Determination of the content of phosphoric acid in a cola drink

Aims of the experiment

- Titration as an analytical examination of foods
- Potentiometric titration to track an acid-base reaction
- Applications for equivalence points, pH values, pKs values
- Titration as a quantitative analytical method
- Properties of polyprotic acids

Principles

In the food industry, many additives and acidifying agents are used to make foods last longer and to fine-tune their flavour. For example, in cola drinks, the acidifying agent E388 is added, which provides phosphoric acid.

In general, for food is a mixture of substances. They often must be separated to investigate individual components, and this can be complicated. Alternatively, in the examination it is a property characteristic of the substance to be analysed that is used. In strong acids such as phosphoric acid, this is the lower pKs value. Therefore, the amount of phosphoric acid can be determined in a simple titration process.

Phosphoric acid is a triprotic acid that is relatively strong in the 1st protolysis step. It ultimately dissociates to phosphate ions and three oxonium ions depending on the pH value in three protolysis steps:

$H_3PO_4 + H_2O \rightleftharpoons H_2PO_4^- + H_3O^+$ 1st Protolysis

$H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{2-} + H_3O^+$ 2nd Protolysis

$HPO_4^{2-} + H_2O \rightleftharpoons PO_4^{3-} + H_3O^+$ 3rd Protolysis

The higher the pH value, the more protolysis steps exist. In the process, each protolysis step represents an equilibrium reaction. This process is typical for polyprotic acids since protons in an anionic species are bound more strongly than in a neutral or cationic species.

The equilibria of the individual protolysis steps can be considered to be independent of one another since the pKs- values of the individual species vary by a factor of 5. Therefore, in a titration of phosphoric acid, three different equivalence points can be observed, each of which corresponds to an equimolar conversion with $NaOH_{(aq.)}$.

In the titration of this experiment, the pH value is plotted as a function of volume. The goal of the experiment is to determine the phosphoric acid concentration in a cola drink. To do so, the 1st equivalence point is used. So, the following formula can be used to calculate the concentration *c* of phosphoric acid in the solution from the volume of sodium hydroxide consumed. Here, *c* describes the concentration in mol/l and *V* describes the volume in litres. The index *S* describes the acid, and the index *B* is the base.

$$c_S \cdot V_S = c_B \cdot V_B$$

Risk assessment

The phosphoric acid concentration in cola drinks is very low, therefore there is no need to take precautionary measures.

Fig. 1: Set-up of the experiment.

Sodium hydroxide is a very strong base and therefore corrosive. Therefore, protective clothing and goggles should be used even with low concentrations.

Sodium hydroxide, 0.1 mol/l	
 **Signal word:** **Hazard**	**Hazard statements** H314 Causes severe skin burns and severe eye damage. H410 Can be corrosive to metals. **Safety statements** 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 carefully with water for several minutes. Remove contact lenses if present and easy to do so. Continue rinsing. P309+P310 IF exposed or you feel unwell: Immediately call a POISON CENTRE or doctor/physician.

Equipment and chemicals

1 Pocket-CASSY 2 Bluetooth 524 018
1 CASSYLab 2 ..... 524 220
1 pH adapter S 524 0672
1 pH sensor, BNC plug 529 672
2 Beakers, Boro 3.3, 400 ml, squat 664 131
1 Beakers, Boro 3.3, 250 ml, squat 664 130
1 Burette, clear glass, 25 ml 665 845
1 Burette clamp, simple 666 559
2 Bosshead S 301 09
1 Universal clamp 0...80 mm 666 555
1 Mini magnetic stirrer 607 105
1 Stirring magnet 666 851
1 Stand base, V-shaped, small 300 02
1 Saddle base 300 11
1 Stand rod 25 cm, 10 mm diam. 301 26
1 Stand rod 50 cm, 10 mm diam. 301 27
1 Wash bottle, PE, 500 ml 661 243
1 Sodium hydroxide, 0.1 mol/l, 500 ml 673 8410
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 required:
1 Computer with Windows XP, Vista, 7, 8,10
1 cola drink

Set-up and preparation of the experiment

Preparation of the experiment

The day before the experiment, a cola drink is made to release its excess hydrogen carbonate. To do so, the cola drink is transferred to a 400 ml [beaker] and stirred for 2 hours.

Alternatively, the cola drink is allowed to stand overnight in the beaker.

