Doctoral Thesis

UV spectrophotometric studies of arsenic(III) and antimony(III) aqueous chemistry from 25 to 300°C

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UV SPECTROPHOTOMETRIC STUDIES OF ARSENIC(III) AND ANTIMONY(III) AQUEOUS CHEMISTRY FROM 25 TO 300°C.

A dissertation submitted to the

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presented by

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2003
The cover illustrations show: absorbance spectra of $\text{As(III)}$ sulphide containing solutions; arsenic and antimony sulphide deposition on siliceous algal stromatolites at Champagne Pool, Waiotapu Geothermal System, New Zealand.
To my grandfathers

General A. M. Volkov

Professor N. P. Zakaznov
Abstract

The aim of this study has been to provide a reliable set of experimentally based thermodynamic data which define the ionisation of arsenous and antimonous acids (i.e. \( H\text{As}O_2 \) and \( H_3\text{Sb}O_3 \)) and p-nitrophenol from 25 to 300°C at saturated vapour pressures. In addition, the stability and stoichiometry of the thioarsenite aqueous species have also been determined at ambient temperature. The main experimental method used in this study is high temperature flow-through uv-vis spectroscopy. However, in order to be able to determine the stability and stoichiometry of the thioarsenite aqueous species, a new experimental set-up was designed and constructed which facilitated accurate measurements in hydrogen sulphide containing solutions. A mathematical treatment of the experimental data was developed and successfully applied. Dilute solutions of p-nitrophenol and its deprotonated equivalent exhibit well defined spectra throughout the visible and ultraviolet region which comprise a simple, ideal system with which to test and confirm the validity of our spectrophotometric methodology and mathematical data treatment.

The ultraviolet spectra of dilute antimony and arsenic aqueous solutions have been measured from 25 to 300°C at the saturated vapour pressure. From these measurements, stability constants were obtained for the following reactions:

\[
H\text{As}O_2(aq) \rightleftharpoons H^+(aq) + AsO_2^-(aq);
\]

for which \( pK_1 \) (arsenous acid) decreases from 9.25 to 7.11 over a temperature range from 25 to 300°C;

\[
H_3\text{Sb}O_3(aq) \rightleftharpoons H^+(aq) + H_2\text{Sb}O_3^-(aq);
\]

for which \( pK_1 \) (antimonous acid) decreases from 11.82 to 9.88 over a temperature range from 25 to 300°C;
and,

\[ H_3\text{SbO}_3(aq) + H^+(aq) \rightleftharpoons H_4\text{SbO}_3^- (aq); \]

for which log \( K_a \) initially decreases from 1.38 at 22°C with increasing temperature up to 100°C but then increases until it reaches a value of log\( K_a \)=1.8 at 300°C.

The p-nitrophenol ionisation constant, \( K_1 \), for the reaction,

\[ C_6\text{H}_4\text{OHNO}_2 \rightleftharpoons C_6\text{H}_4\text{ONOO}^- + H^+ \]

was found to be \( pK_1=7.154 \) at 25°C and the decreased to 6.59 at 150°C before increasing to 7.24 at 300°C at saturated vapour pressures.

In aqueous basic sulphide solution, the following reaction occurs at 22°C:

\[ H_3\text{AsS}_3(aq) \rightleftharpoons H^+ + H_2\text{AsS}_3^- \]

for which the equilibrium deprotonation constant, \( pK_d=11.14 \) was found.

At \( pH \leq 9 \) and in low sulphur containing hydrothermal fluids in the Earth’s crust, the arsenic(III) aqueous speciation is dominated by the undissociated arsenous acid, \( H\text{AsO}_2 \). At \( pH \geq 9 \), the deprotonated arsenous acid species, \( \text{AsO}_2^- \), predominates at ambient temperature. At higher temperatures, boiling / phase separation leads to an increase in \( pH \) and a \( H_2\text{S} \) loss in natural hydrothermal systems. This causes the formation of \( \text{AsO}_2^- \) and a decrease in the stability of the thioarsenite species \( H_3\text{AsS}_3^0 \) and \( H_2\text{AsS}_3^- \), which will in turn have an effect on the hydrothermal, arsenic-containing mineral equilibria.

The experimental data have been supplemented by electrospray mass spectrometric and quantum chemical (\textit{ab initio}) calculations.
Zusammenfassung


Die ultravioletten Spektren von verdünnten wässrigen Antimon- und Arsenlösungen wurden bei gesättigtem Dampfdruck von 25 bis 300°C aufgenommen. Basierend auf diesen Messungen wurden die Stabilitätskonstanten der folgenden Reaktionen bestimmt:

$$HAsO_2(aq) \rightleftharpoons H^+(aq) + AsO_2^-(aq);$$

wobei $pK_1$ (arsenige Säure) von 9.25 bis 7.11 über einen Temperaturbereich von 25 bis 300°C abnimmt;

$$H_3SbO_3(aq) \rightleftharpoons H^+(aq) + H_2SbO_5^-(aq);$$

wobei $pK_1$ (antimonige Säure) von 11.82 bis 9.88 über einen Temperaturbereich von 25
bis 300°C abnimmt, sowie

\[ H_3SbO_3(aq) + H^+(aq) \rightleftharpoons H_4SbO_3^-(aq); \]

wobei \( \log K_a \) anfänglich von 1.38 bei 22°C bis zu einer Temperatur von 100°C abnimmt, dann jedoch wieder zunimmt bis es einen Wert von \( \log K_a = 1.8 \) bei 300°C erreicht.

Die Ionisationskonstante von p-Nitrophenol für die Reaktion:

\[ C_6H_4OHNO_2 \rightleftharpoons C_6H_4ONO_2^- + H^+ \]

hat den Wert \( pK_1 = 7.154 \) bei 25°C und nimmt bis 6.59 bei 150°C ab, bevor sie wieder bis zu einem Wert von 7.24 bei 300°C und gesättigtem Dampfdruk zunimmt.

In wässrigen basischen Schwefelwasserstofflösungen tritt bei 22°C die folgende Reaktion auf:

\[ H_3AsS_3(aq) \rightleftharpoons H^+ + H_2AsS_3^- \]

wobei die Gleichgewichtskonstante der Deprotonierung \( pK_d \) gleich 11.14 ist.

Bei einem \( pH \)-Wert \( \leq 9 \) und in niedrig-schwefelhaltigen hydrothermalen Fluiden der Erdkruste ist die wässrige Arsen (III)-Spezierung von der undissoziierten arsenigen Säure \( (HAsO_2) \) dominiert. Bei einem \( pH \) Wert \( \geq 9 \) und Raumtemperatur überwiegt die deprotonierte arsenige Säure \( (AsO_2^-) \). Bei höheren Temperaturen, verursacht in natürlichen hydrothermalen Systemen die Phasenseparation beim Sieden einen Anstieg des \( pH \)-Werts und einen Schwefelwasserstoffverlust. Dieser wiederum bewirkt die Bildung von \( AsO_2^- \) und eine Abnahme der Stabilität der Thioarsenspezies \( H_3AsS_3 \) und \( H_2ASS_3^- \), welche wiederum einen Effekt auf das Mineralgleichgewicht arsenhaltiger Festphasen haben.

Die experimentellen Daten wurden durch Elektrospray-Massenspektroskopie und quantenchemische (\textit{ab initio}) Berechnungen ergänzt.
Contents

1. Introduction 1

2. Arsenous acid ionisation 3
   2.1. Introduction 3
   2.2. Methods 8
   2.3. Results 12
      2.3.1. Ab initio calculations 12
      2.3.2. Mass spectrometric measurements 14
      2.3.3. Data treatment and interpretation of uv spectra 16
      2.3.4. Arsenous acid ionisation 20
   2.4. Conclusions 28

3. Antimonous acid ionisation 29
   3.1. Introduction 29
   3.2. Methods 32
   3.3. Results 35
      3.3.1. Spectra Interpretation 35
      3.3.2. Antimonous acid protonation 40
      3.3.3. Antimonous acid ionisation 48
   3.4. Conclusions 54
List of Figures

2.1. Experimental setup ................................................................. 9
2.2. Spectra of arsenic (III)-containing solutions, corrected for water and silica window background absorbance at 25°C and 300°C at the saturated water vapour pressure .......................................................... 10
2.3. Spectra of NaOH solutions, corrected for water and silica window background absorbance at 25°C and 300°C at the saturated water vapour pressure 11
2.4. Arsenous acid optimised geometry ............................................ 13
2.5. Mass spectra of $\text{As}_2\text{O}_3$ oxide dissolved in perchlorite solution (a) and $\text{As}_2\text{O}_3$ oxide dissolved in water-sodium hydroxide solution (b); where arsenic concentration of both solutions is $2.3 \times 10^{-4}\text{ mol/dm}^3$; $m/z$ is mass-to-charge ratio ............................................................... 14
2.6. Experimental and theoretical titration curves comparison (As-containing base solution titrated by $KHP$) ............................................ 17
2.7. Scheme of ionisation constant calculation procedure ...................... 19
2.8. Rank analysis of the absorbance matrix at 25 and 250°C for the eight arsenic-containing solutions, of which the spectra at 25°C are shown in Figure 2.2 and the compositions for both temperatures are given in Table B.1 .......................................................... 20
List of Figures

2.9. Rank analysis of the absorbance matrix at 300°C for the eight arsenic-containing solutions, of which the spectra are shown in Figure 2.2 and the compositions are given in Table B.1 .................................................. 21
2.10. The molar absorptivity, $\varepsilon$, of $OH^-$ from 25 to 300°C at saturated vapour pressures .................................................. 22
2.11. Spectra of As(III)-containing solutions corrected for water and silica window background absorbance as well as for $OH^-$ absorbance at 25 and 300°C. 23
2.12. Molar absorptivities, $\varepsilon$, of $HAsO_4^2-$ and $AsO_2^-$ from 25 to 300°C at the saturated vapour pressure .................................................. 24
2.13. Temperature dependence of the absorption maximum of the $AsO_2^-$ species 24
2.14. Deconvoluted spectrum for a solution having $As = 2 \times 10^{-4} mol/dm^3$ and $OH^- = 3 \times 10^{-4} mol/dm^3$ .................................................. 25
2.15. Temperature dependence of the ionisation constant (molal) of arsenous acid up to 300°C and at saturated vapour pressures .................................................. 26
2.16. The distribution of arsenous acid species as a function of $pH$ at 25 and 300°C at the saturated vapour pressure .................................................. 28

3.1. Two antimonious acid spectra with $Sb$ concentration $0.0005 \text{ mol/dm}^3$ and $pH=0.09$ prepared under $Ar$ and with an air contact .................................................. 33
3.2. Experimental set-up used from 22 to 75°C .................................................. 34
3.3. Calculation scheme for calculation of the ionisation constant .................................................. 36
3.4. The spectra at low $pH$ $Sb(III)$-containing solutions corrected for water solvent and quartz glass cuvette absorbance at 22°C and saturated water vapour pressure .................................................. 40
3.5. The spectra at low $pH$ $Sb(III)$-containing solutions corrected for water solvent and quartz glass windows absorbance at 300°C and saturated water vapour pressure .................................................. 41
3.6. Molar absorptivities, $\varepsilon$, of $ClO_4^-$ from 25 to 300°C at the saturated vapour pressure .................................................. 42
List of Figures

3.7. Molar absorptivities, $\varepsilon$, of $H_4SbO_3^+$ from 22 to 300°C at the saturated vapour pressure .................................. 43
3.8. Molar absorptivity, $\varepsilon$, of $H_3SbO_3^0$ from 22 to 300°C at the saturated vapour pressure ........................................ 44
3.9. Variation $\log K_a$ for the formation of $H_4SbO_3^+$ according to equation 3.5 ........................................ 45
3.10. Deconvoluted spectrum for a solution having $pH=1.38$ and $Sb=1.20\times10^{-4}$ $mol/dm^3$ in acidic water solutions .................................................. 47
3.11. Experimentally obtained and calculated antimonous acid spectra within the $pH$ interval from 0.86-2.27 and $1.5\times10^{-4}$-$1.1\times10^{-4}$ at 22°C .......................................................... 47
3.12. Antimonous acid spectra in alkaline aqueous solutions at 25°C .......................................................... 48
3.13. Antimonous acid spectra in alkaline aqueous solutions at 300°C .......................................................... 48
3.14. Rank determination of the absorbance matrix of antimonous acid species at 25 and 300°C .......................................................... 49
3.15. Molar absorptivities, $\varepsilon$, $H_2SbO_3^-$ from 25 to 300°C at the saturated vapour pressure ........................................ 51
3.16. Temperature dependence of the ionisation constant for antimonous acid at the saturated vapour pressure ......................... 52
3.17. Deconvoluted spectrum for a solution having $Sb = 1.40\times10^{-4} mol/dm^3$ and $pH = 11.68$ .......................................................... 53
3.18. The distribution of antimonous acid species as a function of $pH$ at 25 and 300°C at the saturated vapour pressure .......................................................... 54

4.1. Experimental setup used for measurement of spectra of sulphide-containing arsenic(III) solutions .......................................................... 58
4.2. Experimental set-up used to prepare solutions containing $H_2S/HS$ .......................................................... 59
4.3. Glass flow throw flask ("syringe" flask) used to transfer and manipulate hydrogen sulphide solutions .......................................................... 60
4.4. Calibration plot for the "syringe cell"; $H_2S$ absorbance at 190nm versus $H_2S$ concentration .......................................................... 61
List of Figures

4.5. Absorbance spectra of As(III) sulphide containing solutions measured in basic pH range at 22°C and 1 bar, corrected for background absorbance. Compositions of measured solutions, numbered, are given in Table B.10.

4.6. Absorbance spectra of As(III) sulphide containing solutions with the constant sulphur (S=4.6x10^-4 mol/dm^3) concentration and pH varied from 5.70 to 10.35 at 22°C and 1 bar, corrected for background. Solutions compositions are given in Table B.11.

4.7. Absorbance spectra of As(III) sulphide containing solutions spectra with the sulphur concentrations four times greater that that of arsenic at 22°C and 1 bar, corrected for background. Solutions compositions are given in Table B.12.

4.8. Molar absorptivities, $\epsilon$, of $HAsO_2$, $AsO_2^-$, $OH^-$, $H_2S^0$ and $HS^-$ at 22°C and 1 bar.

4.9. Rank analysis of the absorbance matrix created from As – S containing solutions (Figure 4.7) at wavelength from 275 to 400 nm, “tolerance” is estimated instrument error.

4.10. Scheme of thermodynamic constant(s) calculation procedure.

4.11. Flow diagram of decision criteria.

4.12. Molar absorptivities, $\epsilon$, of $H_2As_2S_3^0$ and $HAs_2S_4^-$ obtained with a model.

4.13. Molar absorptivities, $\epsilon$, of $H_3AsS_3^0$ and $H_2AsS_3^-$ at 22°C and 1 bar.

4.14. Deconvoluted spectrum for a solution having $As = 6.6x10^{-4} mol/dm^3$, $S = 2.42x10^{-3} mol/dm^3$ and $NaOH = 2.572x10^{-2} mol/dm^3$.

4.15. Experimentally measured and calculated thioarsenous acid spectra for solutions with the sulphur concentrations four times greater that that of arsenic at 22°C and 1 bar. Solutions compositions are given in Table B.12.

4.16. Thioarsenous acid optimised geometry.

A.1. The structure of p-nitrophenol (from Coleman (1998)).
List of Figures

A.2. Rank of the absorbance matrix created from p-nitrophenol-containing solutions spectra at 25 and 300°C ................................. 84
A.3. Molar absorptivities of p-nitrophenol species at 75°C calculated using two different mathematical procedures ............................... 85
A.4. Spectra (background corrected) of p-nitrophenol solutions of varying pH with p-nitrophenol concentration $7.2 \times 10^{-5}$ mol/dm$^3$ at 25°C ........................................... 87
A.5. Spectra of p-nitrophenol solutions with different concentrations of p-nitrophenol, corrected for water and quartz windows background absorbance at 300°C at saturated water vapour pressure; solutions compositions are given in Table B.18 ........................................... 88
A.6. Spectra of a p-nitrophenol solution (background corrected) from 25°C to 300°C at saturated water vapour pressure ............................... 89
A.7. The molar absorptivities of unionised (fully protonated) p-nitrophenol from 25 to 300°C ......................................................... 90
A.8. The molar absorptivities of deprotonated p-nitrophenol from 25 to 300°C ................................................................. 90
A.9. The temperature dependence of the "blue shifted" absorption maximum of unionised p-nitrophenol species (i.e. protonated) .................... 91
A.10. The temperature dependence of the "red shifted" absorption maximum of deprotonated p-nitrophenol ion ........................................ 91
A.11. Temperature dependence of the p-nitrophenol ionisation constant at equilibrium saturated vapour pressures ............................... 93
A.12. Experimentally obtained and calculated spectra of p-nitrophenol solutions at 90°C; concentration of p-nitrophenol is $7.68 \times 10^{-5}$ mol/dm$^3$. ........................................... 94
List of Figures
List of Tables

2.1. Previously reported values for the ionisation constant of arsenous acid at ambient temperature; $I$ is the ionic strength .......................... 5

2.2. Identification of the peaks in the mass spectra (Figure 2.5a, b) obtained from solutions having $As=2.3 \times 10^{-4} \text{mol/dm}^3$ ........................................ 15

2.3. The ionisation constant (molal) of arsenous acid from 25 to 300°C at the saturated vapour pressure, where the uncertainty is $2\sigma$. ............................. 27

2.4. Thermodynamic data calculated from our experimental data for arsenous acid ionisation (reaction 2.2) at the saturated vapour pressure. Temperature dependence of $\log K_1 = -16.1636 + 0.0312T - 0.0000268T^2$ .............. 27

3.1. Previously reported values for ionisation constants of antimonous acid at ambient temperature .......................................................... 31

3.2. The protonation constant (molal) of antimonous acid from 22 to 300°C at saturated vapour pressures, where the uncertainty is $2\sigma$. .............................. 45

3.3. Ionisation constants of antimonous acid (reaction 3.2) from 25 to 300°C at saturated vapour pressures; the uncertainty is $2\sigma$. The values reported here are related to the hypothetical 1 molal standard state .......................... 51

4.1. Previously reported experimental data on thioarsenite speciation at different temperatures ............................................................. 56
List of Tables

4.2. Nonlinear least squares fits for selected speciation models to the data at 22°C and 1 bar ........................................... 69
4.3. Ab initio calculations of ionisation constant of As – S species ...................................................... 75
A.1. The ionisation constant of p-nitrophenol from 25 to 300°C at equilibrium saturated vapour pressures, where uncertainty is 2σ. The values reported here are related to the hypothetical 1 molal standard state ........................................... 92
B.1. Compositions of experimental solutions used for arsenous acid ionisation constant evaluation from 25 to 300°C ........................................... 96
B.2. Compositions of 60 experimental solutions used for antimonous acid protonation validation at 22°C ........................................... 97
B.3. Compositions of 62 experimental solutions used for antimonous acid protonation validation at 50°C ........................................... 98
B.4. Compositions of 44 experimental solutions used for antimonous acid protonation validation at 75°C ........................................... 99
B.5. Compositions of 8 experimental solutions used for antimonous acid protonation validation from 100 to 300°C ........................................... 100
B.6. Compositions of 6 experimental solutions obtain for calculating molar absorptivities of ClO₄⁻ ion from 25 to 300°C ........................................... 100
B.7. Compositions of experimental solutions used for antimonous acid deprotonation validation at 25°C ........................................... 101
B.8. Compositions of 21 experimental solutions used for antimonous acid deprotonation validation from 50 to 300°C ........................................... 102
B.9. Compositions of four H₂S-containing experimental solutions at 22°C, spectra which were obtained to check the “syringe” cell, also to calculate the molar absorptivity of H₂S ........................................... 103
B.10. Compositions of As(III) sulphide-containing solutions at 22°C, shown in Figure 4.5 ........................................... 104
B.11. Compositions of As(III) sulphide-containing experimental solutions of at 22°C, shown in Figure 4.6 ................................................................. 105
B.12. Compositions of As(III) sulphide-containing experimental solutions of at 22°C, shown in Figure 4.7 ................................................................. 106
B.13. Compositions of Na₂S-containing experimental solutions at 22°C, used to calculate the molar absorptivity of HS⁻ ......................................................... 106
B.15. Compositions of 41 experimental solutions used for p-nitrophenol dissociation validation at 50°C ................................................................. 108
B.16. Compositions of 28 experimental solutions used for p-nitrophenol dissociation validation at 75°C ................................................................. 109
B.17. Compositions of 27 experimental solutions used for p-nitrophenol dissociation validation at 90°C ................................................................. 110
B.18. Compositions of 12 experimental solutions used for p-nitrophenol dissociation validation from 100 to 300°C ................................................................. 111
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List of Symbols

- $K_1$: Ionisation constant of arsenous/antimonous acid
- $K_a$: Protonation constant of antimonous acid
- $K_f$: Formation constant of thioarsenous acid
- $K_d$: Ionisation constant of thioarsenous acid
- $K_w$: Ion product constant of water
- $K_s$: Ionisation constant of hydrogen sulphide
- $K_{ass}$: Association constant for sodium hydroxide
- $[As]$: Total arsenic concentration in $mol/dm^3$
- $[Sb]$: Total antimony concentration in $mol/dm^3$
- $[Na]$: Total sodium concentration in $mol/dm^3$
- $[Cl]$: Total chloride concentration in $mol/dm^3$
- $[ClO_4]$: Total perchlorate concentration in $mol/dm^3$
- $\varepsilon$: Molar absorptivity
- $\Delta H$: Change of enthalpy
- $\Delta S$: Change of entropy
- $\Delta G$: Change of Gibbs free energy
- $K_{HP}$: Potassium hydrogen phthalate
- $\sigma_{[Sb]}$: Standard deviation of total antimony concentration
- $\sigma_{[Na]}$: Standard deviation of total sodium concentration
- $\sigma_{[pN]}$: Standard deviation of total p-nitrophenol concentration
- $\sigma_{[Cl]}$: Standard deviation of total chloride concentration
- $\sigma_{[ClO_4]}$: Standard deviation of total perchlorate concentration
- $\sigma_{K_w}$: Standard deviation of ion product constant of water
1. Introduction

The aqueous chemistry of arsenic(III) and antimony(III) at elevated temperatures and pressures in essentially unknown but it is of fundamental importance to understanding the transport of these elements by fluids migrating throughout the Earth’s crust. Furthermore, the simple aqueous chemistry of antimony(III) at ambient conditions is poorly known. There is only one reported literature value for the ionisation constant of antimonous acid, $H_3SbO_3$, at ambient temperature, the reliability of which is unknown. In addition, the nature of the interaction of $As(III)$ and $Sb(III)$ with aqueous solutions containing reduced sulphur has been the study of numerous studies which are in poor agreement with one another. The stoichiometry of aqueous thioarsenite species is the subject of much controversy and there are no reliable thermodynamic data available. Thus, we are currently unable to model the chemistry of many processes involving arsenic and antimony both in and on the Earth’s crust.

