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PREPARATORY PROBLEMS: PRACTICAL SOLUTIONS AND SUPPLEMENTARY INFORMATION



50th IChO 2018

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SLOVAKIA & CZECH REPUBLIC

BACK TO WHERE IT ALL BEGAN

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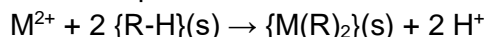


Problem P1. Determination of a metallic ore composition

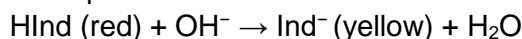
Provide an aqueous sample containing only Zn^{2+} and Cu^{2+} nitrates in a mass ratio of about 1:1; the total concentration of the metals in the solution should be about 35 g dm^{-3} .

I. Determination of the metal ion concentration by alkalimetry and photometry

P1.1 a) Cation exchange between the sample solution and the resin:



b) Indication of the titration endpoint:



P1.2 The column must be washed to neutral pH due to the possible presence of acidic solution in the internal space of the resin. The solution with $\text{pH} < 7$ which remains in the gel, microporous or porous resin, increases the amount of the “released” H^+ ions after the sample ion exchange.

P1.3 A tetraammine complex of Cu^{2+} is formed after adding ammonia. Copper ammine complexes are intensively blue coloured and thus are suitable for the spectrophotometric determination of copper.

P1.4 The concentrations of Cu^{2+} were selected to obtain the absorbance in the range $<0.1; 1.0>$, optimal for the accuracy of the spectrophotometric experiment. Additionally, linear range of Lambert–Beer law is used for the spectrophotometric determination.

P1.5 *Acid–base titration*

Total amount of cations bound to the resin:

$$n = n(\text{Cu}^{2+}) + n(\text{Zn}^{2+})$$

Total amount of released H^+ ions:

$$n(\text{H}^+) = 2 \times n$$

Total amount of OH^- ions determined by alkalimetric titration (abbreviation “at”):

$$n(\text{OH}^-) = c(\text{NaOH}) \times V_{2\text{at}} = n_{\text{at}}(\text{H}^+)$$

Total amount of M^{2+} cations determined by the alkalimetric titration:

$$n_{\text{at}} = n_{\text{at}}(\text{H}^+) / 2 = n(\text{OH}^-) / 2 = c(\text{NaOH}) \times V(\text{NaOH}) / 2$$

Total amount of determined cations bound to the resin, volume V , step I.3:

$$n = n_{\text{at}} \times V_{\text{el}} / V_{1\text{at}}$$

Spectrophotometric analysis

Concentration of Cu^{2+} ions, c_x :

$$c_x = A_x \times (c_{\text{max}} - c_{\text{min}}) / (A_{\text{max}} - A_{\text{min}})$$

Concentration of Cu^{2+} ions in the original sample:

$$c(\text{Cu}^{2+}) = c_x \times (V_{\text{sp}} / V_{\text{pip}}) \times (V_{\text{dil}} / V_{\text{orig}})$$

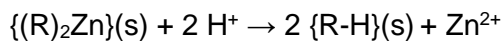
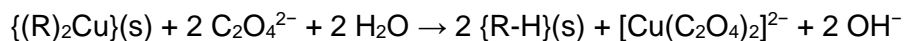
Concentration of Zn^{2+} ions in the original sample:

$$c(\text{Zn}^{2+}) = n / V - c(\text{Cu}^{2+})$$



II. Ion exchange separation and complexometric titration

P1.6 Reactions which occur in the ion exchange (release of the Cu^{2+} and Zn^{2+} ions):



P1.7 Copper oxalate is decomposed by hydrogen peroxide and the released Cu^{2+} ions are determined by complexometric titration with the standard EDTA solution.

P1.8 For both eluates, it is a simple direct titration (reaction stoichiometry ratio for titrant and titrand 1 : 1).



Problem P2. Determination of a carbonate rock composition

Provide a powdered sample prepared by mixing carbonates, so that the sample composition corresponds to the typical values for a dolomite rock. The typical values are (in %, w/w): dolomite 65–75%, calcite 6–10%, ankerite 5–8%, other compounds 10–20% (use sodium bicarbonate).

P2.1 The following calculation is performed for a pure dolomite sample weighing $m_0 = 0.7654$ g. Dolomite (abbreviation “dol”), $\text{CaMg}(\text{CO}_3)_2$

$$n_0 = m_0 / M(\text{dol}) = 0.7654 \text{ g} / 184.41 \text{ g mol}^{-1} = 4.151 \times 10^{-3} \text{ mol}$$



$$n(\text{HCl}) = 4 \times n_0 = 1.660 \times 10^{-2} \text{ mol}$$

$$V(\text{HCl}) = n(\text{HCl}) / c(\text{HCl}) = 0.01660 \text{ mol} / 3 \text{ mol dm}^{-3} = 5.53 \times 10^{-3} \text{ dm}^3$$

10% excess of the calculated volume of the HCl solution used for the quantitative decomposition of the sample: $1.1 \times 5.53 \times 10^{-3} \text{ dm}^3 = 6.08 \times 10^{-3} \text{ dm}^3$

P2.2 The pH will be estimated from the content of a strong acid. The rest of the compounds are weak acids, the influence of which is suppressed by the presence of the strong acid. The excess volume of 3 M HCl is $(6.08 - 5.53) \text{ cm}^3 = 0.55 \text{ cm}^3$, which is diluted to 250 cm^3 :

$$[\text{H}^+] = c(\text{HCl}) \times V(\text{HCl}) / V_0 = 3 \text{ mol dm}^{-3} \times 0.55 \text{ cm}^3 / 250 \text{ cm}^3 = 0.007 \text{ mol dm}^{-3}$$

$$\text{pH} = -\log[\text{H}^+] = 2.2$$

P2.3 Boiling the reaction mixture in step 1 removes dissolved carbon dioxide.