Set-up of the experiment

An apparatus according to Figure 1 is constructed. Here, the apparatus is made up of the stand base with long stand rods, a magnetic stirrer and a 250 ml beaker and burette. The burette is fastened using the burette clamp. In the process, the burette is aligned with the stopcock in such a way that the centre of the volume display can be viewed. The pH sensor is fastened to the saddle base to its associated small stand rod using a bosshead and universal clamp. The height should be adjusted such that in the later measurement, the diaphragm is completely submerged in the solution, but the membrane is not captured by the rotating stirring magnet and damaged as a result.

Now, the pH sensor is connected to the pH adapter S. This is plugged into the input of the Pocket CASSY 2. The Pocket CASSY is connected to a computer via a USB interface.

Load the settings in CASSY Lab.

Calibrating the pH sensor in CASSY Lab

Before it is used, the pH sensor must be calibrated using the associated buffer solutions.

To do so, the CASSY Lab is first started up. In the next step, the sensor is clicked in the program and in Settings, **Correct p*HA*1** is selected. Here, the pH sensor is rinsed with distilled water and dipped into a buffer solution (pH =7). When the pH on the display remains constant, the setpoint of 7.00 is entered and the **Correct Offset/Factor** button is confirmed. Now, the pH sensor is rinsed again with distilled water and dipped into another buffer solution (pH =4). After reaching a constant value, the setpoint 4.00 is entered and **Correct Offset/Factor** is confirmed again.

Note: The stored calibration can be reused for the same CASSY pH sensor and pH adapter. The sequence of buffer solutions is arbitrary.

Performing the experiment

In the first step, the burette is filled with 0.1 M sodium hydroxide, making sure that the meniscus of the solution is at 0 ml. If too much is filled into the burette, the excess solution can be drained into a beaker using the stopcock.

Note: If the stopcock sticks, it can be loosened using a bit of stopcock grease at the joint of the stopcock (do not block the opening).

150 ml of decarbonated cola drink is filled into a 250 ml beaker. The pH sensor is dipped into the beaker and a stirring magnet is added. The magnetic stirrer is turned on and set to a fast rotation speed to ensure thorough mixing. Now, wait until the pH value becomes constant. It should be about 1.9 – 2.2.

Now, start the measurement in the CASSYLab program. The stopcock of the burette is opened so that the dripping rate of sodium hydroxide is constant and not too fast (about 1 – 2 drops per second). During the measurement, a measurement point is manually plotted every 0.5 ml. This can be done using a computer mouse left by clicking on **Record measurement** or by pressing the button on the Pocket CASSY 2. In the process, care must be taken that the measurement points are recorded in 0.5-ml increments.

Now, the semi-automatic generation of the titration curve can be tracked.

After adding a burette (25 ml) of sodium hydroxide, the measurement is ended by pressing the **End measurement** button.

Note: The cola drink may only be titrated at room temperature. Deviating temperatures can lead to distorted results.

If the values are recorded manually in CASSYLab, there should be no appended measurements since they always begin at the end of the prior measurement, which makes it no longer possible to evaluate the experiment as a result.

The experiment should be repeated twice and comparisons should be made to confirm reproducibility of the measurement.

Observation

At the beginning, the cola drink has a low pH value. After continuous addition of sodium hydroxide, it increases slowly and the increase exhibits very large spikes at some points.

The generation of the titration curve can be tracked and interpreted along the way.

Evaluation

Determination of the equivalence points

The determination of equivalence points is easy to do in CASSYLab. Just open the drop-down menu in the diagram by right clicking. Select **Other evaluations** and the sub-point **Determine equivalence point**. Now, the curve area in which one of the equivalence points is assumed is marked. The calculated equivalence point will now display in the diagram. Further information can then be displayed as text and positioned by right clicking **Set mark**, sub-point **Text**. Similarly, this method is also applicable for other equivalence points in the curve plot (see Fig. 2).

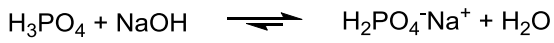
As can be seen in Figure 2, the second equivalence point in the titration curve is difficult to identify. This is due to the low concentration of phosphoric acid in cola drinks. The first equivalence point is sufficient for the evaluation. In this regard, it is the equimolar conversion using NaOH in the first protolysis step that is key.

