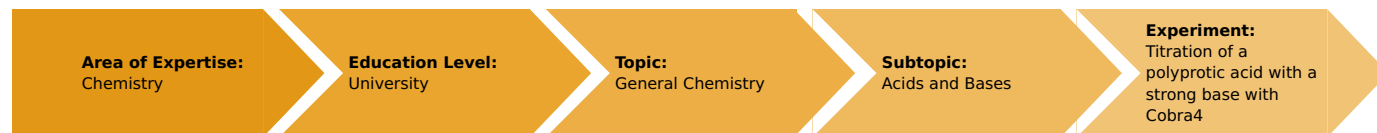


Titration of a polyprotic acid with a strong base with Cobra4

(Item No.: P3121260)

Curricular Relevance



Difficulty



Intermediate

Preparation Time



10 Minutes

Execution Time



10 Minutes

Recommended Group Size



2 Students

Additional Requirements:

- PC with USB interface, Windows XP or higher
- Precision balance, 620 g / 0.001 g

Experiment Variations:

Keywords:

Strong and weak acids and bases, Polyprotic acids, pH value, Law of mass action, Dissociation constant and K_a value, Titration curves, Equivalence point, Potentiometry

Introduction

Short description

Principle:

Phosphoric acid is a multiprotic acid. In aqueous solutions there are three different dissociation steps. The location of the dissociation equilibria is quantitatively described by the K_a or pK_a values which can be determined with potentiometric measurements.

Notes

Any other polyprotic acid (e.g. sulfuric acid) can be used in this procedure in place of phosphoric acid. The pH electrode should be stored in a 3 molar potassium chloride solution when not in use.

Safety instructions



When handling chemicals, you should wear suitable protective gloves, safety goggles, and suitable clothing.

Disposal: The diluted and neutralised solutions of the used acid and base can be disposed by rinsing into the drain.

Ortho-phosphoric acid, 85 %

H314: Causes severe skin burns and eye damage.

H290: May be corrosive to metals.

H314: Causes severe skin burns and eye damage.

P280: Wear protective gloves/protective clothing/eye protection/face protection.

P301+330: IF SWALLOWED: Rinse mouth.

P331: Do NOT induce vomiting.

P305+351: IF IN EYES: Rinse cautiously with water for several minutes.

P338: Remove contact lenses if present and easy to do. Continue rinsing.

P309+310: IF exposed or you feel unwell: Immediately call a POISON CENTER or doctor/physician.

Caustic soda solution, 0.1 N:

H290: May be corrosive to metals.

P234: Keep only in original container.

P280: Wear protective gloves/protective clothing/eye protection/face protection.

Trisodium phosphate solution

H314: Causes severe skin burns and eye damage.

P305+351+338: IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses if present and easy to do – continue rinsing.