P2.4 In step 2, iron is oxidized to Fe^{3+} and the excess of peroxide is removed as it would oxidize the indicators.

P2.5 Iron oxidized to Fe^{3+} is separated by precipitation as a hydroxide.

P2.6 The reaction of EDTA with metal ions has the stoichiometry 1 : 1 in each case. (Abbreviations: “ank” = ankerite; “dol” = dolomite; “cal” = calcite, “admix” = inert impurities)

Content of ankerite in % (w/w), from step 3

$$n(\text{Fe}) / n(\text{EDTA}) = 1/1$$

Ankerite is the only source of iron and contains one iron atom per molecule.

$$n(\text{ank}) = n(\text{Fe}) = V_2 \times c(\text{EDTA}) \times V_0 / V_1$$

$$m(\text{ank}) = n(\text{ank}) \times M(\text{ank}); \quad M(\text{ank}) = 215.95 \text{ g mol}^{-1}$$

$$w(\text{ank}) = m(\text{ank}) / m_0$$

Content of dolomite in % (w/w), from steps 5 and 6

$$n(\text{Me}^{2+}) / n(\text{EDTA}) = 1/1$$

$n(\text{Ca}+\text{Mg})$ is determined in step 5, $n(\text{Ca})$ is determined in step 6

$n(\text{Mg})$ is determined as the difference from steps 5 and step 6

Dolomite is the only source of magnesium and contains one magnesium atom per molecule.

$$n(\text{dol}) = n(\text{Mg}) = n(\text{Ca}+\text{Mg}) - n(\text{Ca})$$



$$n(\text{dol}) = V_6 \times c(\text{EDTA}) \times (V_0 / V_3) \times (V_4 / V_5) - V_8 \times c(\text{EDTA}) \times (V_0 / V_3) \times (V_4 / V_7)$$

$$m(\text{dol}) = n(\text{dol}) \times M(\text{dol}); \quad M(\text{dol}) = 184.41 \text{ g mol}^{-1}$$

$$w(\text{dol}) = m(\text{dol}) / m_0$$

Content of calcite in % (w/w), from step 6

Calcium is present in all three compounds. All the compounds contain one calcium atom per molecule.

The total amount of calcium is determined in step 6:

$$n(\text{Ca}) = n(\text{dol}) + n(\text{ank}) + n(\text{cal}) = V_8 \times c(\text{EDTA}) \times (V_0 / V_3) \times (V_4 / V_7)$$

$$n(\text{cal}) = V_8 \times c(\text{EDTA}) \times (V_0 / V_3) \times (V_4 / V_7) - n(\text{dol}) - n(\text{ank})$$

$$m(\text{cal}) = n(\text{cal}) \times M(\text{cal}); \quad M(\text{cal}) = 100.09 \text{ g mol}^{-1}$$

$$w(\text{cal}) = m(\text{cal}) / m_0$$

Content of inert impurities in % (w/w)

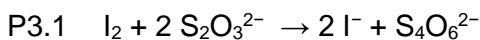
$$w(\text{total}) = w(\text{ank}) + w(\text{dol}) + w(\text{cal})$$

$$w(\text{admix}) = 1 - w(\text{total})$$



Problem P3. Determination and identification of organic acids

I. Determination of sodium thiosulfate concentration in solution



P3.2 $c(S_2O_3^{2-}) = n(S_2O_3^{2-}) / V_2$

$$n(S_2O_3^{2-}) / n(I_2) = 2/1$$

$$n(S_2O_3^{2-}) = 2 \times n(I_2) = 2 \times c(I_2) \times V_1$$

$$c(S_2O_3^{2-}) = 2 \times c(I_2) \times V_1 / V_2$$

II. Identification of an unknown acid in sample solutions A and B and determination of its concentration

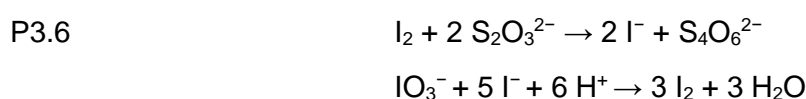
P3.4 Table of the titration results (the data serve as an example only).

Procedure a	Volume of sample solution A or B added to the titration flask $V_{11} = 20.00 \text{ cm}^3$	
	Volumes read from burette (perform only the necessary analyses)	
	Sample A $V_{3a} = 21.00 \text{ cm}^3$ $V_{3b} = 21.00 \text{ cm}^3$ <i>Note/Observation: fast reaction = sharp and stable end point of titration</i>	
	Sample B $V_{4a} = 18.00 \text{ cm}^3$ $V_{4b} = 20.00 \text{ cm}^3$ <i>Note/observation: slow reaction = after the first colour change, the solution resumes its original colour</i>	
	Accepted volumes	$V_3 = 21.00 \text{ cm}^3$ $V_4 = -$
Procedure b	Volume of sample solution A or B added to the titration flask $V_{12} = 20.00 \text{ cm}^3$	
	Volumes read from burette (perform only the necessary analyses)	
	Sample A $V_{5a} = -$ $V_{5b} = -$ <i>Note/Observation: the experiment was omitted based on the results in procedure a</i>	
	Sample B $V_{6a} = 22.00 \text{ cm}^3$ $V_{6b} = 22.00 \text{ cm}^3$ <i>Note/Observation: fast reaction = sharp and stable end point of titration</i>	
	Accepted volumes	$V_5 = 21.00 \text{ cm}^3$ (from procedure a) $V_6 = 22.00 \text{ cm}^3$
Procedure c	Volume of sample solution A or B added to the titration flask $V_{13} = 20.00 \text{ cm}^3$	
	Volumes read from burette (perform only the necessary analyses)	
	Sample A $V_{7a} = -$ $V_{7b} = -$ <i>Note/Observation: Not measured, it is a strong acid, as proved in procedure a</i>	
	Sample B $V_{8a} = 17.00 \text{ cm}^3$ $V_{8b} = 17.00 \text{ cm}^3$ <i>Note/Observation: This measurement is necessary as according to the results in procedures a and b the acid is neither strong nor a hydroxy derivative</i>	



