

In the Classroom

Simplified Treatment of Aqueous Ionic Reactions. Application to Acid–Base Problems

C. FERNÁNDEZ-PEREIRA*, M. ALCALDE, AND J. VALE

E. S. Ingenieros Industriales

Departamento de Ingeniería Química y Ambiental,
Universidad de Sevilla

Sevilla, E-41012 Sevilla, Spain

pereira@esi.us.es

*In principle,
learning about
learners allows
faculty to create
a structure in
which novice
learner skills
more effectively.*

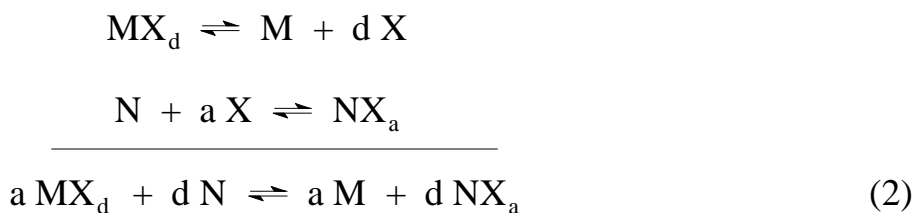
A simplified study of aqueous ionic reactions that treats them as particle-interchange reactions is presented. Most introductory chemistry courses present these reactions separately, though their joint study is of pedagogical interest, as it is coherent and systematic, and it also provides a more global view of ionic reactions. The particle acceptor potential (AP) of a conjugate donor–acceptor pair is defined and used in a graphical method to solve acid–base problems using predominance diagrams. The AP of a conjugate acid–base pair, which measures its tendency to accept protons, allows comparisons between pairs. A treatment valid not only for acid–base reactions, but also for redox, solubility or complexation reactions, and a strategy aimed at solving practical cases are described and applied to different acid–base problems.

The similarities of different aqueous ionic equilibria have been emphasized the most in analytical chemistry textbooks [1–4] and other related publications [5–9]. In this paper, we present a simplified graphical method that easily provides both a rapid estimation of the final acid–base equilibrium, and a technique for solving other equilibrium problems. This approach has pedagogical value for students in an introductory chemistry course. The approach introduced here represents an important step toward attaining the mastery of this subject. In advanced courses, students should be able to attain deeper insight into the resolution of the problem (even in graphic form).

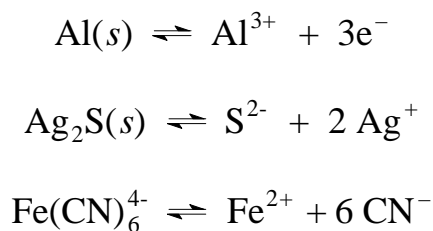
In a previous paper [10], we presented a general procedure for the treatment of aqueous ionic reactions, considering these reactions as interchange equilibria of X particles, between conjugate donor–acceptor pairs. Each pair (i.e., $\text{MX}_d\text{--M}$) is characterized by an equilibrium constant, simplified as:



which allows comparing between pairs. The ionic reactions (mainly acid–base and redox, but also precipitation and complexation) may be regarded as a transfer of different particles (protons, electrons or other charged or uncharged species) between a donor (MX_d) and an acceptor (N) of another pair ($\text{NX}_a\text{--N}$):



The coefficient (d or a) related to the number of particles exchanged within the pair must always be equal to one in acid–base equilibria, but in other ionic equilibria, different values are very common. For example:



In order to establish a common pattern for the four ionic equilibria, we also defined an Acceptance Potential (AP) of a pair which measures the ability of the acceptor to accept particles. Thus, for the $\text{MX}_d\text{-M}$ pair in eq 1 we have:

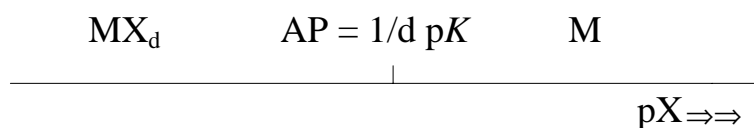
$$\text{AP} = -\log K \frac{1}{d} = \frac{1}{d} \text{p}K \quad (3)$$

Therefore, the larger the AP of a pair is, the stronger will be its acceptor. Conversely, a low AP pair will be formed by a very weak acceptor and a very strong donor. Furthermore, the extent of the overall reaction in eq 2 may be expressed as a function of the difference in the APs:

$$\log (K \alpha \text{AP}_{\text{acceptor}}) - \text{AP}_{\text{donor}}$$

where K is the equilibrium constant for the overall reaction. The larger this difference, the more displaced will be the equilibrium in either direction.

