

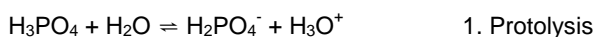
Investigation of triprotic phosphoric acid by titration

Aims of the experiment

- To perform an automatic titration with a drop counter.
- How to determine the equivalence points of phosphoric acid.
- To calculate pH and pK_a values.
- To recognise the buffer effect of solutions (phosphate buffers).

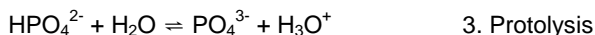
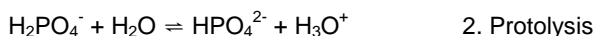
Principles

Every acid is broken down into a hydronium ion and an acid residue when it reacts with water. It is said to dissociate. This also applies to phosphoric acid.



An equilibrium is created between the undissociated phosphoric acid and the dissociated dihydrogen phosphate.

However, phosphoric acid is a triprotic acid. It has three dissociatable hydrogen atoms per molecule. As also with other polyprotic acids, it dissociates step by step. An equilibrium reaction can be drawn up as above for each of these stages (each so-called protolysis stage).



The equilibria can be described in each case using the law of mass action. In this way, the acid dissociation constant K_a and the acid strength (pK_a value) can be calculated for each protolysis stage. Thereby A⁻ is the dissociated form and HA

the undissociated form.

$$K_s = \frac{[\text{H}_3\text{O}^+] \cdot [\text{A}^-]}{[\text{HA}]}$$
$$\text{p}K_a = -\log K_a$$

The pK_a value increases with each protolysis stage. This is typical for polyprotic acids, as the first proton can be split off more easily than the following protons. The most difficult is the separation of the third proton from the already doubly negatively charged HPO₄²⁻ ion.

As the pK_a values for phosphoric acid differ by a factor of five, three equilibrium states can be observed independently from one another. Therefore several equivalence points can be determined during the titration of phosphoric acid. For the first equivalence point, an equivalent amount of sodium hydroxide is required, and for the second equivalence point twice the amount. Because of this behaviour, often not only the molarity (mol/L) is stated for the concentration of acids and bases, but also the normality, which is provided by the number of titratable equivalents multiplied by the molarity.

For the titration in this experiment, the volume-dependent pH





Fig. 1: Set-up of the experiment

value will be plotted. The volume added will be measured using a drop counter. This contains a light barrier which counts each drop. The number of drops can then be converted into a volume in CASSY Lab. The titration curve for phosphoric acid will then be investigated in the evaluation and the buffer effect of the solution established.

Risk assessment

Phosphoric acid and sodium hydroxide solution are corrosive in the concentrations used. Pour these using protective glasses and gloves.

The buffer solution and the thymolphthalein solution are not classified as hazardous substances.

Phosphoric acid, 10 %	
 Signal word: Caution	<p>Hazard statements</p> <p>H315 Causes skin irritation. H319 Causes serious eye irritation.</p> <p>Precautionary statements</p> <p>P280 Wear protective gloves/eye protection. P302+P352 IF ON SKIN: Wash with soap and water. P305+P351+P338 IF IN EYES: Rinse continuously with water for several minutes. Remove contact lenses if present and easy to do. Continue rinsing. P313 Get medical advice/attention.</p>
Sodium hydroxide solution, 1 mol/L	
 Signal word: Hazard	<p>Hazard statements</p> <p>H314 Causes severe skin burns and eye damage. H290 May be corrosive to metals.</p> <p>Precautionary statements</p> <p>P280 Wear protective gloves/protective clothing/eye protection/face protection. P301+ P330 + P331 IF SWALLOWED: Rinse mouth. Do NOT induce vomiting. P305+P351+P338 IF IN EYES: Rinse continuously with water for several minutes. Remove contact lenses if present and easy to do. Continue rinsing. P309 + P310 IF exposed or you feel unwell: Immediately call a POISON CENTER or doctor/physician.</p>

