2). $h^4 + a*h^3 + b*h^2 + c*h + d = 0$
To find the roots, it is necessary to take several steps and make several changes to variables (Утешев А. 2022). The root (h) is given by the equation:

$h = x - a/4$
$x = K/2 + sqrt(D)$
$D = K^2/4 - (t/2 - L)$
$K = sqrt(t - p)$
$L = q/(2*K)$
$t = y - \alpha/3$
$y = 2*(-\Pi/3)^{1/2}*cos(\varphi/3)$
$\varphi = arccos(3*Q*(-3/\Pi)^{1/2}/(2*\Pi))$
$\Pi = \beta - \alpha^2/3$
$Q = 2*\alpha^3/27 + \varepsilon - \alpha*\beta/3$
$\alpha = -p$
$\beta = -4*r$
$\varepsilon = 4*p*r - q^2$
$p = b - 3*a^2/8$
$q = a^3/8 - b*a/2 + c$
$r = d - c*a/4 + b*a^2/16 - 3*a^4/256$

See Appendix#2 for details.
The theoretical titration curve based on the root of the polynomial is presented in Figure 3 b (dashed line).
The second way to construct a theoretical titration curve. Directly from the equation of state $h^4 + (B + K1 + K2)*h^3 + (B*(K1 + K2) + K1*K2 - W - A*K1)*h^2 + (B*K1*K2 - W*(K1 + K2) - 2*A*K1*K2)*h - W*K1*K2 = 0$, by a simple transformation, we obtain the dependence B=f(h):
$B = [(W*K1*K2 - h^4 - h^3*(K1 + K2) - h^2*(K1*K2 - W - A*K1) + h*(K1*W + K2*W + 2*A*K1*K2)]/(h^3 + h^2*(K1 + K2) + h*K1*K2)$ (&&&)

Now we have the theoretical titration curves constructed in two ways: first, by the dependence of the root of the equation of state (h) on the value of B (titrant), which is an independent variable, and second by the dependence of B on the independent variable h using formula (&&&). Both curves are the same (Figure 3 (b).



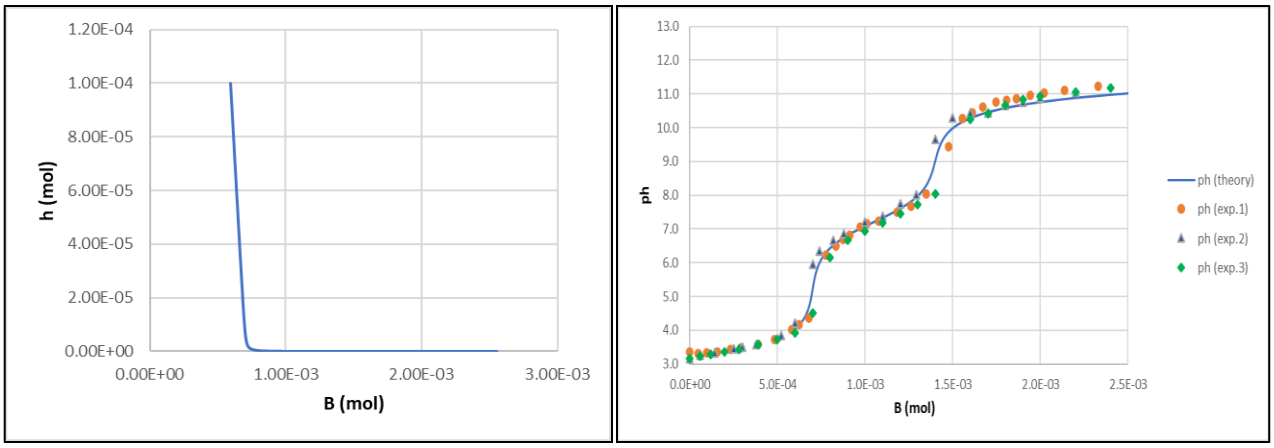
a b

Figure 3 (a, b): A – sulfurous acid, 10^{-3} mol, K1= 0.014, $K2=6.5*10^{-8}$; a- root of the cubic equation h=h(B), b – The theoretical titration curve was obtained by finding the root of the equation of state, dashed line, and by plotting the dependence B=f(h) obtained directly from the equation of state, icons