Arsenic and antimony occur ubiquitously in hydrothermal ore deposits through the Earth’s crust. In addition, both elements occur in appreciable concentrations in active hydrothermal systems such as in New Zealand, Russia (Kamchatka) and the United States. For example, at the Rotokawa and other geothermal systems in New Zealand, hot spring precipitates contain percentage levels of arsenic and antimony (Krupp and Seward, 1987; Weissberg et al., 1979). These surface hot spring environments are also of much interest because of the thermophile biota which they support. Some of these
thermophilic bacteria metabolize dissolved arsenic via a complex set of biochemically mediated redox equilibria which are still inadequately understood. However, the lack of reliable thermodynamic data pertaining to the stability of simple $\text{As(III)}$ and $\text{Sb(III)}$ species in aqueous media means that further insight into fundamental processes in natural waters is inhibited by a paucity of chemical data at conditions from ambient to elevated temperatures.

Finally, it should be noted that some knowledge of the chemistry of arsenic in natural waters sits at the basis of our understanding of the causes and remediation of the contamination of natural waters such as manifest by the catastrophic poisoning of the groundwater system by arsenic in West Bengal and Bangladesh which has affected the health of tens of millions of people.

In order to be able to study more complex natural systems containing arsenic or antimony such as $\text{As}_2\text{O}_3 - \text{H}_2\text{O} - \text{H}_2\text{S}$ (Chapter 4) and $\text{Sb}_2\text{O}_3 - \text{H}_2\text{O} - \text{H}_2\text{S}$, it is first necessary to have reliable data for the hydrolysis equilibria in the simple systems, $\text{As}_2\text{O}_3 - \text{H}_2\text{O}$ and $\text{Sb}_2\text{O}_3 - \text{H}_2\text{O}$ over a range of conditions. The results of such studies are presented in Chapters 2, 3 and 4. Experimental data are also presented for the deprotonation of $p-\text{nitrophenol}$ and results are discussed in Appendix A. Compositions of all experimental solutions are given in Appendix B. A number of computational programs has been written for these studies and these are included in Appendix C.

Thus, the aim of this research has been try to rectify the problem of an adequate data base pertaining to the aqueous chemistry of arsenic and antimony at conditions relevant to those of natural waters over a wide range of conditions of temperature and pressure.
2. Arsenous acid ionisation in aqueous solutions from 25 to 300°C

2.1. Introduction

Arsenic occurs as a trace element in all natural waters both on and in the Earth’s crust at concentrations from 0.5 to 5000 $\mu g/dm^3$, although typical concentrations in fresh waters are generally less that 10 $\mu g/dm^3$. Waters contaminated by mining activity may contain up to 10 000 $\mu g/dm^3$; geothermally influenced waters may contain arsenic concentrations of up to 50 000$\mu g/dm^3$ (Smedley and Kinniburgh, 2002).

Inorganic arsenic occurs in the ambient temperature aquatic environment as either arsenite, $AsO_2^-$, or arsenate, $AsO_4^{3-}$, and their protonated equivalents. The most toxic for human beings is arsenite. Drinking of water contaminated with arsenic is a major threat to human health in a number of countries (West Bengal, India; Bangladesh; China; Taiwan; Chile; Mexico; Argentina) as discussed in recent publications (Nordstrom, 2002; Smedley and Kinniburgh, 2002; Caldwell et al., 2003). Contaminated waters contain in some cases up to 9000$\mu g/dm^3$. The guideline value accepted by WHO (World Health Organisation) for the arsenic content of drinking water is 10 $\mu g/dm^3$ and the sources of arsenic contamination may be natural as well as anthropogenic. Anthropogenic arsenic contamination may originate from the burning of coal, from industrial smelting and the semiconductor industry, from arsenic used for wood preservation and pesticides, as well as release from arsenic-rich ores during mining. High concentrations of arsenic occur in geothermal systems as has been observed in geothermal systems from New Zealand, Iceland, Kamchatka, USA, Japan and numerous other localities (Krupp and Seward,
2.1. INTRODUCTION

Reported arsenic concentrations in the fluids are up to thousands of $\mu g/dm^3$. For example, surface muds and precipitates associated with the Rotokawa geothermal system, New Zealand (Reyes et al., 2003; Krupp and Seward, 1987) comprise up to 250 000 tons of metal enriched material, containing appreciable concentrations of arsenic. In addition, hydrothermal ore systems contain ubiquitous arsenic and antimony sulphide minerals but the transport/deposition chemistry of arsenic and antimony in such environments is not well known (Heinrich and Eadington, 1986). Appreciable quantities of arsenic are also discharged into the atmosphere during active volcanism.

Extensive arsenic contamination occurs in the surficial water of the Second Region of Chile (Romero et al., 2003) where much of the available water comes from the Rio Loa which is in turn fed by Salado river. The waters serve both urban and agricultural use and their poor quality is characterised by elevated salinity and high dissolved arsenic. The Salado is located in the Andes Cordillera and cuts through volcanic rocks, mainly andesite and rhyolitic ignimbrites of Miocene-Holocene age and originates in the El Tatio geothermal region. Physico-chemical parameters and chemical components of the El Tatio geothermal field are given by Romero et al. (2003). Arsenic concentrations in the El Tatio fluids of up to 27 000 $\mu g/dm^3$ have been reported. The Salado river water contains in some parts up to 10 000 $\mu g/dm^3$ arsenic.

A knowledge of aqueous arsenic chemistry is also important to the understanding of biogeochemical reactions. For example, Salmassi et al. (2002) have demonstrated that when geothermal waters (from Hot Creek, California) mix with meteoric waters, As(III) is oxidised to As(V) and this oxidation is bacterially mediated by Agrobacterium albertimagni.

In order to evaluate and model the aqueous arsenic chemistry in natural systems, over a wide range of conditions from ambient to hydrothermal, reliable thermodynamic data are required for arsenous acid. With the exception of the high and apparently spurious value
Table 2.1.: Previously reported values for the ionisation constant of arsenous acid at ambient temperature; $I$ is the ionic strength.

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<thead>
<tr>
<th>$t$ / °C</th>
<th>$pK_1$</th>
<th>$I$</th>
<th>Method</th>
<th>References</th>
</tr>
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<tr>
<td>18</td>
<td>9.21-9.28</td>
<td>0-0.875</td>
<td>Potentiometry</td>
<td>Britton and Jackson (1934)</td>
</tr>
<tr>
<td>25</td>
<td>9.62</td>
<td>0-0.3</td>
<td>Solubility/pH meas.</td>
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<td>Antikainen and Rossi (1959)</td>
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<td>Salomaa et al. (1969)</td>
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<tr>
<td>25</td>
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<td>0.05</td>
<td>Potentiometry</td>
<td>Antikainen and Tevanen (1961)</td>
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<tr>
<td>22</td>
<td>9.32±0.01</td>
<td>0.5</td>
<td>Spectrophotometry</td>
<td>Ivakin et al. (1976)</td>
</tr>
<tr>
<td></td>
<td>9.21±0.01</td>
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<td></td>
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</tr>
<tr>
<td>25</td>
<td>9.32±0.05</td>
<td>0</td>
<td>Potentiometry</td>
<td>Pokrovski (1996)</td>
</tr>
<tr>
<td>25</td>
<td>9.243±0.003</td>
<td>0</td>
<td>Spectrophotometry</td>
<td>Yamazaki et al. (1993)</td>
</tr>
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<td>9.22±0.01</td>
<td>0</td>
<td>Potentiometry</td>
<td>Raposo et al. (2003)</td>
</tr>
</tbody>
</table>

for the ionisation constant reported by Garrett et al. (1940) (i.e. $pK_1=9.62$), the ambient temperature values of $pK_1$ are in the range of $9.2 \leq pK_1 \leq 9.3$. Antikainen and Tevanen (1961) and Yamazaki et al. (1993) have also measured $pK_1$ values up to 45 and 65°C respectively but a few experimentally determined values have been reported at higher temperatures (e.g. Pokrovski, 1996). The available thermodynamic data for arsenous acid ionisation ($K_1$) for the temperature interval around 25°C are summarised in the Table 2.1.

In a number of papers (Antikainen and Rossi, 1959; Yamazaki et al., 1993), arsenous acid has the stoichiometry $\text{HAsO}_2$. On the another hand, there are numerous other studies in which arsenous acid is considered as a moiety comprising one arsenic atom coordinated by three $\text{OH}^-$ ligands (Loehr and Plane, 1968; Pokrovski et al., 1996; Gout et al., 1997; Raposo et al., 2003). This interpretation is supported by the information given by Raman spectra (Loehr and Plane, 1968; Pokrovski et al., 1996; Gout et al., 1997) and the theoretical study by Tossell (1997). Loehr and Plane (1968) studied
As-containing solutions with a different $OH/As$ ratio in a range 3.5 to 15 and interpreted the observed Raman lines in terms of four distinct chemical species, which were assigned to $As(OH)_3^0$, $AsO(OH)_2^-$, $AsO_2(OH)^{2-}$ and $AsO_3^{3-}$. Our own rank analysis of their data indicates the presence of two or three different species. The recent studies by Gout et al. (1997) and Pokrovski et al. (1996) (i.e. Raman measurements from 20°C to 275°C and solubility measurements at 250 and 300°C) are in agreement with Loehr and Plane's (1968) conclusions. These two latter papers essentially rely on the original interpretation and band assignments of Loehr and Plane (1968) in concentrated arsenic-containing solutions. It has also to be mentioned here that the solutions studied in the above mentioned studies were very concentrated. Pokrovski et al. (1996) studied solutions having arsenic concentrations in the range 0.2-6m. Unfortunately Loehr and Plane (1968) did not report the $As$ concentrations of their solutions but state only that $OH + As(III)$ was always $>8$ mol/dm$^3$. Their data do not necessarily represent arsenic(III) hydrolysis behavior in more dilute solutions ($\sim 0.0001m$ and less), which are typical of concentrations in hydrothermal fluids and natural waters. Thus, the validity of Loehr and Plane's (1968) interpretation of arsenous acid band assignments and the applicability to dilute $As(III)$-containing solutions comes into question.

Exafs data may also provide information on the $As(III)$-oxygen coordination environment. Pokrovski et al. (2002) obtained Exafs data $As - OH$ system ($As \sim 0.3m$) and concluded that each atom is surrounded by three oxygens at a distance 1.78Å. The conclusion that arsenous acid exists as $As(OH)_3$ is not conclusive. The Exafs data only provide information about average number of surrounding oxygens. The possibility exists that $As^{3+}$ is coordinated to three, non-equivalent oxygens, that is, two oxygens, one of which is protonated together with a solvated water molecule.

A recent study of Debusschere et al. (2000) of arsenic speciation using capillary zone electrophoresis coupled mass spectrometry supports the $HAsO_2$ stoichiometry. The As-containing species produced in the gas phase had mass-to-charge-ratios ($m/z$) of 107.
and indicated the presence of the $\text{AsO}_2^-$ ion (molecular mass of $\text{AsO}_2^- = 75 + 2 \cdot 16 = 107$).

This study focuses on the determination of the stoichiometry of arsenous acid and its ionisation constant from 25 to 300°C by means of high temperature, flow-through uv spectrophotometry. We have also carried out fundamental ab initio calculations as well as electrospray mass spectrometric measurements on arsenic-containing solutions in order to gain additional insight into arsenous acid stoichiometry.
2.2. Experimental Methods

Mass spectrometric measurements for this study were carried out using the electrospray ionization (ESI) technique which uses an electric field in order to produce a spray of fine droplets. In order to obtain a mass spectrum from an $\text{As}(\text{III})$-containing solution, the sample is passed along a narrow metal capillary tube, the end of which is maintained at a high potential of around 2.5 kV. The high potential and small radius of curvature at the end of the capillary tube creates a strong electric field which causes the emerging liquid to leave the end of the capillary as a mist of droplets mixed with vapour (process of nebulization) and occurs at near atmospheric pressure. Mass spectra of $\text{As}_2\text{O}_3$ dissolved in perchloric acid or sodium hydroxide solution were measured using a Surveyor MSQ (Thermo Finnigan) mass spectrometer.

All solution preparation and handling, as well as the titration of solutions, were carried out in such a way as to exclude any contact with air and under argon in order to avoid oxidation of $\text{As}(\text{III})$ to $\text{As}(\text{V})$ and $\text{CO}_2$ contamination. An arsenic stock solution (0.1877 m) was prepared by dissolving a weighed amount of $\text{As}_2\text{O}_3$ in $\text{NaOH}$ solution. Experimental solutions were prepared by addition (without air contact and employing gas tight Hamilton syringes) of a weighed amount of the stock solution and standardised sodium hydroxide solution to degassed water. The total arsenic concentrations in these samples were determined by ion-chromatography as well as by flame atomic absorption spectroscopy and gravimetric analysis. In order to obtain the precise $\text{Na}^+$ concentrations of the arsenic-containing and blank (no arsenic) $\text{NaOH}$ solutions, they were titrated using pure potassium hydrogen phthalate ($\text{KHP}$). This primary standard has several advantages: it does not absorb moisture readily (i.e. it is non-hygroscopic); it is easily dried; it can be accurately weighed; it can be obtained in very pure form; it has a high molar mass (204.22 g/mole); and it is very soluble in water, reacting in aqueous solution to neutralise the base(i.e. sodium hydroxide). Titrations were performed under argon with a Metrohm 736 GP Titrino autotitrator driven by TiNet 2.3 software. Atomic absorption
analysis of sodium as well as direct pH measurement cannot provide this level of precision.

The ultraviolet spectra were collected using a flow-through Ti – Pd alloy cell which was placed in a Cary 5E double beam spectrophotometer. The optical cell had uv quality quartz glass windows and a thermocouple controlled cooling/heating system which allowed the measurement of spectra from ambient to high temperatures. The flow-through system enables the solution composition to be changed without opening the system and without disturbing to the optical settings such as for example, the path length or the positioning of the cell in the light path. In order to maintain single phase conditions, the pressure was held at 15 bar above the saturated water vapour pressure and controlled by means of a Dynamax SD-300 HPLC pump and an adjustable back pressure regulator. The overall experimental set-up is shown schematically in Figure 2.1.

The uv spectra of $\text{As(III)}$ hydroxide species were recorded from 190 to 300 nm at seven temperatures from 25 to 300°C. Figure 2.2 shows measured spectra of arsenous acid species at 25°C and 300°C. The concentration range of the total dissolved arsenic (III) in the experimental solutions was varied from $1 \times 10^{-4}$ to $2 \times 10^{-3} \text{ mol/dm}^{3}$ and the pH from 4 to
Figure 2.2.: Spectra of arsenic (III)-containing solutions, corrected for water and silica window background absorbance at 25°C and 300°C at the saturated water vapour pressure.
Figure 2.3.: Spectra of NaOH solutions, corrected for water and silica window background absorbance at 25°C and 300°C at the saturated water vapour pressure.

11 by addition of perchloric acid or sodium hydroxide. Figure 2.3 shows the spectra of NaOH solutions (blanks) at 25°C. Table B.1 gives the solution compositions pertaining to the measured spectra. All spectra at all temperatures were corrected for water and silica window background absorbance. To relate the molar concentration scale of the Beer-Lambert law to the molal scale of standard thermodynamic convention, the measured absorbances, $A^{obs}$, were corrected for the isothermal variation of solution density at each temperature. The required density data for experimental solutions because they were diluted were taken as water density from Haar et al. (1984).
2.3. Results and Discussion

2.3.1. Ab initio calculations

In order to provide insight into the stoichiometry and structure of arsenous acid, *ab initio* calculations were also undertaken. In addition, the deprotonation of arsenous acid (i.e. $pK_1$) may also be predicted using *ab initio* methods as outlined by da Silva et al. (1999). The process of losing a proton in the gas phase may be defined by the reaction:

\[
H_3AsO_3(gas) \rightleftharpoons H^+(gas) + H_2AsO_3^-(gas)
\]  

or

\[
HAsO_2(gas) \rightleftharpoons H^+(gas) + AsO_2^-(gas)
\]

The equilibrium ionisation constant for either of these two reactions is related to the standard Gibbs free energy through the relationship,

\[
\Delta G^0 = -2.303RT\log K_1
\]

Since $\Delta G^0$ is a state property, it is determined by the initial and final state of the system and is independent of the path connecting them. Thus we can propose a series of intermediate thermodynamic steps for the whole process.

A thermodynamic cycle is proposed as following:

\[
\begin{align*}
H_3AsO_3(gas) & \xrightarrow{\Delta G_r(gas)} H^+(gas) + H_2AsO_3^-(gas) \\
\Delta G_{solv}(H_3AsO_3) & \quad \Delta G_{solv}(H^+) \quad \Delta G_{solv}(H_2AsO_3^-) \\
\downarrow & \quad \downarrow & \quad \downarrow \\
H_3AsO_3(soln) & \xrightarrow{\Delta G_r(soln)} H^+(soln) + H_2AsO_3^-(soln)
\end{align*}
\]
The Gibbs free energy for the reaction 2.1 in solution is given by:

\[
\Delta G^0_r(\text{soln}) = -\Delta G^0_{\text{solv}}(H_3\text{AsO}_3) - G^0(\text{gas})(H_3\text{AsO}_3) + \Delta G^0_{\text{solv}}(H_2\text{AsO}_3) \\
+ \Delta G^0(\text{gas})(H_2\text{AsO}_3) + \Delta G^0_{\text{solv}}(H^+) \tag{2.4}
\]

Gibbs free energies formation for \(H_3\text{AsO}_3\) and \(H_2\text{AsO}_3^-\) were obtained in this study from ab initio molecular orbital calculations, using G2 model theory with the GAUSSIAN 98 suite of programs. The geometry of each molecule was optimised with MP2 (full)/6-311 G(d) level of theory. Solvation energies were estimated using PCM calculations for each molecule with rigid geometries obtained by MP2 (full)/6-311 G(d) level of theory. The Gibbs free energy of formation for \(H^+\) is equal to zero and solvation energy for \(H^+\) was taken from experimental study of Tissandier et al. (1998). The calculated \(pK_1\) at 25°C for reaction (2.1) is 22.00 and for reaction (2.2), \(pK_1=8.88\), this latter value being close to our experimentally determined value of \(pK_1=9.25\) as well as other reliable literature data. Thus, the ab initio calculations unambiguously support \(H\text{AsO}_2\) form of arsenious acid. The optimised geometry of \(H\text{AsO}_2\) is shown in a Figure 2.4.

**Figure 2.4.: Arsenous acid optimised geometry**
2.3. RESULTS

2.3.2. Mass spectrometric measurements

The mass spectra of two solutions having an arsenic concentration of $2.3 \times 10^{-4} \text{ mol/dm}^3$ (Figure 2.5) are characterised by a number of strong peaks, one of which has $m/z=107$

![Mass spectra of $As_2O_3$ oxide dissolved in perchlorite solution (a) and $As_2O_3$ oxide dissolved in water-sodium hydroxide solution (b); where arsenic concentration of both solutions is $2.3 \times 10^{-4} \text{ mol/dm}^3$; $m/z$ is mass-to-charge ratio](image)

Figure 2.5.: Mass spectra of $As_2O_3$ oxide dissolved in perchlorite solution (a) and $As_2O_3$ oxide dissolved in water-sodium hydroxide solution (b); where arsenic concentration of both solutions is $2.3 \times 10^{-4} \text{ mol/dm}^3$; $m/z$ is mass-to-charge ratio
and is due to the presence of ionised monomeric arsenous acid, \([O = As – OH]\), whereas for \(H_2AsO_3^-\), \(m/z=125\) and was not detected. The other peaks arise inherently from other components in the solutions as shown in Table 2.2.

