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How to solve titration problems

Skills to develop Calculate pH at any time acid base titration. In this section we will see how to make calculations to predict the pH at any moment of weak acid or base titration using methods that we already know about acid-based balance and buffers. Consider the \(\PageIndex{1}\) image from the previous section, showing weak acid or weak base titration curves. PH determines at different points of each curve which species are present at this point. Thus, we need to use different methods to solve the pH depending on how far along the titration is. There are three scenarios we will consider using 50.0 ml of 0.100 ml acetic acid titration with 0.200 M NaOH (figure \(\PageIndex{1a}\)) as an example: pH at the beginning of titration before the titrator ph in the buffer region is added before reaching the equivalence point in the PH equivalence point. , we will use \(pK_a \) 4.76 acetic acid at 25°C (\(K_a = 1.7\fold 10^{-5}\)). Image \(\PageIndex{3}\): (a) low acid titration with a strong base and (b) a weak base with a strong acid. (a) As 0,200 M \(NaOH\) slowly add 50,0 ml of 0,100 M acetic acid, the pH slowly increases at the beginning, then increases rapidly when approaching the point of equivalence, and then increases more slowly. The corresponding titration curve of 50,0 ml of 0,100 M HCl at 0,200 M \(NaOH\) is displayed as a dashed line. (b) As 0,200 M HCl is slowly added to 50,0 ml of 0,100 M NH3, the pH decreases slowly at the beginning, then decreases rapidly as the equivalence point approaches and then decreases more slowly. The corresponding titration curve of 50,0 ml of 0,100 M \(NaOH\) with 0,200 M HCl is displayed as a dashed line. At the beginning of titration we simply have a certain concentration of weak acid or base solution. As discussed in the previous chapter, if we know \ (K_a \ ) or \ (K_b \ ) and the initial concentration of weak acid or weak base, we can calculate the pH by creating an ICE table (i.e. initial concentration, concentration changes and steady state). In this case, the initial concentration of acetic acid shall be 0,100 M. If we define \(x\) as \([/ce{H^{}}]\)} due to acid dissociation, then the 0,100 M acetic acid ionization concentration table is as follows: \[CH_3CO_2H_{(aq)} \rightleftharpoons H^+{aq)} + CH_3CO_2^−\] ICE \([CH_3CO_2H]\) \((.) [H^+]\) \{CH_3CO_2^−]\) initial 0.100 \(1.00 \times 10^{−7}\) 0 change −x +x +x equilibrium 0.100 − x x x , we will ignore \([H^+]\) and \([OH^-]\) due to water authority, calculating the final concentration. (However, you should check whether this assumption is warranted!) Insert expressions final concentration equilibrium equation (and using zooming) \[K_a=\dfrac{[H^+][CH_3CO_2^-]}{[CH_3CO_2H]}=\dfrac{(x)}{0.100 - x} \approx \dfrac{x^2}{0.100}=1.74 \fold 10^{-5}\] Solve this equation gives \(x = [H^+] = 1.32 \fold 10^{-3}\; M\). Thus, the pH of the 0,100 M acetic acid solution 0,100 M solution is as follows: \[pH = −\log(1.32 \times 10^{-3}) = 2879\] Now consider what happens when we start adding \(NaOH\) to \(CH_3CO_2H\) (Image \(\PageIndex{1a}\)). As the neutralisation reaction with strong base revenues until completion, all added \(OH^-\) ions will react with acetic acid, to produce acetate ion and water: \[CH_3CO_2H_ {(aq)} + OH^-_{(aq)} \rightarrow CH_3CO^-_2\;(aq)} + H_2O_{(l)} \label{Eq2}\] All problems of this type must be solved in two stages: stoichiometric calculation followed by a balance calculation. In the first stage, we use neutralization reaction stoichiometry to calculate the base amount of acid and conjugation in the solution after the neutralization reaction. In step 2, we use the equilibrium equation to determine the resulting solution \([\ce{H^{++}}]]\). Example \(\PageIndex{1}\): calculation of pH in the buffer region What is the pH when 5.00 ml of 0,200 M \(NaOH\) is added 50.00 ml 0,100 M \(CH_3CO_2H\) (part (a) in the image \(\PageIndex{1}\)? Step 1: Neutralization stoichiometry to determine the amount of acid and conjugated base in solution 2. Step 1: Solution for equilibrium concentration using ICE table or Henderson-Hasselbalch approximation solution To determine the acid and conjugation base quantity in the solution after neutralization reaction, we calculate the amount of \(\ce{CH_3CO_2H}\) in the initial solution and the amount in the solution \(\ce{OOH}\)). Acetic acid solution was \[50.00 \; \cancel{mL} (0.100 \;mmol (\ce{CH_3CO_2H})/\cancel{mL})=5.00\; mmol (\ce{CH_3CO_2H}) \] The solution in the solution \(\ce{NaOH}\) was 5.00 ml =1.00 mmol \(NaOH\) When comparing quantities, it shows that \(CH_3CO_2H\) is superior. Because \(OH^-\) responds with a CH_3CO_2H 1:1 1 in the sichichiometry, the excess amount of \(CH_3CO_2H\) is as follows: 5.00 mmol \(CH_3CO_2H\) − 1.00 mmol \(OH^-\) = 4.00 mmol \(CH_3CO_2H\) Each 1 mmol \(OH^-\) reacts to 1 mmol acetate, so the final amount of \(CH_3CO_2−^\) is 1.00 mmol. Reaction stoichiometry is summarised in the following table, which shows the number of moles of different species rather than their concentration. \[\ce{CH3CO2H(aq) + OH^{−} (aq) <=> CH3CO2^{-}(aq) + H2O(l)}\] ICE \([\ce{CH_3CO_2H}]]\) \([\ce{OH^{−}}}}}}}}}}\(\ce{CH_3CO_2H}}}}}\) \(\ce{CH_3CO_2H}}}}\) \(\ce{OH^{−}}}}}}}}}}}}}}\(\ce{</BISA}}}}}}}\) \(\ce{CH_3CO_2H}}}}}\) \(\ce{OH^{−}}}}}\) \(\ce(0)}\) \(ce(CH3CO2)}\) \(40007) [\ce{CH_3CO_2^{-}}]]] 1.00 mmol 0 mmol variation −1.00 mmol −1.00 mmol +1.00 mmol end 4.00 mmol 0 mmol 1.00 mmol This ICE table gives an initial amount and the final amount of \(OH^-\) ions as 0. Since the aqueous solution of acetic acid always contains at least a small amount of acetate ions in equi weight with acetic acid, the initial acetate concentration is not actually 0. However, you can override the value in this calculation because the amount of \(CH_3CO_2^−\) in balance is insignificant compared to the added value of \(OH^-).\. In addition, due to the autoionization of water, no aqueous solution may contain 0 mmol \(OH^-), but the amount \(OH^-)) due to water autoionization is insignificant compared to the amount \(OH^-)) added. We use initial amounts of reagents to determine the reaction stoichiometry and postpone the balance until the second side of the problem. Now that we have started to have a mixture of \(\ce{CH_3CO_2H}\) and \(\ce{CH3CO2^{−}}}}\) in the solution, we know that this titration point is in the buffer region. Therefore, we can use the equilibrium method or the Henderson-Hasselbalch equation. To calculate \([\ce{H^{+}}]]]) using the acid ionization balance, you must first calculate [\(\ce{CH_3CO_2H}}}]) and \([\ce{CH3CO2{−}}}}]\) using the number of each millimole and the total volume of solution in this at titration: \[final \;volume=50.00 \;mL+5.00 \;mL=55.00 \;mL\] \[\left [CH_{3}CO_{2}H \right] = \dfrac{4.00\; mmol \; CH_{3}CO_{2}H}{55.00\; ml} =7.27 \fold 10^{-2} \; \m \] \[\left [CH_{3}CO_{2}^{-} \right] = \dfrac{1.00\; mmol\; M\\left[10^\right]\right]=dfrac{1.00\;mmol\; CH_{3}CO_{2}^{-} }{55.00\; ml} =1.82\fold 10^{-2} \; M \] Knowing the concentration of acetic acid and acetate ions at equilibrium and \(K_a\) acetic acid (\(1,74 \fold 10^{-5}\)), we can calculate \([H^+]]) \) at balance: \[K_ {a}=\dfrac(\left[CH_{3}CO_{2}^{-} \right]\left [H^{+} \right]}{\left [CH_{3}CO_{2}^{-} \right]\left [H^{+}+CH_{3}CO_{2} K_ CH_{3}CO_{2}} H\right]}{\left [CH_{3}CO_{2}^{-} \right]} = \dfrac{\left (1.72 \times 10^{-5} \right)\left (7.27 \ times 10^{-2} \; M\right)} {\left(1.82\fold 10^(-2)\right)}}=6.95\fold 10^{-5}\; M\] Calculating \(−\log[\ce{H^{+}}}}\) gives \[pH = −\log(6.95 \times 10^{-5}) = 4158.