Triprotic Acid (AH_3)

As we have seen from the previous paragraph, the titration curve can be calculated in two ways based on the equation of state. Here we will not look for the roots of the fifth-degree polynomial, but we will use the second way. We express B directly from the equation of state and plot the titration curve (Figure 4 b) in the coordinates ph - B: $B = [W*K12*K2*K3 – h^5-h^4*(K1 + K2 + K3) – h^3*(K1*K2 + K1*K3 + K2*K3 – W – A*K1) – h^2*(K1*K2*K3 – W*(K1 + K2 + K3) – A*(2*K1*K2 + K1*K3)) + h*(W*(K1*K2 + K1*K3 + K2*K3) + 3*A*K1*K2*K3)]/(h^4 + h^3*(K1 + K2 + K3) + h^2*(K1*K2 + K1*K3 + K2*K3) + h*K1*K2*K3)$. (&&&&).

It is easy to see that for K3=0 (&&&&) goes into (&&&).



a b

Figure 4 (a, b): A – phosphoric acid, $7*10^{-4}$ mol, K1= $6.9*10^{-3}$, K2=$6.2*10^{-8}$; K3=$4.8*10^{-13}$; panel a – h versus B dependence, panel b – ph versus B dependence, solid line is the calculation, and symbols are the experimental data

The theoretical curve agrees well with the experiment.

CONCLUSION

The method has been developed for constructing the equation of state for solutions of weak acids and a strong base, solutions of weak bases and a strong acid, and, solutions of weak acids and weak bases. The titration curves obtained based on the general equations of state are continuous monotonic functions, which is an advantage over the currently used piecewise continuous ones.

Checking the correctness of the theoretical model was carried out in several ways:

1) It is shown that the previously published Charlot equation is a special case of the general equation of state and is derived from it.
2) Theoretical titration curves constructed based on the general equation of state are in good agreement with the experimental data.
3) Independently calculated or known singular points of the titration curve (in particular equivalence points) coincide with these points of the theoretical curve.

Prospects for the Future

It is planned to use the equations of state as a tool for studying electrolyte solutions and for predicting their behavior.

Abbreviations

K1, K2, and K3 - dissociation constants
A – A number of moles of acid added to the solution.
B – A number of moles of base added to the solution.
h – A number of moles of hydrogen ions (H^+) in solution
W – The Water Ionization Constant (Kw)
W/h - A number of moles of hydroxide ions (OH^-) in solution

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Appendix# 1

To find the roots of a cubic equation, it is necessary to take several steps and make several changes to variables (Утешев А. 2022).

$h^3 + a*h^2 + b*h + c = 0$

let $h = y + k$, and $k = -a/3$ (first changing of variable) ->

$\mathbf{y^3 + p*y + q = 0}$ were

$p = b – a^2/3$, and

$q = 2*a^3/27 – a*b/3 + c$

$y = u + v$ and let $u*v = -p/3$ (second changing of variable) ->

$u^3 + v^3 + q = 0$

$u^3*v^3 = -p^3/27$ ->

u^3 and v^3 are the roots (t1, t2) of the quadratic equation: $t^2 + t*q – p^3/27 = 0$, its discriminant is D.

$D = q^2/4 + p^3/27$ – Discriminant of a cubic polynomial. In all cases considered by us, the discriminant of the cubic equation was negative. So, to find the roots, we need to use a complex number: $a + i*b = r*(\cos(\varphi) + i*\sin(\varphi))$ where "i" is the imaginary unit.

Theorem. In the case of $D < 0$, the real roots of the polynomial $y^3 + p*y + q$ are given by the formulas:

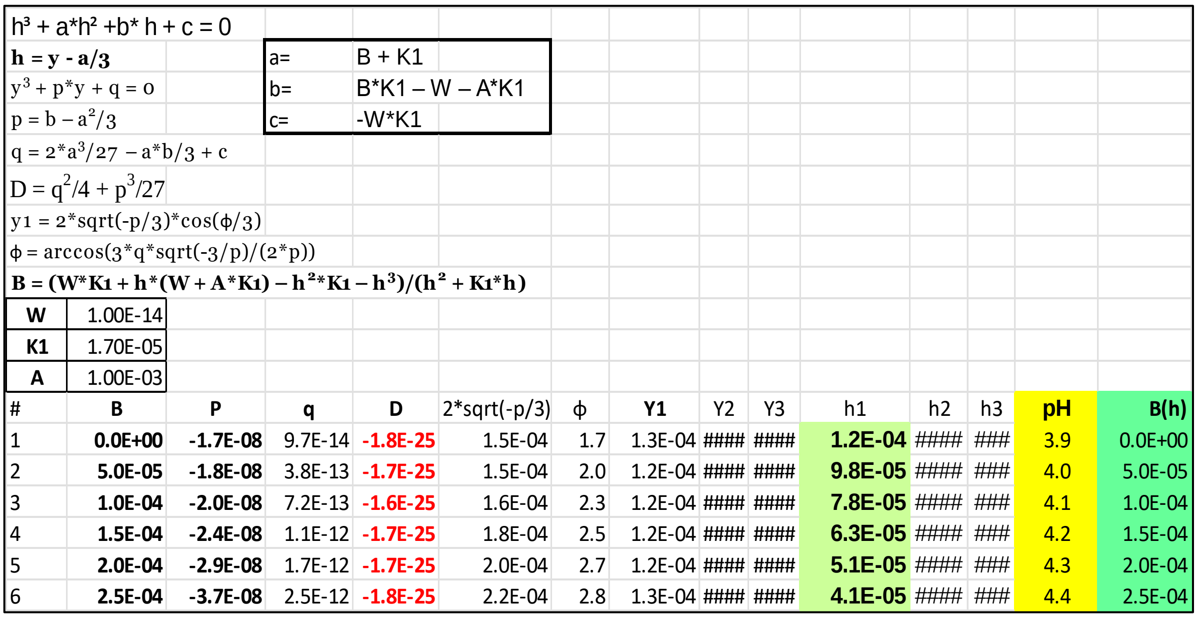
$y1 = 2*\mathrm{sqrt}(-p/3)*\cos(\varphi/3)$

$y2 = 2*\mathrm{sqrt}(-p/3)*\cos(\varphi/3+ 2*\pi/3)$

$y3 = 2*\mathrm{sqrt}(-p/3)*\cos(\varphi/3+ 4*\pi/3)$ were $\pi=3.14…$

$\varphi = \arccos(3*q*\mathrm{sqrt}(-3/p)/(2*p))$

The desired **h** is related to **y** by the relation: $\mathbf{h = y - a/3}$



$h^3 + a*h^2 + b*h + c = 0$

$\mathbf{h = y - a/3}$

$y^3 + p*y + q = 0$

$p = b – a^2/3$

$q = 2*a^3/27 – a*b/3 + c$

$D = q^2/4 + p^3/27$

$y1 = 2*\mathrm{sqrt}(-p/3)*\cos(\phi/3)$

$\phi = \arccos(3*q*\mathrm{sqrt}(-3/p)/(2*p))$

$\mathbf{B = (W*K1 + h*(W + A*K1) – h^2*K1 – h^3)/(h^2 + K1*h)}$

a=	B + K1
b=	B*K1 – W – A*K1
c=	-W*K1

W	1.00E-14
K1	1.70E-05
A	1.00E-03

#	**B**	**P**	**q**	**D**	2*sqrt(-p/3)	ϕ	**Y1**	Y2	Y3	h1	h2	h3	**pH**	**B(h)**
1	**0.0E+00**	**-1.7E-08**	9.7E-14	**-1.8E-25**	1.5E-04	1.7	1.3E-04	####	####	**1.2E-04**	####	###	3.9	0.0E+00
2	**5.0E-05**	**-1.8E-08**	3.8E-13	**-1.7E-25**	1.5E-04	2.0	1.2E-04	####	####	**9.8E-05**	####	###	4.0	5.0E-05
3	**1.0E-04**	**-2.0E-08**	7.2E-13	**-1.6E-25**	1.6E-04	2.3	1.2E-04	####	####	**7.8E-05**	####	###	4.1	1.0E-04
4	**1.5E-04**	**-2.4E-08**	1.1E-12	**-1.7E-25**	1.8E-04	2.5	1.2E-04	####	####	**6.3E-05**	####	###	4.2	1.5E-04
5	**2.0E-04**	**-2.9E-08**	1.7E-12	**-1.7E-25**	2.0E-04	2.7	1.2E-04	####	####	**5.1E-05**	####	###	4.3	2.0E-04
6	**2.5E-04**	**-3.7E-08**	2.5E-12	**-1.8E-25**	2.2E-04	2.8	1.3E-04	####	####	**4.1E-05**	####	###	4.4	2.5E-04