Table 2.2.: Identification of the peaks in the mass spectra (Figure 2.5a, b) obtained from solutions having \(As=2.3 \times 10^{-4} \text{ mol/dm}^3\).

<table>
<thead>
<tr>
<th>(m/z), in (a)</th>
<th>formula</th>
<th>(m/z), in (b)</th>
<th>formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>99</td>
<td>(^{35}\text{ClO}_4^-)</td>
<td>99</td>
<td>(^{35}\text{ClO}_4^-)</td>
</tr>
<tr>
<td>101</td>
<td>(^{37}\text{ClO}_4^-)</td>
<td>101</td>
<td>(^{37}\text{ClO}_4^-)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>77</td>
<td>(^{77}\text{As}) or (^{13}\text{CO}_4)</td>
</tr>
<tr>
<td>107</td>
<td>(\text{AsO}_2^-)</td>
<td>107</td>
<td>(\text{AsO}_2^-)</td>
</tr>
<tr>
<td>123</td>
<td>(\text{As(V)O}_3^-)</td>
<td>123</td>
<td>(\text{As(V)O}_3^-)</td>
</tr>
</tbody>
</table>

Insight into the ionisation mechanism of arsenous acid may also be obtained from the calculated free energies for the relevant protonation reactions as shown below:

\[
H_3\text{AsO}_3(gas) \rightleftharpoons H_3O^+(gas) + \text{AsO}_2(gas) \quad \Delta G^0_r(gas) = 794 \text{ kJ} \quad (2.5)
\]

\[
H_3\text{AsO}_3(gas) + H_2O(gas) \rightleftharpoons H_3O^+(gas) + H_2\text{AsO}_3^- \quad \Delta G^0_r(gas) = 751 \text{ kJ} \quad (2.6)
\]

\[
\text{HAsO}_2(gas) + H_2O(gas) \rightleftharpoons H_3O^+(gas) + \text{AsO}_2^- \quad \Delta G^0_r(gas) = 728 \text{ kJ} \quad (2.7)
\]

or, in terms of a simple deprotonation,

\[
H_3\text{AsO}_3(gas) \rightleftharpoons H^+(gas) + H_2\text{AsO}_3^- \quad \Delta G^0_r(gas) = 1437 \text{ kJ} \quad (2.8)
\]

\[
\text{HAsO}_2(gas) \rightleftharpoons H^+(gas) + \text{AsO}_2^- \quad \Delta G^0_r(gas) = 1414 \text{ kJ} \quad (2.9)
\]

The most energetically favorable ionisation mechanism as judged from these calculations will be either by reaction 2.7 or 2.9. Both reactions products are \(\text{AsO}_2^-\). This again supports existence of \(\text{HAsO}_2^-\) in aqueous solutions.
2.3. RESULTS

2.3.3. Data treatment and interpretation of uv spectra

The first part of the data treatment considers the potentiometrical titrations, from which pH and sodium concentrations are obtained for each arsenic containing solution. The second part deals with the interpretation of the uv spectroscopic data.

The potentiometric titrations permitted the determination of the pH and sodium concentration. The mathematical treatment involved the solution six equations containing seven variables which included charge and mass balance equations as well as the expressions for the ion product constant for water and the ionisation constants of potassium hydrogen phthalate (KHP) and arsenous acid. The relevant equations are,

\[ K_1 = \frac{\left[AsO_2^-\right] \gamma_{AsO_2^-} \left[H^+\right] \gamma_{H^+}}{\left[HAsO_2^+\right] \gamma_{HAsO_2^+}} \] (2.10)

\[ [As]_{tot} = [AsO_2^-] + [HAsO_2^+] \] (2.11)

\[ K_w = [H^+] \gamma_{H^+} [OH^+] \gamma_{OH^-} \] (2.12)

\[ K_{KHP} = \frac{[H^+] [P^{2-}]}{[HP^-]} \] (2.13)

\[ [Phtal]_{tot} = [HP^-] + [P^{2-}] \] (2.14)

\[ [K^+] + [Na^+] + [H^+] = [OH^-] + [AsO_2^-] + [HP^-] + 2[P^{2-}] \] (2.15)

where the terms in square brackets are molar concentrations (mol/dm³); [As]_{tot} is the total arsenic concentration; [Phtal]_{tot} is the total potassium hydrogen phthalate concentration; \( K_1 \) is the ionisation constant for arsenous acid; \( K_w \) is the ion product constant of water and \( K_{KHP} \) is stability constant for the reaction:

\[ HP^- \rightleftharpoons P^{2-} + H^+. \] (2.16)

Because the solutions were basic, the ionisation of arsenous acid has an influence on the equivalent point of the titration curve and must be considered. The total arsenic concentration, [As]_{tot}, \( K_w \) and \( K_{KHP} \) are known, as is the concentration of the standard
2.3. RESULTS

Figure 2.6.: Experimental and theoretical titration curves comparison (As-containing base solution titrated by \textit{KHP})

\textit{KHP} solution and the volume of \textit{KHP} solution added at the equivalent point and hence, \([Phtal]_{tot}\).

The mathematical solution of the above system of equations to obtain \(pH\) and the concentrations of \(Na^+\) was facilitated using a set of programmes developed using the \textsc{MATLAB} and \textsc{MAPLE} computational platforms. The principle of looking for a solution is based on the minimisation of the sum of squares of the differences between the experimental and theoretical titration curves (Figure 2.6) as a function of \(Na^+\) concentrations, bearing
in mind that the pH is given by the concentration of sodium hydroxide in the solution. The concentration of Na\(^+\) was used to obtain the ionisation constant for arsenous acid at higher temperatures since the direct experimental measurement of OH\(^-\) concentrations or pH in such solutions, was not possible.

Before we can proceed to the refinement of the equilibrium constants, it is necessary to validate the model in both a chemical and statistical sense. The validation is based on the analysis of the absorbance matrix for the number of absorbing species at each temperature. Since absorbance is a linear function of concentration for a given absorbing species at a specified wavelength, the maximum number of linearly independent columns of the absorbance matrix (i.e. the rank of the absorbance matrix) gives the number of absorbing species in solution at a particular temperature, providing that no two species have identical molar absorptivities. Figure 2.7 shows the iterative calculation scheme. The chemical model includes the ionisation of arsenous acid (reaction 2.2 in aqueous media), the ionisation of water and the ion pairing of sodium hydroxide. The mathematical model for arsenous acid speciation to obtain \(K_1\) (equation 2.10) requires consideration of the mass balance equations: (2.11) and (2.12), as well as the charge balance equation,

\[
[H^+] + [Na^+] = [OH^-] + [AsO_2^-]
\]  

(2.17)

and the equilibrium expression for the association constant,

\[
K_{ass} = \frac{[NaOH] \gamma_{NaOH}}{[Na^+] \gamma_{Na^+} [OH^-] \gamma_{OH^-}}
\]  

(2.18)

where \(K_{ass}\) is the association constant of sodium hydroxide; the terms in square brackets are molar concentrations of species in \(mol/dm^3\); \(\gamma\) is the activity coefficient.

The aim of the iterative calculation procedure is to refine the equilibrium constant for arsenous acid, \(K_1\). It has two features that distinguish it from conventional computation schemes:

- the correction for the OH\(^-\) absorbance at every iteration step.
CHAPTER 2. ARSENOUS ACID IONISATION

2.3. RESULTS

Figure 2.7.: Scheme of ionisation constant calculation procedure

- the solution of the overdetermined system of linear equations has to carried out in a stable way using Tikhonov regularization technique since system is ill-conditioned and ill-posed.
2.3.4. Arsenous acid ionisation

The measured spectra represent the overlay of the total absorbance of all species existing in the measured arsenic solutions from pH 4 to 11 (Figure 2.2). Figure 2.8 demonstrates that the rank analysis of the absorbance versus wavelength matrix created from the spectra at 25°C and 250°C for the wavelength intervals from 197 to 220nm at 25°C and from 208 to 240nm at 250°C, is three. There are thus three species in solution (i.e. the rank is three), one of which can be attributed to the hydroxide ion through its charge-
Figure 2.9.: Rank analysis of the absorbance matrix at 300°C for the eight arsenic-containing solutions, of which the spectra are shown in Figure 2.2 and the compositions are given in Table B.1.

transfer-to-solvent transition and associated absorption band in the stated wavelength range as shown in Figures 2.3 and 2.10. At 300°C, the rank of the absorbance matrix for the interval 220-240 nm is 2, indicating the presence of only two absorbing species (i.e. $OH^-$ and an arsenous acid species), whereas for the interval 240-250 nm, the rank was one, indicating the presence of only one absorbing arsenous acid species (Figure 2.9).
2.3. RESULTS

CHAPTER 2. ARSENOUS ACID IONISATION

The molar absorptivities of hydroxide from 25 to 300°C at saturated vapour pressures were obtained from uv spectroscopic measurements of the sodium hydroxide-water system and are shown on the Figure 2.10. We are now left with the task of determining the identity of the two remaining species. The spectra collected from pH 4 to 8 (i.e. spectra a and b in Figure 2.2) were identical, given the small differences in the solutions composition. This arises because the same species is absorbing and the concentration of this species is independent of pH in the acid to near neutral region. This species can be ascribed to ionised $HAsO_2^+$. If one also considers the ionisation of arsenous acid (i.e. reaction 2.2 in the aqueous phase), then in addition to $OH^-$, the other two absorbing species would be $HAsO_2^+$ and $AsO_2^-$. The molar absorptivity of $HAsO_2$ at any given temperature was obtained by absorbance measurements in acid solutions (i.e. in the absence of any other absorbing species). Figure 2.11 shows the spectra, corrected for hydroxide ion absorbance at 25 and 300°C. Thus, the absorbances are due only to the presence of arsenic(III) species. Figure 2.12 illustrates molar absorptivities of $HAsO_2^+$ and $AsO_2^-$ at different temperatures. The molar absorptivity of $AsO_2^-$, as a result of substraction of
Figure 2.11.: Spectra of As(III)-containing solutions corrected for water and silica window background absorbance as well as for $\text{OH}^-$ absorbance at 25 and 300°C.
2.3. RESULTS

CHAPTER 2. ARSENOUS ACID IONISATION

Figure 2.12.: Molar absorptivities, $\varepsilon$, of $HAsO_2^-$ and $AsO_2^-$ from 25 to 300°C at the saturated vapour pressure

Figure 2.13.: Temperature dependence of the absorption maximum of the $AsO_2^-$ species

The total absorbance with $OH^-$ and $HAsO_2$ molar absorptivities, shows a strong red shift of the band position with increasing temperature. Such behavior of $AsO_2^-$ absorbance in aqueous solutions is typical of a charge-transfer-to-solvent (ctts) type of transition. One of the key features of ctts transitions is the strong dependence of the position of the absorption band maximum on temperature. In Figure 2.13, the strong red shift of...
the $\text{AsO}_2^-$ band position with increasing temperature is shown. The linear dependence of the absorption maximum with temperature and indicates the presence of the charge-transfer-to-solvent transition. The absorption maximum at 25°C for the undissociated arsenous acid species is at the edge of the vacuum uv region at approximately 186nm. For the deprotonated arsenous acid species, the band maximum is shifted to 202nm.

Figure 2.14 shows the deconvoluted spectrum at 25°C and for a solution having a total arsenic concentration of $2 \times 10^{-4} \text{mol/dm}^3$ and $\text{OH}^- = 3 \times 10^{-4} \text{mol/dm}^3$. The values of the equilibrium constants obtained in the non-linear least squares refinement are summarised in Table 2.3 and presented together with the Figure 2.15. On this Figure is shown the trend of decreasing first ionisation constant with increasing temperature which is the general trend among weak acids. Data from this study are in good agreement with other data at 25°C (Table 2.1) and with the data from Yamazaki et al. (1993) up to 65°C as well as with the data extrapolated to a zero ionic stength from Antikainen and Tevanen (1961) up to 45°C. In addition, the equilibrium stability constant for the deprotonation of arsenous acid from SUPCRT92 (Johnson et al., 1992) as well as the estimated values given by Smith et al. (1986) are also shown in Figure 2.15. These values differ from our
2.3. RESULTS

CHAPTER 2. ARSENOUS ACID IONISATION

Figure 2.15.: Temperature dependence of the ionisation constant (molal) of arsenous acid up to 300°C and at saturated vapour pressures experimentally determined values by up to 1.5 orders of magnitude at 300°C. The values for $pK_1$ reported by Pokrovski (1996) are similarly discrepant.

In order to derive the thermodynamic functions for the ionisation constants from our experimental data, the values of $\log K_1$ as a function of temperature were fitted to different forms of,

$$
\log K_1 = A + BT + CT^2 + D/T + E\log T.
$$

(2.19)

A three term expression (see Table 2.4) was found to best fit the data and was subsequently differentiated to provide values of the standard enthalpy and entropy change of arsenous acid ionisation.

It is important to mention here that corrections for activity coefficients were made using an extended Debye-Hückel equation (Robinson and Stokes, 1968) although in fact, they
are negligible and less than the experimental error. At high temperatures, the association of sodium hydroxide becomes more significant (Ho et al., 2000), but at the concentrations used in our work, it affects the last (in this case, the second) decimal place of $pK_1$ at 300°C and is again lower than the experimental error.

Table 2.3.: The ionisation constant (molal) of arsenous acid from 25 to 300°C at the saturated vapour pressure, where the uncertainty is 2σ.

<table>
<thead>
<tr>
<th>$t/\degree C$</th>
<th>$pK_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>9.25 ±0.05</td>
</tr>
<tr>
<td>50</td>
<td>8.90 ±0.05</td>
</tr>
<tr>
<td>100</td>
<td>8.25 ±0.05</td>
</tr>
<tr>
<td>150</td>
<td>7.80 ±0.09</td>
</tr>
<tr>
<td>200</td>
<td>7.40 ±0.17</td>
</tr>
<tr>
<td>250</td>
<td>7.21 ±0.23</td>
</tr>
<tr>
<td>300</td>
<td>7.11 ±0.04</td>
</tr>
</tbody>
</table>

Table 2.4.: Thermodynamic data calculated from our experimental data for arsenous acid ionisation (reaction 2.2) at the saturated vapour pressure. Temperature dependence of $logK_1 = -16.1636 + 0.0312T - 0.0000268T^2$

<table>
<thead>
<tr>
<th>$t/\degree C$</th>
<th>$\Delta G^e/kJmol^{-1}$</th>
<th>$\Delta H^e/kJmol^{-1}$</th>
<th>$\Delta S^e/Jmol^{-1}K^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>52.80</td>
<td>25.82</td>
<td>-90.5</td>
</tr>
<tr>
<td>50</td>
<td>55.06</td>
<td>27.65</td>
<td>-84.8</td>
</tr>
<tr>
<td>100</td>
<td>58.94</td>
<td>29.70</td>
<td>-78.3</td>
</tr>
<tr>
<td>150</td>
<td>63.19</td>
<td>28.99</td>
<td>-80.8</td>
</tr>
<tr>
<td>200</td>
<td>67.03</td>
<td>24.74</td>
<td>-89.4</td>
</tr>
<tr>
<td>250</td>
<td>72.21</td>
<td>16.17</td>
<td>-107.1</td>
</tr>
<tr>
<td>300</td>
<td>78.02</td>
<td>2.52</td>
<td>-131.7</td>
</tr>
</tbody>
</table>
2.4. Conclusions

Undissociated arsenous acid exists in water solutions as \( H\text{As}O_2 \). This stoichiometry is supported by both the mass spectrometric measurements and the \textit{ab initio} calculations. The experimentally determined ionisation constant, \( pK_1 \), decreases from 9.25 to 7.11 over a temperature range from 25 to 300°C. At low temperatures and for the \( pH \leq 9 \), the speciation is dominated by the unionised arsenous acid (Figure 2.16). In low sulphur containing hydrothermal fluids in the Earth’s crust, the arsenic chemistry will also be dominated by the two arsenous acid species, \( H\text{As}O_2 \) and \( \text{As}O_2^- \). At \( pH \geq 9 \), the deprotonated \( \text{As}O_2^- \) species predominates at ambient temperature. For example, in semi-arid or arid environments, high \( pH > 8.5 \) conditions may evolve as a result of mineral weathering and strong evaporation (Smedley and Kinniburgh, 2002). At higher temperatures, boiling / phase separation leads to an increase in \( pH \) and \( H_2S \) loss in natural hydrothermal systems. This causes the formation of \( \text{As}O_2^- \) which will in turn have an effect on the hydrothermal, arsenic-containing mineral equilibria.

Figure 2.16: The distribution of arsenous acid species as a function of \( pH \) at 25 and 300°C at the saturated vapour pressure.
3. Antimonous acid ionisation in aqueous solutions from 25 to 300°C

3.1. Introduction

Antimony is an important component of hydrothermal systems. For example, in Rotokawa geothermal system, New Zealand (Krupp and Seward, 1987), hot spring precipitates contain some 250-500 tonnes of antimony. Antimony is a chalcophile, occurring with sulphur and metals such as copper, lead, silver and iron in many hydrothermal ore deposits. There are more than one hundred antimony containing minerals, although antimony mostly occurs in $Sb(III)$ state in stibnite ($Sb_2S_3$).

Antimony concentrations in hydrothermal fluids are in a range from 0.1 to 0.45 ppm (i.e. $0.82 - 3.70 \, \mu mol/dm^3$) (Weissberg et al., 1979); this is an enrichment in comparison with antimony concentrations in natural waters, which typically contain less than $1 \, \mu mol/dm^3$ are (Filella et al., 2002).

In order to understand the conditions and processes (transport and precipitation mechanisms) that control hydrothermal ore deposition, it is necessary to have reliable thermodynamic information pertaining to the speciation of antimony in geothermal waters, including the formation of thioantimonite complexes, which are mainly responsible for antimony transport in hydrothermal solutions. However, there is no agreement as to which complexes antimony forms with sulphur in aqueous solutions at high temperatures.
This problem has long been emphasized in literature, however, published experimental data and theoretical predictions still remain controversial. The lack of thermodynamic data means that reliable modelling of antimony transport and mineral deposition in hydrothermal systems is fraught with uncertainty. Thus, the aim of this study was to obtain the necessary thermodynamic information on antimony (III) speciation in aqueous solutions from ambient to high temperatures to be able to predict the distribution and behavior of antimony in hydrothermal solutions.

In order to be able to study more complex high temperature systems containing antimony (± sulphur), it is necessary to first consider the simple Sb(III) hydrolysis equilibria in aqueous media. However, the aqueous chemistry of antimonous acid $H_3SbO_3$ (or antimony hydroxide $Sb(OH)_3$) is not well characterised. There are a few published data at 25°C but almost no data are available at high temperatures. Zotov et al. (2003) obtained experimental data up to 450°C on the solubility of antimony trioxide in high temperatures aqueous solutions but considered the presence of only one species, $Sb(OH)_3$.

Up to now, no study has attempted to characterise the ionisation of antimonous acid, and consequently to define antimony speciation at high temperatures. Therefore, this study focuses on the determination of the stability constants for antimonous acid protonation/deprotonation at temperatures from 22 to 300°C at equilibrium saturated vapour pressure.

Two equilibria may be defined which describe antimonous acid protonation/deprotonation in aqueous solutions; i.e.,

$$H_3SbO_3(aq) + H^+(aq) \rightleftharpoons H_4SbO_5^-(aq) \quad K_a \quad (3.1)$$

and

$$H_3SbO_3(aq) \rightleftharpoons H^+(aq) + H_2SbO_3^-(aq) \quad K_1 \quad (3.2)$$

where $K_a$ and $K_1$ are the equilibrium constants for reactions 3.1 and 3.2, respectively. The
Chapter 3. Antimonous Acid Ionisation

3.1. Introduction

Table 3.1.: Previously reported values for ionisation constants of antimonous acid at ambient temperature.

<table>
<thead>
<tr>
<th>t /°C</th>
<th>pK_a</th>
<th>pK_1</th>
<th>I</th>
<th>Method</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>-1.13</td>
<td>11.82</td>
<td>0</td>
<td>Solubility</td>
<td>recalculated from Gayer and Garrett (1952)</td>
</tr>
<tr>
<td>25</td>
<td>-1.19</td>
<td>5</td>
<td>M</td>
<td>Solubility</td>
<td>recalculated from Ahrland and Bovin (1974)</td>
</tr>
<tr>
<td>25</td>
<td>-1.42</td>
<td>0</td>
<td></td>
<td>Spectrophotom.</td>
<td>Mishra and Gupta (1968)</td>
</tr>
</tbody>
</table>

published experimentally derived thermodynamic data for antimonous acid ionisation ($K_a$ and $K_1$) at the temperature interval around 25°C are summarised in the Table 3.1.