An almost pure monotone increase in pH value is seen at the equivalence points. At the turning point, equilibrium then takes effect between the acid and the base. There is barely any increase to be seen between the equivalence points, which are caused by the protolysis steps for phosphoric acid. This is because of a buffer effect in the individual protolysis steps for phosphoric acid. In buffer solutions, there are both greater amounts of a weak acid and of the corresponding base. In the process, polyprotic acids indicate as many buffer ranges as they have protons to shed.

The pH value of the first equivalence point is within the acidic range at 4.2.

Determining the amount of phosphoric acid

Only the first protolysis step is considered in the determination of phosphoric acid. Thus, according to



in the aqueous solution, the dihydrogen phosphate anion will not be found in the salt formula, but will rather exist in a dissociated form as sodium cation and dihydrogen phosphate anion. In the process, an equivalent of sodium hydroxide is consumed in order to deprotonate phosphoric acid once. Accordingly, the concentration of the phosphoric acid can be determined as follows:

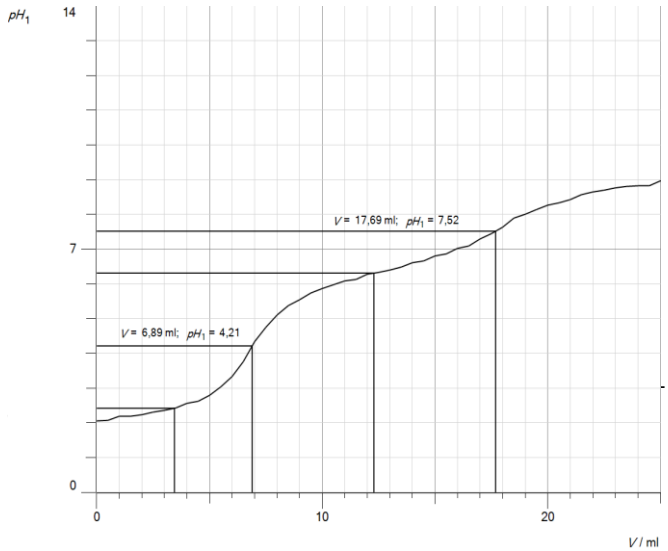
$$c_s \cdot V_s = c_B \cdot V_B$$

Conversion according to the acid concentration sought yields:

$$c_s = \frac{c_B \cdot V_B}{V_S}$$

The concentration sought is that of phosphoric acid. Entering the values determined provides the following concentration of phosphoric acid in the sample

$$c_s = \frac{0.00689\ l \cdot 0.1 \frac{mol}{l}}{0.150\ l} 9 = 4.59 \frac{mmol}{l}$$



Now, this value is converted according to the following equation using the molar mass *M* (98 g/mol) of phosphoric acid to obtain the exact amount *m*.

$$m = c \cdot M = 0.00459 \frac{mol}{l} \cdot 98 \frac{g}{mol} = 0{,}450 \frac{g}{l} \equiv 450 \frac{mg}{l}$$

Results

Equivalence points and pH range

The titration curve contains two equivalence points, only the first of which is clearly recognisable. For the first point, a volume of V_{eq} = 6.9 ml of 0.1 M sodium hydroxide was added. For the second point, a volume of V_{eq} = 17.7 ml was added. As can be seen, the second equivalence point is not at twice the addition of sodium hydroxide. For this reason, only the first equivalence point is used for further calculations.

Determining the amount of phosphoric acid

The cola sample has a phosphoric acid content of 450 mg/l. In the sample investigated (150 ml) there is 67.5 mg of phosphoric acid.

Literature values for the amount of phosphoric acid (E338) in cola drinks for the Coca-Cola as the producer come to 170 mg/l and other databases indicate a general maximum concentration of 700 mg/l in foods.

Cleaning and disposal

The contents of the beaker can be disposed of down the drain, as can excess dilute sodium hydroxide solution. Then, rinse away with plenty of water. All glass equipment used are rinsed multiple times with distilled water, which is disposed of down the drain. The pH sensor is rinsed with distilled water, the cap with the 3M KCl solution is placed on it, and it is stored away.

Note on storage of pH sensors: pH sensors must not be allowed to dry out. They must always be immersed in a 3-molar KCl solution and stored away. Instead of plastic caps, a better option would be to store them in a storage vessel (for example 667 4195).

Notes

Other questions can be investigated using this experimental set-up as well, for example comparing cola drinks from different producers or cola drinks from a single producer (normal vs. diet varieties).

Also, carbonated cola can be compared with decarbonated cola.