

Investigating the Effect of a Buffer Using Systematic Equilibria

Systematic equilibria is a purely quantitative approach to equilibria. Using a known concentration, all known dissociation equations, and some equations of Conservation of Charge and Conservation of Mass, systematic equilibria is a method that can be used to find the concentration of all species at equilibria.

Using this method, the effect of including the KHT buffer is investigated.

A step-by-step method of systematic equilibria will be used:

Step 1. Write all chemical reactions.

Step 2. Write the charge balance equation.

Step 3. Write all mass balance equations.

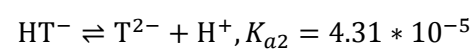
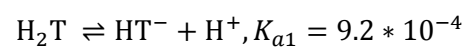
Step 4. Write all equilibrium expressions.

Step 5. Count equations and unknowns. There must be as many or more equations than unknowns or else the problem cannot be solved.

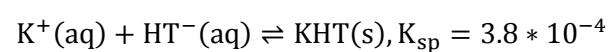
Step 6. Use algebraic expressions to solve for species concentrations using standard methods.

Step 1. Write all chemical reactions.

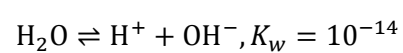
Consider the dissociation of H_2T – a diprotic, weak acid, with given dissociation constants for each dissociation:



In grapes, there also exists a naturally occurring buffer, involving K^+ naturally present in grapes, HT^- , and a salt called KHT, which exists in the following solubility equilibrium:



Also consider the autoprotolysis of water, with given K_w constant:



Step 2. Write the charge balance equation.

Due to the Law of Conservation of Charge, the sum of the concentrations of all positive charges and all negative charges must be equal to 0 in a solution; this is the same as saying that the sum of the concentration of all positive charges is equal to the sum of the concentration of all negative charges in a solution:

$$n_1[\text{C}_1] + n_2[\text{C}_2] + \dots n_m[\text{C}_m] = n_1[\text{A}_1] + n_2[\text{A}_2] \dots n_m[\text{A}_m]$$

, where C_m is the m th cation, A_m is the m th anion and n_m is the magnitude of the charge of the m th cation or anion.

Inputting all cations and anions into a charge balance equation yields:

$$(1) [\text{H}^+] + [\text{K}^+] = [\text{OH}^-] + [\text{HT}^-] + 2[\text{T}^{2-}]$$

There is a coefficient of 2 in front of the concentration of T^{2-} because the concentration of negative charge from one T^{2-} is two times as much the concentration of the ion.

Step 3. Write all mass balance equations.

Due to the Law of the Conservation of Mass, in a chemical reaction, no matter can be created nor destroyed. A mass balance equation shows that the quantity of all species in a solution containing a particular atom (or group of atoms) must equal the amount of that atom (or group) delivered to the solution, meaning the initial concentration of a species must be equal to the concentration of that species in all its forms at equilibrium:

$$C_A = [A] + [A'] + \cdots [A^{n'}]$$

, where C_A is the initial concentration of a species A added and $[A^{n'}]$ is the concentration of the species A in all its forms at equilibrium.

If there was an initial concentration of C_1 of H_2T , then the mass balance equation of H_2T and its ions in all forms would be:

$$(2) C_1 = [H_2T] + [HT^-] + [T^{2-}] + [KHT]$$

, since HT^- , T^{2-} and KHT are all the forms of the tartrate ion (T^{2-}). The concentration of H_2T is also included in the equation because there would be some concentration of H_2T left over from its initial concentration C_1 after dissociation.

In there was an initial concentration C_2 of K^+ before equilibrium, then the mass balance equation of K^+ in all its forms would be:

$$(3) C_2 = [K^+] + [KHT]$$

, since KHT is one of the forms of K^+ .

Step 4. Write all equilibrium expressions.