Antimony(III) oxide solubility at ambient temperature has been studied by Gayer and Garrett (1952) in water, sodium hydroxide and hydrochloric acid solutions under nitrogen atmosphere. The solubility of antimonous trioxide in water was found to be $5.2 \times 10^{-5} \text{mol/kg}$. In basic solutions, the solubility increases to $99.8 \times 10^{-5} \text{mol/kg}$. Solubility also increases in acidic media to $10.2 \times 10^{-5} \text{mol/kg}$. We have derived values for $pK_a$ and $pK_1$ from the data Gayer and Garrett (1952) and these value is given in Table 3.1. Baes and Mesmer (1976) refer to the value from Mishra and Gupta (1968) value as the most precisely known stability constant for antimonous acid protonation.

Jander and Hartmann (1965) and Ahrland and Bovin (1974) determined the speciation of antimony (III) in aqueous solutions at ambient temperature. Jander and Hartmann (1965) carried out ionophoresis, ion exchange and diffusion measurements at very high ionic strength in basic ($16 \text{M NaOH}$) and acidic ($11 \text{M HClO}_4$) media and demonstrated that there were apparently no polymeric species formed and that one species ($H_2SbO_7^{2-}$) existed in basic solutions and one in acidic solutions ($H_4SbO_6^{4+}$). Ahrland and Bovin (1974) studied the hydrolysis of antimony (III) in perchloric and nitric acid solutions at ionic strength $I=5M$ at 25°C using the solubility method.
3.2. METHODS

CHAPTER 3. ANTIMONOUS ACID IONISATION

In previous studies which have employed the solubility method, the stoichiometry of antimony complexes have been written in different forms, however, with solubility measurements alone, it is impossible to define whether the complex is stoichiometrically $\text{SbO}^+$, $\text{Sb(OH)}_2^+$, or $\text{H}_4\text{SbO}_5^+$. Throughout this paper, we write the $\text{Sb(III)}$ hydrolytic equilibria as acid ionisation as defined by equations (3.1) and (3.2) bearing in mind the strong acidic properties of antimony(III) at low pH.

3.2. Experimental Methods

Antimony trioxide behaves as a hydrophobic solid and is sparingly soluble in water ($5.2 \times 10^{-5} \text{ m}$ from Gayer and Garrett, 1952). In addition, $\text{Sb(III)}$ solutions are sensitive to the presence of atmospheric oxygen, forming $\text{Sb(V)}$. Thus, some considerable care must be taken in the preparation of $\text{Sb(III)}$-containing solutions.

$\text{Sb}_2\text{O}_3$ was dissolved in a three neck flask under an argon atmosphere at 65°C, taking a one to three days to yield either saturated or near saturated solutions. Solutions were then filtered under an argon atmosphere. All solutions were prepared with degassed (no $\text{CO}_2$ or $\text{O}_2$) double distilled (in quartz glass) water. Degassing of water was carried out in an ultrasonic bath by repeated evacuation from a sealed flask and subsequent bubbling by argon. Oxidation of $\text{Sb(III)}$ can occur because of trace impurities in the argon gas due to the long time (days) required for dissolving of antimony trioxide in water solutions. Gmelin (1950), suggested boiling $\text{Sb}_2\text{O}_3$ in water under argon for 24 hours but in our experience, this method accumulates $\text{O}_2$ in the solution, causing the formation of $\text{As(V)}$. For solubility measurements, this may be a minor effect, but for spectrophotometric measurements it is critical, because $\text{Sb(V)}$ species also absorb intensely in the ultraviolet region. The prepared solutions were pumped from the preparation flasks to the optical cell which had previously been evacuated and flushed with argon. The following experiment demonstrates the importance of this effect: the same solution was filtered with and without contact with air (i.e. under $\text{Ar}$). Figure 3.1 illustrates the two spectra.
Figure 3.1.: Two antimonous acid spectra with Sb concentration 0.0005 mol/dm³ and pH=0.09 prepared under Ar and with an air contact

obtained from these solutions with the same Sb concentration and pH, but prepared using different methods. The dashed line shows an additional band at the wavelength 235nm compared with the solid line (oxygen free), and in general, it has a slightly more intense and broad spectrum. Solutions prepared under Ar (4.5 grade) typically showed a small band at 235nm, and these solutions were discarded. Thus, in order to obtain good quality spectra of in Sb(III)-containing solutions, experiments have to be done under argon and the argon purity has to be very high, since even small impurities of oxygen in the Ar will lead to the cumulative oxidation of Sb(III) to Sb(V). All experiments in this study were prepared only with the highest purity Ar (Ar 6.0 grade) and with an additional purification, which was carried out by passing the argon through a column of elemental copper maintained at 400°C.
Spectrophotometric titrations were used to obtain $Sb$ solution spectra from 22 to 75°C, using an experimental setup as shown in Figure 3.2. $Sb$-containing solutions under constant $Ar$ flow were transferred to a titration vessel, which was in turn connected with the automatic titrator (Metrohm) and HPLC pump (Dynamax, Varian) and a flow-through quartz glass cuvette. This cuvette is placed within a Cary 5 Spectrophotometer (Varian) and the temperature regulated with the help of thermostat to temperatures from 22 to 75°C ($\pm 0.1^\circ$C). Titrations were carried out with constant stirring and constant volume. Constant volume was achieved by a simply returning the solution after measurement of each spectrum to the titration vessel (i.e. closed system). All connecting tubing are made from oxygen impermeable teflon. The solution within the cuvette and tubes created a “dead volume”, which was measured and added to the total volume of titrated solution.

$HClO_4$ and $NaOH$ stock solutions used for spectrophotometric titrations were standardised under deoxygenated argon by acid/base titration using tris-hydroxymethyl-aminomethane with phenolphtalein for the acid and potassium hydrogen phthalate ($KHP$) with methyl orange for the base.
Experimental facility used for the high temperature spectrophotometric measurements (from 150 to 300°C) is similar to the one discussed in the Chapter 2. And solutions were prepared as described above. After each measurement, the solutions could not be returned to the original solution reservoir, because after heating to 300°C at 110 bar pressure, there was a possibility of a contamination from the stainless steel outlet tubing (however, the inlet is lined with gold). For each run, around 400 ml of solution was consumed. The spectra were collected in a flow-through mode at all temperatures.

The antimony concentrations of both saturated and unsaturated stock solutions was determined by atomic absorption analysis with a precision ±2%. The solutions used for spectrophotometric measurements were prepared by dilution by weight with deoxygenated water under an argon atmosphere.

Thus, spectra were obtained from 22 to 300°C over a wide range of pH from 0.8 to 12.5 and of Sb(III) concentrations around 0.0001 mol/dm³. And corrected for background absorbance (i.e. water and quartz windows). To relate the molar concentration scale of the Beer-Lambert law to the molal scale of standard thermodynamic convention, the measured absorbances, $A_{obs}$, were corrected for the isothermal variation of solution density at each temperature. The solutions were all in the dilute range and were treated as water with the required density data being taken from Haar et al. (1984).

3.3. Results and Discussions

3.3.1. Spectra Interpretation

Interpretation of the spectra obtained from antimony-containing solutions with pH from 9 to 12.5 is similar to the procedure outlined for arsenous acid in Chapter 2. Figure 3.3 shows the calculation scheme used in this study. Absorbance is a linear function of the concentrations of all absorbing species at a given wavelength. The number of independent
3.3. RESULTS

CHAPTER 3. ANTIMONOUS ACID IONISATION

Figure 3.3.: Calculation scheme for calculation of the ionisation constant

\[ F = \sum_{i=1}^{m} \sum_{k=1}^{s} (A_{i,k}^{\text{obs}} - A_{i,k}^{\text{calc}})^2 \]

Optimisation
\[ n = n + 1 \]

If \( K_1^{(n+1)} - K_1^{(n)} < d \)

Yes

\[ K_1 \]

No
columns in the absorbance matrix (i.e. the rank) gives the number of absorbing species. Thus, the first step after creating the absorbance matrix ($A_{abs}$ with “$i$” number of solutions and “$k$” number of measured wavelength points), is to determine the rank of the matrix. Establishing the number of absorbing species allows one to create a chemical model, which in turn is used to develop a mathematical model based on the charge and mass balance relations, and the various equilibrium constant expressions.

The mathematical model for antimonous acid speciation requires consideration of mass and charge balance expressions at,

a) low $pH$:

\[
[Sb] = [H_4SbO_5^+] + [H_3SbO_6^0] \quad (3.3)
\]

\[
[H_4SbO_5^+] + [H^+] + [Na^+] = [OH^-] + [ClO_4^-] \quad (3.4)
\]

and also mass action:

\[
K_a = \frac{[H_4SbO_5^+][H_3SbO_6^0]}{[H^+][Na^+] [OH^-]} \quad (3.5)
\]

\[
K_w = [H^+][OH^-] \quad (3.6)
\]

b) high $pH$:

mass balance:

\[
[Sb] = [H_3SbO_3^0] + [H_2SbO_3^-] \quad (3.7)
\]

charge balance:

\[
[H^+] + [Na^+] = [OH^-] + [H_2SbO_3^-] \quad (3.8)
\]

mass action:

\[
K_1 = \frac{[H_2SbO_3^-][H^+] [H_3SbO_3^0]}{[H_3SbO_3^0][H_2SbO_3^-]} \quad (3.9)
\]

and additionally, $NaOH$ association defined by equation:

\[
K_{ass} = \frac{[NaOH][Na^+][OH^-]}{[Na^+][OH^-]} \quad (3.10)
\]

and the ion product of water:

\[
K_w = [H^+][OH^-] \quad (3.11)
\]
where $K_a$ and $K_1$ are antimonous acid protonation and ionisation constants respectively; $K_{ass}$ is the association constant of sodium hydroxide; $K_w$ is ion product constant of water; the terms in square brackets are molar concentrations of species in $mol/dm^3$; $\gamma$ is activity coefficient. The necessary activity coefficients, were calculated using the extended Debye-Hückel equation (Robinson and Stokes, 1968):

$$\log \gamma_i = \frac{-A z_i^2 \sqrt{I}}{1 + \hat{a} B \sqrt{I}} \quad (3.12)$$

where $A$ and $B$ constants are taken from Bradley and Pitzer (1979); Helgeson and Kirkham (1974) respectively; $\hat{a}$ is taken from Kielland (1937). But, it should be noted that the studied ionic strength most of solutions studied was always $\leq 0.01$ and the activity coefficients term was small. Sodium hydroxide association constants were taken from Ho et al. (2000).

Assuming a value for $K_a$ and taking the known values for the other equilibrium constant is known, the mass and charge balance equations can be solved and concentrations of all existing species in solutions calculated. The next step is the calculation of molar absorptivities, using the constrained non-negative least squares method of optimisation. Optimisation has to be constrained such that the molar absorptivities are positive, (i.e. there is no negative absorbance). Thus, the theoretical absorbance can be calculated. After this, a second optimisation process determines the least squares minimum. During the second optimisation, care must be taken in order to avoid values of the stability constant corresponding to a local minimum. This can happen when the initial guesses are wrong or too divergent from the real value. To avoid this problem, it is necessary to try a number of initial guesses and, if they give different values of stability constants, the one with a smallest sum of squares is accepted.

Uncertainty calculations were done using the Gaussian error propagation rule:

$$\sigma_K = \sqrt{\left(\frac{\partial K}{\partial [Sb]} \sigma_{[Sb]}\right)^2 + \left(\frac{\partial K}{\partial [Na]} \sigma_{[Na]}\right)^2 + \left(\frac{\partial K}{\partial K_w} \sigma_{K_w}\right)^2} \quad (3.13)$$
where \( \frac{\partial K}{\partial [\text{Sb}]} \), \( \frac{\partial K}{\partial [\text{Na}]} \), and \( \frac{\partial K}{\partial K_w} \) are the partial derivatives of a ionisation constant with respect to each given parameter, (i.e. total antimony concentration, total sodium concentration (or total perchlorate concentration)) and the ionisation constant of water, respectively. \( \sigma_{[\text{Sb}]} \), \( \sigma_{[\text{Na}]} \), and \( \sigma_{K_w} \) are standard deviations of total antimony concentration, total sodium concentration (or total perchlorate concentration) and the ionisation constant of water.

Partial derivatives were obtained using a "brute-force" approach with a "central differences" method. For example, the partial derivative of \( K \) with respect to the parameter [Sb] at a point \([\text{Sb}]_i\) is estimated by solving the model (optimisation) at two points \(((\text{Sb})_i - h)\) and \(((\text{Sb})_i + h)\), where \( h \) is a small number (i.e. \( 10^{-9} \)) and the respective outputs are obtained as \( K_{i1} \) and \( K_{i2} \). The partial derivative is then given by

\[
\frac{\partial K}{\partial [\text{Sb}]} \approx \frac{K_{i1} - K_{i2}}{2h}; \quad h \to 0. \tag{3.14}
\]

In the same way, the partial derivative of \( K \) with respect to others parameters such as [Na] and the ionisation constant of water are obtained.

Each spectrum was obtained at a different antimony and sodium concentration with different corresponding uncertainties. This means that the partial derivative of \( K \) with respect to each parameter's value with a given standard deviation has to be taken into account. This was done by taking an average value of all partial derivatives with respect to one parameter, multiplied by its standard deviation, i. e.

\[
\left( \frac{\partial K}{\partial [\text{Sb}]} \sigma_{[\text{Sb}]} \right)_{av} = \frac{\sum_{k=1}^{n} \frac{\partial K}{\partial [\text{Sb}]} \sigma_{[\text{Sb}]} k}{n} \tag{3.15}
\]

where \( n \) is the number of solutions.
3.3. RESULTS

3.3.2. Antimonous acid protonation

From solubility measurements at 25°C Gayer and Garrett (1952), it is known that a protonated form of antimonous acid, $H_4SbO_3^+$, occurs in acidic aqueous solutions. In order to further study the formation of this species, the spectra of $Sb(III)$-containing solutions were measured at low pH and at temperatures from 22 to 75°C using spectrophotometric titration method.

Figure 3.4 shows spectra of $Sb$-containing solutions within the acidic range at 22°C. Compositions of solutions used to measure spectra at temperatures 22, 50 and 75°C are given in the Tables B.2, B.3 and B.4, respectively. Spectra at high temperatures (i.e. 100, 150, 200, 250 and 300°C) were collected using a Ti – Pd alloy optical cell as described.

Figure 3.4.: The spectra at low pH $Sb(III)$-containing solutions corrected for water solvent and quartz glass cuvette absorbance at 22° and saturated water vapour pressure
Figure 3.5.: The spectra at low pH Sb(III)-containing solutions corrected for water solvent and quartz glass windows absorbance at 300°C and saturated water vapour pressure previously. Figure 3.5 shows spectra of Sb-containing solutions within the acidic range at 300°C and saturated water vapour pressure and Table B.5 gives the compositions of the acidic antimony-containing solutions for which spectra were measured from 100 to 300°C.

Rank analysis of the absorbance matrix at each temperature demonstrated that three absorbing species were present at all measured temperatures. However, at 250 and 300 contribution to the total absorbance from the third species was very weak.

In order to understand which species were contributing to the overall absorbance envelope, spectra of aqueous solutions containing only perchloric acid with concentration between 0.0110 to 0.2595 mol/dm³ (see Table B.6) were obtained from 25 to 300°C. For the study of the protonation of antimonous acid, aqueous antimony solutions were prepared with
3.3. RESULTS

CHAPTER 3. ANTIMONOUS ACID IONISATION

Figure 3.6.: Molar absorptivities, ε, of ClO$_4^-$ from 25 to 300°C at the saturated vapour pressure.

Perchloric acid concentrations up to 0.2218 mol/dm$^3$. The molar absorptivities, ε, of ClO$_4^-$ are shown in the Figure 3.6 and are typical of a charge-transfer-to-solvent (ctts) type of transition. The absorbance maximum of perchlorate ion occurs at a shorter wavelengths within the uv region and was not determined. The low energy absorption edge undergoes the expected red shift with increasing temperature (Figure 3.6).

The ClO$_4^-$ ion absorbs in the wavelength interval 190-240 nm. Consequently, one of absorbing species is present in solutions is the perchlorate ion, ClO$_4^-$. However, ClO$_4^-$ ion absorbs weakly, in comparison with the ctts spectra of OH$^-$ and Cl$^-$ ions. Nevertheless, at ClO$_4^-$ concentrations of 0.1-0.2 mol/dm$^3$, there is a significant contribution from perchlorate ion absorbance to the total measured absorbance. Therefore, this contribution was subtracted from the spectra of all solutions containing perchloric acid at all temperatures.
The chemical model for acidic antimony-containing solutions is given by the reaction (3.1). At 22°C, the first ten spectra from pH=0.85 to 1.00 were identical; that is, the concentration of the Sb(III)-containing species is independent of pH in this range. Thus, the second of three absorbing species can be ascribed to the protonated antimonous acid, $H_4SbO_3^+$.

Figure 3.7 shows the calculated molar absorptivity of the protonated antimonous acid species. It absorbs intensely at low temperatures. With increasing temperature, perchlorate ion molar absorptivity increases at a given wavelength, although the molar absorptivity for the band maximum for the $ClO_4^-$ ion presumably decreases with increasing temperature. The molar absorptivity of the protonated antimonous acid species, $H_4SbO_3^+$, decreases with decreasing temperature. This makes calculation of molar absorptivities at temperatures between 150-300°C less accurate and evaluation of protonation constant difficult.

The third absorbing species is neutral antimonous acid. The molar absorptivities determined in this study are shown in the Figure 3.8. The spectra broaden as temperature...
3.3. RESULTS

CHAPTER 3. ANTIMONOUS ACID IONISATION

Figure 3.8.: Molar absorptivity, $\varepsilon$, of $H_3SbO_3^0$ from 22 to 300°C at the saturated vapour pressure

increases up to 300°C. At 22, 50 and 75°C, the maximum absorption and band position is well defined and at about 190 nm. With increasing temperature, the spectra are overlapped by the red-shifted $ClO_4^-$ contribution and the water continuum absorption, which obscure the band maximum for $H_3SbO_3^0$.

The values of the equilibrium constants obtained by the non-linear, non-negative least squares refinement are summarised in Table 3.2. These values given as a function of temperature, were fitted to the equation:

$$ R \ln K_1 = a + b/T + c \ln T + dT + eT^2 $$

(3.16)

where $a = 23581; b = -5.4763 \cdot 10^5; c = -4300.3; d = 10.258; e = -0.0039975$. The five term form of this equation was found to best fit the data.

In Figure 3.9, it can be seen that the protonation constant initially decreases with increasing temperature up to 100°C but then increases until it reaches a value of $logK_a=1.8$ at 300°C. Uncertainties in the determination of the protonation constant at 22, 50 and 75°C
Figure 3.9.: Variation $\log K_a$ for the formation of $H_4SbO_3^+$ according to equation 3.5

Table 3.2.: The protonation constant (molal) of antimonous acid from 22 to 300°C at saturated vapour pressures, where the uncertainty is $2\sigma$.

<table>
<thead>
<tr>
<th>$t$ / °C</th>
<th>$\log K_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>1.385 ±0.012</td>
</tr>
<tr>
<td>50</td>
<td>1.236 ±0.008</td>
</tr>
<tr>
<td>75</td>
<td>1.078 ±0.009</td>
</tr>
<tr>
<td>100</td>
<td>0.94 ±0.08</td>
</tr>
<tr>
<td>150</td>
<td>1.04 ±0.15</td>
</tr>
<tr>
<td>200</td>
<td>1.1 ±0.3</td>
</tr>
<tr>
<td>250</td>
<td>1.5 ±0.3</td>
</tr>
<tr>
<td>300</td>
<td>1.8 ±0.3</td>
</tr>
</tbody>
</table>

temperatures are remarkably low (see Table 3.2), because a large number of experimental solutions (up to 60) were studied which allowed a statistically rigorous definition of the spectra for all three species, $ClO_4^-$, $H_4SbO_3^+$ and $H_3SbO_3^2$. For constants obtained from
3.3. RESULTS

CHAPTER 3. ANTIMONOUS ACID IONISATION

100 to 300°C, uncertainties increase. The difference between uncertainties at 100°C and at 75°C is explained by the smaller number of solutions studied. With increasing temperature, increasing uncertainty can be explained by a combination of changes of molar absorptivities of all three species and probable decomposition of perchloric acid at the highest temperatures, despite having collected the spectra in a flow-through mode. The molar absorptivity of ClO$_4^-$ (Figure 3.6) is red shifted with increasing temperature and strongly overlaps with the absorbance of $H_4SbO_3^+$ (Figure 3.7), which is also decreases with increasing temperature. The absorbance of $H_4SbO_3^+$ becomes weaker, introducing further uncertainty in the spectra interpretation.

Unfortunately, there is no available thermodynamic data on perchloric acid association. At temperatures below 100°C, estimates of perchloric acid ionisation are controversial (Haase et al., 1965; Quist et al., 1965)). However, association of perchloric acid at high temperatures has already been observed by Ratcliffe and Irish (1984) who studied the Raman spectra of perchloric acid and found traces of molecular HClO$_4$ in concentrated acid solutions. Henderson et al. (1971) studied the kinetics of thermal decomposition of 1.1-6.6 m perchloric acid at 295-322°C. the suggested products of decomposition were $O_2$, $Cl_2$, $HCl$. Since there are no data on perchloric acid association, correction for association was not included in the calculations, and the assumption was made that all perchloric acid is dissociated. The rank of the absorbance matrix is three, indicate the no decomposition products such $Cl_2(aq)$ or $ClO^-$ are present.