\] Alternatively, because the concentration of each component is high, compared to \(K_a\), we can use Henderson-Hasselch approximation when treating the system as a buffer: \[pH=pK_a+\log \left(\dfrac{[A^−]}{[HA]} \right)\] \[pH= 4.76+\log \left(\d (1.00 mmol){{pH= 4.00 mmol} = 4.76 + (-0.602) = 4,158 \right)\] This approach is mathematically equivalent to the first , but note that there is no need to convert millimeters into molar concentrations to use the Henderson-Hasselbalch equation, which makes this method a little simpler. Exercise \(\PageIndex{1}\) Calculate the pH of the solution prepared by adding 125.0 0 ml of 0.213 M HCl solution 0,150 M ammonia solution. Ammonia \(pK_b\) is 4.75 at 25°C. Answer 9.23 (Note that since ammonia is about half neutralized at this point, this pH is very close to \(pK_a\) ammonium, 9.25!) Any pH point for titration before complete neutralisation of a weak acid can be solved by the above method. However, the equivalence point no longer has a significant amount of starting acid and the sample is no longer buffer. Rather, the sample consists mainly of a base of weak acid conjugation. the pH is determined by the concentration of this base and \(pK_b\) and can be resolved using a base dissociation balance. In the example of \(\PageIndex{2}\), we calculate the pH of acetic acid titration curves at the equivalence point. Example \(\PageIndex{2}\): When calculating pH equivalence point What is the pH of the solution after 25,00 ml 0,200 M \(NaOH\) is added 50,00 ml of 0,100 M acetic acid? Given: volume and molarity of base and acid Requested: pH strategy: Write a balanced chemical equation for the reaction. Then calculate the initial number of millimeters \(OH^-\) and \(CH_3CO_2H\). Determine which species, if any, are superior. The results in the table showing the initial numbers, changes and final figures of millimoly. If after a reaction with \(OH-\), write the acetate reaction equation with water to the acetate reaction. A table format shall be used to obtain the concentration of all species present. Calculate \(K_b\) by using the \(K_w = K_aK_b\). Calculate [OH−] and use it to calculate the pH of the solution. SOLUTION Ignoring viewer ion (\(Na^+\)), the equation for this response is as follows: \[CH_3CO_2H_{ (aq)} + OH^-(aq) \rightarrow CH_3CO_2^-^-(aq) + H_2O(l)\] The original number of millimeters \(OH^-\) and \(CH_3CO_2H\\ are as follows: 25.00 ml (0.200 mmol \ (OH-\) / mL) = 5,00 mmol \(OH-\) \[50.00 \; ml (0,100 mmol CH_3CO_2 H / mL) = 5,00 mmol \; CH_3CO_2H \] The number of millimoles \(OH^-\) is equal to the number of millimols \ (CH_3CO_2H \), so no species is exceeded. B Since the number of millimols added \(OH^-\) corresponds to the number of millimols of acetic acid in the solution, this is the point of equivalence. The results of the neutralisation reaction can be summarised in tabular form. \[CH_3CO_2H_{(aq)}+OH^-_{(aq)} \rightleftharpoons CH_3CO_2^{-}(aq)+H_2O(l)\] ICE \([\ce{CH3CO2H}]]) \ (\ce{OH^{−}}}}}) \(\ce{CH3CO2^{−}}}}}}}) initial tsle 5.00 mmol 5.00 mmol 0 mmol change −5.00 mmol −5.00 mmol +5.00 mmol end 0 mmol 0 mmol 5.00 mmol C Because the neutralization reaction results in a weak base, we should consider the weak base reaction with water, to calculate the pH of the [H+] at equilibrium and thus the final pH of the solution. The initial acetate concentration is obtained from response: \[[\ce {CH_3CO_2}]=\dfrac{5.00\;mmol\; CH_3CO_2 ^{-}}{(50.00+25.00) \; ml}=6.67\times 10^{-2} \; M \] The equilibrium reaction of acetate with water is as follows: \[\ce{CH_3CO^{-}2(aq) + H2O(l) <=> CH3CO2H(aq) + OH^{-} (aq)} \] The equilibrium constant of this reaction is \[K_b = \dfrac{K_w}{K_a} \label{16.18}\], where \(K_a\) is the acetic ionization constant. Therefore, we define the x as \([\ce{OH^{−}}]]) caused by the reaction of acetate with water. Here is the completed table of concentrations: \[H_2O_{(l)}+CH_3CO^−{2(aq)} \rightleftharpoons CH_3CO_2H_{(aq)} +OH^−_{(aq)} \] \([ce{CH3CO2^{−}}]]\) \([\ce{CH3CO2H}]\) \([ce{OH^{−}}]]) initial 00667 0 1.00 × 