	Accepted volumes	$V_7 = -$	$V_8 = 17.00 \text{ cm}^3$
Indicate with a ✓ the identified component in sample A			
HCl ✓		CH_3COOH	$(\text{R}(\text{OH})_x(\text{COOH})_y)$
Indicate with a ✓ the identified component in sample B			
HCl		CH_3COOH ✓	$(\text{R}(\text{OH})_x(\text{COOH})_y)$

- P3.5 - Strong hydrochloric acid will give the same result in all the procedures.
- Weak acids react slowly in Procedure **a**, the equivalence point is not indicated properly.
 - In Procedure **b**, hydroxy derivative acts as a strong acid and the equivalence point can be indicated as for the strong acid in Procedure **a**.



- P3.7 Calculation in Procedure **a** (for a strong acid)

$$n(\text{S}_2\text{O}_3^{2-}) / n(\text{I}_2) = 2/1$$

$$n(\text{I}_2) = (1/2) \times n(\text{S}_2\text{O}_3^{2-}) = (1/2) \times c(\text{S}_2\text{O}_3^{2-}) \times V(\text{S}_2\text{O}_3^{2-})$$

$$n(\text{H}^+) / n(\text{I}_2) = 6/3 = 2$$

$$n(\text{H}^+) = 2 \times n(\text{I}_2) = 2 \times (1/2) \times n(\text{S}_2\text{O}_3^{2-}) = n(\text{S}_2\text{O}_3^{2-}) = c(\text{S}_2\text{O}_3^{2-}) \times V(\text{S}_2\text{O}_3^{2-})$$

$$c(\text{HCl}) = c(\text{S}_2\text{O}_3^{2-}) \times V(\text{S}_2\text{O}_3^{2-}) / V(\text{HCl})$$

$$c(\text{HCl}) = c(\text{S}_2\text{O}_3^{2-}) \times V_3 / V_{11}$$

Justification: A strong acid can be determined using the simplest procedure (although all three procedures are possible) – direct titration and minimized number of added compounds minimize the possible error sources.

- P3.8 Calculation in the case of Procedure **b** (shown for citric acid H_3A)

$$n(\text{S}_2\text{O}_3^{2-}) / n(\text{I}_2) = 2/1$$

$$n(\text{I}_2) = 1/2 \times n(\text{S}_2\text{O}_3^{2-}) = 1/2 \times c(\text{S}_2\text{O}_3^{2-}) \times V(\text{S}_2\text{O}_3^{2-})$$

$$n(\text{H}^+) / n(\text{I}_2) = 6/3 = 2$$

$$n(\text{H}^+) = 2 \times n(\text{I}_2) = 2 \times 1/2 \times n(\text{S}_2\text{O}_3^{2-}) = n(\text{S}_2\text{O}_3^{2-}) = c(\text{S}_2\text{O}_3^{2-}) \times V(\text{S}_2\text{O}_3^{2-})$$

$$n(\text{H}^+) / n(\text{H}_3\text{A}) = 3/1$$

$$n(\text{H}_3\text{A}) = 1/3 n(\text{H}^+)$$

$$c(\text{H}_3\text{A}) = 1/3 \times c(\text{S}_2\text{O}_3^{2-}) \times V(\text{S}_2\text{O}_3^{2-}) / V(\text{H}_3\text{A})$$

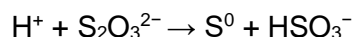
$$c(\text{H}_3\text{A}) = 1/3 \times c(\text{S}_2\text{O}_3^{2-}) \times V_6 / V_{12}$$

Justification: The addition of Ca^{2+} increases the strength of hydroxy acid species. The direct titration then works well.

- P3.9 As there is excess of thiosulfate in Procedure **c**, the equilibrium of the reaction iodate/iodide is shifted to the reaction products due to the consumption of iodine by the reaction with thiosulfate present in the mixture.



P3.10 In an acidic solution, thiosulfate undergoes an undesired side reaction (elemental sulfur can be observed):



Thiosulfate must be added as last, when the concentration of H^+ is decreased due to the reaction with the mixture iodate/iodide

P3.11 Calculation when weak acid (for example acetic acid) is determined – Procedure **c**.

There are two sources of iodine in the titration flask: the added I_2 solution ($n_1(\text{I}_2)$) and I_2 formed in reaction of H^+ with the mixture iodate/iodide ($n_2(\text{I}_2)$).

