

## Titration and phosphates in the environment (question 3, 2007 paper)

### Video transcript

This question is about phosphate levels in our environment.

The question begins by providing some background information into the problems that can be caused by excess phosphate levels in both water supplies and blood. The introduction then moves on to explain how the concentration of phosphate ions in solution can be determined by addition of ammonium molybdate to the solution of phosphate ions, forming ammonium molybdophosphate, with each mole of ammonium molybdophosphate containing one phosphate unit. The concentration of ammonium molybdophosphate formed can be determined by titration with sodium hydroxide using phenolphthalein indicator. One mole of ammonium molybdophosphate requires 23 moles of sodium hydroxide for neutralisation. Parts (a) and (b) of the question look at the chemistry of this titration.

#### Part a

Part (a) of the question asks you to choose two statements out of a choice of five which explain why so many moles of sodium hydroxide are needed to neutralise each mole of ammonium molybdophosphate. If we take each of these statements in turn we can see which ones we think are correct.

Statement A is that sodium hydroxide is a weak alkali. You should know that sodium hydroxide is probably the best known example of a strong alkali and so we can disregard this statement. Also since the indicator for the titration is phenolphthalein we know that sodium hydroxide cannot be a weak alkali, as the phenolphthalein is not a suitable indicator for titrations with weak alkalis, owing to the colour change taking place at a pH above the equivalence point. This supports our decision that Statement A is incorrect and hence can be disregarded.

Statement B is that ammonium molybdophosphate has a very high molecular mass. Although we do not know the formula of the compound we can imagine that this is probably true. However the mass of the compound would not explain why so many moles of base were needed as with titrations it is the number of moles of the compounds involved which is important.

Statement C is that the molybdenum-containing species is acidic. This must be true for neutralisation to be possible by the addition of base. Although it doesn't help us to explain why so many moles of hydroxide are needed it does help us to explain why hydroxide is needed and so we can tick this as one of our two statements.

Statement D states that phosphate ions are acidic. By definition, a Brønsted-Lowry acid is a substance that can donate a proton. Looking at the formula of a phosphate ion,  $\text{PO}_4^{3-}$  it clearly has no protons to donate and hence we can rule out statement D.

Finally then, statement E is that the molybdophosphate ion contains many molybdenums. Although we do not fully know the structure of the ammonium molybdophosphate complex, since the phosphate is not acidic then it must be the ammonium molybdo bit which is. Ammonium ions are weakly acidic, but since one mole of hydroxide reacts with one mole of acid then we know that the

ammonium molybdo bit must contain many moles of acid and so we can say that this statement, statement E does help to explain why so many moles of hydroxide are needed per mole of ammonium molydophosphate. Hence our answer is C and E.

### Part b

Part (b) of the question then asks you to use the information given about the titration to calculate the concentration of phosphate in  $10 \text{ cm}^3$  of treated blood serum, given that when the blood serum was reacted with an excess of ammonium molybdate, the precipitated ammonium molybdophosphate required  $17.25 \text{ cm}^3$  of a  $0.0100 \text{ mol dm}^{-3}$  solution of sodium hydroxide for neutralisation. We can calculate the number of moles of sodium hydroxide required for the neutralisation using the equation, moles = concentration  $\times$  volume. Applying the concentration of hydroxide of  $0.0100 \text{ mol dm}^{-3}$  and the volume of  $17.25 \text{ cm}^3$  or  $(17.25 / 1000) \text{ dm}^3$  we can calculate the number of moles of sodium hydroxide needed to be  $1.725 \times 10^{-4} \text{ mol}$ .