Equipment and chemicals

1	Sensor-CASSY 2.....	524 013
1	CASSY Lab 2	524 220
1	pH Adapter S.....	524 0672
1	pH electrode with plastic shaft, BNC	667 4172
1	Timer S.....	524 074
1	Drop counter	337 4681
1	Magnetic stirrer mini.....	607 105
2	Beaker, DURAN, 250 mL, squat.....	664 103
1	Graduated pipette 10 mL.....	665 997
1	Pipetting ball (Peleus ball).....	666 003
1	Burette, clear glass, 50 mL, side tap	665 847
1	Funnel, PP, 25 mm diam.....	665 816
1	Burette clamp for 1 burette, roller clamp	666 559
1	Stand base, V-shaped, small	300 02
1	Stand rod 75 cm, 12 mm diam.	300 43
1	Saddle base	300 11
1	Stand rod 25 cm, 10 mm diam.	301 26
2	Boshead S.....	301 09
2	Universal clamp 0...80 mm.....	666 555
1	Stopcock grease, 60 g.....	661 082
1	Phosphoric acid, 10 %, 100 mL.....	674 3440
1	Sodium hydroxide solution 1 mol/L, 500ml.....	673 8421
1	Buffer solution pH 4.00, 250 mL.....	674 4640
1	Buffer solution pH 7.00, 250 mL.....	674 4670
1	Water, pure, 1L.....	675 3400
Additionally recommended:		
1	Thymolphthalein solution, 0.1 %, 50 mL.....	675 1600
also required:		
1	PC with Windows XP, Vista, 7 or 8	

Set-up and preparation of the experiment

Set-up of the experiment

Build a titration apparatus from the stand base with the long stand rod together with a magnetic stirrer, beaker and burette (see Fig. 1). Also attach the drop counter to the stand using a boshead and a universal clamp. Set up the drop counter and the burette so that the drops will fall centrally through the drop counter.

Fix the pH electrode to the small stand, consisting of a base and a stand rod. Adjust the height of the pH electrode so that the glass membrane on the one hand is completely immersed in the solution afterwards, but on the other hand cannot be damaged by the rotating stirrer magnet.

Connect the pH electrode to the pH Adapter S. Insert the pH adapter S into the upper input (Input A) of the Sensor-CASSY. Insert the Timer S into the lower input (Input B). Connect the drop counter to this. Connect the Sensor-CASSY with a computer running CASSY Lab software.

Preparation of the drop counter in CASSY Lab

1. Using the funnel, fill the burette to above the zero mark with 1 molar sodium hydroxide solution (measuring solution). Place the beaker on the magnetic stirrer under the burette.

Note: Check that the burette tap can be freely turned before starting the titration. If necessary, lubricate with a small (!) amount of stopcock grease. Make sure that the burette does not drip and that the tip of the burette is filled with measuring solution. The graduations on the burette should be clearly legible over the entire length.

2. [Load CASSY Lab settings.](#)

3. To check whether the drop counter is counting correctly, set the burette to drop liquid and count the drops.

Note: If not every drop is counted, check whether the drops are being detected by the light barrier. The drops should

briefly light up red. If this does not happen, shift the burette and/or the drop counter.

4. For calibration (determination of the drop size), allow 10 mL of sodium hydroxide solution to drip out and the drops to be counted.

5. The average volume of a drop of NaOH solution will be calculated in CASSY Lab using a formula. The general formula for this is "NB1 * V0 / N0". Where NB1 is the number of drops (e.g. 188), V0 the total volume added (here: 10 mL) and N0 the number of drops counted for 10 mL. Enter the values for NB1 and V0.

6. Fill the burette again up to the zero mark.



Calibrating the pH electrode in CASSY Lab

For accurate measurements, the pH electrode must first be calibrated:

1. Select the setting pH A1 **Correction**.
2. Rinse the pH electrode with distilled water and immerse it into the pH 7.00 buffer solution.
3. Enter 7.00 for the first target value and press the **Offset** button when a stable measurement value has been reached.
4. Rinse the pH electrode with distilled water and immerse it into the pH 4.00 buffer solution.
5. Enter 4.00 for the second target value and press the **Correct factor** button when a stable measurement value has been reached.

Note: The stored calibration can be used again for the same CASSY, pH electrode and pH Adapter.

Performing the experiment

1. Place approximately 100 mL of distilled water into the beaker and using the pipette add exactly 10 mL of phosphoric acid (10 %, approx. 1.1 M).
2. To make it easier to identify the transition point (equivalence point), a few drops of thymolphthalein (transition point pH 9.3...10.5) can be added as an indicator.
3. Start the measurement series with .
4. Carefully open the burette tap, allowing the sodium hydroxide solution to drip slowly.
5. A measurement value is recorded automatically every five seconds (volume and pH value). Take care to ensure a constant drop frequency.
6. A titration curve is now automatically generated.
7. After 40 mL of NaOH solution have been added, close the tap and stop the measurements with .



Note: The calibration can now be checked by reading off and entering the total number of drops (N0) and the exact volume of NaOH added (V0). Alternatively, only the calibration can be carried out here.