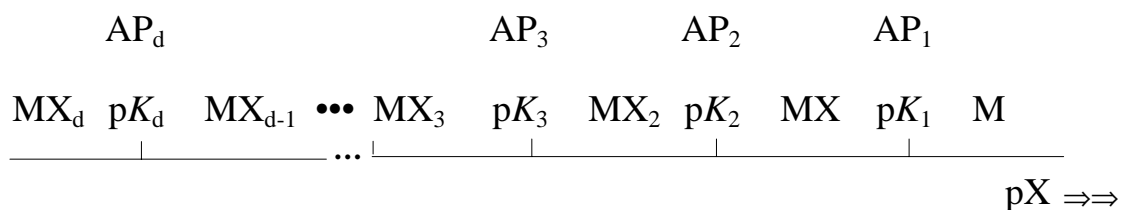
The acceptance potential is also an interesting tool when considering the equilibria of particle interchange in a graphic form, since it represents the $\text{p}X$ ($-\log [X]$) value which separates the intervals or zones of predominance of the donor form and of the acceptor form of a pair that exchanges X particles:¹



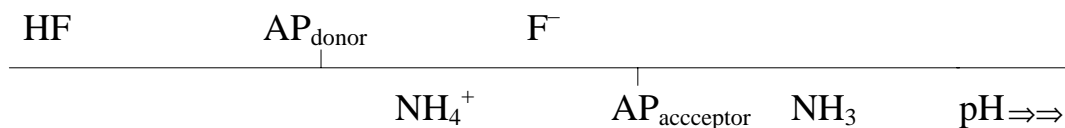
Provided that successive species exist, it is necessary to establish the predominance intervals of all the (stable) species of the family, without dealing with the intervals in an overall way. Thus, when M can form various species MX_i with X (where i can adopt values from 1 to d) we get the predominance diagram that follows:²

¹ Although this interpretation is strictly valid only for mononuclear species in solution, the predominance zone concept may also be extended to other species (polynuclear, pure solid or liquid) with slight modifications of the predominance term.

² Successive $\text{p}K$ s (or APs) are ordered inversely in acid–base equilibria.

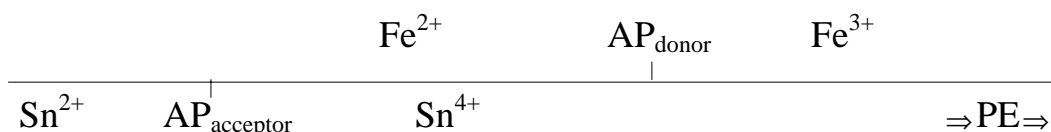


Earlier we proposed a simplified graphic estimation of the equilibrium [10]. Thus, for a system that originally contains HF and NH₃, the diagram could be:



and, from its mere observation, the species that can coexist, and the direction and extent of the reactions that will take place can be deduced. If the species do not have a common interval (e.g., HF and NH₃), they cannot exist simultaneously as predominant species and an interchange reaction will form species with a common interval and the equilibrium will be reached.

To the contrary, the following redox diagram shows that the simultaneous coexistence of Sn⁴⁺ and Fe²⁺ is possible, because they have a common predominance zone (between both APs):



This paper presents a treatment of acid–base reactions that can be generalized to other kinds of ionic equilibria. The treatment provides a rapid “view” of what happens in solution (through the use of the diagrams) and simplifies the calculus of concentrations, without using numerous formulas for the different cases, as is sometimes shown in some introductory texts.

Although it is now easier to find computer programs that give an accurate resolution of complex mixtures of acids and bases, and graphical methods that provide a very close estimate of equilibrium pH (pH_{eq}), the proposed method has the virtue of simplicity and, along with a rapid estimation of the equilibrium pH, elucidates the reaction taking

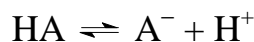
place and the nature of the final equilibrium, in which, by simple stoichiometry, the concentrations of the predominant species may be obtained.

With little further development, always in an approximate form, the results may be quantified and the pH_{eq} be determined using only two expressions, as described below.

For all these reasons, we think that the main objectives of an introductory course dealing with acid–base chemistry are more than fulfilled with the proposed method.