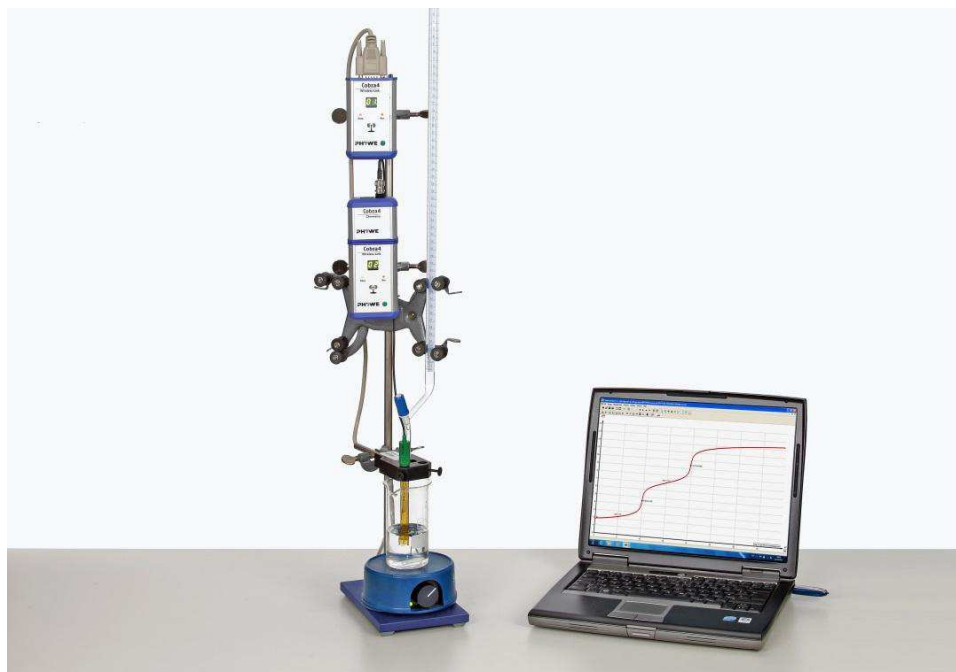
Equipment

Position No.	Material	Order No.	Quantity
1	Cobra4 Wireless/USB-Link incl. USB cable	12601-10	2
2	Cobra4 Sensor-Unit Chemistry	12630-00	1
3	curricuLAB measureLAB	14580-61	1
4	Holder for Cobra4 with support rod	12680-00	2
5	USB charger for Cobra4 Mobile-Link 2 and Wireless/USB-Link	07932-99	2
6	Cobra4 Sensor-Unit Drop Counter	12636-00	1
7	Storage flask for pH electrodes, filled with 250 ml 3.0 M KCl solution	18481-20	1
8	pH-electrode, plastic body, gel, BNC	46265-15	1
9	Retort stand, h = 750 mm	37694-00	1
10	Right angle boss-head clamp	37697-00	3
11	Magnetic stirrer without heating, 3 ltr., 230 V	35761-99	1
12	Magnetic stirring bar 15 mm, cylindrical	46299-01	1
13	Burette, lateral stopcock, Schellbach, 50 ml, graduations 0, 1 ml	36513-01	1
14	Burette clamp, roller mount., 2 pl.	37720-00	1
15	Funnel, d.40 mm, f.burettes	36888-00	1
16	Volumetric pipette, 10 ml	36578-00	1
17	Pipettor	36592-00	1
18	Funnel, glass, top dia. 55 mm	34457-00	1
19	Volumetric flask 100 ml, IGJ12/21	36548-00	1
20	Beaker, high, BORO 3.3, 50 ml	46025-00	2
21	Beaker, high, BORO 3.3, 150 ml	46032-00	1
22	Beaker, low, BORO 3.3, 150ml	46060-00	1
23	Beaker, low, BORO 3.3, 100 ml	46053-00	1
24	Pasteur pipettes, 250 pcs	36590-00	1
25	Rubber caps, 10 pcs	39275-03	1
26	Wash bottle, plastic, 500 ml	33931-00	1
27	Buffer solution, pH 4.62 1000 ml	30280-70	1
28	Buffer solution, pH 9 1000 ml	30289-70	1
29	Caustic soda sol., 0.1M 1000 ml	48328-70	1
30	Ortho-phosphoric acid 85% 250 ml	30190-25	1
31	Water, distilled 5 l	31246-81	1

Task

Titration is used to determine the unknown concentration of an identified analyte.

1. Measure the alteration of the pH value during a titration of an aqueous solution of phosphoric acid with a 0.1 molar sodium hydroxide solution at constant temperature using the Cobra4 system.
2. From the titration curve read the equivalence points and pKa values.
3. Determine the concentration of the acid.



Set-up and procedure

Set-up



- Set up the experiment as shown in Fig. 1.

