IChO Veszprém - Budapest 1987

500 mg of a hydrated sodium salt of phosphoric acid are dissolved in 50.0 ml of 0.1 molar sulphuric acid. This solution is diluted with distilled water to 100.0 ml and 20.0 ml thereof are titrated with 0.100 molar NaOH solution using thymolphthalein as indicator. The average of the burette reading is 26.53 ml. The pH at the end-point is 10.00. The cumulative protonation constants are given by

$$K_n = \frac{[H_nPO_4^{n-3}]}{[PO_4^{3-}][H^+]^n}$$

where $pK_1 = -11.70$; $pK_2 = -18.6$; $pK_3 = -20.6$. Relative atomic masses are: Na = 23.0 and P = 31.0

a) Calculate the percentage distribution, by moles, of all protonated $H_nPO_4^{n-3}$ species at the end point.

b) What is the stoichiometric formula of the salt ?

IChO Oslo 1994 (Prep. Prob.)

Fosfor moodustab kaks klooriidi, PCl_3 ja PCl_5, vahetul reaktsionil elementide vahel.

a) Kijeldage P_4, PCl_3 ja PCl_5 molekulide geomeetriat.

b) Arvutage, milline on saadud lahuse pH, kui 0,1 molli PCl_3 lahustatakse 1 cm^3 vees.

c) Arvutage, milline on saadud lahuse pH, kui 0,1 mooli PCl_3 lahustatakse 450 cm^3 1 M NaOH lahuses. $K_{a1}(H_3PO_3) = 1{,}6\cdot10^{-2}$; $K_{a2}(H_3PO_3) = 7\cdot10^{-7}$

IChO Oslo 1994 (Prep. Prob.)

Tuntuimad fosfori oksiidid P_4O_6 ja P_4O_{10}. Need oksiidid on tuntuimate oksohapete anhüdriidid. P_4O_{10} lisamisel suuremale kogusele veele moodustub kolmealuliseline ortofosforhape, mille dissotsioonikonstandid on: $K_{a1}(H_3PO_4) = 7{,}1\cdot10^{-3}$; $K_{a2}(H_3PO_4) = 6{,}2\cdot10^{-8}$; $K_{a3}(H_3PO_4) = 4{,}5\cdot10^{--13}$

a) Arvutage 0,015 M Na_3PO_4 vesilahuse pH.

Meil on 4 katseklaasi (A-D), igaühes on 1,00 dm^3 0,020 M HCl lahus. Katseklassidesse lisatakse tahket Na_3PO_4. Lahuse ruumala jääb konstantseks.

b) Katseklassi A lisatakse 0, 015 mooli Na_3PO_4. Leidke lahuse pH.

c) Katseklassi B lisatakse 0, 020 mooli Na_3PO_4. Leidke lahuse pH.

d) Katseklassi C lisatakse 0, 0050 mooli Na_3PO_4. Leidke lahuse pH.

e) Peale Na_3PO_4 lisamist katseklaasi D oli seal lahuse pH 6,65. Kui palju Na_3PO_4 lisati?

Teatmikus on toodud hõbefosfaadi lahustuvuskorrutis $Ksp(Ag_3PO_4) = 1{,}0\cdot10^{-16}$.

f) Näidake, et fosfaatanirooniprotolüüsi ei või jätta arvestamata, kui arvutatakse hõbefosfaadi lahustuvust vees.

g) Arvutage hõbefosfaadi lahustuvus vees eeldades, et teisi mittelahustuvaid sooli ei moodustu.

IChO Oslo 1994 (Prep. Prob.)

Loodusliku vee proovis tuleb soolhappega potentsiomeetrilise tiitrimise teel määrata vesinikkarbonaat- ja karbonaatioonide sisaldused. 50 ml weeproovi (alikvoodi) tiitrimisel 0,01M soolhappega olid tiitrimiskõvera käänupunktid 12,35 ja 41,15 ml juures.
Määrake vesinikkarbonaat- ha karbonaatioonide kontsentratsioonid veeproovis.