Observation

The phosphoric acid solution is colourless at the start of the experiment. The pH value is approx. 1.5. By adding sodium hydroxide solution, the pH value slowly increases. At a pH value of about 9.5, the solution turns blue in colour. Blue streaks can already be seen before this at the point of entry of the drops, which however disappear again on further stirring. The titration curve is characterised by two equivalence points (points of inflection in the curve).

Evaluation

Determination of the equivalence points

The equivalence points ($V = V_{eq}$) are easily determined in CASSY Lab. Open the context menu by right-clicking on the diagram. Under  **Further evaluation**, select the subitem  **Determine equivalence point**. Mark the curve range within which the equivalence point is to be determined. The calculated equivalence point will now be displayed in the diagram. The associated values can be found in the status line and can be transferred as text to any desired point in the diagram using the mouse. Perform this also for the second equivalence point (see Fig. 2).

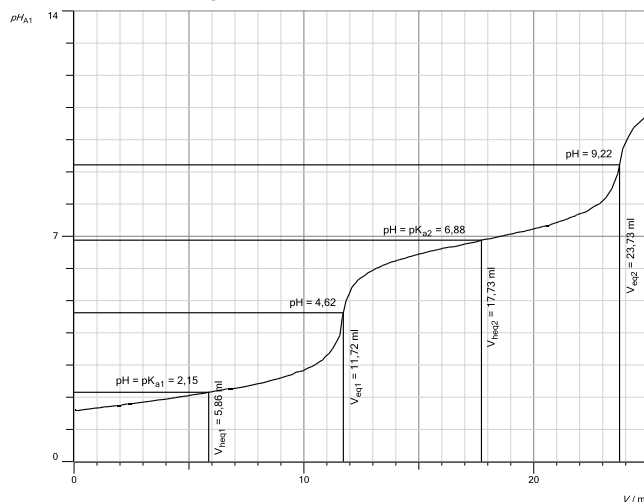


Fig. 2: Titration curve with equivalence points and the half equivalence point drawn in.

pKa values of the protolysis stages

The half equivalence points (V_{heq}) are shown in CASSY Lab in addition (see Fig. 2). These correspond to the pKa value of each protolysis stage in accordance with the Hendersen-Hasselbalch equation. On the addition of exactly half the amount of base needed for complete neutralisation of the acid, acid and base are present in equal concentrations.

$$pH = pK_s + \log_{10} \frac{c(A^-)}{c(HA)}, \text{ with } c(A^-) = c(HA)$$



$$pH = pK_a + \log_{10}(1), \text{ with } \log_{10}(1) = 0$$

$$pH = pK_a$$

The pKa values are summarised in Table 1. The pKa value for the third stage cannot be determined, as phosphoric acid is never fully dissociated in aqueous solution.

The buffer ranges of phosphate

The pH value changes very little between the two equivalence points over a large volume range. The solution acts as a buffer. In buffer solutions, large amounts of a weak acid and its conjugate base are present concurrently. Polyprotic acids display as many buffer ranges as the protons they can donate. The buffer range in every case lies around the pKa value (see Table 1).

The pH value also increases slightly in the buffer ranges. The increase can be visualised using a line of best fit. The display option "Straight line evaluation" has been prepared in CASSY Lab for this purpose. After right-clicking in the diagram and selecting the menu item  **Make adjustment** →  **Line of best fit**, mark a small area of the curve in one of the buffer zones symmetrical to the relevant half equivalent point V_{heq} . Do this also for the other two buffer zones. On the basis of the Hendersen-Hasselbalch equation (see above), the three

straight lines should be almost parallel (see Fig. 3). There might, however, be small inaccuracies caused by changes in the volume through adding the NaOH solution and reaching the measurement range limits of the pH electrode.

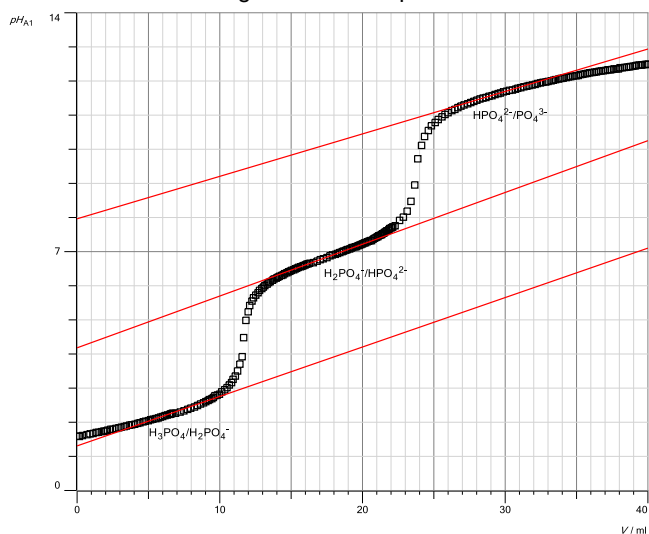


Fig. 3: Titration curve with buffer linear slope lines added.