10−7 change −x +x +x equilibrium (0.0667 − x) x x x D into the expressions for the final values from this table Equation \ref{16.18} , \[K_{b}= \dfrac{K_w}{K_a} =\dfrac{1.01 \times 10^{-14}}{1.74 \times 10^{-5}} = 5.80 \times 10^{-10}=\dfrac{x^{2}}{0.0667} \label{16.23}\] We can obtain \(K_b\) by rearranging Equation \ref{16.23} and substituting the known values: \[K_b=K_wK_a=(1.01×10^{−14}) (1.74×10^{−5})=5.80×10^{−10}=x20.0667 \] which we can solve to get \(x = 6.22 \times 10^{−6}\). Thus \([OH^{−}] = 6,22 \times 10^{−6}\, M\) and the pH of the final solution is 8,794 (Image \(\PageIndex{3a}\)). As intended for titration of weak acid, the pH at the equivalence point is greater than 7,00 because the titration product is a base, acetate ion, which then reacts with water to obtain \(\ce{OH^-}}}). Exercise \(\PageIndex{2}\) Calculate the pH of the solution prepared by adding 88.0 ml of 0,213 M HCl solution to 125,0 ml of the 0,150 M ammonia solution. Ammonia \(pK_b\) is 4.75 at 25°C. 5.14 When a strong base is added to the polyproic acid solution, the neutralisation reaction is gradual. The most acidic group is titrated first, followed by the next most acidic, and so on. If the \(pK_a\) values are separated by at least three \(pK_a\) units, the total titration curve shows well-resolved actions corresponding to titrating each proton. Titration of Trirotic acid \(H_3PO_4\) with \(NaOH\) is shown in the figure \(\PageIndex{2}\) and shows two well-defined actions: the first midpoint corresponds to \(pK_a\)1 and the second midpoint corresponds to \(pK_a\)2. Because HPO42− is such a weak acid, \(pK_a\)3 has such a value that the third action cannot be resolved using 0,100 M \(NaOH\) as a titrant. Image of \(\PageIndex{2}\): Titration curve for phosphoric acid (\(H_3PO_4\), a typical polyprotic acid. A curve of titration of 25.0 ml of a 0,100 M solution H_3PO_4 of 0,100 M \(NaOH\) with a species in each Of The Ka is shown. Two different equivalence points corresponding to the proprotonation of \(H_3PO_4\) at pH ≈ 4.6 and at pH ≈ 9.8. Because \(HPO_4^{2−}\) is a very weak acid, the third equivalence point at pH ≈ 13 is not well defined. The titration curve for the polypotcical base response with a strong acid is a mirror image of the curve shown in the figure shown in the figure \ (\PageIndex{2}\). The initial pH is high, but as the acid is added, the pH decreases gradually if the sequential \(pK_b\) values are well separated. When calculating the pH, titration of polyprotic acid or base, it is important to know which \(pK_a\) or \(pK_b\) value to use based on reaction stoichiometry is of interest. \(\PageIndex{3}{3}) Calculate the pH of the solution prepared by adding 55,0 ml of the 0,120 M \(NaOH\) solution to 100,0 ml of the 0,0510 M solution of oxalic acid (\(HO_2CCO_2\)H), diprotanoic acid (abbreviated as H2ox). Oxalic acid, the simplest dicarbonic acid, is found in rhubarb and many other plants. Rhubarb leaves are toxic because they contain calcium salt of fully deprotoned oxalic acid, oxalate ions (−O2CCO2−, abbreviated \ (ox^{2-}\)). Oxalate salts are toxic for two reasons. First, oxilate salts of bi-worthy cations, such as \(Ca^{2+}\)) are insoluble at neutral pH, but soluble at low pH. As a result, calcium oxalate dissolves in the diluted acid of the stomach, allowing the oxalate to be absorbed and transported into cells where it can react with calcium to form tiny calcium oxalate crystals that damage the tissues. Secondly, oxalate forms stable complexes with metal ions, which can change the distribution of metal ions in biological liquid. Taking into account: volume and concentration of acid and base Required: pH strategy: Calculate the initial millimeters of acid and base. Use the table format to determine the quantity of all species in the solution. Calculate the concentrations of all species in the final solution. Identify \(\ce{[H{+}]}}}} and