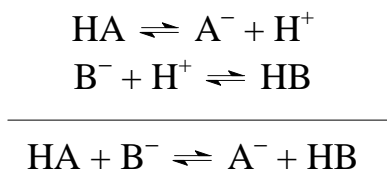
Acid–Base Equilibria

Acid–base equilibria are usually considered (Brønsted-Lowry) as proton (H^+) interchange reactions. An acid, HA, and its conjugate base (A^-) are the components of a donor–acceptor pair



that has a relative tendency to be displaced in one direction or another according to its AP, which in this case, will be equal to $\text{p}K$, (K is the acidity constant of HA, K_{HA}). As mentioned, the equilibrium constants used here always refer to successive species, so, for polyprotic acids and bases, the stoichiometric coefficient of H^+ in the pair is always one.

Acid–base reactions take place when a proton donor (acid) such as HA, and a proton acceptor (base) such as B^- coexist in solution, so that a transfer or interchange reaction can occur:



The extent of the global reaction will be determined by the difference between the acceptance potentials of the two pairs ($\text{AP}_{\text{base}} - \text{AP}_{\text{acid}}$), in other words, $\text{p}K_{\text{HB}} - \text{p}K_{\text{HA}}$.

Strategy For The Resolution Of Acid–Base Problems

1. It is always necessary to establish a proton-exchange reaction between the

strongest acid (lower AP) and the strongest base (higher AP) present, because that reaction is the most thermodynamically favored (highest equilibrium constant) of all the possible reactions.³ The transformations considered are particle-interchange reactions between a donor from one pair and an acceptor of the same or another pair, which after the exchange are converted into their respective conjugates. Occasionally, water may be the strongest donor or acceptor, and in this case, it must be considered part of an ordinary donor–acceptor pair.

2. In the proposed treatment, the acid–base reactions can only be one of these:

- a) An almost complete reaction (very high equilibrium constant), occurring when the reactants (acid and base) do not have a common predominance zone.
- b) A practically nonexistent reaction (very low equilibrium constant), if the acid and the base are simultaneously the predominant species of their respective pairs in a common pH interval.

Although these behaviors are simplifications, a great number of real acid–base systems fit well into the above classifications.

3. Different proton exchange reactions are possible when several acids and bases are present in a solution and do not have common predominance zones. In such a case, the reactions must be considered successively, beginning with the strongest acid and base—those that have their predominance zones farthest apart. After a reaction takes place (a complete reaction), a solution equivalent to the previous one is obtained, and the process repeats itself until the system reaches the final equilibrium. All the equivalent solutions are similar acid–base problems and can be solved in the same manner.

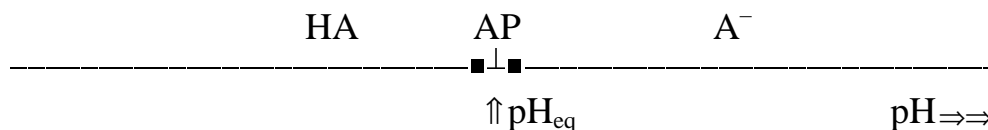
4. When all the acid–base reactions have been completed and the system arrives to the final equilibrium, all of the predominant species from each pair must coexist in a common pH zone. At this moment, the pH-determining equilibrium is that resulting from the strongest acid and the strongest base present in the system.

³ This treatment is not valid when very concentrated and very dilute species are found side by side. Concentrations must be similar in order to use this treatment.

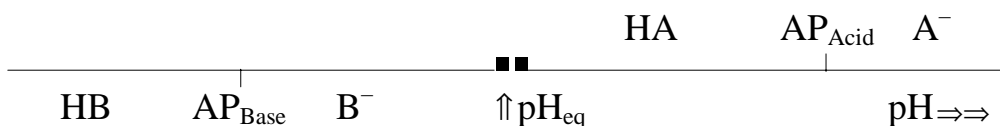
This supposes only one of two possibilities:

a) The strongest acid and base belong to the same pair, and they form an acid–base buffer: HA and A^- . In this case, pH_{eq} will be close to the AP of the pair:

$$pH_{eq} \approx AP$$



b) The strongest acid and base, HA and B^- , belong to different pairs. In this case, both must have a common predominance zone (if they did not have a common zone, there would be an exchange reaction and the system would not have reached the final equilibrium) and consequently there will be practically no reaction and pH_{eq} will be found between the APs of both pairs, AP_{acid} and AP_{base} , in the middle zone (far from the zones of predominance of A^- and HB, which are present only in very small proportions). In acid–base reactions, this implies a pH near the arithmetic mean of both APs:



Calculation of pH_{eq}

Once the predominant species and their concentrations in the final equilibrium have been obtained, the concentration of the exchanged particle $[H^+]_{eq}$ or pH_{eq} , may be determined using *only two expressions*:

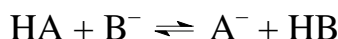
The pH_{eq} is approximately equal to one AP

The strongest acid and base belong to the same pair. The “reaction” simply refers to the equilibrium between the two: pH_{eq} will be approximately AP and $[H^+]_{eq}$ can be obtained from the expression of the equilibrium constant of the pair:

$$[\text{H}^+]_{\text{eq}} = K_{\text{HA}} \frac{[\text{HA}]}{[\text{A}^-]} \quad \text{or} \quad \text{pH}_{\text{eq}} = \text{AP} - \log \frac{[\text{HA}]}{[\text{A}^-]} \quad (4)$$

The pH_{eq} is between two APs

The strongest donor and acceptor belong to different pairs. In this case the exchange reaction:



will occur to a limited degree (a practically nonexistent reaction), but, in any case, the number of particles donated by HA (one mole per mole of A^-) will be the same as that accepted by B^- (one mole per mole of HB), that is:

$$[\text{A}^-] = [\text{HB}]$$

and starting from the respective equilibrium constants (K_{HA} and K_{HB}) we obtain:

$$\frac{K_{\text{HA}}[\text{HA}]}{[\text{H}^+]} = \frac{[\text{B}^-][\text{H}^+]}{K_{\text{HB}}}$$

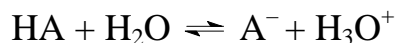
From which:

$$[\text{H}^+]_{\text{eq}} = \sqrt{K_{\text{HA}} K_{\text{HB}} \frac{[\text{HA}]}{[\text{B}^-]}} \quad \text{or} \quad \text{pH}_{\text{eq}} = \frac{\text{AP}_{\text{acid}} + \text{AP}_{\text{base}}}{2} - \frac{1}{2} \log \frac{[\text{HA}]}{[\text{B}^-]} \quad (5)$$

since there is barely a reaction, the concentrations of HA and B^- in the equilibrium can be considered the initial ones.

Role of the Solvent (Intervention of Water)

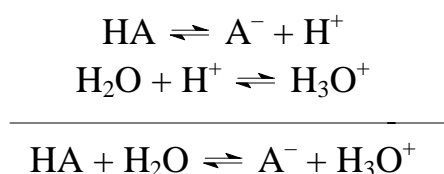
Water may act as a base (acceptor). In fact, the values of the equilibrium constants (or APs) which measure the strengths of acids (and inversely the strengths of their conjugate bases) are determined in aqueous solution, corresponding to the reaction:



Bearing in mind that, in ideal (dilute) solutions, activities can be equal either to molar concentrations of solutes, or to one in the case of the solvent ($a_{\text{H}_2\text{O}} = 1$), the constant of the cited equilibrium would be:

$$K_{\text{HA}} = \frac{[\text{A}^-][\text{H}_3\text{O}^+]}{a_{\text{H}_2\text{O}}[\text{HA}]} = \frac{[\text{A}^-][\text{H}_3\text{O}^+]}{[\text{HA}]}$$

Accordingly, the experimental value which characterizes each pair really refers to an equilibrium constant between two donor–acceptor pairs:



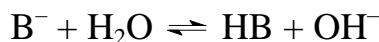
where the solvent acts as a base. Thus, an H_3O^+ – H_2O donor–acceptor pair, characterized by its AP, must be introduced, so that:



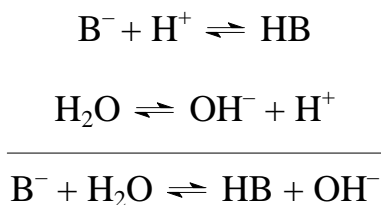
A common problem in these and other donor–acceptor equilibria is due to the impossibility of accomplishing an isolated proton-donating reaction without a proton-accepting reaction being produced simultaneously, which implies that the constant of a single pair cannot be determined. These cases are solved by assigning an arbitrary value to the constant of a reference pair and defining the values of the other pairs according to it. For acid–base equilibria:

$$K_{\text{H}_3\text{O}} = \frac{[\text{H}^+]}{[\text{H}_3\text{O}^+]} = 1$$

Water may also act as a donor, i.e., an acid:



and the previous equation may be considered as an interchange of protons between the (HB and B⁻) and (H₂O and OH⁻) pairs:



neither of whose constants, K_{HB} and $K_{\text{H}_2\text{O}}$ respectively, can be determined separately. Nevertheless, we know the value of the equilibrium constant for autoionization of water:

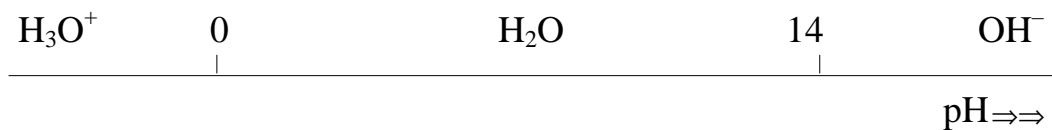
$$2 \text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{H}_3\text{O}^+$$

$$K_w = 10^{-14} (25^\circ \text{C}) = \frac{[\text{OH}^-][\text{H}_3\text{O}^+]}{(a_{\text{H}_2\text{O}})^2} = [\text{OH}^-][\text{H}^+] \frac{[\text{H}_3\text{O}^+]}{\text{H}^+} = K_{\text{H}_2\text{O}} / K_{\text{H}_3\text{O}^+}$$

which, according to the adopted value for $K_{\text{H}_3\text{O}^+}$, lead us to:



Water is both acidic and basic (it is an ampholyte), and its predominance diagram is similar to that corresponding to a polyprotic acid:

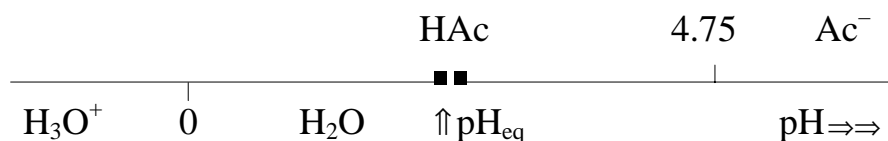


As strong acids and bases are completely dissociated in diluted solution, it is not possible to distinguish in the aqueous environment between acids stronger than H₃O⁺ or weaker than H₂O (bases stronger than OH⁻). In other words, all those pairs with AP > 14 (strong bases) or AP < 0 (strong acids) will be treated in the same way. In the proposed treatment it is not necessary to handle strong acids or bases differently than the weak ones, as is common in elementary textbooks. All the pairs, including those formed by H₂O (in this case with the explanations given below) are dealt with similarly.

The participation of water as an acid or as a base can be ignored whenever another acid or base is present in the solution. Acids and bases weaker than water (i.e., acids such as NH_3 , $\text{Na}^+(\text{aq})$ or $\text{K}^+(\text{aq})$, or bases such as Cl^- or NO_3^-), the conjugates of strong bases and acids respectively, will never be the strongest acid or base because water will always play this role instead; accordingly, their acid–base properties may be ignored.

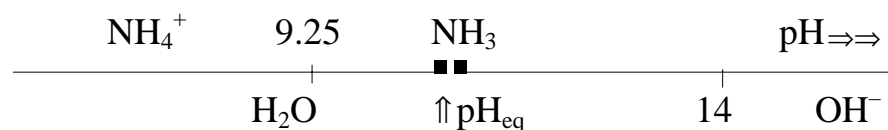
When water acts as an acid ($\text{AP} = 14$) or as a base ($\text{AP} = 0$), some peculiarities must be taken into account:

1. H_2O may intervene in a practically nonexistent reaction, e.g., with a weak acid:



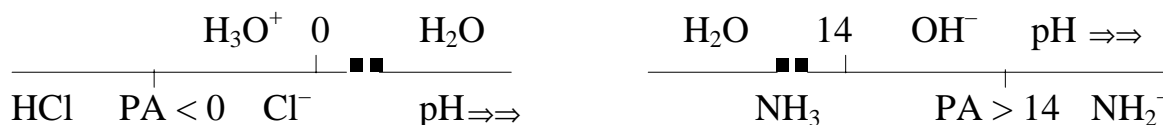
$$\text{pH}_{\text{eq}} \approx \frac{4.75 + 0}{2} = 2.37$$

or with a weak base:



$$\text{pH}_{\text{eq}} \approx \frac{14 + 9.25}{2} = 11.62$$

Water may also react in an almost complete reaction, with a strong acid or base. In that case, H_2O is always (in diluted solution) the reagent in excess, so pH_{eq} will always be around the AP of water. Furthermore, in diluted solution that supposes that pH_{eq} will be in the zone of predominance of H_2O :



that is: $\text{pH} > 0$ in the (strong acid + H_2O) case and $\text{pH} < 14$, in the (H_2O + strong base) case.