IChO Oslo 1994

Lactic acid is formed in the muscles during intense activity (anaerobic metabolism). In the blood, lactic acid is neutralized by reaction with hydrogen carbonate ions. This will be illustrated by the following calculations:

Lactic acid, written HL, is monoprotic, and the acid dissociation constant is K_{HL} = I.4 x 10^{-4}.

The acid dissociation constants for carbonic acid are: K_{a1} = 4.5 x 10^{-7} and K_{a2} = 4.7 x 10^{-11}. All carbon dioxide remains dissolved during the reactions.

a) Calculate the pH of a 3.00 x 10^{-3} M solution of HL.

b) Calculate the value of the equilibrium constant for the reaction between lactic acid and hydrogen carbonate ions.

c) 3.00 x 10^{-3} mol of lactic acid (HL) is added to 1.00 L of 0.024 M solution of $NaHCO_3$ (no change in volume, HL completely neutralized). Calculate the pH of the solution of $NaHCO_3$ before HL is added. Calculate the pH of the solution after the addition of HL.

d) The pH of the blood in a person changed from 7.40 to 7.00 due to the lactic acid which formed during physical activity. Let an aqueous solution having pH = 7.40 and [HCO_3^-] = 0.022 M represent blood in the following calculation and in f). Calculate the number of moles of lactic acid which must be added to 1.00 L of this solution so that the pH becomes7.00.

e) In a saturated aqueous solution of $CaCO_3$(s) the pH is measured as 9.95. Calculate the solubility of calcium carbonate in water and show that the calculated value for the solubility product constant K_{sp} is 5 x 10^{-9}.

f) Blood contains calcium ions. Calculate the maximum concentration of "free" calcium ions in the solution given in d). (pH = 7.40, [HCO_3^-] =0.022 M)

IChO Moscow 1996

Potassium dichromate is one of the most widely used precipitating reagents. The following equilibria are established in aqueous solutions of Cr(VI).

$HCrO_4^- = H^+ + CrO_4^{2-}$ pK_1 = 6.50

$2HCrO_4^- = Cr_2O_7^{2-} + H_2O$ pK_2 = -1.36

All other equilibrium involving chromium should be ignored.

a) Evaluate the equilibrium constants for the following reactions:

i) $CrO_4^{2-} + H_2O \rightarrow HCrO_4^- + OH^-$ ii) $Cr_2O_7^{2-} + 2OH^- \rightarrow 2CrO_4^{2-} + H_2O$

b) The solubility product of $BaCrO_4$ K_s = 1.2 x 10^{-10}. $BaCr_2O_7$ is very soluble in water.

In what direction will the equilibrium (1b) shift upon the addition of the following reagents to a moderately concentrated aqueous solution of potassium dichromate?

i) KOH ii) $BaCl_2$ iii) HCl iv) H_2O (consider all the above equilibria)

c) Dissociation constant of acetic acid K_a = 1.8 x 10^{-5}. Calculate the pH value of:

i) 0.010 M K_2CrO_4 ii) 0.010 M $K_2Cr_2O_7$ iii) 0.010 M $K_2Cr_2O_7$ + 0.100 M CH_3COO

d) Calculate the equilibrium concentrations of the following ions in a solution of 0.010 M $K_2Cr_2O_7$ + 0.100 M CH_3COOH

i) CrO_4^{2-} ii) $Cr_2O_7^{2-}$

IChO Bangkok 1999 (Preb. Prob.)

a) Phosphoric acid, H_3PO_4, is a triprotic acid. If a solution of 0.100 M H_3PO_4 is titrated with 0.100 M NaOH, estimate the pH at these points:

(i) Halfway between the initial point and the first equivalent point.

(ii) At the second equivalent point.

(iii) Why might it be difficult to define the titration curve after the second end point?