Total amount of iodine in the titration flask:

$$n(\text{I}_2) = n_1(\text{I}_2) + n_2(\text{I}_2)$$

The iodine reacts with the thiosulfate added by the pipette $n_1(\text{S}_2\text{O}_3^{2-})$ and by the burette $n_2(\text{S}_2\text{O}_3^{2-})$.

$$n(\text{S}_2\text{O}_3^{2-}) = n_1(\text{S}_2\text{O}_3^{2-}) + n_2(\text{S}_2\text{O}_3^{2-}) = (V_{23} + V_8) \times c(\text{S}_2\text{O}_3^{2-})$$

The corresponding amount of iodine: $n(\text{S}_2\text{O}_3^{2-}) / n(\text{I}_2) = 2/1$

$$n(\text{I}_2) = (1/2) \times n(\text{S}_2\text{O}_3^{2-}) = (1/2) \times (V_{23} + V_8) \times c(\text{S}_2\text{O}_3^{2-})$$

Iodine originated from the reaction of the acid sample

$$n_2(\text{I}_2) = n(\text{I}_2) - n_1(\text{I}_2) = 1/2 \times (V_{23} + V_8) \times c_1 - c(\text{I}_2) \times V_{33}$$

The corresponding acid:

$$n(\text{H}^+) / n_2(\text{I}_2) = 6/3 = 2$$

$$n(\text{H}^+) = 2 \times n_2(\text{I}_2)$$

$$c(\text{HAc}) = n(\text{H}^+) / V_{13}$$

Justification: Weak acid must be determined by back titration, when equilibrium is shifted due to the iodine consumption by the reaction with added thiosulfate.

III. Identification of an unknown hydroxy carboxylic acid in the sample

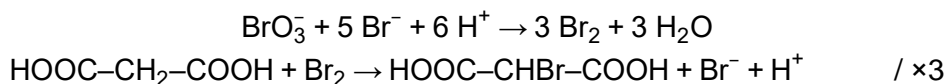
P3.13 For example, when the acids are neutralized to 50%, the values of pH are 3.71 for tartaric acid, 3.86 for lactic acid, 4.28 for malic acid, and 4.78 for citric acid.

Other points of titration curves can be used for this purpose from the region of partially neutralized acid with NaOH solution.

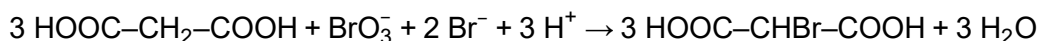


Problem P4. A chemical oscillator and its activation energies

P4.1 The yellow colour observed is due to Br_2 formation and its disappearance due to malonic acid bromination:



Overall:

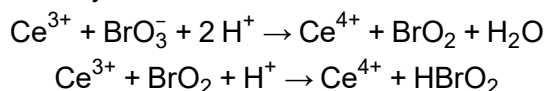


P4.2 A typical $t = 114.25 \text{ s}$ (may depend significantly on the reactor geometry, stirring rate etc.)

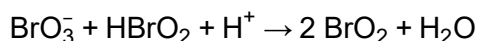
$$[\text{Br}^-] = 5.0 \text{ mM}, \text{ thus } d[\text{Br}^-]/dt = 5.0 / 114.25 \text{ mM s}^{-1} = 4.38 \times 10^{-2} \text{ mM s}^{-1}.$$

The average period of oscillation in the BZ oscillator with the same temperature and the same $[\text{Ce(III)}]$ was 96.19 s , consuming $96.19 \times 4.38 \times 10^{-2} \text{ mM s}^{-1} = 4.21 \text{ mM Br}^-$. According to the stoichiometry shown above, this corresponds to 6.32 mM malonic acid. The bromide for each cycle comes from the oxidative degradation of bromomalonic acid.

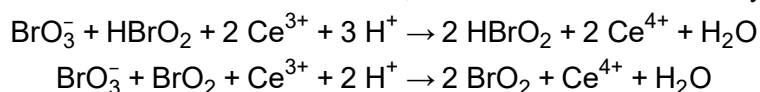
P4.3 In the list of the bromine-containing species, we need to look at the bromine oxidation states and at the numbers of bromine atoms. Only two of the species can be combined with the one-electron oxidation of Ce^{3+} to Ce^{4+} to give the desired $1:1:n$ stoichiometry for the reactants and an integer stoichiometric coefficient for the reduced bromine-containing product. The two species are BrO_3^- and BrO_2 , capable of undergoing one-electron reduction to BrO_2 and HBrO_2 , respectively:



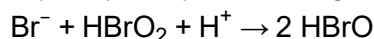
However, the oxidation must proceed with BrO_2 , because plenty of BrO_3^- was observed to be present side by side with the reduced Ce^{3+} during the Br-inhibited reaction in part I.1. BrO_2 is produced from BrO_3^- and HBrO_2 :



The equations for Ce^{3+} oxidation and BrO_2 production can be combined in two ways, eliminating either BrO_2 or HBrO_2 . Nevertheless, both results are autocatalytic:



Bromide ions inhibit the autocatalytic cycle by consuming HBrO_2 :



P4.4 A typical set of results is as follows:

[Ce] / mM	Induction period / s	Periods of oscillation / s			
		1 st	2 nd	3 rd	Average
2.5	152.18	88.43	86.55	86.23	87.07
5.0	149.78	96.97	94.92	96.69	96.19

As the concentration of cerium was doubled, the induction period was practically not affected, it decreased only negligibly. On the contrary, the average period of oscillations increased slightly. The increase was, however, only by about 10%. These results suggest that the reactions of cerium are the fast ones, and not rate-determining.