Figure 3.10 shows an example of a deconvoluted spectrum of antimonous acid solution at 22°C with a total concentration of $Sb = 1.20 \times 10^{-4} \text{mol/dm}^3$ and $pH = 1.38$. Figure 3.11 shows experimentally obtained and calculated (dots) antimonous acid spectra at room temperature and illustrates the excellent agreement between the calculated and experimental spectra. This suggests that the chosen chemical model and developed mathematical description are credible.
CHAPTER 3. ANTIMONOUS ACID IONISATION

3.3. RESULTS

Figure 3.10.: Deconvoluted spectrum for a solution having $pH=1.38$ and $Sb=1.20\times10^{-4}$ mol/dm$^3$ in acidic water solutions

Figure 3.11.: Experimentally obtained and calculated antimonous acid spectra within the $pH$ interval from 0.86-2.27 and $1.5\times10^{-4}$-$1.1\times10^{-4}$ at 22°C
3.3.3. Antimonous acid ionisation

Spectra were collected at temperatures 25, 50, 100, 150, 200, 250 and 300°C in alkaline solutions. Figure 3.12 shows measured spectra of a series of alkaline $Sb$-containing solutions.

Figure 3.12.: Antimonous acid spectra in alkaline aqueous solutions at 25°C

Figure 3.13.: Antimonous acid spectra in alkaline aqueous solutions at 300°C
Figure 3.14.: Rank determination of the absorbance matrix of antimonous acid species at 25 and 300°C

solutions at 25°C. The compositions of the solutions are given in the Table B.7. Figure 3.13 shows spectra of Sb-containing solutions obtained at 300°C and saturated water vapour pressure. The solutions compositions are given in Table B.8. In both cases, the absorbance increases with increasing sodium hydroxide concentration.

Rank analysis of the absorbance matrix at temperatures from 25 to 300°C was carried out for all spectra. the rank of the matrix is two at all temperatures from 25 to 300°C as illustrated for 25 and 300°C in Figure 3.14.
3.3. RESULTS

Now we are left to assign the two absorbing species. The solutions contained high concentrations of sodium hydroxide. The hydroxide ion absorbs strongly in the uv as shown previously (see Figure 2.10) from 190 to 220 nm at 25°C and from 190 to 250 nm at 300°C. That means that it does not absorb in the wavelength range from 220 to 240 nm from 25 to 250°C, but it absorbs at 240-250 nm at 300°C, where spectra of Sb-containing solutions spectra were measured, and where results of the rank analysis indicated that two absorbing species to be present. From the study of the speciation of antimonous acid in acidic solutions (this study), it is known that $H_3SbO_3$ absorbs in the wavelength interval, 190-240 nm at 250°C, broadening to 190-250 nm with increasing temperature to 300°C. Thus, the one of absorbing species in the alkaline antimony-containing solutions from 25 to 250°C can be assigned to $H_3SbO_3$. At 300°C, the first absorbing species can be assigned to the hydroxide ion, since $H_3SbO_3$ has almost no contribution to the total absorbance at this temperature. This conclusion is based not only on analysis of absorbance interval, but is also supported by the chemical/mathematical model used in the calculation of the deprotonation constant. Thus, the presence of $H_3SbO_3$ as an absorbing species at 300°C is not consistent with the trends observed at other temperatures.

The second absorbing species at all measured temperatures is assigned to the deprotonated antimonous acid ion, $H_2SbO_5^-$. The formation of the polynuclear species is considered unlikely because the concentration of antimony in the solutions was low and always less than 0.00026 mol/dm³. The strong red shift of the low energy absorption edge of the deprotonated antimonous acid species with increasing temperature is characteristic of a charge-transfer-to-solvent (ctts) type of electron transition. Therefore, the deprotonation reaction (reaction 3.2) describes this system. The molar absorptivities for the deprotonated antimonous acid species, $H_2SbO_5^-$, from 25 to 300°C at the saturated vapour pressure are shown in Figure 3.15. Although the maximum of absorbance could not be measured.

The values of the equilibrium constants for the reaction 3.2 were obtained by the non-
CHAPTER 3. ANTIMONOUS ACID IONISATION

3.3. RESULTS

Figure 3.15.: Molar absorptivities, $\varepsilon$, $H_2SbO_3^-$ from 25 to 300°C at the saturated vapour pressure

linear non-negative least squares refinement and are summarised in Table 3.3.

Table 3.3.: Ionisation constants of antimonous acid (reaction 3.2) from 25 to 300°C at saturated vapour pressures; the uncertainty is 2σ. The values reported here are related to the hypothetical 1 molal standard state.

<table>
<thead>
<tr>
<th>t°C</th>
<th>$pK_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>11.82 ±0.02</td>
</tr>
<tr>
<td>50</td>
<td>11.52 ±0.04</td>
</tr>
<tr>
<td>100</td>
<td>11.05 ±0.02</td>
</tr>
<tr>
<td>150</td>
<td>10.56 ±0.03</td>
</tr>
<tr>
<td>200</td>
<td>10.19 ±0.02</td>
</tr>
<tr>
<td>250</td>
<td>9.99 ±0.02</td>
</tr>
<tr>
<td>300</td>
<td>9.88 ±0.02</td>
</tr>
</tbody>
</table>
Figure 3.16 shows the temperature dependence of antimonous acid deprotonation constant. With increasing temperature, the deprotonation constant of the antimonous acid decreases in a manner similar to that observed for arsenous acid and other weak acids.

![Graph showing temperature dependence of antimonous acid](image)

Figure 3.16.: Temperature dependence of the ionisation constant for antimonous acid at the saturated vapour pressure

Figure 3.17 shows an example of a deconvoluted spectrum of antimonous acid solution at 25°C with a total concentration of $Sb = 1.40 \times 10^{-4} \text{mol/dm}^3$ and $pH = 11.68$.

The values of ionisation constants as a function of temperature were fitted to a form of the extended Van’t Hoff equation to determine temperature dependence:

$$ R \ln K_1 = a + b/T + c \ln T + dT + eT^2 \quad (3.17) $$

where $a = 295.88; b = -5901.4; c = -64.704; d = 0.26307; e = -0.00014659$. 
Figure 3.17: Deconvoluted spectrum for a solution having $Sb = 1.40 \times 10^{-4} \text{mol/dm}^3$ and $pH = 11.68$
3.4. Conclusions

The protonation and deprotonation of antimonous acid from ambient to high temperatures have been studied spectrophotometrically. Precise values of the equilibrium constants were obtained for protonation of antimonous acid at 22, 50 and 75°C with values of lower precision from 150 to 300°C. The log\(K_a\) varied from 1.38 to 0.94 over a temperature interval from 22 to 100°C and then increased up to 1.8 at 300°C. The deprotonation constant for antimonous acid decreases dramatically with temperature in a way similar to that observed for arsenous acid. The \(pK_1\) of the deprotonation constant varied from 11.82 to 9.88 from 25 to 300°C. Figure 3.18 shows the distribution of antimonous acid species in aqueous solutions at 25 and 300°C as a function of \(pH\).
4. The formation of thioarsenite species in aqueous solutions

4.1. Introduction

Most active hot spring systems and deep geothermal environments are characterised by the presence of reduced sulphur (i.e. $H_2S$ and $HS^-$). The interaction of $As(III)$ with $H_2S/HS^-$ leads to the precipitation of arsenic sulphide minerals including orpiment and realgar as well as other phases such duranusite ($As_4S$), dimorphite ($As_4S_3$), uzonite ($As_4S_5$) and alacranite ($As_8S_9$) in addition to amorphous $As_2S_3$, depending upon temperature and $pH$. However, the reaction of aqueous arsenic($III$) species (e.g. arsenous acid) with $H_2S/HS^-$ also leads to the formation of thioarsenite species in solution.

In order to understand the speciation of arsenic in geothermal and natural waters, it is necessary to have thermodynamic data on aqueous arsenic speciation. The current lack of data means that the reliable modelling of arsenic transport and mineral deposition in hydrothermal systems is fraught with uncertainty. Processes responsible for arsenic deposition and transport in hydrothermal solutions have been the subject of many studies and we have recently (Chapter 2, this thesis) determined the first ionisation constant of arsenous acid, $HAsO_2$, up to 300°C at the saturated vapour pressures.

The stoichiometry and stability of thioarsenite species in aqueous media have been the subject of a number of previous studies. Unfortunately, the stiochiometries proposed
4.1. INTRODUCTION

CHAPTER 4. THIOARSENITE SPECIES

Table 4.1.: Previously reported experimental data on thioarsenite speciation at different temperatures

<table>
<thead>
<tr>
<th>species</th>
<th>t / °C</th>
<th>pH</th>
<th>method</th>
<th>references</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{AsS}_2^{2-}; \text{AsS}_3^{2-}$</td>
<td>20</td>
<td>6-9</td>
<td>solubility</td>
<td>Babko and Lisetskaya (1956)</td>
</tr>
<tr>
<td>$\text{As}_3\text{S}_6^{3-}; \text{As}_2\text{S}_4^{4-}$</td>
<td>20</td>
<td>4-12</td>
<td>potent./cryosc.</td>
<td>Angeli and Souchay (1960)</td>
</tr>
<tr>
<td>$\text{AsS}_2^{2-}$</td>
<td>25-200</td>
<td>alkaline</td>
<td>solubility</td>
<td>Weissberg et al. (1966)</td>
</tr>
<tr>
<td>$\text{H}_2\text{AsS}_4$</td>
<td>25?</td>
<td>0-8</td>
<td>gravimetry</td>
<td>Srivastava and Ghosh (1958)</td>
</tr>
<tr>
<td>$\text{As}_3\text{S}_6^{3-}; \text{As}_2\text{S}_4^{4-}$</td>
<td>22</td>
<td>7.97-11.98</td>
<td>spectrophotometry</td>
<td>Vorob'eva et al. (1977)</td>
</tr>
<tr>
<td>$\text{H}_2\text{AsO}_3^0; \text{As}_3\text{S}_6^{3-}$</td>
<td>22</td>
<td>7.45-8.76</td>
<td>solubility</td>
<td>Ivakin et al. (1979)</td>
</tr>
<tr>
<td>$\text{H}_2\text{As}_2\text{S}_4^2; \text{HAs}_2\text{S}_4^2$</td>
<td>90</td>
<td>1.2-7.9</td>
<td>solubility</td>
<td>Mironova and Zotov (1980)</td>
</tr>
<tr>
<td>$\text{As}_2\text{S}_4^{2-}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{H}_2\text{AsO}_3^0$</td>
<td>25-150</td>
<td>1.2-5.4</td>
<td>solubility</td>
<td>Mironova et al. (1983)</td>
</tr>
<tr>
<td>$\text{AsS}_2^{2-}$</td>
<td>25</td>
<td>2-7.4</td>
<td>potentiometry</td>
<td>Prasad (1987)</td>
</tr>
<tr>
<td>$\text{H}_2\text{As}_3\text{S}_6^0; \text{H}_2\text{As}_3\text{S}_6^0$</td>
<td>25-300</td>
<td>1-12.8</td>
<td>recalculation from</td>
<td>Spycher and Reed (1989)</td>
</tr>
<tr>
<td>$\text{HAs}_3\text{S}_6^{2-}$</td>
<td></td>
<td></td>
<td>literature data</td>
<td></td>
</tr>
<tr>
<td>$\text{H}_2\text{AsO}_3^0; \text{H}_2\text{As}_2\text{S}_3^0^0$</td>
<td>25-150</td>
<td>1.2-9.0</td>
<td>solubility</td>
<td>Mironova et al. (1990)</td>
</tr>
<tr>
<td>$\text{HAs}_2\text{S}_4^2; \text{As}_2\text{S}_4^{2-}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{H}_2\text{AsO}_3^0; \text{H}_2\text{As}_2\text{S}_3^0^0$</td>
<td>25, 90</td>
<td>1.16-7.31</td>
<td>solubility</td>
<td>Webster (1990)</td>
</tr>
<tr>
<td>$\text{H}_3\text{AsO}_3^0; \text{H}_2\text{As}_3\text{S}_6^0$</td>
<td>25-90</td>
<td>2-8</td>
<td>solubility</td>
<td>Eary (1992)</td>
</tr>
<tr>
<td>$\text{As(SH)}_2^{2-}; \text{As}_2\text{S}_2^2; \text{AsS}_3^2$</td>
<td>room</td>
<td>alkaline</td>
<td>Raman, Exafs</td>
<td>Helz et al. (1995)</td>
</tr>
<tr>
<td>$\text{As}_2\text{S}_3^2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Seven unidentified species reported</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{As(OH)}_2(SH)^0$</td>
<td>25</td>
<td>7.01-10.90</td>
<td>ion chromatograph-</td>
<td>Wilkin et al. (2003)</td>
</tr>
<tr>
<td>$\text{As(OH)}_2^S; \text{As(OH)}_2\text{S}_2^2$</td>
<td></td>
<td></td>
<td>ICP-MS</td>
<td></td>
</tr>
<tr>
<td>$\text{AsS}_2^2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

for thioarsenite species in aqueous solutions are in poor agreement as shown in Table 4.1. Most of the previous studies have involved the measurements of solid or amorphous arsenic sulphide solubility (Webster, 1990; Mironova et al., 1990; Eary, 1992) in aqueous solutions. Other potentiometric, Raman and Exafs studies have been carried out by Prasad (1987), Wood et al. (2002) and Helz et al. (1995). In addition, ab initio
CHAPTER 4. THIOARSENITE SPECIES

4.1. INTRODUCTION

calculations have been reported by Helz et al. (1995) and Tossell (2001). Proposed stoichiometries for thioarsenite complexes in aqueous solutions at low temperature vary from author to author. In general, it is accepted that in the acidic range of the pH, the thioarsenite species is associated arsenous acid (Webster, 1990; Mironova et al., 1990; Eary, 1992). In alkaline solutions, two possible stoichiometries have been suggested by various authors from solubility studies (i.e. the dimer or trimer $\text{As}_2\text{S}_4^{2-}$ and $\text{As}_3\text{S}_6^{3-}$). High concentrations of arsenic in alkaline solution may give rise to the formation of polynuclear species. A fundamental weakness of the solubility method in this case is that the measured solubilities may be in a concentration range where polynuclear species predominate. The study of thioarsenite formation at low (constant) arsenic concentrations over a wide pH range is therefore not possible.

Spectroscopic methods can provide knowledge on a structure of species. The combined Exafs and Raman study Helz et al. (1995) of 0.016-0.08 $M$ total arsenic in 1 $M$ NaHS suggested the presence of an $\text{AsS}_3^{-}$. This observation is in agreement with the potentiometric study of Prasad (1987). The recent study (Wilkin et al., 2003) suggested numerous combinations from oxygen containing thioarsenites to the tetrahydrosulphidoarsenic(III) species, $\text{As}(\text{HS})_3^{-}$. However, in Wilkin et al. (2003), the interaction with the eluent may have occurred which will affect the thioarsenite speciation. In addition, no information concerning the calculation of stability constants was presented. The main conclusion from this study was that many possible combinations of $\text{As, O, S, H}$ may occur. The Raman study by Wood et al. (2002) suggested that a complex mixture of thioarsenite species occurs within the pH range 7-13. Some previous studies have perhaps also suffered from the unidentified presence of $\text{As}_2\text{S}_3$ colloid dispersed as a sol as well as from oxidation of $\text{As(III)}$ to $\text{As(V)}$ and hence the formation of $\text{As(V)}$ thioarsenite species.

The aim of this study has therefore been to determine the stoichiometry and deprotonation of thioarsenous acid in dilute solutions at ambient conditions by means of flow-throw uv-vis spectrophotometry.
4.2. Experimental methods

The experimental apparatus used in this study is shown in Figure 4.1. The spectra were recording using a Cary 5 spectrophotometer. A specially built “syringe” flask was connected to an automatic titrator (Metrohm) and HPLC pump (Dynamax, Varian) and flow-through quartz glass cuvette, thermostated at 22°C. Titrations were facilitated with a constant volume (closed) system, in which the solution was returned (by pumping) after spectrum measurement to the “syringe” flask. All connecting tubing were made from teflon in order to minimise diffusive ingress of atmospheric oxygen into the system. The volume of the cuvette and tubing creates an additional volume (i.e. “dead” volume) in the system which was also measured and included in the total volume when adjusting the composition of the titrated solution.

An As(III) stock solution solution (0.0096 mol/dm³) was prepared by dissolving a weighed amount of As₂O₃ in degassed water. Solution preparation and handling was carried out in such a way as to exclude any contact with air (i.e. CO₂ and O₂) in order to avoid oxidation of As(III) to As(V) and interference with pH by carbonate equilibria.
High purity water (triple distilled in quartz glass) was degassed under vacuum in an ultrasonic bath and then flushed with ultra pure argon (grade 6.0) which had been additionally "cleaned" by passing through a high temperature (400°C) copper trap. This evacuation and argon purging procedure was repeated five times.

Hydrogen sulphide solutions were prepared using a procedure similar to the Kipp's gas generator (Figure 4.2). This avoided the possibility of contamination by trace organic compounds which may be present in commercially available cylinders of \( H_2S \) and which might absorb in the ultraviolet region. Crystals of fresh \( Na_2S \cdot 9H_2O \) (from a sealed bottle, stored in the refrigerator) were quickly added to the reaction flask which was then flushed with argon for 20 minutes. This flask was connected to another flask containing phosphoric acid which was maintained under a constant argon flow. Small aliquots of phosphoric acid were then added to the sodium sulphide crystals to produce high purity \( H_2S \). The resulting \( H_2S \) solutions were taken up in a gas tight Hamilton syringe and subsequently analysed.
for total sulphide by iodometric back titration using a standardised iodine solution (0.05 M) diluted in acetate buffer (pH=4.15). A starch indicator was employed and the excess iodine was back-titrated using 0.05 M $Na_2S_2O_3$ solution.

The flask containing a movable piston (i.e. “syringe flask”, Figure 4.3) permitted the transfer of aliquots of $H_2S$ stock solution such that the solutions remaining in the flask did not change composition because of the increase in the residual vapour space. As solution was extracted from the flask, the piston moved to maintain contact with the
CHAPTER 4. THIOARSENITE SPECIES  4.2. EXPERIMENTAL METHODS

liquid phase and prevent the creation of a vapour space into which $H_2S$ could partition from the liquid phase, thus changing the concentration of $H_2S$ in the remaining solution. When a portion of sulphide solution was removed or added to the flask, the piston moved down or up to ensure that no gas phase was present. The addition of degassed, standardised $As(III)$ and $NaOH$ solutions, as well as aliquots of $H_2S$ stock solution (Figure 4.2) was facilitated with gas tight Hamilton syringes.

Figure 4.4 shows a calibration plot for the “syringe” cell, developed for this study. For this purpose, four $H_2S$ solutions were prepared and their spectra were measured. An $H_2S$ stock solution contained in a Hamilton syringe (with volume 50ml) was iodometrically back titrated (to determine the total sulphur) and then aliquots of this analysed titrated solution were added to the “syringe” cell filled with degassed water. $pH$ and $H_2S$ concentrations for each solution are given in Table B.9. The prepared solutions had $pH=5-5.3$, and over this $pH$ range, $H_2S(aq)$ there is the only one absorbing species. The absorbances of $H_2S$ solutions prepared in this way (no $H_2S$ gas losses) at a given wavelength have to be linearly dependent on $H_2S$ concentrations, according to the Beer-Lambert law. The measured data points (absorbance of four $H_2S$ solutions at 190 nm plotted versus $H_2S$

![Figure 4.4: Calibration plot for the “syringe cell”; $H_2S$ absorbance at 190nm versus $H_2S$ concentration.](image)

61
concentrations) exhibit a linear dependence (Figure 4.4). Thus, there was no losses of \( \text{H}_2\text{S} \) during solution preparation and measurement.

### 4.3. Results and discussions

Spectra of arsenic- and sulphur-containing solutions were obtained at 22°C over the \( \text{pH} \) range from 5.70 to 12.83 and corrected for background absorbance (i.e. water and quartz glass windows). Spectra for the solutions studied (Tables B.10, B.11, B.12) are given in Figures 4.5, 4.6, 4.7 respectively.