2. The convention for the solvent in diluted solutions is applied to H_2O , so an activity always equal to one is used instead of its molar concentration.

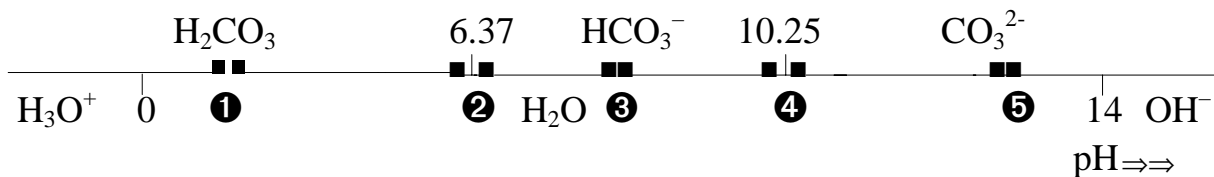
The resolution of some acid–base problems, following the strategy of equivalent solutions, is shown in Tables 1–4.

Strong acids and bases may also be transformed directly, before considering any reaction, in H_3O^+ and OH^- respectively. Nevertheless, for different reasons we consider it more elucidating to handle these substances initially without dissociation. Thus, although the species that intervene in the reactions are H_3O^+ and OH^- , the reagents are HCl and NaOH . Though it is not possible to compare different acids or bases in an aqueous solution, the treatment allows to evidence differences (HClO_4 is stronger than HCl), Finally, with the recommended procedure it is not necessary to deal with strong acids and bases as a special case.

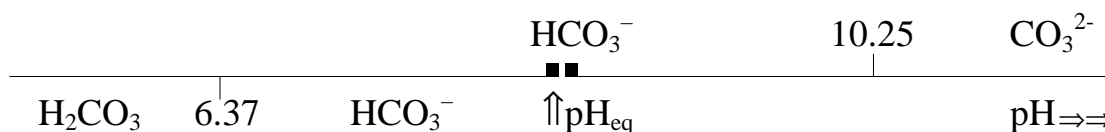
Polyprotic Acids and Bases

Polyprotic acids and bases can also be treated by considering them respectively as a mixture of acids or bases of very different strengths. Taking into account that the difference between the successive acceptance potentials (the successive $\text{p}K$) is usually large enough (frequently 4–5 units) as only the strongest acid and base in solution need be considered, only one or two species of the family will be present in the solution at appreciable concentrations.

In the course of the titration of a polyprotic acid (e.g., 0.1M H_2CO_3) with NaOH , the pH_{eq} expressions corresponding to the intermediate situations at any stage in the addition of NaOH , are either of the “ pH_{eq} approximately equal to one AP” kind (when the molar concentration of NaOH is: $0 < C_{\text{base}} < 0.1$ ② or $0.1 < C_{\text{base}} < 0.2$ ④) or of the “ pH_{eq} between two APs” kind (when C_{base} is: 0 ① ; 0.1 ③ and 0.2 ⑤).



Thus, 0.1 M H_2CO_3 (e.g., 0.1 M $\text{H}_2\text{CO}_3 + \text{H}_2\text{O}$, $a_{\text{H}_2\text{O}}=1$) has an approximate pH of $(0 + 6.37)/2 = 3.18$; 0.1 M $\text{H}_2\text{CO}_3 + 0.07$ M NaOH is equivalent to 0.03 M $\text{H}_2\text{CO}_3 + 0.07$ M HCO_3^- (pH near 6.37), and 0.1 M $\text{H}_2\text{CO}_3 + 0.1$ M NaOH is equivalent to 0.1 M HCO_3^- . The intermediate species, semineutralized acids or bases (ampholytes) are conveniently dealt with by considering them as an equimolecular mixture of an acid and a base that have a common interval. Thus, in a sodium bicarbonate solution, HCO_3^- is simultaneously the strongest acid and the strongest base:



$$\text{pH}_{\text{eq}} = \frac{6.37 + 10.25}{2} - \frac{1}{2} \log \frac{[\text{HCO}_3^-]}{[\text{HCO}_3^-]} = \frac{6.37 + 10.25}{2} = 8.31$$

Also the cases of $\text{H}_2\text{CO}_3 + \text{NaOH}$ (in excess), after the equivalence point, and that of $\text{Na}_2\text{CO}_3 + \text{HCl}$ (in excess), occurring after the equivalence point in the titration of Na_2CO_3 with HCl, may be easily dealt with, considering respectively only the excess of NaOH or HCl, and solving the problem as a NaOH + H_2O (strong base) or a HCl + H_2O (strong acid) problem.