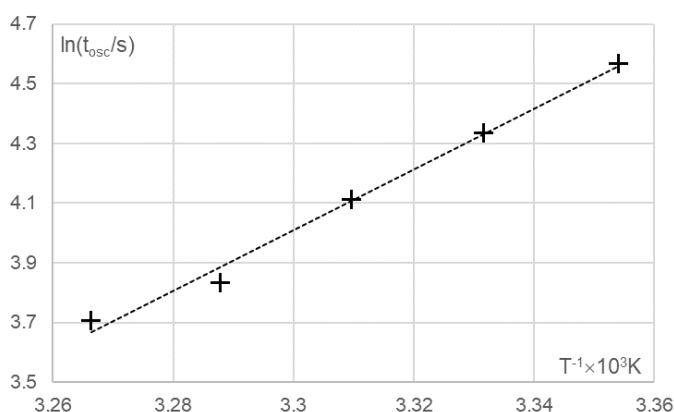
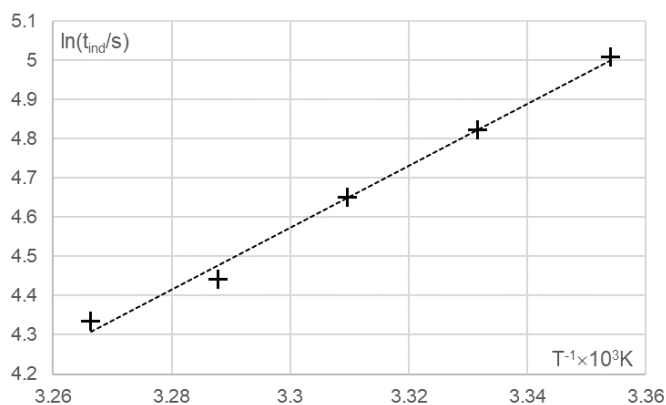
P4.5 A typical set of results is as follows:

Temperature / °C	Induction period / s	Periods of oscillation / s			
		1 st	2 nd	3 rd	Average
25.0	149.78	96.97	94.92	96.69	96.19
27.0	124.26	76.92	75.23	77.12	76.42
29.0	104.56	61.09	61.18	60.81	61.03
31.0	84.92	46.90	45.90	45.78	46.19
33.0	76.36	41.30	40.26	40.70	40.75

This yields the following values of $1/T$ and natural logarithms:

$T^{-1} / 10^{-3} \text{ K}^{-1}$	$\ln(\text{induction period} / \text{s})$	$\ln(\text{period of oscillations} / \text{s})$
3.354	5.00917	4.5664
3.332	4.82238	4.3363
3.310	4.64976	4.1113
3.288	4.4417	3.8328
3.267	4.3355	3.7075

We obtain two graphs that look very similar, but they yield different values of E_a :



The slope of the graph with the induction periods is 7 890 K, therefore the corresponding activation energy is $7\,890 \text{ K} \times R = 65.6 \text{ kJ mol}^{-1}$. The slope of the graph made for the periods of oscillation is 10 140 K, thus the activation energy is $10\,140 \text{ K} \times R = 84.3 \text{ kJ mol}^{-1}$. The activation energy determined from the induction periods is closer to the reference value for cerium, whereas the activation energy determined for the periods of oscillation is closer to the reference value for ferroin, despite the fact that cerium is in large excess.



Problem P5. Kinetics of a chemical wave front propagation

P5.1 Typical experimental results look like this:

Set	[H ₂ SO ₄]	[BrO ₃ ⁻]	Times from accepted replicates / s			v / mm min ⁻¹
#1	0.50 M	0.10 M	61.58	63.41	60.18	4.81
			63.14	62.00	63.57	
#2	0.35 M	0.10 M	108.10	106.75	109.26	2.80
			107.22	106.93	104.78	
#3	0.50 M	0.13 M	56.32	53.45	55.42	5.41
			56.48	56.12	54.71	
#4	0.50 M	0.070 M	78.22	75.60	76.25	3.89
			77.99	78.37	76.32	

P5.2 Non-zero values of q would suggest that alternative parallel reaction pathways capable of affecting the autocatalysis may exist side by side with the production of **X** dependent on bromate(V). If q is positive, there may be additional autocatalytic pathways capable of making **X** without bromate(V). If q is negative, there may be reactions inhibiting the autocatalysis, as if not all bromate(V) was effectively contributing to the reaction.

The usual calculation of slope and intercept applies:

$$p = \frac{v_{\#3}^2 - v_{\#4}^2}{[\text{BrO}_3^-]_{\#3} - [\text{BrO}_3^-]_{\#4}} = \frac{5.41^2 - 3.89^2}{0.13 - 0.07} \text{ mm}^2 \text{ min}^{-1} \text{ M}^{-1} = 235.6 \text{ mm}^2 \text{ min}^{-2} \text{ M}^{-1}$$

$$q = v_{\#3}^2 - p [\text{BrO}_3^-]_{\#3} = (29.27 - 235.6 \times 0.13) \text{ mm}^2 \text{ min}^{-2} = -1.4 \text{ mm}^2 \text{ min}^{-2}$$

The calculation above also demonstrates how the individual terms contribute: while $p[\text{BrO}_3^-]$ represents $30.6 \text{ mm}^2 \text{ min}^{-2}$, the value of q is much smaller, making up around 5% of the total at 0.13 M and around 9% at 0.070 M bromate(V). Such contributions could easily come from other factors of measurement, and they cannot be regarded as significant.