![Absorbance spectra of As(III) sulphide containing solutions measured in basic pH range at 22°C and 1 bar, corrected for background absorbance. Compositions of measured solutions, numbered, are given in Table B.10](image)

Figure 4.5.: Absorbance spectra of As(III) sulphide containing solutions measured in basic \( \text{pH} \) range at 22°C and 1 bar, corrected for background absorbance. Compositions of measured solutions, numbered, are given in Table B.10

In order to evaluate the spectra of possible thioarsenite species in As(III)-containing sulphide solutions, one must know the molar absorptivities of all the other absorbing species which may also be present. These include the two arsenous acid species, \( \text{HAsO}_2^- \) and \( \text{AsO}_2^- \) as well as the \( \text{OH}^- \), the spectra of which we have been previously studied (see Chapter 2). \( \text{H}_2\text{S}^0 \) and \( \text{HS}^- \) are also present in such solutions and their molar
CHAPTER 4. THIOARSENITE SPECIES

4.3. RESULTS

As=1.1x10^{-4} \text{mol/dm}^3
S=4.6x10^{-4} \text{mol/dm}^3
NaOH=4x10^{\text{to } 6.8x10^{-4}} \text{mol/dm}^3

Figure 4.6.: Absorbance spectra of As(III) sulphide containing solutions with the constant sulphur \((S=4.6x10^{-4}\text{mol/dm}^3)\) concentration and \(pH\) varied from 5.70 to 10.35 at 22°C and 1 bar, corrected for background. Solutions compositions are given in Table B.11.

As=5.7 to 6.7x10^{-4} \text{mol/dm}^3
S=2.08 to 2.45x10^{-4} \text{mol/dm}^3
NaOH=2.050x10^{\text{to } 6.972x10^{-4}} \text{mol/dm}^3

Figure 4.7.: Absorbance spectra of As(III) sulphide containing solutions spectra with the sulphur concentrations four times greater that that of arsenic at 22°C and 1 bar, corrected for background. Solutions compositions are given in Table B.12.
absorptivities were obtained in the present study and are consistent with those reported by Suleimenov and Seward (1997). Spectra of pure \( H_2S \) and \( Na_2S \) solutions at 22°C were measured and compositions of measured solutions are given in the Tables B.9 and B.13. The relevant molar absorptivities for the above mentioned species are given in Figure 4.8.

There are a number of problems that arise in the study thioarsenite formation using uv spectroscopy. Firstly, there are a number of other species which absorb strongly at ultraviolet wavelengths (see above) and solution compositions (i.e. \( As(III) \) and sulphide concentrations and \( pH \)) must be chosen to minimise the spectral contributions of these other species and to maximise the contributions due to the thioarsenite species. This is particularly important in alkaline solutions in which contributions from the very intense charge-transfer-to-solvent spectra of both \( HS^- \) and \( OH^- \) may “swamp” the component(s) due to thioarsenite species. For example, the spectra of \( As(III) \) sulphide containing solutions given in Figure 4.5 clearly represent the superposition of arsenous acid species and hydrogen sulphide species. Secondly, care must be taken to avoid solution composi-

![Figure 4.8: Molar absorptivities, \( \varepsilon \), of \( HAsO_2^0 \), \( AsO_2^- \), \( OH^- \), \( H_2S^0 \) and \( HS^- \) at 22°C and 1 bar](image)

64
tions in the acid to near neutral region in which the solubility of colloidal (or crystalline) 
$As_2S_3$ is very low. At $As(III)$ and sulphide concentrations which yield spectra of 
suitable absorbance, dilute colloidal dispersions of $As_2S_3$ may form which appear clear 
and transparent. Nevertheless, light scattering from such “colloidal solutions” give rise to 
erroneous spectra which cannot be interpreted in terms of homogeneous solution equilibria. A number of such spectra affected by colloid light scattering are shown in Figure 4.6. 
The spectra are broad and also characterised by an enhanced baseline absorbance which 
cannot be removed by subtraction of the solvent and window background. Such spectra 
were typically at $pH \leq 9$ (for $\sum As(III) = 1.0x10^{-5}$ to $1.0x10^{-3}$ and $\sum S = 1.0x10^{-5}$ 
to $1.0x10^{-3}$) and were not used in this study of thioarsenite formation.

Figure 4.7 shows chosen measured spectra of thioarsenite-containing solutions (which 
contain no colloidal species). Solution for these spectra were prepared with the arsenic 
($As=5.7x10^{-4}$ to $6.7x10^{-4} \, mol/dm^3$) and with increasing sodium hydroxide concentra-
tions at a total sulphur concentration four times higher than arsenic ($S=2.08x10^{-3}$ to 
$2.45x10^{-3}\, mol/dm^3$). The $pH$ values for the solutions shown in the figure are the values 
calculated assuming the presence of all the species present according to the model which 
best fitted the data as discussed later.
4.3. RESULTS

4.3.1. Mathematical treatment

Before proceeding to the refinement equilibrium constants, it is necessary to validate the model in both a chemical and mathematical sense. The validation is based on the analysis of the absorbance matrix for the number of absorbing species at each temperature. Since absorbance is a linear function of concentration for a given absorbing species at a specified wavelength, the maximum number of linearly independent columns of the absorbance matrix (i.e. the rank of the absorbance matrix) gives the number of absorbing species in solution at a particular temperature, providing that no two species have identical molar absorptivities. Figure 4.9 shows that the rank of the matrix created from the measured spectra at 22°C over the wavelength interval from 275 to 400nm, is two.

![Graph showing rank analysis](image)

Figure 4.9.: Rank analysis of the absorbance matrix created from As – S containing solutions (Figure 4.7) at wavelength from 275 to 400nm, “tolerance” is estimated instrument error.

Figure 4.10 shows the proceeded scheme of calculation. Determination of the number of absorbing species allows the creation a chemical model, which in turn will give a mathematical model, based on mass action, mass balance and charge balance equations. A number of speciation models were fitted to the obtained experimental data (Table 4.2).
CHAPTER 4. THIOARSENITE SPECIES

4.3. RESULTS

Absorbance matrix, $A_{obs}^{(i \times k)}$

Number of absorbing species / rank ($r$) analysis of $A_{obs}^{(i \times k)}$

Chemical Model; mass and charge balance equations

Initial guess for unknown constant(s) / $K_i^*$

Equilibrium concentrations species in solutions for example: $H^+$, $OH^-$, $H_2S^0$, $HS^-$, $H_3AsS_3^0$ and $H_2AsS_3^-$

Concentration matrix $C^{(i \times r)}$ of absorbing species

Solution of overdetermined system of linear equations

$\varepsilon = (C \cdot C^\top)^{-1}C \cdot A_{obs}^{(i \times k)}, \; \ell = 1$

Calculated absorbance matrix $A_{calc}^{(i \times k)} = C \cdot \varepsilon$

$F = \sum_{i=1}^{m} \sum_{k=1}^{s} (A_{i,k}^{obs} - A_{i,k}^{calc})^2$

$\forall_{k^{(n+1)} - k^{(n)} < d}$

Optimisation $n = n + 1$

$(\kappa, K^*_{(n+1)} - K^*_{(n)}) < d$

Yes

No

K_i

Figure 4.10.: Scheme of thermodynamic constant(s) calculation procedure
As example of the mathematical model for a given chemical model is given as follows for
the model 10 which was found to best fit the experimental data. The relevant relations
are for the mass action (i.e. equilibrium expressions):

$$K_d = \frac{[H_2AsS_3^-] \gamma_{H_2AsS_3^-} [H^+] \gamma_{H^+}}{[H_3AsS_3^0] \gamma_{H_3AsS_3^0}} \quad (4.1)$$

$$K_s = \frac{[HS^-] \gamma_{HS^-} [H^+] \gamma_{H^+}}{[H_2S(aq)] \gamma_{H_2S}} \quad (4.2)$$

for mass balance:

$$[As] = [H_3AsS_3^0] + [H_2AsS_3^-] \quad (4.3)$$

$$[S] = [H_3AsS_3^0] + [H_2AsS_3^-] + [H_2S(aq)] + [HS^-] \quad (4.4)$$

for charge balance:

$$[H^+] + [Na^+] = [OH^-] + [H_2AsS_3^-] + [HS^-] \quad (4.5)$$

and additionally, for NaOH association defined by equation:

$$K_{ass} = \frac{[NaOH] \gamma_{NaOH}}{[Na^+] \gamma_{Na^+} [OH^-] \gamma_{OH^-}} \quad (4.6)$$

for water ionisation equation:

$$K_w = [H^+] \gamma_{H^+} [OH^-] \gamma_{OH^-} \quad (4.7)$$

where $K_d$ is thioarsenous acid ionisation constant; $K_s$ is ionisation constant of hydrogen
sulphide; $K_{ass}$ is the association constant of sodium hydroxide; $K_w$ is ion product constant
of water; the terms in square brackets are molar concentrations of species in $mol/dm^3$; $\gamma$
is the relevant activity coefficient. Activity coefficients were calculated using an extended
Debye-Hückel equation of the form (Robinson and Stokes, 1968), shown in the equation
(3.12).

The chemical models listed in Table 4.2 in addition to the thioarsenite formation and
ionisation reactions include other chemical reactions: the models 1, 5, 6, 7, 8, 9 include
ionisation of water, hydrogen sulphide and arsenous acid, the reaction (2.2); the chemical
Table 4.2.: Nonlinear least squares fits for selected speciation models to the data at 22°C and 1 bar.

<table>
<thead>
<tr>
<th>model</th>
<th>species</th>
<th>reaction</th>
<th>logK</th>
<th>ε</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>HAsOS⁺, HAsS₂⁻</td>
<td>HAsO₂ + H₂S(aq) ⇌ HAsOS + H₂O(l)</td>
<td>no converg.</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HAsOS + H₂S(aq) ⇌ HAsS₂ + H₂O(l)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>As(HS)⁺⁺, As(HS)⁺⁺⁺</td>
<td>As³⁺ + HS⁻ ⇌ As(HS)⁺⁺</td>
<td>no converg.</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>As(HS)⁺⁺ + HS⁻ ⇌ As(HS)⁺⁺⁺</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>As(HS)⁺⁺⁺, As(HS)⁺⁺⁺⁺</td>
<td>As³⁺ + 2HS⁻ ⇌ As(HS)⁺⁺⁺</td>
<td>-9.11 unrealistic*</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>As(HS)⁺⁺⁺ + HS⁻ ⇌ As(HS)⁺⁺⁺⁺</td>
<td>19.53</td>
<td>&quot;</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>HAsS₂⁺, H₂AsS₄⁻</td>
<td>HAsS₂ + HS⁻ ⇌ H₂AsS₄⁻</td>
<td>-8.8 unrealistic*</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>H₃AsS₃⁺, H₂AsS₄⁻</td>
<td>HAsO₂ + 3H₂S(aq) ⇌ H₃AsS₃ + 2H₂O(l)</td>
<td>no converg.</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H₃AsS₃ ⇌ H₂AsS₄⁻ + H⁺</td>
<td>&quot;</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>H₂AsS₄⁻, HAsS₂⁺⁺⁺⁺</td>
<td>HAsO₂ + 3H₂S(aq) ⇌ H₂AsS₄⁺⁺⁺⁺ + 2H₂O(l) + H⁺</td>
<td>no converg.</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H₂AsS₄⁺⁺⁺⁺ ⇌ HAsS₂⁺⁺⁺⁺ + H⁺</td>
<td>&quot;</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>HAsS₂⁺⁺⁺⁺, AsS₃⁻⁻</td>
<td>HAsO₂ + 3H₂S(aq) ⇌ HAsS₂⁺⁺⁺⁺ + 2H₂O(l) + 2H⁺</td>
<td>no converg.</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HAsS₂⁺⁺⁺⁺ ⇌ AsS₃⁻⁻ + H⁺</td>
<td>&quot;</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>HAsS₂⁺⁺⁺⁺, AsS₃⁻⁻</td>
<td>HAsO₂ + 2H₂S(aq) ⇌ HAsS₂ + 2H₂O(l)</td>
<td>22.64 unrealistic*</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HAsS ⇌ HAsS₂⁻ + H⁺</td>
<td>-7.49</td>
<td>&quot;</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>H₂As₂S₄⁺⁺⁺⁺, H₂As₂S₄⁺⁺⁺⁺⁺</td>
<td>2HAsO₂ + 4H₂S(aq) ⇌ H₂As₂S₄⁺⁺⁺⁺⁺ + 4H₂O(l)</td>
<td>21.04 unrealistic*</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H₂As₂S₄⁺⁺⁺⁺⁺ ⇌ H₂As₂S₄⁺⁺⁺⁺⁺ + H⁺</td>
<td>-9.33</td>
<td>&quot;</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>H₃AsS₃⁺⁺⁺⁺, H₂AsS₄⁻⁻</td>
<td>H₃AsS₃ ⇌ H₂AsS₄⁻⁻ + H⁺</td>
<td>-11.14 realistic 0.0001</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>11</td>
<td>AsS₃⁻⁻, H₂AsS₄⁻⁻</td>
<td>AsS₃⁻⁻ + HS⁻ ⇌ H₂AsS₄⁻⁻</td>
<td>1.46 realistic 0.0006</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

F is the optimisation objective function value; ε is the molar absorptivity of the relevant thioarsenite species; the asterisk, *, indicates that the computed molar absorptivities have no physical meaning.

Models 2, 3, 4, 10 do not include arsenous acid ionisation, but include ionisation of water and hydrogen sulphide; the chemical model 11 includes only the ionisation of water. The results of fits using above models are listed in a Table 4.2. As indicated in bold font, the fit assuming the model 10 gave the lowest value of F, where F is the optimisation objective function value, defined by,

\[ F = \sum_i \sum_k (A_{ik}^{obs} - A_{ik}^{calc})^2. \]
The evaluation of the chemical model which best fitted the ultraviolet spectroscopic data was based on a number of criteria, which included,

1) convergence criteria: did the optimisation converge to an interior (global) minimum?
2) molar absorptivity criteria: are the calculated molar absorptivities physically possible and meaningful?
3) goodness of fit criteria: which model has the lowest optimisation objective function value?

Based on these criteria, the acceptance/rejection of a given model was considered using a procedure summarised briefly in Figure 4.11. The results obtained for different models (Table 4.2) demonstrate that models 1, 2, 5, 6 and 7 do not converge to a global optimum and do not reasonably describe the observed data. The models clearly fail to account for the measured spectra. In some cases, the optimisation procedure is capable
of finding a global minimum but the resulting molar absorptivities are unrealistically large (e.g. $\geq 10^{19}$), as with models 3, 4, 8 and 9 (Figure 4.12). Such large values for molar absorptivities have never been measured or computed and are considered to be a mathematical artefact with no physical meaning. In case of a model 9, for example, the values of $\varepsilon$ for $HAs_2S_4^-$ were ridiculously large whereas the corresponding values of $\varepsilon$ for $H_2As_2S_4$ were miniscule. Computations that converged to a global minimum and yielded meaningful molar absorptivities, fulfilled the criteria to be considered as the "true" model that explains the data, as is the case for models 10 and 11. The model (i.e. model 10) with the lowest objective function value, $F$, was then chosen as the one which best fitted the observed spectra.

Considering the the above mentioned decision criteria, only models 10 and 11 are considered to be chemically and mathematically meaningful. Since the optimised objective function value of model 10 is six times smaller than that for model 11, model 10 was considered to most reliably account for the measured spectra.
4.3.2. Thioarsenous acid ionisation

Figure 4.13 shows the molar absorptivities, $\varepsilon$, of $H_3AsS_3^0$ and $H_2AsS_3^-$ at 22°C and 1 bar. Both species absorb in the ultraviolet region from 280 to 380 nm. The band maxima occur at vacuum ultraviolet wavelengths (i.e. at $\lambda < 280$ nm) and were not determined in this study.

![Figure 4.13: Molar absorptivities, $\varepsilon$, of $H_3AsS_3^0$ and $H_2AsS_3^-$ at 22°C and 1 bar](image)

Figure 4.14 shows an example of a deconvoluted spectrum at 22°C of arsenic containing solution. And Figure 4.15 shows a comparison between measured and calculated spectra of the thioarsenous acid species at 22°C and illustrates the excellent agreement between them.
CHAPTER 4. THIOARSENNITE SPECIES

4.3. RESULTS

Figure 4.14.: Deconvoluted spectrum for a solution having $As = 6.6 \times 10^{-4} \text{mol/dm}^3$, $S = 2.42 \times 10^{-3} \text{mol/dm}^3$ and $NaOH = 2.572 \times 10^{-2} \text{mol/dm}^3$

Figure 4.15.: Experimentally measured and calculated thioarsenous acid spectra for solutions with the sulphur concentrations four times greater than that of arsenic at $22^\circ C$ and 1 bar. Solutions compositions are given in Table B.12
4.3. RESULTS

CHAPTER 4. THIOARSENNITE SPECIES

4.3.3. Ab initio calculations

The ionisation process of thioarsenous acid, (i.e. absolute pK value), in aqueous solution can also be predicted using ab initio calculations using approach similar to that of da Silva et al. (1999). An additional aim was to obtain information pertaining to thioarsenous acid structure. The gas phase deprotonation of thioarsenous acid may be defined by the equilibrium:

\[ H_3\text{AsS}_3(gas) \rightleftharpoons H^+(gas) + H_2\text{AsS}_3^-(gas) \] (4.8)

The equilibrium ionisation constant for reaction 4.8, \( K_a \), is related to the standard Gibbs free energy through the relationship

\[ \Delta G^0 = -2.303RT \log K_a \] (4.9)

Since \( \Delta G^0 \) is a state property, it is determined by the initial and final state of the system and is independent of the path connecting them. Thus, we can propose a series of intermediate steps thermodynamic for the whole process. The following thermodynamic cycle can be created:

\[
\begin{align*}
H_3\text{AsS}_3(gas) & \xrightarrow{\Delta G^0(gas)} H^+(gas) + H_2\text{AsS}_3^-(gas) \\
\downarrow & \downarrow & \downarrow \\
H_3\text{AsS}_3(soln) & \xrightarrow{\Delta G^0(soln)} H^+(soln) + H_2\text{AsS}_3^-(soln)
\end{align*}
\]

Gibbs free energy for the reaction 4.8 in solution is given by,

\[ \Delta G^0(soln) = -\Delta G^0_{solv}(H_3\text{AsS}_3) - G^0(gas)(H_3\text{AsS}_3) + \Delta G^0_{solv}(H_2\text{AsS}_3) + \Delta G^0(gas)(H_2\text{AsS}_3) + \Delta G^0_{solv}(H^+) \] (4.10)

The Gibbs free energies of formation for thioarsenite species were calculated in this study using ab initio molecular orbital calculations. These calculations were carried out using G2 model theory with the GAUSSIAN 98 suite of programs. The geometry of each molecule was optimised with MP2 (full)/6-311 G(d) level of theory. Solvation energies
Table 4.3.: Ab initio calculations of ionisation constant of As – S species

<table>
<thead>
<tr>
<th>protonated species</th>
<th>reaction number</th>
<th>pK</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_3\text{AsS}_3^0$</td>
<td>(4.11)</td>
<td>9.46</td>
</tr>
<tr>
<td>$\text{HAsS}_2^0$</td>
<td>(4.12)</td>
<td>1.16</td>
</tr>
<tr>
<td>$\text{HAsO}_2^0$</td>
<td>(4.13)</td>
<td>7.19</td>
</tr>
<tr>
<td>$\text{H}_3\text{AsO}_2^0$</td>
<td>(4.14)</td>
<td>15.02</td>
</tr>
</tbody>
</table>

were estimated using PCM calculations for each molecule with rigid geometries obtained by MP2 (full)/6-311 G(d) level of theory. The Gibbs free energy of formation for $H^+$ is equal to zero and solvation energy (experimentally determined) for $H^+$ was taken from Tissandier et al. (1998). The following reactions and species were considered:

$$H_3\text{AsS}_3^0 \rightleftharpoons H^+ + H_2\text{AsS}_3^- \quad (4.11)$$
$$\text{HAsS}_2^0 \rightleftharpoons H^+ + \text{AsS}_2^- \quad (4.12)$$
$$\text{HAsO}_2^0 \rightleftharpoons H^+ + \text{AsOS}^- \quad (4.13)$$
$$\text{H}_3\text{AsO}_2^0 \rightleftharpoons H^+ + H_2\text{AsO}_2^- \quad (4.14)$$

The calculated $pK$ at $22^\circ C$ for the reaction 4.11 is 9.46 (Table 4.3) which is consistent with the experimentally determined value of $pK = 11.14$ (Table 4.2), given the appreciable uncertainties in the *ab initio* calculated values. The first deprotonation step of the other hypothetical arsenous acid species are many orders of magnitude discrepant from the experimentally determined value for $H_3\text{AsS}_3^0$. Thus, the *ab initio* calculations support $H_3\text{AsS}_3$ form of thioarsenous acid. The optimised geometry of $H_3\text{AsS}_3$ is shown in Figure 4.16.
4.4. CONCLUSIONS

4.4. Discussion and Conclusions

Recent studies by Wilkin et al. (2003) and Wood et al. (2002) emphasized the complexity of the possible forms of thioarsenite species. Wilkin et al. (2003) suggests the speciation of thioarsenite based on a stepwise formation. Wood et al. (2002) did not determine the stoichiometry of observed species. The comparison between obtained results by Wilkin et al. (2003) and present study is difficult due to the different conditions of experiments and chosen models/species (consequently one can not compare the stability constants). We have observed only two distinct absorbing species in basic pH range. In acidic and neutral solutions, the spectrophotometric data did not show the presence of any of thioarsenite species except dilute colloidal dispersions, which are the dominant forms responsible for $As(III) - H_2S$ interaction in near neutral and acidic solutions at the arsenic concentrations of our study (i.e. $As=1.1x10^{-4}mol/dm^3$ and $pH=5.70-9.62$). The oxidation of the prepared solutions due to contact with eluent probably occurred in the study of Wilkin et al. (2003) which accounts for the presence of $As(V)$ in their solutions. It is not clear how stoichiometries/models were established and hence, we are unable to discuss their results in more detail. Helz et al. (1995) demonstrated also existence
of thioarsenous acid using Exafs measurements (\( \sim 0.02 \) and \( \sim 0.08 \) m) and in this case the unambiguous presence of three sulphurs in the first shell was detected, suggesting an \( \text{AsS}_3 \) moiety. There was no evidence for oxygen in a first shell and also no significant evidence for \( \text{As-As} \) interactions in a second shell. Thus, it appears from both our results and those of Helz et al. (1995) and Prasad (1987) that arsenic is coordinated to three sulphurs as thioarseous acid species, \( \text{H}_3\text{AsS}_3 \), \( \text{H}_2\text{AsS}_3^- \) and probably \( \text{HAsS}_3^{2-} \) in aqueous media over a wide range of total dissolved arsenic concentrations at \( pH \geq 9 \).