From our initial equation, written using the information in the introduction, we know that 1 mole of ammonium molybdophosphate requires 23 moles of sodium hydroxide before the end point is reached. Therefore if we know that the number of moles of sodium hydroxide involved in the reaction is  $1.725 \times 10^{-4} \text{ mol}$ , we can calculate that the number of moles of ammonium molydophosphate formed by the reaction of the phosphate in the  $10 \text{ cm}^3$  of blood serum with the ammonium molybdate, is equal to  $1.725 \times 10^{-4} \text{ mol} / 23 = 7.5 \times 10^{-6} \text{ mol}$ . In the introduction, we are told that one mole of ammonium molydophosphate contains one phosphate unit. Therefore we know that this  $7.5 \times 10^{-6} \text{ mol}$  is also equal to the number of moles of phosphate ion present in the  $10 \text{ cm}^3$  of blood serum. Finally then, if there are  $7.5 \times 10^{-6} \text{ mol}$  of phosphate present in  $10 \text{ cm}^3$  of the blood serum, we can calculate the concentration of phosphate in the blood serum to be  $7.5 \times 10^{-6} \text{ mol} \div 0.010 \text{ dm}^3 = 7.5 \times 10^{-4} \text{ mol dm}^{-3}$ .

### Part c

Part (c) of the question introduces you to the fact that the degree to which a phosphate ion is protonated in aqueous solution, depends on the pH of the solution. The question provides the acid dissociation constants for each of the three dissociation steps of phosphoric acid, and asks you to calculate which form of phosphate is prevalent in blood serum at pH 7.4. If we start off by looking at the dissociation of a weak acid HA into  $\text{H}^+$  and  $\text{A}^-$ , we know that the acid dissociation constant  $K_a = [\text{H}^+][\text{A}^-] / [\text{HA}]$ .

In order to determine which form of phosphate is prevalent in blood serum, we need to determine the ratio of the deprotonated to the protonated form for each of the dissociation steps at the pH given. This can be represented by  $[\text{A}^-] / [\text{HA}]$ . Rearranging our equation for  $K_a$  given above, this ratio can therefore be calculated as  $K_a / [\text{H}^+]$ . Since  $\text{pH} = -\log[\text{H}^+]$  we can calculate the  $[\text{H}^+]$  at pH 7.4 to be  $10^{-7.4}$  or  $3.98 \times 10^{-8} \text{ mol dm}^{-3}$ . With this value to hand, we can now run through each of the dissociation steps and calculate the ratio of  $[\text{A}^-] / [\text{HA}]$  by dividing the acid dissociation constant by the concentration of  $[\text{H}^+]$ . So, for the first dissociation, dividing  $K_{a1}$  by  $[\text{H}^+]$ ,  $3.98 \times 10^{-8} \text{ mol dm}^{-3}$  we calculate that  $[\text{H}_2\text{PO}_4^-] / [\text{H}_3\text{PO}_4] = 198439$ , ie the predominant species is  $\text{H}_2\text{PO}_4^-$  and the equilibrium lies to the right.

Similarly, for the second dissociation step, dividing the acid dissociation constant,  $K_{a2}$  by the concentration of  $[\text{H}^+]$  we calculate that  $[\text{HPO}_4^{2-}] / [\text{H}_2\text{PO}_4^-] = 1.55$ . In this case the equilibrium is

much more balanced with  $\text{HPO}_4^{2-}$  slightly dominating. Finally then, for the final dissociation,  $[\text{PO}_4^{3-}] / [\text{HPO}_4^{2-}] = K_{a3} / 3.98 \times 10^{-8} \text{ mol dm}^{-3} = 1.11 \times 10^{-5}$ . In this case the equilibrium lies far to the left and  $\text{HPO}_4^{2-}$  dominates. So what do these calculations tell us about the phosphate species present at pH 7.4? The first dissociation lies to the right and  $\text{H}_2\text{PO}_4^-$  dominates. The second dissociation step however tells us that this  $\text{H}_2\text{PO}_4^-$  dissociates further into  $\text{HPO}_4^{2-}$ . However, the  $\text{HPO}_4^{2-}$  doesn't dissociate any further because the third dissociation step lies to the left at this pH and hence we can say from the data, that the form of phosphate which is prevalent at pH 7.4 is  $\text{HPO}_4^{2-}$ .

#### Part d

The final part of the question moves on to look at some treatments for high phosphate levels in the blood, known as hyperphosphataemia, and for high phosphate levels in ponds. In both cases the excess phosphate ions are removed as precipitates, in blood as a precipitate of lanthanum phosphate formed by the addition of lanthanum carbonate which is marketed as the drug Fosrenol or in pond water as a precipitate of aluminium sulphate formed by the addition aluminium sulfate.