Conclusions

The consideration of acceptance potentials of acceptor–donor pairs and the use of predominance diagrams are interesting tools for the rapid resolution of ionic equilibrium problems and for understanding the reactions that take place. Acid–base reactions are considered in this general treatment as proton transfer reactions. The proposed method first determines the concentrations of the predominant species and the approximate pH in the final equilibrium. After that, pH_{eq} can be calculated (and from it, the concentrations of the other species), using only two expressions. The same two expressions allow us to obtain a rapid estimation of the pH in acid–base reactions, PE (or *E*) in redox reactions, the ligand concentration in complexation and the cation and anion concentrations in precipitation reactions.

TABLE 1. Evolution Through Equivalent Solutions.

<u>Problem</u>		<u>Initial</u>			<u>1</u>		<u>Equilibrium</u>	
Regents	Concn	AP	Acid/ base	Concn	Acid/ base	Concn	Acid/ base	Concn
HNO ₂	0.1	3.37	HNO ₂	0.1				
KIO	0.2	8.69	HBrO	0.1	H ₂ S	0.1		
NH ₄ Cl	0.3	9.25	NH ₄ ⁺	0.3	NH ₄ ⁺	0.3	NH ₄ ⁺	0.3
H ₂ S	0.1				HIO	0.1	HIO	0.2
			K ⁺	0.2	K ⁺	0.2	K ⁺	0.2
			Cl ⁻	0.3	Cl ⁻	0.3	Cl ⁻	0.3
					NO ₂ ⁻	0.1	NO ₂ ⁻	0.1
							HS ⁻	0.1
		10.64	IO ⁺	0.2	IO ⁺	0.1		

$H_{\text{eq}} (\text{approx}) \approx (9.25 + 8.69) / 2 = 8.97$

$$pH_{\text{eq}} = \frac{9.25 + 8.69}{2} - \frac{1}{2} \log \frac{[\text{NH}_4^+]}{[\text{BrO}^-]} = 8.97 - \frac{1}{2} \log \frac{0.3}{0.1} = 8.73$$

TABLE 2. Evolution Through Equivalent Solutions.

<u>Problem</u>			<u>Initial</u>		<u>1</u>		<u>2</u>		<u>Equilibrium</u>	
Regents	Concn	AP	Acid/ base	Concn	Acid/ base	Concn	Acid/ base	Concn	Acid/ base	Concn
NaOH	0.1	4.75	HAc	0.02						
NaBrO	0.04	9.31	HCN	0.03	HCN	0.03				
HCN	0.03						H ₂ O	a = 1	H ₂ O	a = 1
NaF	0.05		Na ⁺	0.09	Na ⁺	0.11	Na ⁺	0.14	Na ⁺	0.19
HAc	0.02	3.45	F ⁻	0.05	F ⁻	0.05	F ⁻	0.05	F ⁻	0.05
		8.69			Ac ⁻	0.02	Ac ⁻	0.02	Ac ⁻	0.02
			BrO ⁻	0.04	BrO ⁻	0.04	BrO ⁻	0.04	BrO ⁻	0.04
							CN ⁻	0.03	CN ⁻	0.03
		>14	NaOH	0.1	NaOH	0.08	NaOH	0.05	OH ⁻	0.05

$$\text{pH}_{\text{eq}}(\text{approx})^a 14(>14)$$

$$\text{pH}_{\text{equil}} = 14 - \log \frac{1}{0.05} = 12.70$$

TABLE 3. Resolution Procedure For A Solution Containing a Strong Acid.

	H_3O^+	AP = 0	H_2O	AP=14	OH^-
INITIAL SOLUTION	HNO_3	AP < 0	NO_3^-		
	$HClO$		AP = 7.2	ClO^-	
	NH_4^+		AP = 9.2	NH_3	
	HF	AP = 3.17	F^-		
	HAc	AP = 4.74	Ac^-		
	Na^+				AP > 14