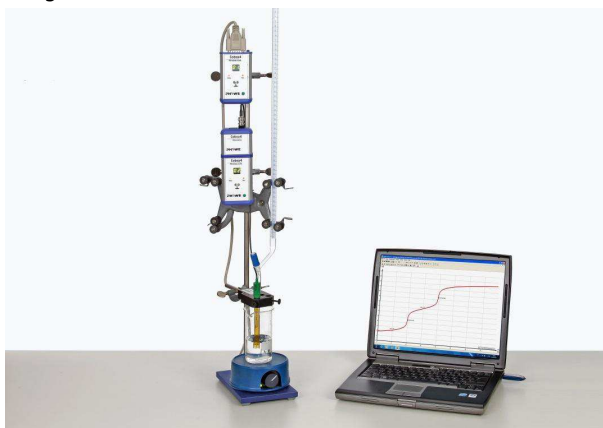


Fig. 1

- Combine the Cobra4 Sensor Unit Chemistry and the Cobra4 Drop Counter with the Cobra4 Wireless-Links.
- Attach them to the retort stand with the holders for Cobra4 and right angle clamps.
- Connect the pH electrode to the pH input of the Cobra4 Sensor Unit Chemistry and the temperature probe to temperature input T1.
- Start the PC and connect the Cobra4 Wireless Manager with a USB socket of the computer.
- Switch on the Cobra4 Wireless/USB-Link (). Connect your computer via WiFi with the Wireless/USB-link (maximum range 50m) or attach the Cobra4 device to the computer with the USB cable.
- Start the software . The Cobra4 measuring device will be automatically detected.
- Boot the experiment "Titration of a polyprotic acid with a strong base with Cobra4" (Load experiment). The measurement parameters for this experiment are loaded now.

Calibrate the pH electrode:

To do so, use the buffer tablets for the two pH values to perform two-point calibrations.

If the electrode has already been calibrated recently, a new calibration is not necessary.

Go to settings and select pH Sensor. Click on Calibration (Fig. 2) and perform a 2-point calibration by using two buffer solutions, e.g. pH 4.0 and pH 10.0 (Fig. 3).

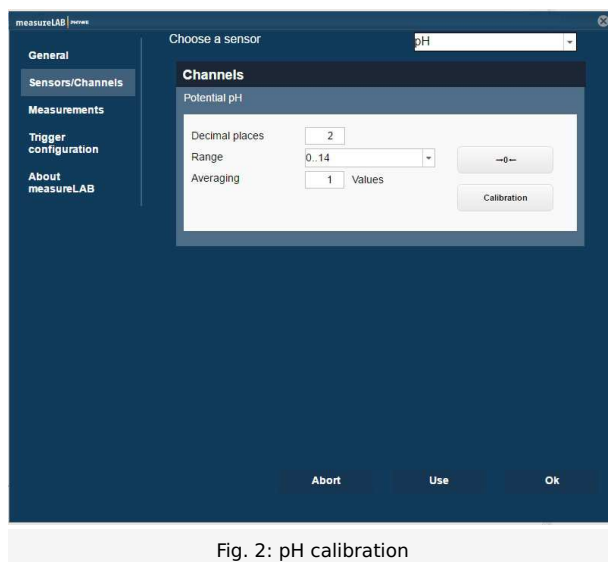


Fig. 2: pH calibration

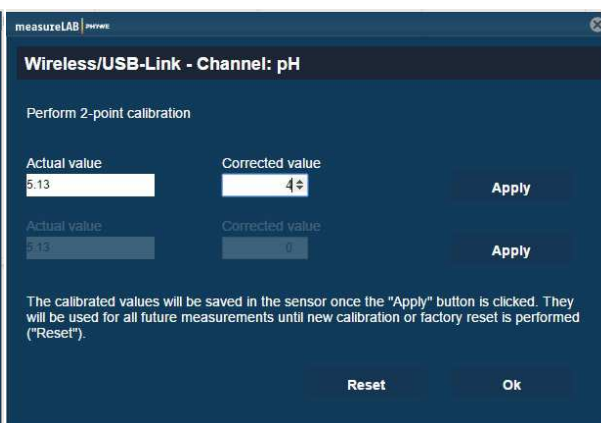


Fig. 3: pH Calibration (Correction of values)

Preparation of necessary solutions to conduct experiment:

0.1 molar H_3PO_4 solution: Weigh 1.153 g of 85 % ortho-phosphoric acid into a 50 ml beaker. Transfer this amount of acid in a 100 ml volumetric flask quantitatively and make up to the mark with distilled water.