Part (d) of the question asks you to write an equation for the reaction between lanthanum carbonate and the hydrochloric acid present in your stomach. This first thing to do in this question is to work out the correct formula for the lanthanum carbonate. Since we are told in the introduction that lanthanum phosphate has a formula of  $\text{LaPO}_4$ , then we know that a lanthanum ion must carry a 3+ charge. Since a carbonate ion has a 2- charge and knowing that the overall charge on an ionic compound must be equal to zero, then we know that the two ions must combine in a ratio of 2:3 giving the formula of lanthanum carbonate as  $\text{La}_2(\text{CO}_3)_3$ .

Now, when a carbonate reacts with an acid, the products of the reaction are a salt, carbon dioxide and water. Using this equation then, we can write that when lanthanum carbonate reacts with hydrochloric acid the products of the reaction are a salt, lanthanum chloride (which must have a formula  $\text{LaCl}_3$ ), carbon dioxide and water. Finally then, balancing the equation, looking at the lanthanum ions first, each equivalent of lanthanum carbonate contains two lanthanum ions and hence we must form two equivalents of lanthanum chloride. Each equivalent of lanthanum chloride contains three chloride ions and so we know the reaction must involve six equivalents of hydrochloric acid. Looking now at the carbonate ions, each equivalent of lanthanum carbonate contains three carbonate ions and hence three equivalents of carbon dioxide must be formed. Finally then balancing the hydrogen atoms we can see that we must also form three equivalents of water.

#### Part e

The final part of the question then moves on to look at the solubility of the phosphate salts formed in the precipitation reactions. The question introduces something the solubility product of a salt,  $K_{sp}$  and tells us that it is equal to the product of the concentrations of each of the ions in the salt at the point of saturation. So for lanthanum phosphate, the product from the precipitation reaction between lanthanum carbonate and excess phosphate ions,  $K_{sp} = [\text{La}^{3+}]_{\text{sat}} [\text{PO}_4^{3-}]_{\text{sat}}$ .

Part (e) of the question asks you to use these values to calculate the concentration of a saturated solution of lanthanum phosphate. Since the formula for lanthanum phosphate is  $\text{LaPO}_4$  then each mole of lanthanum phosphate contains an equal number of lanthanum and phosphate ions. Therefore at saturation, we know that  $[\text{La}^{3+}] = [\text{PO}_4^{3-}]$ . Knowing this then, we can say that  $7.08 \times 10^{-27} \text{ mol}^2 \text{ dm}^{-6} = \text{either } [\text{La}^{3+}]^2 \text{ or } [\text{PO}_4^{3-}]^2$  and hence at saturation the concentration of each of these

ions is  $8.41 \times 10^{-14} \text{ mol dm}^{-3}$ . Since each mole of lanthanum phosphate contains one mole of each ion, then the concentration of each ion at saturation is equal to the concentration of the salt at saturation and hence the concentration of lanthanum phosphate at saturation is  $8.41 \times 10^{-14} \text{ mol dm}^{-3}$ .

Finally in part (f) of the question you are asked, if an equimolar solution of aluminium and lanthanum ions is added slowly to a solution of phosphate ions, which of the two possible phosphates, aluminium phosphate or lanthanum phosphate would precipitate first. A salt precipitates out when its concentration goes above the concentration of the saturated solution; the solution can 'hold' no more salt. So, from the calculation in part(e) we know that lanthanum phosphate would precipitate out at a concentration of  $8.41 \times 10^{-14} \text{ mol dm}^{-3}$ . If we do an identical calculation for  $\text{AlPO}_4$  since it too contains an equal number of  $\text{Al}^{3+}$  and  $\text{PO}_4^{3-}$  ions, we can say that  $[\text{Al}^{3+}] = [\text{PO}_4^{3-}] = [\text{AlPO}_4]_{\text{sat}} = \text{square root of } K_{\text{sp}}(\text{AlPO}_4)$  and hence calculate that the aluminium phosphate would precipitate out at a concentration of  $9.91 \times 10^{-11} \text{ mol dm}^{-3}$ . Finally then, from our calculations we can see that the concentration of lanthanum phosphate at saturation is lower than the concentration of aluminium phosphate at saturation and hence lanthanum phosphate would precipitate first.