The dissociation of H_2T and HT^- , as well as the autoprotolysis of water, may be written in an equation such that their dissociation constants are the subject of the equation:

$$(4) K_{a1} = 9.2 * 10^{-4} = \frac{[HT^{-}][H^{+}]}{[H_2T]}$$

$$(5) K_{a2} = 4.31 * 10^{-5} = \frac{[T^{2-}][H^{+}]}{[HT^{-}]}$$

$$(6) K_w = 10^{-14} = [H^{+}][OH^{-}]$$

There is also the solubility constant of KHT, however K_{sp} is conditional. The precipitate appears only if the reaction quotient for the dissolution reaction is higher than the K_{sp} . Thus:

$$(7) [K^{+}][HT^{-}] \leq 3.8 * 10^{-4} = K_{sp}$$

Example calculation: On Week 1, adding 25 mL of tartaric acid to the must yielded a total acidity of 0.02025 M, which was found via sodium hydroxide titrations:

This solution also had a pH, measured by the pH probe, of 2.64.

Finding the hydrogen ion concentration:

$$[H^{+}] = 10^{-pH}$$

$$[H^{+}] = 10^{-2.64}$$

$$[H^{+}] = 2.291 * 10^{-3}$$

Substituting all of this information into the system of equations:

$$(1) (2.291 * 10^{-3}) + [K^{+}] = [OH^{-}] + [HT^{-}] + 2[T^{2-}]$$

$$(2) 0.02025 = [H_2T] + [HT^{-}] + [T^{2-}] + [KHT]$$

$$(3) C_2 = [K^{+}] + [KHT]$$

$$(4) K_{a1} = 9.2 \cdot 10^{-4} = \frac{[HT^-](2.291 \cdot 10^{-3})}{[H_2T]}$$

$$(5) K_{a2} = 4.31 \cdot 10^{-5} = \frac{[T^{2-}](2.291 \cdot 10^{-3})}{[HT^-]}$$

$$(6) K_w = 10^{-14} = (2.291 \cdot 10^{-3})[OH^-]$$

$$(7) [K^+][HT^-] \leq 3.8 \cdot 10^{-4} = K_{sp}$$

Step 5. Count equations and unknowns. There must be as many or more equations than unknowns or else the problem cannot be solved.

From all the equations, there are seven unknown concentration of species: H_2T , HT^- , T^{2-} , OH^- , K^+ , KHT and C_2 . There are also seven equations above. Since the number of equations is equal to the number of variables needed to be solved, these set of equations are solvable. Therefore, the process of simultaneous equations will be used to find the concentrations of each species.

Step 6. Use algebraic expressions to solve for species concentrations using standard methods.

To solve these system of equations, calculator was used. Since the solver only takes inputs of single-letter variables, each species was assigned a variable. x denoted $[H_2T]$, y denoted the $[HT^-]$, z denoted the $[T^{2-}]$, a denoted C_a , b denoted the $[OH^-]$, c denoted the $[K^+]$ and d denoted the $[KHT]$:

solve {	$0.0022908676527678 + c = b + y + 2 \cdot z$, {x,y,z,a,b,c,d}
	$0.02025 = x + y + z + d$	
	$a = d + c$	
	$9.2 \cdot 10^{-4} = \frac{y \cdot 0.0022908676527678}{x}$	
	$4.31 \cdot 10^{-5} = \frac{z \cdot 0.0022908676527678}{y}$	
	$10^{-14} = 0.0022908676527678 \cdot b$	
	$c \cdot b \leq 3.8 \cdot 10^{-4}$	
$x = -0.709648 \cdot (c3 - 0.02025)$ and $y = -0.284991 \cdot (c3 - 0.02025)$ and $z = -0.005362 \cdot (c3 - 0.02025)$ and $a = 0.704286 \cdot$		

Due to the presence of an inequality sign, the calculator generates a constant "c3" that has an infinite number of solutions to a finite set of equations. What needed to be found, however, was the range of

possible values for "c3", thus, another set of equations had to be made for this value in order find its range.

To do this, some simple, intuitive chemical limits were placed on the value of "c3".