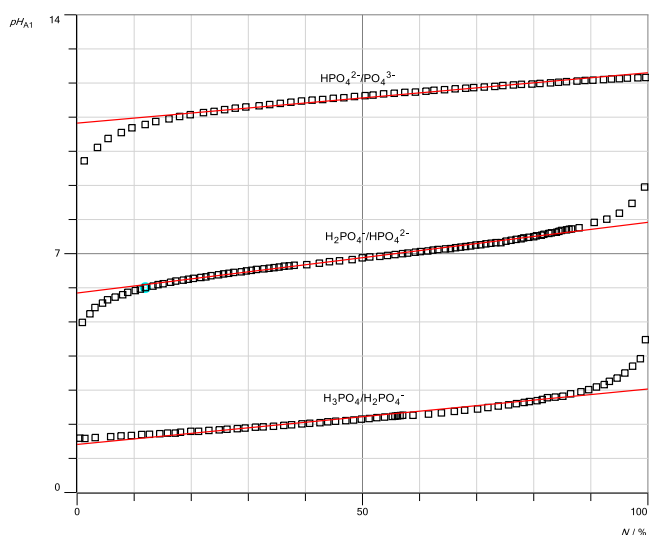


Fig. 4: Buffering curves with buffer linear slope lines added.

The buffering curves of phosphate

If one plots the pH value against the percentage of neutralisation N at each of the buffer stages, the relevant buffer range is presented more clearly. For this, the three equivalence points must first be entered into CASSY Lab. Take the first

and the second equivalence points from the "Standard" diagram and enter these as parameters. The third equivalence point is calculated from the first using a formula.

The degree of neutralisation N is calculated in CASSY Lab from the equivalence points. In the "Buffering curves" display, the three sections of the titration curve are placed one above the other in a diagram. For further evaluation, the linear slopes of the buffer curves as described above can be inserted into the diagram.

Results

Equivalence points and pK_a values

The titration curve contains two equivalence points. For the first point, an approximate volume of $V_{eq1} = 11.7$ mL of sodium hydroxide solution was added. For the second equivalence point, a volume of $V_{eq2} = 23.7$ mL was added, i.e., approximately twice the amount (see Table 1).

With a value of 4.6, the pH at the first equivalence point is in the acidic range, as the first protolysis stage of the phosphoric acid is more acidic than the sodium hydroxide solution is basic. The second equivalence point is at pH 9.2. Here, the sodium hydroxide solution is a stronger base than the second protolysis stage is an acid.

The measured pK_a values (half equivalence points) have been entered into Table 1. No value can be determined for the third stage.

Buffer effect and pK_a values

The area in which the phosphates can be used as buffers can be easily read from the buffering curves in Fig. 4. The data has been summarised in Table 1. The buffer from the second protolysis stage is used particularly frequently, for example in biology, as solutions can be kept neutral in these.

Cleaning and disposal

Empty the contents of the beaker with the titrated solution into the laboratory drain and flush well with water. Allow the remaining contents of the burette to run away into a beaker and pour this also into the laboratory drain and flush well. Rinse the burette out several times with distilled water and allow it to dry. Rinse the pH electrode with distilled water and place it into the cap with 3 M KCl solution for storage.

Notes on the maintenance of pH electrodes: pH electrodes must not be allowed to dry out. They must always be stored in a 3 M KCl solution. Storage containers (e.g. 667 4195) are more suitable for this than plastic caps.

Tab. 1: Summary of the results of the titration of phosphoric acid with sodium hydroxide solution.

	Acid	Conjugate base	Equivalence point	pK_a value (measured)	pK_a value (literature)	Buffer range
1. Protolysis	H_3PO_4	$H_2PO_4^-$	11.7 mL	2.2	2.1	pH 1 - 3
2. Protolysis	$H_2PO_4^-$	HPO_4^{2-}	23.7 mL	6.9	7.1	pH 6 - 8
3. Protolysis	HPO_4^{2-}	PO_4^{3-}	35.1 mL	--	12.3	--