P5.3 This is a usual calculation of partial reaction orders:

$$a = \frac{\log(v_{\#1}/v_{\#2})}{\log([\text{H}_2\text{SO}_4]_{\#1}/[\text{H}_2\text{SO}_4]_{\#2})} = \frac{\log(4.81/2.80)}{\log(0.50/0.35)} = 1.517$$

$$b = \frac{\log(v_{\#3}/v_{\#4})}{\log([\text{BrO}_3^-]_{\#3}/[\text{BrO}_3^-]_{\#4})} = \frac{\log(5.41/3.89)}{\log(0.13/0.070)} = 0.533$$

The value of b is in a good agreement with the expected value of 0.5, corresponding to the first order kinetics with respect to bromate.

On the other hand, the value of a does not agree. In fact, $a \approx 1.5$ suggests a third-order dependence of the reaction rate on [H₂SO₄]. This can be interpreted as the partial reaction order with respect to [H⁺], if the same dissociation degree of H₂SO₄ is assumed in 0.50 M and 0.35 M solutions. In this concentration range, rate equation (3) needs to be reconsidered.



Note: Reaction conditions were chosen deliberately in this range with increased sensitivity to the acid concentration. Above 0.50 M H₂SO₄, the expected value of a ≈ 0.5 would be obtained.

P5.4 Based on (2) and (3), we can calculate the rate constant in the following way:

$$k = \frac{v^2}{4D[\text{BrO}_3^-][\text{H}^+]} \approx \frac{v^2}{4D[\text{BrO}_3^-][\text{H}_2\text{SO}_4]}$$

Converting the values of v to cm s^{-1} and evaluating the formula above, we find:

	Set #1	Set #2	Set #3	Set #4
$v / 10^{-2} \text{ cm s}^{-1}$	8.02	4.67	9.02	6.48
$k / \text{M}^{-2} \text{ s}^{-1}$	16.1	7.78	15.6	15.0

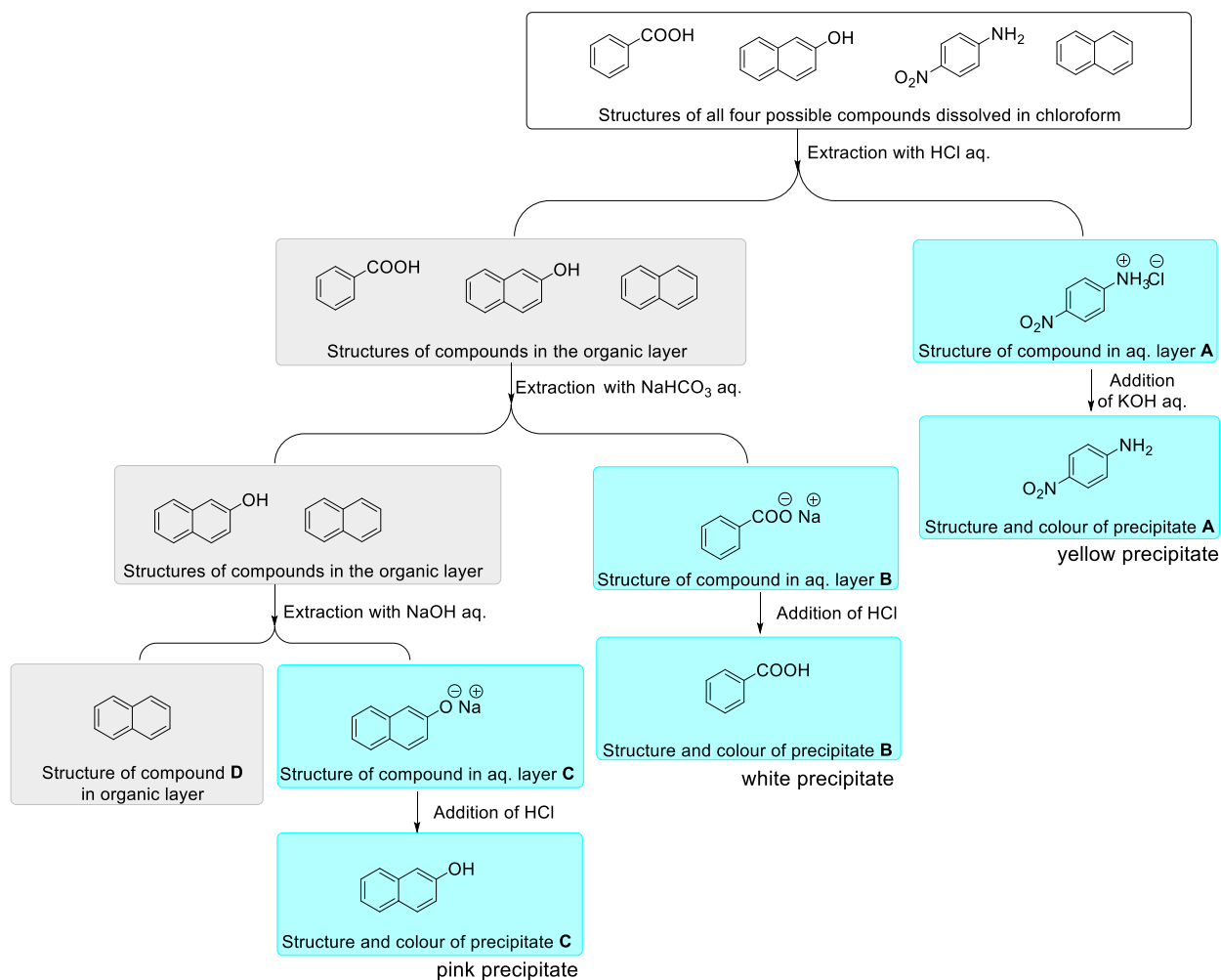
The values of k found from concentration sets #1, #3 and #4 are in relatively good agreement with the reference value of $20 \text{ M}^{-2} \text{ s}^{-1}$. The value from concentration set #2 is considerably smaller and confirms a different mode in the kinetics of the reaction under these conditions.