$K_1 = 7.1 \times 10^{-3}$ $K_2 = 6.2 \times 10^{-8}$ $K_3 = 4.4 \times 10^{-13}$

b) A solution contains 530 millimoles of sodium thiosulfate and an unknown amount of potassium iodide. When this solution is titrated with silver nitrate, 20.0 millimoles are added before the first turbidity of silver iodide persists. How many millimoles of potassium iodide are present? A final volume is 200 mL.

$Ag(S_2O_3)_2^{3-} \rightleftharpoons Ag^+ + 2S_2O_3^{2-}$ (aq) $K_d = 6.0 \times 10^{-14}$

AgI (s) $\rightleftharpoons Ag^+$(aq) + I^-(aq) $K_{sp} = 8.5 \times 10^{-17}$

IChO Bangkok 1999

A diprotic acid , H_2A , undergoes the following dissociation reactions:

$H_2A \rightleftharpoons HA^- + H^+$; $K_1 = 4.50 \times 10^{-7}$

$HA^- \rightleftharpoons A^{2-} + H^+$; $K_2 = 4.70 \times 10^{-11}$

A 20.00 mL aliquot of a solution containing a mixture of Na2A and NaHA is titrated with 0.300 M hydrochloric acid. The progress of the titration is followed with a glass electrode pH meter. Two points on the titration curve are as follows :

mL HCl added	pH
1.00	10.33
10.00	8.34

a) On adding 1.00 mL of HCl, which species reacts first and what would be the product?

b) What is the amount (mmol) of the product formed in (2-1)?

c) Write down the main equilibrium of the product from (2-1) reacting with the solvent ?

d) What are the amounts (mmol) of Na_2A and NaHA initially present?

e) Calculate the total volume of HCl required to reach the second equivalence point.

Solutions I, II and III contain a pH indicator HIn ($K_{In} = 4.19 \times 10^{-4}$) and other reagents as indicated in the table. The absorbance values at 400 nm of the solutions measured in the same cuvette are also given in the table. K_a of CH_3COOH is 1.75×10^{-5}.

	Solution I	Solution II	Solution III
Total concentration of indicator Hin	1.00×10^{-5} M	1.00×10^{-5} M	1.00×10^{-5} M
Other reagents	1.00 M HCl	0.100 M NaOH	1.00 M CH_3COOH
Absorbance at 400 nm	0.000	0.300	?

f) Calculate the absorbance at 400 nm of Solution III.

g) Apart from H_2O, H^+ and OH^-, what are all the chemical species present in the solution resulting from mixing Solution II and Solution III at 1:1 volume ratio?

h) What is the absorbance at 400 nm of the solution in g)?

i) What is the transmittance at 400 nm of the solution in g)?

IChO Mumbai 2001

Phosphoric acid is of great importance in fertiliser production. Besides, phosphoric acid and its various salts have a number of applications in metal treatment, food, detergent and toothpaste industries.

2.1 The pK values of the three successive dissociations of phosphoric acid at 25°C are:

pK_{1a} = 2.12 pK_{2a} = 7.21 pK_{3a} = 12.32

Write down the conjugate base of dihydrogen phosphate ion and determine its pK_b value.

Small quantities of phosphoric acid are extensively used to impart the sour or tart taste to many soft drinks such as colas and root beers. A cola having a density of 1.00 g mL^{-1} contains 0.05 % by weight of phosphoric acid.

2.2 Determine the pH of the cola (ignoring the second and the third dissociation steps for phosphoric acid). Assume that the acidity of the cola arises only from phosphoric acid.

2.3 Phosphoric acid is used as a fertiliser for agriculture. 1.00 x 10^{-3} M phosphoric acid is added to an aqueous soil suspension and the pH is found to be 7.00. Determine the fractional concentrations of all the different phosphate species present in the solution. Assume that no component of the soil interacts with any phosphate species.

2.4 Zinc is an essential micronutrient for plant growth. Plants can absorb zinc in water soluble form only. In a given soil water with pH = 7.0, zinc phosphate was found to be the only source of zinc and phosphate. Calculate the concentration of [Zn^{2+}] and [PO_4^{3-}] ions in the solution. K_{sp} for zinc phosphate is 9.1×10^{-33}.