convert this value to pH. Solution: In Table E5, the oxalic acid \(pK_a\) values are given as 1,25 and 3,81. Again we continue by fixing the millimoles of acid and base originally present: \[100.00 \cancel (mL) \ left (\ dfrac (0,510 \; mmol \; H_{2}ox}{\cancel{mL}} \right)= 5.10 \;mmol\; H_{2} \] \[55.00 \cancel{mL} \left (\dfrac{0.120 \;mmol\; NaOH) (\cancel{mL}} \right)= 6.60 \;mmol\; NaOH \] Strongest acid (\(H_2ox\)) reacts with the base first. It leaves (6.60 - 5.10) = 1.50 mmol \(OH ^-)) to react with Hox−, forming ox2- and H2O. Reactions can be written as follows: \[\underset{5.10\mmol}{H_{2}ox}+\underset{6.60\;mmol}{OH^{-}} \rightarrow \underset{5.10\;mmol}{{Hox^{-}}} subset of {5.10\mmol}{H_{2}O} \} \] [\ underset (5.10 \ mmol) (Hox^ (-)) + subset (1,50 \; mmol) (OH^()\rightarrow\underset(1.50\mmol;) (ox^ (2-) + \underset {1.50\;; mmol {H_{2}O} \] Inr table, \(\ce{H2ox}\) \(\ce{OH^{-}}}}) \(\ce{Hox^{−}}}})\(\ce{ox^{2−}}\) initial 5.10 mmol 6.60 mmol 0 mmol 0 mmol (step 1) −5.10 mmol −5.10 mmol +5.10 mmol 0 ,.0 mmol final (step 1) 0 mmol 1.50 mmol 5.10 mmol 0 changes (step 2) – −1.50 mmol −1.50 mm the balance between weak acid (\\ce{Hox^{-}}}}) and its conjugation base (\(\ce{ox^{2-}}}}) in the final solution is determined by the size of the second ionisation constant. , \(K_{a2} = 10^{-3.81} = 1.6 \times 10^{-4}\). To calculate the pH of a solution, we need to know \(\ce{[H^{++}]}}}) that is determined using exactly the same method as acetic acid titration example \(\PageIndex{2}\): final volume of solution = 100,0 ml + 55,0 5 mL = 155,0 ml Thus \(\ ce{Hox^{-}}}}) and \(\ce{ox^{2-}}}}) have the following concentrations: \[\left [Hox^{-} \right] = \dfrac{3.60 \; mmol \; Hox^{-}}{155.0\; ml} = 2.32 \fold 10^{-2} \; M\] \[\left [ox^{2-} \right] = \dfrac{1.50 \; mmol \; ox^{2-}}{155.0 \; mL} = 9.68 \times 10^{-3\} M \] Now we can calculate [H+] at balance, using the following equation: \[K_ {a2} =\dfrac{\left [ox^{2-} \right]\left [H^{+} \right] }{\left [Hox^{-} \right]} \] Rearranging this equation and replacing \(\ce{Hox^{−}}) and \(\ce{ox^{2−}}), \[\left [H^{}} right] =\dfrac{K_{a2}\left [Hox^{{ \right]}{\left [ox^{2-} \right]} = \dfrac{\left (1.6\times 10^{-4} \right] = dfrac (\ left (1.6\ fold 10^ (-4) \right) \left (2.32\times 10^{-2} \right)}{\left (9.68\times 10^{-3} \right)}=3.7\times 10^{-4} \; M\] So \[pH = -\log \left [H^{+} \right]= -\log\left (3.7 \times 10^{-4} \right)= 3.43 \] This response has a chemical significance because the pH is between the first and second \(pK_a\) values of oxalic acid as it should be. We added enough hydroxide ions to fully titrate the first, more acidic proton (which gives us a pH greater than \(pK_{a1}\)), but we added just enough to titrate less than half of the second, less acidic proton, with \(pK_{a2}\). If we had added just enough hydroxide to fully titrate the first proton plus half of the second, we would have titrated in the middle of the second step, and the pH would be 3.81, equal to \(pK_{a2}\). Exercise \(\PageIndex{3}\): Piperazine Piperazine is a diprotic base used to control intestinal parasites (worms) in pets and humans. A dog is given 500 mg (5.80 mmol) piperazine (\(pK_{b1}\) = 4.27, \(pK_{b2}\) = 8.67). If the dog has initially 100 ml of 0,10 M HCl (pH = 1,00), calculate the pH of the stomach after swallowing piperazine. Answer pH = 4,9 Plots of acid-based titration generates titration curves that can be used to calculate pH, pOH, \(pK_a\) and \(pK_b\) systems. In order to calculate the pH at any time of titration, the quantities of all species must first be determined using the neutralisation reaction stoichiometry. Equilibrium methods can then be used to determine the pH. Polyprotic acid or base titration in case of neutralisation usually occurs in discrete stages, which can be processed separately to calculate the pH. Ph.

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