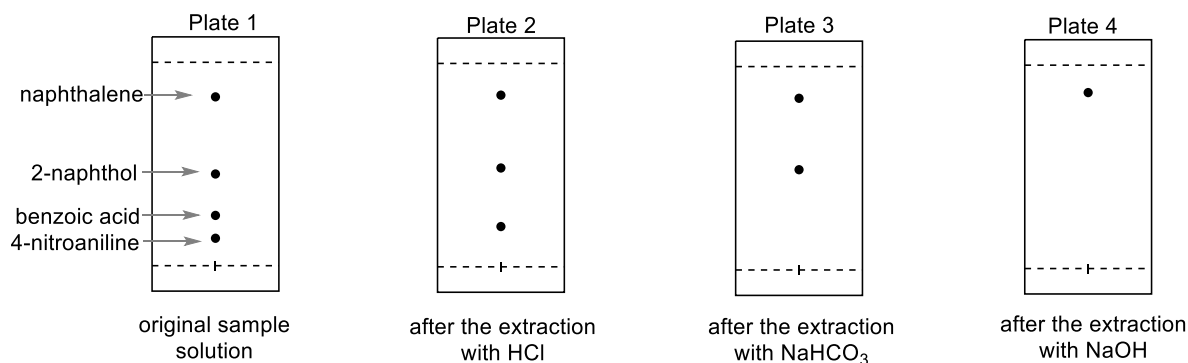
Problem P6. Separation of acidic, basic and neutral organic compounds

Prepare samples which may contain 3–4 of the following compounds: benzoic acid, 4-nitroaniline, naphthalene-2-ol and naphthalene, mixed in ratio w/w 1:1:1:1 for a four-component mixture, or 0:1:1:1, 1:1:1:0 or 1:1:0:1 for three-component mixtures. Note that 4-nitroaniline has to be present in any sample. The following solution is given for a 4-component mixture.

P6.1

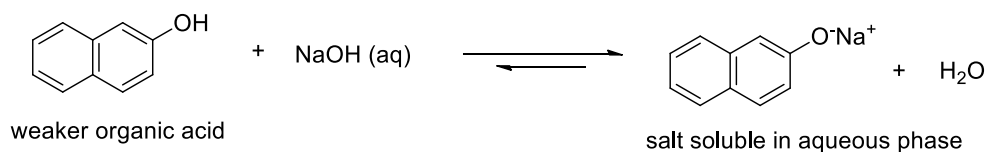
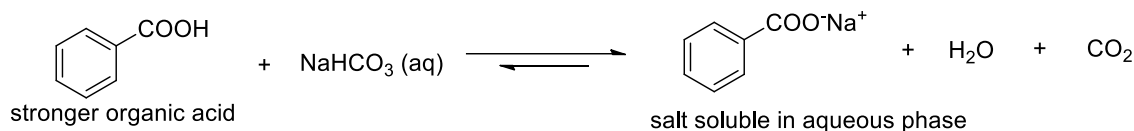
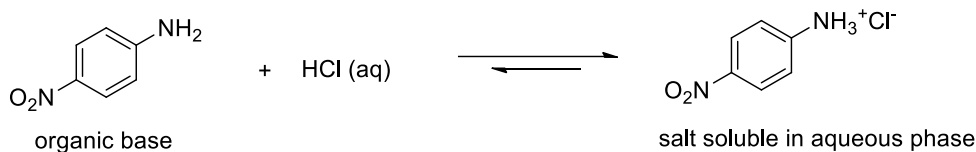


P6.2 Comparison of the TLC plates shows that after each extraction one of the compounds “disappears” from the organic phase as it is extracted into the aqueous phase of an appropriate pH (one component would be missing in three-component mixtures).

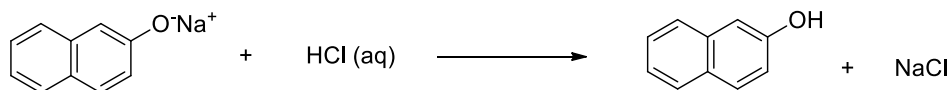
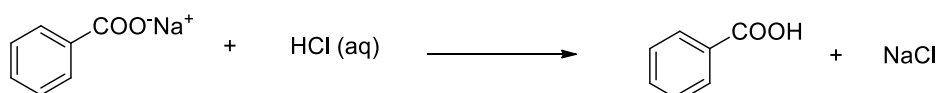
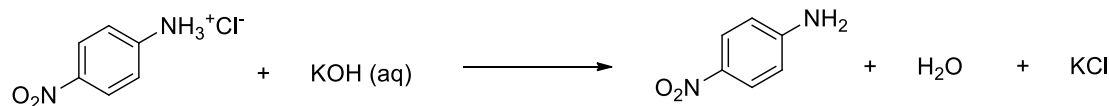


P6.3

SEPARATION EQUATIONS



ISOLATION EQUATIONS



P6.4 The use of NaHCO₃ for the second extraction is necessary to separate compound **B** (benzoic acid) from compound **C** (2-naphthol). A stronger organic acid (benzoic acid) is extracted into the bicarbonate solution as its conjugate base. A weaker organic acid (2-naphthol) remains in the organic phase. If the first extraction were performed with hydroxide solution, both organic acids (benzoic acid and 2-naphthol) would be extracted into the basic aqueous phase as conjugate bases and they would not get separated.