We were able to demonstrate the presence of two arsenite species and stability constant for the reaction between them. In our solutions, the reduced sulphur concentrations was four times greater that that of arsenic and hence all arsenous acid species reacted to thioarsenite.

The thioarsenious species, \( \text{H}_3\text{AsS}_3^0 \) and \( \text{H}_2\text{AsS}_3^- \), were found to be the dominant \( \text{As}(\text{III}) \) sulphide species in dilute aqueous solutions at ambient temperature and pressure. The ionisation constant, \( K_1 \), for the thioarsenious acid was obtained, and (i.e. \( pK_1 = 11.14 \pm 0.04 \)).

In low sulphur hydrothermal fluids in the Earth’s crust, the simple arsenious acid, \( \text{HAsO}_2^0 \) and \( \text{AsO}_2^- \), species will be the dominant arsenic species. However, in sulphide-containing fluids, the fully protonated \( \text{H}_3\text{AsS}_3 \) species will be present at \( pH \leq 9 \). In acidic to neutral solutions, the addition of \( \text{H}_2\text{S} \) to \( \text{As}(\text{III}) \) solutions may also lead to the formation of \( \text{As}_2\text{S}_3(\text{solid}) \) which may be transported as a dispersed sol. At elevated temperatures, however, little is currently known of the stability and deprotonation of thioarsenite species. This will be subject of our continuing studies.
4.4. CONCLUSIONS

CHAPTER 4. THIOARSENITE SPECIES
5. Conclusions

The study presents the results on the experimental determination of the ionisation constants of arsenous and antimonous acids from 25 to 300°C at the equilibrium saturated vapour pressure. In addition, the stoichiometry of the arsenous acid was evaluated using electrospray mass spectrometric measurements and ab initio calculations and concluded to be $H_3AsO_2$. The speciation of thioarsenite species in aqueous solutions within the wide pH range at 22°C was also studied spectrophotometrically. The stoichiometry of thioarsenous acid was found to be $H_3AsS_3$ and the ionisation (deprotonation) constant was $pK_1=11.14$.

In natural low temperature waters at $pH \leq 9$ and low oxidation potential, the dominant As(III) species present will be the unionised arsenous acid, $HAsO_2$. At $pH \geq 9$, the deprotonated $AsO_2^-$ species will also be present. If reduced sulphur (i.e. $H_2S/HS^-$) is present, then thioarsenous acid, $H_3AsS_3$, will form. $pK_1$ of thioarsenous acid is 11.14 and hence, the deprotonated $H_2AsS_3^-$ will not be important in natural waters having $pH \leq 10$. In low sulphur geothermal fluids, the arsenous acid species, $HAsO_2$, will predominate in fluids having $pH \leq 6$, however, for high temperature fluids (e.g. at 300°C), the $AsO_2^-$ species will be more important at $pH \geq 6$ with $HAsO_2$ and $AsO_2^-$ being in approximately equal concentrations at $pH=7.2$. In reduced sulphur containing geothermal fluids, the fully protonated thioarsenous acid, $H_3AsS_3$, will form over a wide range of $pH$ values where $pH \leq 10$, however there are no reliable data available on the stability or deproto-
nation of this species under hydrothermal conditions.

Unionised antimonous acid, $H_3SbO_3$, will predominate in natural, low temperatures waters at $pH \leq 10$ whereas at $pH \geq 10$, $H_3SbO_3$ starts to become important. In hydrothermal fluids (e.g. at 300°C), $H_3SbO_3$ predominates at $pH \leq 9$ but significant $H_2SbO_3^-$ occurs at $pH \geq 8$. Of particular interest in the modelling of the transport and deposition of antimony in high sulphidation, epithermal depositing systems in which luzonite-enargite-famatinite phases occur, is the possible role of $H_4SbO_3^+$ which is stable at $1 \leq pH \leq 3$. The stability of the thioantimonite species at elevated temperatures and pressures is currently poorly known.

Finally, we have used experimental approaches developed in this project to generate a precise and accurate set of deprotonation constants for the organic indicator, p-nitrophenol from 25 to 300°C at saturated vapour pressures.

More fundamental thermodynamic data on the stability of both thioarsenite and thioantimonite species in aqueous media from ambient to hydrothermal conditions are required before the transport and deposition chemistry of these two elements can be modelled in natural systems at extreme conditions. The data in this thesis provide a first step in this direction.
A. P-nitrophenol ionisation from 25 to 300°C and saturated vapour pressures

A.1. Introduction

P-nitrophenol is widely used in chemistry and biology as a pH indicator. It belongs to the phenol group and is characterised by an aromatic ring with hydroxyl group attached. P-nitrophenol is obtained by substitution the nitro group $NO_2$ on the aromatic ring (Figure A.1). P-nitrophenol is an acidic phenol because of stabilisation of the phenolate by the nitro group. The ionisation of p-nitrophenol has been at well studied 25°C (Bates and Schwarzenbach, 1954; Allen et al., 1962) with the generally accepted value for the ionisation (deprotonation) constant of $pK=7.15$ at 25°C. The ionisation reaction for p-nitrophenol can be written as follows:

$$C_6H_4OHN0_2 \rightleftharpoons C_6H_4O\text{NO}^-_2 + H^+ \quad (A.1)$$

There are studies of p-nitrophenol ionisation which have been carried out from ambient to high temperatures. Allen et al. (1962) and Pavlyuk and Smolyakov (1974) studied p-nitrophenol spectrophotometrically up to 60 and 175°C respectively. Over this temperature range, their data are in good agreement. However, the more recent values of $pK$ reported by Shin et al. (1997) are in apparent disagreement with the extrapolated data of Allen et al. (1962) and Pavlyuk and Smolyakov (1974) at temperatures $\geq 125$°C.
A.1. INTRODUCTION

APPENDIX A. P-NITROPHENOL IONISATION

Very few organic pH indicators have been adequately characterised in aqueous media at elevated temperatures and pressures. Thermodynamic data pertaining to the deprotonation of such "indicator" molecules under extreme conditions is necessary to study (spectrophotometrically) the hydrolytic behavior of metal cations as well as pH dependent heterogeneous reaction kinetics in hydrothermal systems. For example, the equilibrium and kinetic aspects of silicate mineral solubilities and hydrolysis could in principle be studied in situ by spectrophotometrically monitoring the pH of the hydrothermal solution phase with stable, organic pH indicators. Unfortunately, the hydrolytic equilibria of most organic indicator molecules at high temperatures and pressures remain essentially unstudied.

The aim of this study has therefore been to provide a reliable set of experimentally based thermodynamic data which define the ionisation of p-nitrophenol from 25 to 300°C at saturated vapour pressures. In addition, dilute solutions of p-nitrophenol and its deprotonated equivalent exhibit well defined spectra throughout the visible and ultraviolet region and comprise a simple, ideal system with which to test and confirm the validity of our spectrophotometric methodology and mathematical data treatment.
A.2. Methods

Spectra were recorded in the range from 190 to 700 nm using a Cary 5 Spectrophotometer which was "in line" with a computer interfaced, automatic titrator and HPLC pump. The system operated in a flow through mode and employed a sealed quartz glass cuvette at lower temperatures (i.e. 25, 50, 75 and 90°C) and a titanium/palladium alloy cell for measurements at higher temperatures (i.e. 100, 150, 200, 250 and 300°C). Uncertainties at lower temperature were less than ±0.1°C whereas the temperatures of the higher regime were ±1°C of the stated value.

The p-nitrophenol solutions studied were in the range from 5x10^-5 to 1.2x10^-4 mol/dm^3. The solutions were prepared from triple distilled (in quartz glass) water from which atmospheric oxygen had been removed by boiling under vacuum in an ultrasonic bath. The titre reagent solutions (i.e. HCl and NaOH) were similarly de-gassed. All handling and transfer of the solutions was carried out under an atmosphere of oxygen-free argon (grade 6.0) which had been further de-oxygenated by being passed through a 50 cm long column of elemental copper filings at 400°C.

A.2.1. Spectra Interpretation

The interpretation of the spectra has already been discussed in some detail in previous chapters. The data treatment may be summarised as follows:

1. Correction of spectra for background (water and cuvette/windows absorbance); and at temperatures ≥100°C a correction for density was done. Density corrections are carried out because all solution concentrations were obtained on molar scale at room temperature (the Beer-Lambert law: absorbance is proportional to the concentration, which is in molar units, i.e. number of moles per volume unit). Due to the thermal expansion of liquid, the density of liquid decreases and consequently the total concentration of solution must therefore be corrected for volume change.
Density data for corrections at high temperatures were taken as water density from Haar et al. (1984).

2. Determination of the number of absorbing species (i.e. the rank of the absorbance matrix, $A^{obs}(ixk)$ with “i” number of solutions and “k” number of measured wavelength points). The rank of absorbance matrix created from p-nitrophenol-containing solutions spectra is shown in Figure A.2. Over a wide range of tolerance, the rank is two for temperatures 25 and 300°C (also for other temperatures within the temperature range from 25 to 300°C).

3. Development of realistic chemical models (in the case of an unknown chemical system, a number of chemical models have to be created); the chemical model consists of all chemical reactions occurring (or significant) in the solutions and the definition of the species which absorb within the system. The model has to be consistent with the number of absorbing species and have to deal with all absorbing species; ideally, the number of existing species should be equal to the number of absorbing species.
APPENDIX A. P-NITROPHENOL IONISATION

A.2. METHODS

1. Developing of a mathematical model from a chemical model. The mathematical model consists of mass action, mass balance and charge balance equations. It is important to mention here that corrections for activity coefficients are included in the mathematical model and were made using extended Debye-Hückel equation (3.12) (Robinson and Stokes, 1968) though in fact they are negligible; it should be noted that the studied ionic strength most of all solutions studied was always $\leq 0.001$.

2. Verification of relationships between concentrations of existing species in prepared aqueous solutions, using a computational program (already existing or newly created), based on the developed mathematical model (see step (4)).

3. Calculation of molar absorptivities: calculation of pseudo molar absorptivities from an assumed equilibrium constant (i.e. an "initial guess") using a non-linear, constrained, (non-negative) least squares method in optimization; for example, on Figure A.3, the molar absorptivities obtained without constrained optimisation at the wavelength interval 375-475 nm are negative. Equilibrium constants obtained with-
A.2. METHODS

APPENDIX A. P-NITROPHENOL IONISATION

out constrained optimisation have no physical meaning.

7. Determination of the objective function, i.e., a function of the difference between calculated (molar absorptivities multiplied by concentrations at assumed equilibrium constant (i.e. "initial guess") and observed spectra, i.e. the objective function value:

\[ F = \sum_i \sum_k (A_{ik}^{\text{obs}} - A_{ik}^{\text{calc}})^2 \]

8. Determination of the stability constant: iterative calculation to obtain the constant, i.e. a second optimization, constraining objective function value to the minimum.

9. Determination of true molar absorptivities by constrained optimisation (see step (6)), using the resulting equilibrium constant.

10. Calculation of uncertainty using the Gaussian error propagation rule:

\[
\sigma_K = \sqrt{\left(\frac{\partial K}{\partial [pN]} \sigma_{[pN]}\right)^2 + \left(\frac{\partial K}{\partial [Na]} \sigma_{[Na]}\right)^2 + \left(\frac{\partial K}{\partial [Cl]} \sigma_{[Cl]}\right)^2 + \left(\frac{\partial K}{\partial K_w} \sigma_{K_w}\right)^2} \quad (A.2)
\]

where \( \frac{\partial K}{\partial [pN]} \), \( \frac{\partial K}{\partial [Na]} \), \( \frac{\partial K}{\partial [Cl]} \), \( \frac{\partial K}{\partial K_w} \) are the partial derivatives of the equilibrium constant with respect to each given parameter, i.e. total p-nitrophenol concentration, total sodium concentration, total hydrochloric acid concentration and the ionisation constant of water; \( \sigma_{[pN]} \), \( \sigma_{[Na]} \), \( \sigma_{[Cl]} \), \( \sigma_{K_w} \) are standard deviations of p-nitrophenol total concentration, sodium total concentration, hydrochloric acid total concentration and the dissociation constant of water.
A.3. Results and Discussions

Spectra of p-nitrophenol solutions at 25°C are shown in Figure A.4. Compositions of the solutions used to obtain these spectra are listed in Table B.14. Compositions of solutions for which spectra were measured at 50, 75, 90, 100-300°C are given in the Tables B.15, B.16, B.17 and B.18, respectively. Spectra obtained at 300°C are shown in Figure A.5 and exhibit a wide absorbance interval and high intensities. At 25°C, details of the spectra within the wavelength interval between 200 and 360 nm are discussed below. Spectra from solutions with pH=4 to 5.5 show a major absorption band for wavelength interval 260-340 nm with the maximum absorbance at 316 nm at 25°C, whereas it occurs at 300 nm at 300°C. With increasing pH, absorbance within the interval 270-340 nm decreases, and starts increase within the interval 350-500 nm.

Figure A.4.: Spectra (background corrected) of p-nitrophenol solutions of varying pH with p-nitrophenol concentration $7.2 \times 10^{-5} \text{ mol/dm}^3$ at 25°C
The rank analysis of the absorbance matrices for all measured temperatures is two (Figure A.2), indicating the presence of two absorbing species. There is also the possibility to check for the existence of two absorbing species using a graphical method. An isosbestic points are those at which all the spectra have the same absorbance. The occurrence of one isosbestic point indicates a good probability of having two absorbing species, and the occurrence of more than one isosbestic point is extremely strong evidence for two species. In our system of spectra (see spectra at 25°C, on the Figure A.4), five isosbestic points occur at 209, 215, 231, 268, 347 nm, confirming the existence of two absorbing species. The spectra at 300°C also exhibit a number of isosbestic points (Figure A.5), although they are not as clearly defined due to different total concentrations of p-nitrophenol in solutions.
The spectra collected within the pH=4 to 5 range were identical at 25°C as well as at other temperatures. This is because only the protonated (undissociated) p-nitrophenol is present in this pH range at all temperatures studied and its concentration remains essentially constant. The second absorbing species, the deprotonated p-nitrophenol ion becomes important as the pH approaches the value of the pK (i.e. pH increases) and predominates at the highest pH's of the measurements.

With increasing temperature, the relation between these two absorbing species changes as illustrated in Figure A.6. At low temperature and at pH=9.61, there is only one absorbing species, the deprotonated p-nitrophenol ion. With increasing temperature to 300°C, the pH decreases to 7.14 and the bands characteristic for unprotonated p-nitrophenol start to appear. In addition, the absorbance strongly decreases with temperature.
Figure A.7: The molar absorptivities of unionised (fully protonated) p-nitrophenol from 25 to 300°C.

Figure A.8: The molar absorptivities of deprotonated p-nitrophenol from 25 to 300°C.

Figure A.7 and Figure A.8 illustrate the molar absorptivities of the fully protonated and ionised (deprotonated) p-nitrophenol species from 25 to 300°C at saturated water vapour pressure. With increasing temperature, the absorption bands of these two species behave differently.
Figure A.9.: The temperature dependence of the “blue shifted” absorption maximum of unionised p-nitrophenol species (i.e. protonated)

Figure A.10.: The temperature dependence of the “red shifted” absorption maximum of deprotonated p-nitrophenol ion

These shifts are shown in Figure A.9 and A.10. The absorption band for the associated p-nitrophenol molecule exhibits a blue shift with increasing temperature whereas the band for the anionic form undergoes a red shift.
Table A.1: The ionisation constant of p-nitrophenol from 25 to 300°C at equilibrium saturated vapour pressures, where uncertainty is 2σ. The values reported here are related to the hypothetical 1 molal standard state

<table>
<thead>
<tr>
<th>t / °C</th>
<th>pK_a</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>7.154 ± 0.005</td>
</tr>
<tr>
<td>50</td>
<td>6.96 ± 0.01</td>
</tr>
<tr>
<td>75</td>
<td>6.75 ± 0.01</td>
</tr>
<tr>
<td>90</td>
<td>6.68 ± 0.01</td>
</tr>
<tr>
<td>100</td>
<td>6.65 ± 0.27</td>
</tr>
<tr>
<td>150</td>
<td>6.59 ± 0.12</td>
</tr>
<tr>
<td>200</td>
<td>6.60 ± 0.03</td>
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<tr>
<td>250</td>
<td>6.82 ± 0.03</td>
</tr>
<tr>
<td>300</td>
<td>7.24 ± 0.04</td>
</tr>
</tbody>
</table>

The values of the equilibrium constants for the reaction A.1 obtained by the non-linear non-negative least squares method are summarised in Table A.1 and in Figure A.11. In this figure, a parabolic trend of decreasing pK\textsubscript{1} with increasing temperature to 300°C is observed. This behavior is characteristic of weak acids and has also been observed for formic, acetic, phosphoric and \textit{H}_2\textit{S} acids.

The values of ionisation constant as a function of temperature were fitted to a form of the equation,

\[ R \ln K_1 = a + a/T + c \ln T + cT + eT^2 \quad (A.3) \]

such that \( a = 1510.8; \ b = -38464; \ c = -278.19; \ d = 0.72581; \ e = -0.00033326. \) The five-term form of this equation was found to best fit the data. The ratio of the regression sum of squares to the total sum of squares, the \( R \)-square value, \( (R^2) \), is equal to 0.99.
A.4. Conclusions

The value of $pK=7.154\pm0.005$ is in excellent agreement with the generally accepted "best values" for the $pK$ reported in the literature (e.g. Bates and Schwarzenbach, 1954; Allen et al., 1962; Pavlyuk and Smolyakov, 1974; Ege, 1994). However, the value of $pK=7.24\pm0.04$ at 300°C (this study) differs from the given temperature dependences from data of Pavlyuk and Smolyakov (1974) and Shin et al. (1997) by up to 0.5 log unit at 300°C. The data of Allen et al. (1962), extend from 0 to 60°C are in good agreement with our data.

In addition, the p-nitrophenol ionisation constant has demonstrated that experimental methods used in this study are reliable and values obtained at ambient temperature in agreement with literature and as well provided a new data up 300°C. Figure A.12
Figure A.12.: Experimentally obtained and calculated spectra of p-nitrophenol solutions at 90°C; concentration of p-nitrophenol is $7.68 \times 10^{-5} \text{mol/dm}^3$.

This illustrates the goodness of fit of the data obtained from a range of experiments at 90°C.