Figure 1: **An example of an EXCEL spreadsheet for calculating the roots of a cubic equation**

At the request of a client, we develop and supply spreadsheet templates for calculations and plotting titration curves.

Appendix# 2

To find the roots of a quartic equation, it is necessary to take several steps and make several changes to variables (Утешев А. 2022).

Week diprotic acid (AH_2). $h^4 + a*h^3 + b*h^2 + c*h + d = 0$

Having made the change of variable $h = x - a/4$, we get the equation:

$\mathbf{x^4 + x^2*p + x*q + r = 0}$ (#), where

$p = b – 3*a^2/8$

$q = a^3/8 - b*a/2 + c$

$r = d – c*a/4 + b*a^2/16 - 3*a^4/256$

Add and subtract the expression $(x^2*t + t^2/4)$ to (#) to get the sum of two perfect squares:

$(x^2 + t/2)^2 = (t-p)*x^2 – q*x + (t^2/4 – r)$ (##)

The right part of the equation will be perfect square $(t-p)*x^2 – q*x + (t^2/4 – r) \equiv (K*t + L)^2$ at $K=\mathrm{sqrt}(t-p)$, and $L=-q/(2*K)$ if

$D = q^2 – 4*(t-p)*(t^2/4 – r) = 0 = t^3 – p*t^2 – 4*r*t + (4*p*r – q^2)$

$t^3 – p*t^2 – 4*r*t + (4*p*r – q^2) = 0$ This cubic equation is the **Ferrari Resolvent**.

$t^3 + \alpha*t^2 + \beta*t + \varepsilon = 0$

$\alpha = -p$

$\beta = -4*r$

$\varepsilon = 4*p*r – q^2$

Let's find the root of the Resolvent (see appendix#1), for this, we will make the change of variable $t = y + \Upsilon = y - \alpha/3$ and get the equation:

$\mathbf{y^3 + \Pi*y + Q = 0}$ (###), where

$\Pi = \beta – \alpha^2/3$

$Q = 2* \alpha^3/27 + \varepsilon - \alpha* \beta/3$

$D = Q^2/4 + \Pi^3/27$ – Discriminant of cubic polynomial

$D < 0 \Rightarrow y = 2*(- \Pi/3)^{1/2}*\cos(\varphi/3)$

where $\varphi = \arccos(3*Q*(-3/\Pi)^{1/2}/(2* \Pi))$

if $D > 0$, the only real root is computed using Cardano's formula (Утешев А. 2022). But in all our cases, D was negative.

Now we have one chosen root "**y**".

Go back to equation (##):

$t = y -\alpha/3$

$K = (t-p)^{1/2}$

$L = -q/(2*K)$

$(x^2 + t/2)^2 = (t-p)*x^2 - q*x + (t^2/4 - r) = (t-p)*x^2 - q*x + (t^2/4 - r) = (K*x + L)^2 \rightarrow$