Procedure

- Position the magnetic stirrer under the stand and pipette 10 ml of the 0.1 molar phosphoric acid in the 150 ml beaker and slip a magnetic stirring rod in.
- Fill the burette up to the 50 ml mark with 0.1 molar sodium hydroxide solution.
- Position the beaker containing the **phosphoric acid solution** on the magnetic stirrer so that the pH measuring electrode dips into the solution (*Note:* The pH electrode must dip at least so deep in the solution that the diaphragm is completely immersed in the solution. Add more water if necessary).
- Position the tap of the burette so that sodium hydroxide solution can drop into the beaker. Also ensure that individual drops will be recorded by the drop counter.
- Adjust the stirrer to a medium stirring speed (*Note:* Do not allow the magnetic stirring bar to hit against the measuring electrode.)
- Start measurement with a click on  in the icon strip.
- Add sodium hydroxide solution drop-wise to the phosphoric acid solution from the burette. (*Note:* Take care that the addition of the drops is not so rapid that the light barrier cannot register individual drops.)
- When about 50 ml of sodium hydroxide has been so added, close the tap of the burette and click on  the icon to terminate the measurement.
- Save your experiment data using  in the top bar.

Results and evaluation

Results

Fig. 4 shows the graph as presented by the programme, the measurement curve of a titration of 10 ml of 0.1 molar phosphoric acid with sodium hydroxide solution ($c = 0.1 \text{ mol/l}$). To have the equivalence points and pK_a values displayed use  in the top bar of the diagram.