pH $\Rightarrow \Rightarrow$

Evolution Through Equivalent Solutions

<u>Problem</u>		<u>Initial</u>		<u>1</u>		<u>2</u>		<u>Equilibrium</u>	
Reagents	Concn	Acid/ base	Concn	Acid/ base	Concn	Acid/ base	Concn	Acid/ base	Concn
HNO_3	0.1	HNO_3	0.1	HNO_3	0.08	HNO_3	0.04		
$HClO$	0.03							H_3O^+	0.04
NH_3	0.02	HF	0.05	HF	0.05	HF	0.05	HF	0.05
HF	0.05					HAc	0.04	HAc	0.04
NaAc	0.04	HClO	0.03	HClO	0.03	HClO	0.03	HClO	0.03
				NH_4^+	0.2	NH_4^+	0.02	NH_4^+	0.02
		Na^+	0.04	Na^+	0.04	Na^+	0.04	Na^+	0.04
				NO_3^-	0.02	NO_3^-	0.06	NO_3^-	0.1
		Ac^-	0.04	Ac^-	0.04	H_2O	a = 1	H_2O	a = 1
		NH_3	0.02						

pHeq(approx) ^a 0(>0)

pHequil = $0 - \log \frac{0.04}{1} = 1.40$

TABLE 4. Resolution Procedure For A Solution Containing Several Acids And Bases.

	H_3O^+	AP = 0	H_2O	AP=14	OH^-		
	HCl	AP < 0	Cl^-				
INITIAL SOLUTION	H_3PO_4	AP = 2.12	$H_2PO_4^-$	AP = 7.21	HPO_4^{2-}	AP = 12.67	PO_4^{3-}
	NH_4^+		AP = 9.25		NH_3		
	Na^+				AP > 14	NaOH	
	pH $\Rightarrow \Rightarrow$						

Evolution Through Equivalent Solutions

Added Species		Initial		1		2		3		4		Equilibrium	
Regents	Concn	Acid/ base	Concn	Acid/ base	Concn	Acid/ base	Concn	Acid/ base	Concn	Acid/ base	Concn	Acid/ base	Concn
HCl	0.2	HCl	0.2	HCl	0.15	HCl	0.05						
H₃PO₄	0.1	H_3PO_4	0.1	H_3PO_4	0.1	H_3PO_4	0.1	H_3PO_4	0.1	H_3PO_4	0.05		
NH₃	0.1									$H_2PO_4^-$	0.05	$H_2PO_4^-$	0.15
(NH₄)₃PO₄	0.1	NH_4^+	0.3	NH_4^+	0.3	NH_4^+	0.3	NH_4^+	0.35	NH_4^+	0.4	NH_4^+	0.4
NaOH	0.05			Na^+	0.05	Na^+	0.05	Na^+	0.05	Na^+	0.05	Na^+	0.05
				Cl^-	0.05	Cl^-	0.15	Cl^-	0.2	Cl^-	0.2	Cl^-	0.2
						HPO_4^{2-}	0.1	HPO_4^{2-}	0.1	HPO_4^{2-}	0.1	HPO_4^{2-}	0.05
		NH_3	0.1	NH_3	0.1	NH_3	0.1	NH_3	0.05				
		PO_4^{3-}	0.1	PO_4^{3-}	0.1								
		NaOH	0.05										

$pH_{eq}(\text{approx})^a 7.21$

$pH_{equil} = 7.21 - \log \frac{0.15}{0.05} = 6.73$

REFERENCES

1. Charlot, G. *Chimie Analytique Generale*, Part I; Masson: Paris, 1967.
2. Sillén, L. G. in *Treatise on Analytical Chemistry*; Kolthoff, I. M.; Elving, P. J., Eds.; Interscience: New York, 1966; Part 1, Vol. 1, Chapter 8.
3. Inczédy, J. *Analytical Applications of Complex Equilibria*; Ellis Horwood: Chichester, 1976.
4. Ringbom, A. *Complexation in Analytical Chemistry*; Interscience: New York, 1963.
5. Stumm, W.; Morgan, J. E. *Aquatic Chemistry. An Introduction Emphasizing Chemical Equilibria in Natural Waters*; Wiley-Interscience: New York, 1981.
6. Pankow, J. F. *Aquatic Chemistry Concepts*; Lewis: Chelsea, 1991.
7. Morel F. M. M.; Hering, J. G. *Principles and Applications of Aquatic Chemistry*; Wiley-Interscience: New York, 1993.
8. Elenkova, N. G. *Talanta* **1980**, 27, 699.
9. Kauffman, G. B. *J. Chem. Educ.* **1988**, 65, 28.
10. Vale, J.; Fernández-Pereira C.; Alcalde, M. J. *Chem. Educ.* **1993**, 70, 790.