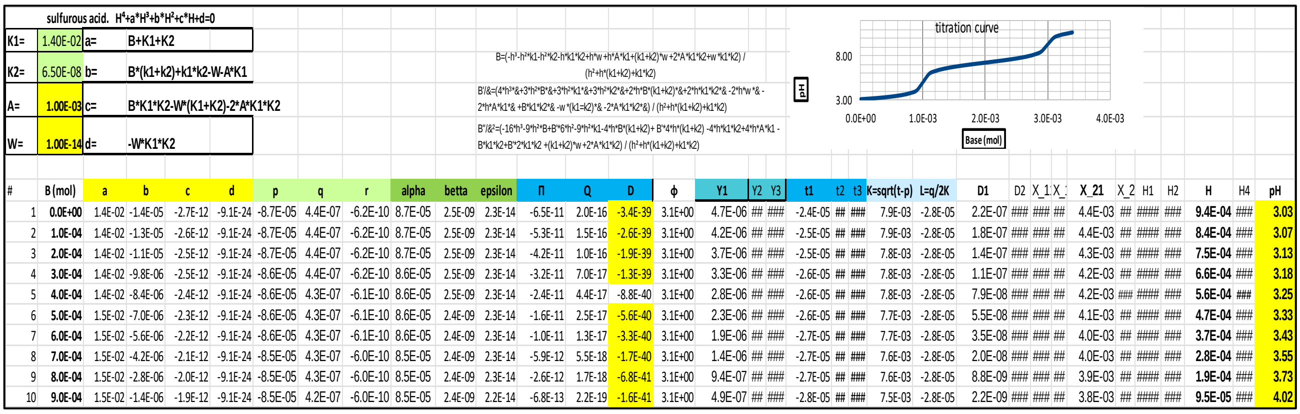
$(x^2 + t/2)^2 = ((t-p)^{1/2}*x - q/(2*K))^2 \rightarrow$

$x^2 + t/2 = \pm(K*x + L) = \pm((t-p)^{1/2}*x - q/(2*K))$

Now we have two quadratic equations and two discriminants D1 and D2:

D1=K2/4-(t/2+L), D2=K2/4-(t/2-L), and hence four roots: x1, x2, x3 and x4.

We choose one root so that $h = x -a/4 > 0$. Finally, we get the functional dependence h = f(B, A, K1, K2), and the theoretical titration curve ph= f(B, A, K1, K2).



sulfurous acid. $H^4+a*H^3+b*H^2+c*H+d=0$

K1= 1.40E-02 a= B+K1+K2

K2= 6.50E-08 b= B*(k1+k2)+k1*k2-W-A*K1

A= 1.00E-03 c= B*K1*K2-W*(K1+K2)-2*A*K1*K2

W= 1.00E-14 d= -W*K1*K2

$B=(-h^3-h^2*k1-h^2*k2-h*k1*k2+h*w+h*A*k1+(k1+k2)*w+2*A*k1*k2+w*k1*k2) / (h^2+h*(k1+k2)+k1*k2)$

$B'/\&=(4*h^3*\&+3*h^2*B*\&+3*h^2*k1*\&+3*h^2*k2*\&+2*h*B*(k1+k2)*\&+2*h*k1*k2*\& -2*h*w*\& - 2*h*A*k1*\& +B*k1*k2*\& -w*(k1=k2)*\& -2*A*k1*k2*\&) / (h^2+h*(k1+k2)+k1*k2)$

$B''/\&^2=(-16*h^3-9*h^2*B+B'*6*h^2-9*h^2*k1-4*h*B*(k1+k2)+ B'*4*h*(k1+k2) -4*h*k1*k2+4*h*A*k1 - B*k1*k2+B'*2*k1*k2 +(k1+k2)*w+2*A*k1*k2) / (h^2+h*(k1+k2)+k1*k2)$