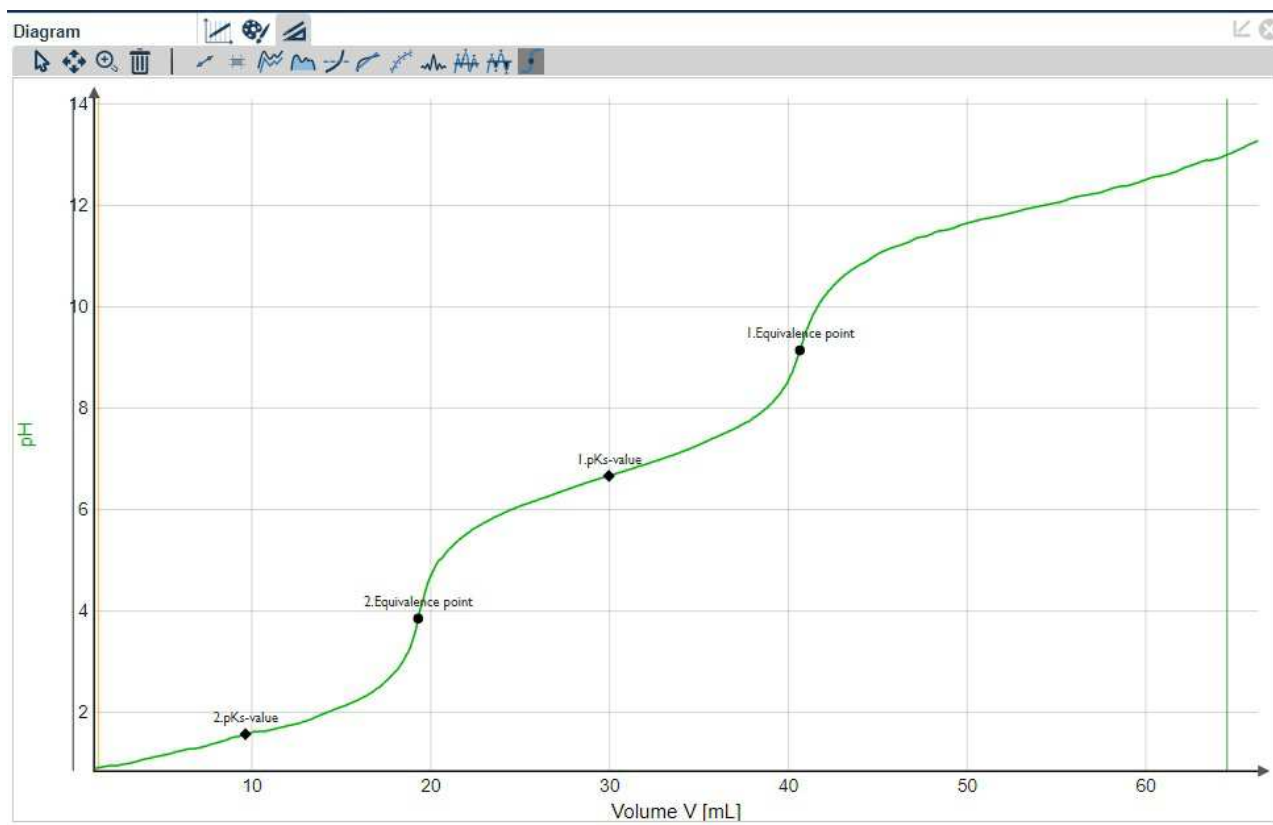


Fig. 4: Exemplary result

- Fig. 4 shows the typical curve of a titration of a polyprotic acid against a strong base. The last equivalent point cannot be determined under the present experimental conditions.
- At the beginning the pH value is not as low as that of a strong acid like hydrochloric acid. That's because the phosphoric acid is only partly dissociated.
- During the performance of the titration the oxonium ions are neutralised because of the reaction with the added hydroxide ions. The used oxonium ions are replaced because of further dissociation of acid molecules.
- Because of the logarithmical presentation of the concentration ($\text{pH} = -\log c(\text{H}_3\text{O}^+)$) and because of the establishment of a buffer system the rising of the curve is at first very low. The buffer system in this area consists of not dissociated phosphoric acid molecules and formed dihydrogenphosphate ions.



- Near the first point of equivalence the pH value shows an abrupt rise because in this area more and more of the phosphoric acid molecules are dissociated now and the buffer system doesn't exist anymore. The first equivalence point of a titration at given conditions should be at 10 ml of added caustic soda solution.
- The pK_a values are calculated with the so called half equivalence point method. Here the Henderson-Hasselbalch equation, which describes the pH value of buffer solutions, is used:

$$\text{pH} = \text{p}K_a - \log \frac{c(\text{HA})}{c(\text{A}^-)}$$

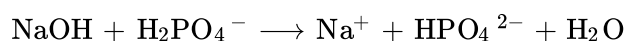
- At the first half equivalence point the concentrations of the dihydrogenphosphate ions and the not dissociated phosphoric acid molecules are equal:

$$c(\text{HA}) = c(\text{A}^-)$$

$$-\log \frac{c(\text{HA})}{c(\text{A}^-)} = 0$$

$$\text{pH} = \text{p}K_{\text{a}}$$

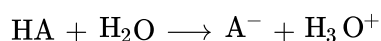
- During the further performance of the titration a second buffer system is established because of the second dissociation step of phosphoric acid. The buffer system in this area consists of dihydrogen phosphate ions and formed hydrogen phosphate ions.



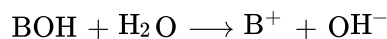
- Near the second point of equivalence the pH value shows another abrupt rise because in this area more and more of the dihydrogen phosphate ions are dissociated and this buffer system doesn't exist anymore.
- The second equivalence point of a titration at given conditions should be at 20 ml of added caustic soda solution. The $\text{p}K_{\text{a}}$ value for the second dissociation step is calculated as shown above.
- In the end of the titration the rise of the pH value is low again.