Since "c3" is a value used in the calculation of the concentration of species, it does not make sense to have a negative concentration of a species, thus the set of equations including the value "c3" had to be greater than or equal to 0:

$$[H_2T], [HT^-], [T^{2-}], [KHT], [K^+], [OH^-], C_2 \geq 0$$

The appearance of "c3" in an equation that calculates the concentration of all species in the equilibrium also suggests that "c3" is itself a concentration. Since, again, it does not make sense to have a negative concentration, "c3" must be greater than or equal to 0:

$$c_3 \geq 0$$

From the mass balance equation, it also does not make sense for a species to produce a greater concentration than the initial concentration before equilibrium, as this would violate the Law of Conservation of Mass. Thus:

$$[KHT] \leq C_2$$

, and:

$$[H_2T], [HT^-], [T^{2-}], [KHT] \leq 0.02025$$

Inputting these equations into the calculator for the value of "c3" yielded:

solve	$-0.709648 \cdot (x-0.02025) \geq 0$	$\{x\}$	$0 \leq x \leq 0.012503$
	$-0.284991 \cdot (x-0.02025) \geq 0$		
	$-0.005362 \cdot (x-0.02025) \geq 0$		
	$0.704286 \cdot (x+0.00525) \geq 0$		
	$-0.295714 \cdot (x-0.012503) \geq 0$		
	$-0.295714 \cdot (x-0.012503) \leq 0.02025$		
	$-0.295714 \cdot (x-0.012503) \leq 0.704286 \cdot (x+0.00525)$		
	$-0.709648 \cdot (x-0.02025) \leq 0.02025$		
	$-0.284991 \cdot (x-0.02025) \leq 0.02025$		
	$-0.005362 \cdot (x-0.02025) \leq 0.02025$		
	$x \geq 0$		

Thus the range of possible values for "c3" is $0 \leq c_3 \leq 0.012503$.

The significance of these values relates to the buffering capacity of KHT. "0" represents that none of the K^+ ions have precipitated with the HT^- to form KHT, meaning that the buffer has not activated and has not resisted a change in pH. "0.012503" represents the maximum concentration of K^+ ions to precipitate with HT^- ions to form KHT, meaning the buffer is resisting a change in pH to its maximum potential.

If, for example, the buffer did not activate, then "c3" would have to equal 0, and calculating the concentration of every species:

$x=-0.709648 \cdot (0-0.02025)$	$x=0.01437$
$y=-0.284991 \cdot (0-0.02025)$	$y=0.005771$
$z=-0.005362 \cdot (0-0.02025)$	$z=0.000109$
$a=0.704286 \cdot (0+0.00525)$	$a=0.003698$
$b=4.36516E-12$	$b=4.36516E-12$
$c=-0.295714 \cdot (0-0.012503)$	$c=0.003697$
$d=0$	$d=0$

Thus the $[H_2T]$ is equal to 0.021437 M, the $[HT^-]$ 0.005771 M, the $[T^{2-}]$ is 0.000109 M, the $[OH^-]$ is $4.3651 \cdot 10^{-12}$ M, the $[K^+]$ is 0.003697 M, the $[KHT]$ is 0 (since the buffer has not activated) and C_2 is equal to 0.003698 M.

If the buffer maximised its buffering potential by precipitating all the K^+ ions and HT^- ions into KHT, then "c3" would have to equal its maximum 0.012503 and the concentration of every species would be:

$x=-0.709648 \cdot (0.012503-0.02025)$	$x=0.005498$
$y=-0.284991 \cdot (0.012503-0.02025)$	$y=0.002208$
$z=-0.005362 \cdot (0.012503-0.02025)$	$z=0.000042$
$a=0.704286 \cdot (0.012503+0.00525)$	$a=0.012503$
$b=4.36516E-12$	$b=4.36516E-12$
$c=-0.295714 \cdot (0.012503-0.012503)$	$c=0.$
$d=0.012503$	$d=0.012503$

Thus the $[H_2T]$ is equal to 0.005498 M, the $[HT^-]$ is 0.002208 M, the $[T^{2-}]$ is 0.000042 M, the $[OH^-]$ is $4.3651 \cdot 10^{-12}$ M, the $[K^+]$ is 0 M (since the buffer has maximised its potential to resist a change in pH, precipitating all the K^+ ions) , the $[KHT]$ is 0.012503 (its maximum) and C_2 is equal to 0.012503 M.

As can be seen, for example, the concentration has H_2T has decreased noticeably from 0.01437 M to 0.005498 M when the buffer was put in place. This means a decrease in acidity occurred, thus a decrease in the concentration of H^+ and therefore an increase in pH.

What can be concluded is that if a buffer is to be considered in calculating the pH of a solution, then one would obtain a higher pH than without a buffer, due to the resistance in the change of pH.