#	B (mol)	a	b	c	d	p	q	r	alpha	betta	epsilon	Π	Q	D	ϕ	Y1	Y2	Y3	t1	t2	t3	K=sqrt(t-p)	L=q/2K	D1	D2	X_1	X_	X_21	X_2	H1	H2	H	H4	pH
1	**0.0E+00**	1.4E-02	-1.4E-05	-2.7E-12	-9.1E-24	-8.7E-05	4.4E-07	-6.2E-10	8.7E-05	2.5E-09	2.3E-14	-6.5E-11	2.0E-16	-3.4E-39	3.1E+00	4.7E-06	##	###	-2.4E-05	##	###	7.9E-03	-2.8E-05	2.2E-07	###	###	##	4.4E-03	##	####	###	**9.4E-04**	###	**3.03**
2	**1.0E-04**	1.4E-02	-1.3E-05	-2.6E-12	-9.1E-24	-8.7E-05	4.4E-07	-6.2E-10	8.7E-05	2.5E-09	2.3E-14	-5.3E-11	1.5E-16	-2.6E-39	3.1E+00	4.2E-06	##	###	-2.5E-05	##	###	7.9E-03	-2.8E-05	1.8E-07	###	###	##	4.4E-03	##	####	###	**8.4E-04**	###	**3.07**
3	**2.0E-04**	1.4E-02	-1.1E-05	-2.5E-12	-9.1E-24	-8.7E-05	4.4E-07	-6.2E-10	8.7E-05	2.5E-09	2.3E-14	-4.2E-11	1.0E-16	-1.9E-39	3.1E+00	3.7E-06	##	###	-2.5E-05	##	###	7.8E-03	-2.8E-05	1.4E-07	###	###	##	4.3E-03	##	####	###	**7.5E-04**	###	**3.13**
4	**3.0E-04**	1.4E-02	-9.8E-06	-2.5E-12	-9.1E-24	-8.6E-05	4.4E-07	-6.2E-10	8.6E-05	2.5E-09	2.3E-14	-3.2E-11	7.0E-17	-1.3E-39	3.1E+00	3.3E-06	##	###	-2.6E-05	##	###	7.8E-03	-2.8E-05	1.1E-07	###	###	##	4.2E-03	##	####	###	**6.6E-04**	###	**3.18**
5	**4.0E-04**	1.4E-02	-8.4E-06	-2.4E-12	-9.1E-24	-8.6E-05	4.3E-07	-6.1E-10	8.6E-05	2.5E-09	2.3E-14	-2.4E-11	4.4E-17	-8.8E-40	3.1E+00	2.8E-06	##	###	-2.6E-05	##	###	7.8E-03	-2.8E-05	7.9E-08	###	###	##	4.2E-03	###	####	###	**5.6E-04**	###	**3.25**
6	**5.0E-04**	1.5E-02	-7.0E-06	-2.3E-12	-9.1E-24	-8.6E-05	4.3E-07	-6.1E-10	8.6E-05	2.4E-09	2.3E-14	-1.6E-11	2.5E-17	-5.6E-40	3.1E+00	2.3E-06	##	###	-2.6E-05	##	###	7.7E-03	-2.8E-05	5.5E-08	###	###	##	4.1E-03	##	####	###	**4.7E-04**	###	**3.33**
7	**6.0E-04**	1.5E-02	-5.6E-06	-2.2E-12	-9.1E-24	-8.6E-05	4.3E-07	-6.1E-10	8.6E-05	2.4E-09	2.3E-14	-1.0E-11	1.3E-17	-3.3E-40	3.1E+00	1.9E-06	##	###	-2.7E-05	##	###	7.7E-03	-2.8E-05	3.5E-08	###	###	##	4.0E-03	##	####	###	**3.7E-04**	###	**3.43**
8	**7.0E-04**	1.5E-02	-4.2E-06	-2.1E-12	-9.1E-24	-8.5E-05	4.3E-07	-6.0E-10	8.5E-05	2.4E-09	2.3E-14	-5.9E-12	5.5E-18	-1.7E-40	3.1E+00	1.4E-06	##	###	-2.7E-05	##	###	7.6E-03	-2.8E-05	2.0E-08	###	###	##	4.0E-03	##	####	###	**2.8E-04**	###	**3.55**
9	**8.0E-04**	1.5E-02	-2.8E-06	-2.0E-12	-9.1E-24	-8.5E-05	4.3E-07	-6.0E-10	8.5E-05	2.4E-09	2.3E-14	-2.6E-12	1.7E-18	-6.8E-41	3.1E+00	9.4E-07	##	###	-2.7E-05	##	###	7.6E-03	-2.8E-05	8.8E-09	###	###	##	3.9E-03	##	####	###	**1.9E-04**	###	**3.73**
10	**9.0E-04**	1.5E-02	-1.4E-06	-1.9E-12	-9.1E-24	-8.5E-05	4.2E-07	-6.0E-10	8.5E-05	2.4E-09	2.2E-14	-6.8E-13	2.2E-19	-1.6E-41	3.1E+00	4.9E-07	##	###	-2.8E-05	##	###	7.5E-03	-2.8E-05	2.2E-09	###	###	##	3.8E-03	##	####	###	**9.5E-05**	###	**4.02**

Figure 1: An example of an EXCEL spreadsheet for calculating the roots of a quartic equation

At the request of a client, we develop and supply spreadsheet templates for calculations and plotting titration curves.