Evaluation

- An acid reacts with water and forms an anion and an oxonium ion:

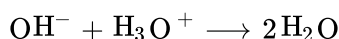


- Sodium hydroxide as a strong base dissociates in water completely:



with $\text{B} = \text{Na}$

- In neutralisation reactions oxonium ions and hydroxide ions react quantitatively to water:



- The pH value and the pOH value are measures for the concentrations of oxonium and hydroxide ions in aqueous solutions.

$$\text{pH} = -\log c(\text{H}_3\text{O}^+)$$

$$\text{pOH} = -\log c(\text{OH}^-)$$

$$\text{p}K_{\text{w}} = \text{pH} + \text{pOH} = 14$$

- For practical applications, it is often important to exactly determine the equivalence point of acidbase titrations. Since the pH of the solution changes suddenly at the equivalence point, it is simple to determine using electrochemical pH measurements. The titration curves of acid-base titrations are easily understood, and the unknown concentrations [i.e. $c(\text{H}^+)$, $c(\text{OH}^-)$, $c(\text{HA})$, $c(\text{A}^-)$, $c(\text{BOH})$ and $c(\text{B}^+)$] are described by the following equations:

- Law of mass action:

$$c(\text{H}^+) \cdot c(\text{OH}^-) = K_{\text{w}}$$

$$\frac{c(\text{H}^+) \cdot c(\text{A}^-)}{c(\text{HA})} = K_{\text{a}}$$

$$\frac{c(\text{B}^+) \cdot c(\text{OH}^-)}{c(\text{BOH})} = K_{\text{b}}$$

2. Charge neutrality:

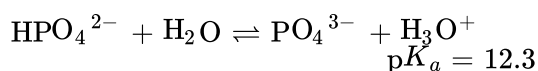
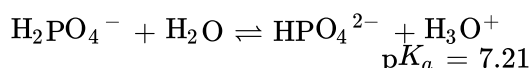
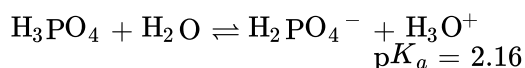
$$c(\text{H}^+) + c(\text{B}^+) = c(\text{OH}^-) + c(\text{A}^-)$$

3. Conservation of mass:

$$c(\text{HA}) + c(\text{A}^-) = c_{\text{A}}$$

$$c(\text{BOH}) + c(\text{B}^+) = c_{\text{B}}$$

- For multibasic phosphoric acid, a number of equivalent points result according to the following dissociation steps:



$$\text{with: } \text{p}K_a = -\log K_a$$

- The pH measurement is a potentiometric measurement and can only be carried out, when the potential of the indicator electrode is measured against that of a reference electrode. Both electrodes are contained in single-rod pH measuring systems. A glass electrode is used as the indicator electrode. When this is immersed in an aqueous solution, a swelling layer (gel) is formed at the pH sensitive glass membrane. This also occurs at the inner side of the membrane, which is in contact with a defined buffer solution, commonly of pH 7. According to the pH of the test solution, hydronium ions diffuse either out of, or into, the outer swelling layer, whereby the potential of this layer changes. The pH, and so also the potential, of the inner side of the glass membrane remains constant while this occurs. With regard to the pick-up electrode, the same system is chosen as for the reference electrode (AgCl), so that the potential difference between the two electrodes is equal to zero. The voltage measured with the single-rod measuring system therefore results from the potential difference between the inside and outside swelling layers of the glass electrode.
- When the system is dipped into a test solution of pH 7, then a potential of 0 mV should be given, as the inner potential is equal to the outer potential. Theoretically, when the pH changes by a single unit, the voltage should change by 59.16 mV. This can be calculated using the Nernst equation, which is as follows for hydrogen:

$$E = E_0 + 2.3 \cdot \frac{RT}{F} \cdot \log \alpha(\text{H}^+)$$

where

$$E^0 = 0$$

$$\log \alpha(\text{H}^+) \cong \log c(\text{H}^+) = -\text{pH}$$

$$2.3 \cdot \frac{RT}{F} = 59.16 \text{ mV} \quad (\text{at } T = 298.15 \text{ K})$$

From this it follows that: $E = -59.16 \text{ mV} \cdot \text{pH}$

T Absolute temperature
 R Universal gas constant
 F Faraday constant

- This rise in the pH-characteristic line is called the slope of the single-rod pH measuring system. The slope of real pH measuring systems deviates like the zero point from the theoretical value given by the Nernst equation.