P6.5

Compound	R_f	m (g) ^a	Compound name
A	0.21–0.22	0.112–0.141 (60–75%)	4-nitroaniline
B	0.33–0.34	0.109–0.131 (58–70%)	benzoic acid
C	0.53–0.54	0.151–0.166 (59–83%)	2-naphthol
D	0.85–0.86	0.110–0.155 (59–83%)	naphthalene

^a isolated yields of dried compound obtained from 1:1:1:1 mixture

P6.6 Students should find out that the ratio of the compounds in the sample was 1:1:1:1 and that the sum of the masses of the isolated compounds is smaller than the original sample weight. Some of the material is lost in each step: transfers of material, imperfect layer separation during extractions, loss occurring during the precipitation, filtration, etc.



Problem P7. Meerwein–Ponndorf–Verley reduction

P7.1–P7.4 Characteristics and yield of the product:

TLC analysis (silica gel, hexanes/ethyl acetate 6:1): $R_f(\text{ketone}) = 0.37$; $R_f(\text{alcohol}) = 0.13$

Product: white crystals, yield after crystallization from hexanes 145 mg (72%), melting point 72.0–73.0 °C (hexanes).

P7.5 $m(\text{iPrOH}) = V(\text{iPrOH}) \times d(\text{iPrOH})$

$$m(\text{iPrOH}) = 4 \text{ cm}^3 \times 0.786 \text{ g cm}^{-3} = 3.144 \text{ g}$$

$$m(\text{H}_2\text{O}) = m(\text{iPrOH}) \times w(\text{H}_2\text{O})$$

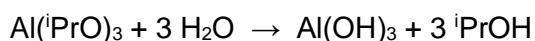
$$m(\text{H}_2\text{O}) = 3.144 \text{ g} \times 0.002 = 6.3 \times 10^{-3} \text{ g}$$

$$n(\text{H}_2\text{O}) = m(\text{H}_2\text{O}) / M(\text{H}_2\text{O})$$

$$n(\text{H}_2\text{O}) = 6.3 \times 10^{-3} \text{ g} / 18.01 \text{ g mol}^{-1} = 3.5 \times 10^{-4} \text{ mol} = 0.35 \text{ mmol}$$

The number of moles of water present in 4 cm³ of isopropyl alcohol is 0.35 mmol.

P7.6 The products of aluminium isopropoxide hydrolysis are aluminium hydroxide and isopropyl alcohol.



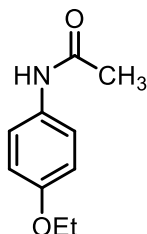
P7.7 The spot of the alcohol product has a lower retention factor (shorter distance of the spot from the start) compared to the starting ketone. This is caused by the higher polarity of the alcohol product and the ability of alcohol to act as a H-bonding donor, resulting in a higher affinity to the stationary phase.

P7.8 2-Acetonaphthone can be converted to 1-(2-naphthyl)ethanol by the treatment with hydrides such as LiAlH₄, NaBH₄ or DIBAL-H. Another method for the reduction of ketones is a transition metal catalyzed hydrogenation. Platinum or ruthenium are common catalysts. Complexes of transition metals (e.g. Wilkinson catalyst) can be used in homogeneous catalysis. Complexes with chiral ligands allow stereoselective reduction of ketones.

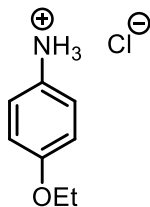


Problem P8. Transformation of a drug to a sweetener

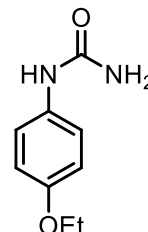
P8.1 Structures:



A: Phenacetin



B



C: Dulcin

$$\text{P8.2 } n(\mathbf{P}) = m(\mathbf{P}) / M(\mathbf{P}) = 1.00 \text{ g} / 151.17 \text{ g mol}^{-1} = 6.615 \times 10^{-3} \text{ mol}$$

$$n(\mathbf{C}) = n(\mathbf{P})$$

$$m(\text{theor. } \mathbf{C}) = n(\mathbf{C}) \times M(\mathbf{C}) = 6.615 \times 10^{-3} \text{ mol} \times 180.21 \text{ g mol}^{-1} = 1.19 \text{ g}$$

P8.3 $\text{Exp. yield}(\mathbf{C}) = m(\text{actual yield } \mathbf{C}) / m(\text{theor. } \mathbf{C})$; expressed in %, rounded to integers

The yield of the isolated phenacetin (**A**) is 85–90% (not marked). A typical yield of the isolated dulcin (**C**) after thorough drying is 0.50 g (42% yield from paracetamol). If recrystallization from organic solvents is required, the yield drops to ca 0.20 g (17% yield from paracetamol), but essentially pure white crystalline material is obtained.

P8.4 M.p.(**C**) = 173.0–174.0 °C; impurities lower the m.p. dramatically.

$$\text{P8.5 } R_f(\mathbf{P}) = 0.37$$

$$R_f(\mathbf{A}) = 0.46$$

$$R_f(\mathbf{C}) = 0.19$$

- P8.6
- NaOH deprotonates the OH group of paracetamol to give a coloured phenolate.
 - The deprotonated, anionic substrate is much more reactive than the neutral paracetamol.
 - Acetamide functional group is stable towards a base (NaOH in 95% EtOH).
 - Aryl ethyl ether functional group is stable towards an aqueous acid (aq. HCl).
 - Product **B** is a salt (it contains a cation and an anion).

P8.7 d) Isocyanic acid, H–N=C=O