It has to be mentioned here that the spectrophotometric determination of pH at high temperature with p-nitrophenol indicator is very promising, provided that the indicator species do not participate in side reactions with the components of the reaction being studied.
B. Analytical data

The following section presents the compositions of solutions for which spectra were measured at different temperatures (up to $300^\circ$), and were used in this study.
Table B.1.: Compositions of experimental solutions used for arsenous acid ionisation constant evaluation from 25 to 300°C

<table>
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<tr>
<th>solution</th>
<th>total $\text{As}$ concentrations, $\text{mol/dm}^3$</th>
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</tr>
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</tr>
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<tr>
<td>3</td>
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APPENDIX B. ANALYTICAL DATA

Table B.2.: Compositions of 60 experimental solutions used for antimonous acid protonation validation at 22°C

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</table>

$Sb$ is a total antimony concentration in \textit{mol} dm$^{-3}$; $ClO_4$ is a total perchlorate concentration in \textit{mol} dm$^{-3}$; $Na$ is a total sodium concentration in \textit{mol} dm$^{-3}$; pH is calculated from balance equations.
Table B.3.: Compositions of 62 experimental solutions used for antimonous acid protonation validation at 50°C

<table>
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<th>$Na$</th>
<th>solution</th>
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</tr>
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<td>0.1416</td>
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</tr>
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<td>0.1411</td>
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<td>0.07883</td>
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<td>0.08028</td>
</tr>
<tr>
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<td>0.1390</td>
<td>0.08172</td>
</tr>
<tr>
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<td>0.1385</td>
<td>0.08315</td>
</tr>
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<td>0.03509</td>
<td>50</td>
<td>0.0001314</td>
<td>0.1380</td>
<td>0.08457</td>
</tr>
<tr>
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<td>0.1552</td>
<td>0.03689</td>
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<td>0.0001309</td>
<td>0.1374</td>
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</tr>
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<td>21</td>
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<td>0.1369</td>
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<td>0.1533</td>
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<td>0.0001295</td>
<td>0.1359</td>
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<tr>
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<td>0.04905</td>
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<td>0.10720</td>
</tr>
<tr>
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<td>0.0001431</td>
<td>0.1502</td>
<td>0.05073</td>
<td>59</td>
<td>0.0001199</td>
<td>0.1259</td>
<td>0.11810</td>
</tr>
<tr>
<td>29</td>
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<td>0.1496</td>
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<td>0.1242</td>
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<tr>
<td>31</td>
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<td>0.1484</td>
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<td>62</td>
<td>0.0001179</td>
<td>0.1238</td>
<td>0.12390</td>
</tr>
</tbody>
</table>

$Sb$ is a total antimony concentration in moles/dm³; $ClO_4$ is a total perchlorate concentration in moles/dm³; $Na$ is a total sodium concentration in moles/dm³.
## APPENDIX B. ANALYTICAL DATA

Table B.4.: Compositions of 44 experimental solutions used for antimonous acid protonation validation at 75°C

<table>
<thead>
<tr>
<th>solution</th>
<th>Sb</th>
<th>ClO₄</th>
<th>Na</th>
<th>solution</th>
<th>Sb</th>
<th>ClO₄</th>
<th>Na</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.1677</td>
<td>-</td>
<td>23</td>
<td>0.000144</td>
<td>0.1512</td>
<td>0.04603</td>
</tr>
<tr>
<td>2</td>
<td>0.000159</td>
<td>0.1669</td>
<td>0.00231</td>
<td>24</td>
<td>0.000143</td>
<td>0.1505</td>
<td>0.04791</td>
</tr>
<tr>
<td>3</td>
<td>0.000158</td>
<td>0.1661</td>
<td>0.00459</td>
<td>25</td>
<td>0.000143</td>
<td>0.1498</td>
<td>0.04977</td>
</tr>
<tr>
<td>4</td>
<td>0.000157</td>
<td>0.1653</td>
<td>0.00686</td>
<td>26</td>
<td>0.000142</td>
<td>0.1492</td>
<td>0.05162</td>
</tr>
<tr>
<td>5</td>
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<td>0.1645</td>
<td>0.00911</td>
<td>27</td>
<td>0.000142</td>
<td>0.1485</td>
<td>0.05344</td>
</tr>
<tr>
<td>6</td>
<td>0.000156</td>
<td>0.1637</td>
<td>0.01133</td>
<td>28</td>
<td>0.000141</td>
<td>0.1479</td>
<td>0.05526</td>
</tr>
<tr>
<td>7</td>
<td>0.000155</td>
<td>0.1629</td>
<td>0.01353</td>
<td>29</td>
<td>0.000140</td>
<td>0.1472</td>
<td>0.05705</td>
</tr>
<tr>
<td>8</td>
<td>0.000154</td>
<td>0.1621</td>
<td>0.01570</td>
<td>30</td>
<td>0.000140</td>
<td>0.1466</td>
<td>0.05883</td>
</tr>
<tr>
<td>9</td>
<td>0.000154</td>
<td>0.1613</td>
<td>0.01786</td>
<td>31</td>
<td>0.000139</td>
<td>0.146</td>
<td>0.06060</td>
</tr>
<tr>
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<td>0.02000</td>
<td>32</td>
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<td>0.1453</td>
<td>0.06235</td>
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<td>0.1598</td>
<td>0.02211</td>
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<td>0.000138</td>
<td>0.1447</td>
<td>0.06408</td>
</tr>
<tr>
<td>12</td>
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<td>0.02421</td>
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<td>0.06580</td>
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<td>13</td>
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<td>0.000137</td>
<td>0.1435</td>
<td>0.06751</td>
</tr>
<tr>
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<td>0.02835</td>
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<td>0.1429</td>
<td>0.06920</td>
</tr>
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<td>0.1423</td>
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<tr>
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</tr>
<tr>
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<td>0.000134</td>
<td>0.1411</td>
<td>0.07419</td>
</tr>
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<td>0.1547</td>
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<td>40</td>
<td>0.000134</td>
<td>0.1405</td>
<td>0.07582</td>
</tr>
<tr>
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<td>0.03835</td>
<td>41</td>
<td>0.000129</td>
<td>0.1349</td>
<td>0.09145</td>
</tr>
<tr>
<td>20</td>
<td>0.000146</td>
<td>0.1533</td>
<td>0.04030</td>
<td>42</td>
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<td>0.1297</td>
<td>0.10590</td>
</tr>
<tr>
<td>21</td>
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<td>0.1526</td>
<td>0.04223</td>
<td>43</td>
<td>0.000119</td>
<td>0.1249</td>
<td>0.11920</td>
</tr>
<tr>
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<td>0.1519</td>
<td>0.04414</td>
<td>44</td>
<td>0.000118</td>
<td>0.1239</td>
<td>0.12180</td>
</tr>
</tbody>
</table>

Sb is a total antimony concentration in mol/dm³; ClO₄ is a total perchlorate concentration in mol/dm³; Na is a total sodium concentration in mol/dm³;
APPENDIX B. ANALYTICAL DATA

Table B.5.: Compositions of 8 experimental solutions used for antimonous acid protonation validation from 100 to 300°C

<table>
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<tr>
<th>solution</th>
<th>Sb</th>
<th>ClO₄⁻</th>
</tr>
</thead>
<tbody>
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<td>0.22180</td>
</tr>
<tr>
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<td>0.000083</td>
<td>0.18963</td>
</tr>
<tr>
<td>3</td>
<td>0.000094</td>
<td>0.15424</td>
</tr>
<tr>
<td>4</td>
<td>0.000092</td>
<td>0.10967</td>
</tr>
<tr>
<td>5</td>
<td>0.000087</td>
<td>0.08572</td>
</tr>
<tr>
<td>6</td>
<td>0.000076</td>
<td>0.05326</td>
</tr>
<tr>
<td>7</td>
<td>0.000103</td>
<td>0.04827</td>
</tr>
<tr>
<td>8</td>
<td>0.000083</td>
<td>0.02713</td>
</tr>
</tbody>
</table>

Sb is a total antimony concentration in mol/dm³; ClO₄⁻ is a total perchlorate concentration in mol/dm³;

Table B.6.: Compositions of 6 experimental solutions obtain for calculating molar absorptivities of ClO₄⁻ ion from 25 to 300°C

<table>
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<tr>
<th>solution</th>
<th>ClO₄⁻</th>
</tr>
</thead>
<tbody>
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<tr>
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</tr>
<tr>
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</tr>
<tr>
<td>4</td>
<td>0.1158</td>
</tr>
<tr>
<td>5</td>
<td>0.1661</td>
</tr>
<tr>
<td>6</td>
<td>0.2595</td>
</tr>
</tbody>
</table>

ClO₄⁻ is a total perchlorate concentration in mol/dm³;
Table B.7.: Compositions of experimental solutions used for antimonous acid deprotonation validation at 25°C

<table>
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<th>solution</th>
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<th>$Na$</th>
</tr>
</thead>
<tbody>
<tr>
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</tr>
<tr>
<td>2</td>
<td>0.000089</td>
<td>0.002528</td>
</tr>
<tr>
<td>3</td>
<td>0.000097</td>
<td>0.002570</td>
</tr>
<tr>
<td>4</td>
<td>0.000097</td>
<td>0.002804</td>
</tr>
<tr>
<td>5</td>
<td>0.000097</td>
<td>0.003088</td>
</tr>
<tr>
<td>6</td>
<td>0.000097</td>
<td>0.003972</td>
</tr>
<tr>
<td>7</td>
<td>0.000097</td>
<td>0.005572</td>
</tr>
<tr>
<td>8</td>
<td>0.000097</td>
<td>0.006992</td>
</tr>
</tbody>
</table>

$Sb$ is a total antimony concentration in $mol/dm^3$; $Na$ is a total sodium concentration in $mol/dm^3$;
### Table B.8: Compositions of 21 experimental solutions used for antimonous acid deprotonation validation from 50 to 300°C

<table>
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<th>Sb</th>
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</tr>
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<tr>
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<td>0.000162</td>
</tr>
<tr>
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<td>0.000105</td>
<td>0.000189</td>
</tr>
<tr>
<td>4</td>
<td>0.000096</td>
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<tr>
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<td>0.000138</td>
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</tr>
<tr>
<td>6</td>
<td>0.000094</td>
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</tr>
<tr>
<td>7</td>
<td>0.000144</td>
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</tr>
<tr>
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</tr>
<tr>
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</tr>
<tr>
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</tr>
<tr>
<td>11</td>
<td>0.000120</td>
<td>0.001332</td>
</tr>
<tr>
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<td>0.001513</td>
</tr>
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<tr>
<td>14</td>
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</tr>
<tr>
<td>16</td>
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<td>0.002570</td>
</tr>
<tr>
<td>17</td>
<td>0.000097</td>
<td>0.002804</td>
</tr>
<tr>
<td>18</td>
<td>0.000097</td>
<td>0.003088</td>
</tr>
<tr>
<td>19</td>
<td>0.000097</td>
<td>0.003972</td>
</tr>
<tr>
<td>20</td>
<td>0.000097</td>
<td>0.005572</td>
</tr>
<tr>
<td>21</td>
<td>0.000097</td>
<td>0.006992</td>
</tr>
</tbody>
</table>

*Sb* is a total antimony concentration in *mol/dm³*; *Na* is a total sodium concentration in *mol/dm³*.
Table B.9.: Compositions of four \(H_2S\)-containing experimental solutions at 22°C, spectra which were obtained to check the “syringe” cell, also to calculate the molar absorptivity of \(H_2S\).

<table>
<thead>
<tr>
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<th>(S)</th>
<th>(pH)</th>
</tr>
</thead>
<tbody>
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</tr>
<tr>
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<td>5.39</td>
</tr>
<tr>
<td>3</td>
<td>0.00026</td>
<td>5.30</td>
</tr>
<tr>
<td>4</td>
<td>0.00100</td>
<td>5.00</td>
</tr>
</tbody>
</table>

\(S\) is the total sulphur concentration in \(mol/dm^3\).
APPENDIX B. ANALYTICAL DATA

Table B.10.: Compositions of As(III) sulphide-containing solutions at 22°C, shown in Figure 4.5

<table>
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<tr>
<th>solution</th>
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<th>S</th>
<th>Na</th>
</tr>
</thead>
<tbody>
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<td>-</td>
<td>-</td>
</tr>
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<td>0.00006</td>
</tr>
<tr>
<td>3</td>
<td>0.00012</td>
<td>0.00006</td>
<td>0.00012</td>
</tr>
<tr>
<td>4</td>
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<td>0.00009</td>
<td>0.00018</td>
</tr>
<tr>
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<td>0.00012</td>
<td>0.00024</td>
</tr>
<tr>
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</table>

As is the total arsenic concentration in mol/dm³; S is the total sulphur acid concentration in mol/dm³; Na is the total sodium concentration in mol/dm³;
APPENDIX B. ANALYTICAL DATA

Table B.11.: Compositions of As(III) sulphide-containing experimental solutions of at 22°C, shown in Figure 4.6

<table>
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<th>solution</th>
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<th>Na</th>
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As is the total arsenic concentration in mol/dm³; S is the total sulphur acid concentration in mol/dm³; Na is the total sodium concentration in mol/dm³;
Table B.12.: Compositions of \( \text{As(III)} \) sulphide-containing experimental solutions of at 22°C, shown in Figure 4.7

<table>
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<th>( Na )</th>
</tr>
</thead>
<tbody>
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<td>0.00234</td>
<td>0.03301</td>
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<tr>
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<td>0.04284</td>
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<td>0.05509</td>
</tr>
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<td>0.00057</td>
<td>0.00208</td>
<td>0.06972</td>
</tr>
</tbody>
</table>

\( \text{As} \) is the total arsenic concentration in \( \text{mol/dm}^3 \); \( S \) is the total sulphur concentration in \( \text{mol/dm}^3 \); \( Na \) is the total sodium concentration in \( \text{mol/dm}^3 \);

Table B.13.: Compositions of \( \text{Na}_2\text{S} \)-containing experimental solutions at 22°C, used to calculate the molar absorptivity of \( \text{HS}^- \)

<table>
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<tr>
<th>solution</th>
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<th>( Na )</th>
<th>( pH )</th>
</tr>
</thead>
<tbody>
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</tr>
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</table>

\( S \) is the total sulphur concentration in \( \text{mol/dm}^3 \); \( Na \) is the total sodium concentration in \( \text{mol/dm}^3 \).
### APPENDIX B. ANALYTICAL DATA

Table B.14.: Compositions of 26 experimental solutions used for p-nitrophenol deprotonation at 25°C

<table>
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<tr>
<th>solution</th>
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<th>$Cl$</th>
<th>$Na$</th>
<th>$pH$</th>
</tr>
</thead>
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<td>-</td>
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</tr>
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</tr>
<tr>
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<td>0.000016</td>
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</tr>
<tr>
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</tr>
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</tr>
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<td>0.000039</td>
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</tr>
<tr>
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</tr>
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</table>

$p – \text{nitrophenol}$ is the total p-nitrophenol concentration in mol/dm³; $Cl$ is the total hydrochloric acid concentration in mol/dm³; $Na$ is the total sodium concentration in mol/dm³; $pH$ is the calculated pH with $pK_1$ of p-nitrophenol equal to 7.15
Table B.15.: Compositions of 41 experimental solutions used for p-nitrophenol dissociation validation at 50°C

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<th>Na</th>
<th>sol.</th>
<th>$p$-nitrophenol</th>
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<td>0.000088</td>
<td>0.000093</td>
<td>0.000260</td>
</tr>
<tr>
<td>21</td>
<td>0.000088</td>
<td>0.000094</td>
<td>0.000130</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

"sol." is solution number

$p$-nitrophenol is the total p-nitrophenol concentration in mol/dm$^3$;

Cl is the total hydrochloric acid concentration in mol/dm$^3$;

Na is the total sodium concentration in mol/dm$^3$;
Table B.16.: Compositions of 28 experimental solutions used for p-nitrophenol dissociation validation at 75°C

<table>
<thead>
<tr>
<th>solution</th>
<th>$p$-nitrophenol</th>
<th>$Cl$</th>
<th>$Na$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.000085</td>
<td>0.000096</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>0.000085</td>
<td>0.000096</td>
<td>0.0000078</td>
</tr>
<tr>
<td>3</td>
<td>0.000085</td>
<td>0.000096</td>
<td>0.0000156</td>
</tr>
<tr>
<td>4</td>
<td>0.000085</td>
<td>0.000096</td>
<td>0.0000233</td>
</tr>
<tr>
<td>5</td>
<td>0.000085</td>
<td>0.000096</td>
<td>0.0000311</td>
</tr>
<tr>
<td>6</td>
<td>0.000085</td>
<td>0.000096</td>
<td>0.0000389</td>
</tr>
<tr>
<td>7</td>
<td>0.000085</td>
<td>0.000096</td>
<td>0.0000466</td>
</tr>
<tr>
<td>8</td>
<td>0.000085</td>
<td>0.000096</td>
<td>0.0000544</td>
</tr>
<tr>
<td>9</td>
<td>0.000085</td>
<td>0.000096</td>
<td>0.0000622</td>
</tr>
<tr>
<td>10</td>
<td>0.000085</td>
<td>0.000096</td>
<td>0.0000699</td>
</tr>
<tr>
<td>11</td>
<td>0.000085</td>
<td>0.000096</td>
<td>0.0000777</td>
</tr>
<tr>
<td>12</td>
<td>0.000085</td>
<td>0.000096</td>
<td>0.0000855</td>
</tr>
<tr>
<td>13</td>
<td>0.000085</td>
<td>0.000096</td>
<td>0.0000932</td>
</tr>
<tr>
<td>14</td>
<td>0.000085</td>
<td>0.000096</td>
<td>0.0001010</td>
</tr>
<tr>
<td>15</td>
<td>0.000085</td>
<td>0.000096</td>
<td>0.0001088</td>
</tr>
<tr>
<td>16</td>
<td>0.000085</td>
<td>0.000096</td>
<td>0.0001165</td>
</tr>
<tr>
<td>17</td>
<td>0.000085</td>
<td>0.000096</td>
<td>0.0001243</td>
</tr>
<tr>
<td>18</td>
<td>0.000085</td>
<td>0.000095</td>
<td>0.0001320</td>
</tr>
<tr>
<td>19</td>
<td>0.000085</td>
<td>0.000095</td>
<td>0.0001398</td>
</tr>
<tr>
<td>20</td>
<td>0.000085</td>
<td>0.000095</td>
<td>0.0001475</td>
</tr>
<tr>
<td>21</td>
<td>0.000085</td>
<td>0.000095</td>
<td>0.0001553</td>
</tr>
<tr>
<td>22</td>
<td>0.000085</td>
<td>0.000095</td>
<td>0.0001630</td>
</tr>
<tr>
<td>23</td>
<td>0.000085</td>
<td>0.000095</td>
<td>0.0001708</td>
</tr>
<tr>
<td>24</td>
<td>0.000085</td>
<td>0.000095</td>
<td>0.0001785</td>
</tr>
<tr>
<td>25</td>
<td>0.000085</td>
<td>0.000095</td>
<td>0.0001863</td>
</tr>
<tr>
<td>26</td>
<td>0.000085</td>
<td>0.000095</td>
<td>0.0001940</td>
</tr>
<tr>
<td>27</td>
<td>0.000085</td>
<td>0.000095</td>
<td>0.0002018</td>
</tr>
<tr>
<td>28</td>
<td>0.000085</td>
<td>0.000095</td>
<td>0.0002095</td>
</tr>
</tbody>
</table>

$p$-nitrophenol is the total p-nitrophenol concentration in $mol/dm^3$; $Cl$ is the total hydrochloric acid concentration in $mol/dm^3$; $Na$ is the total sodium concentration in $mol/dm^3$. 
Table B.17.: Compositions of 27 experimental solutions used for p-nitrophenol dissociation validation at 90°C

<table>
<thead>
<tr>
<th>solution</th>
<th>$p$–nitrophenol</th>
<th>Cl</th>
<th>Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0000768</td>
<td>0.0000960</td>
<td>0.0000000</td>
</tr>
<tr>
<td>2</td>
<td>0.0000768</td>
<td>0.0000959</td>
<td>0.0000067</td>
</tr>
<tr>
<td>3</td>
<td>0.0000768</td>
<td>0.0000959</td>
<td>0.000133</td>
</tr>
<tr>
<td>4</td>
<td>0.0000768</td>
<td>0.0000959</td>
<td>0.000200</td>
</tr>
<tr>
<td>5</td>
<td>0.0000768</td>
<td>0.0000959</td>
<td>0.000267</td>
</tr>
<tr>
<td>6</td>
<td>0.0000768</td>
<td>0.0000959</td>
<td>0.000333</td>
</tr>
<tr>
<td>7</td>
<td>0.0000768</td>
<td>0.0000959</td>
<td>0.000400</td>
</tr>
<tr>
<td>8</td>
<td>0.0000768</td>
<td>0.0000959</td>
<td>0.000466</td>
</tr>
<tr>
<td>9</td>
<td>0.0000768</td>
<td>0.0000959</td>
<td>0.000533</td>
</tr>
<tr>
<td>10</td>
<td>0.0000768</td>
<td>0.0000959</td>
<td>0.000599</td>
</tr>
<tr>
<td>11</td>
<td>0.0000768</td>
<td>0.0000959</td>
<td>0.000666</td>
</tr>
<tr>
<td>12</td>
<td>0.0000768</td>
<td>0.0000959</td>
<td>0.000733</td>
</tr>
<tr>
<td>13</td>
<td>0.0000768</td>
<td>0.0000959</td>
<td>0.000799</td>
</tr>
<tr>
<td>14</td>
<td>0.0000768</td>
<td>0.0000959</td>
<td>0.000866</td>
</tr>
<tr>
<td>15</td>
<td>0.0000768</td>
<td>0.0000959</td>
<td>0.000932</td>
</tr>
<tr>
<td>16</td>
<td>0.0000768</td>
<td>0.0000959</td>
<td>0.000999</td>
</tr>
<tr>
<td>17</td>
<td>0.0000768</td>
<td>0.0000958</td>
<td>0.001065</td>
</tr>
<tr>
<td>18</td>
<td>0.0000768</td>
<td>0.0000958</td>
<td>0.001132</td>
</tr>
<tr>
<td>19</td>
<td>0.0000768</td>
<td>0.0000958</td>
<td>0.001198</td>
</tr>
<tr>
<td>20</td>
<td>0.0000767</td>
<td>0.0000958</td>
<td>0.001265</td>
</tr>
<tr>
<td>21</td>
<td>0.0000767</td>
<td>0.0000958</td>
<td>0.001331</td>
</tr>
<tr>
<td>22</td>
<td>0.0000767</td>
<td>0.0000958</td>
<td>0.001398</td>
</tr>
<tr>
<td>23</td>
<td>0.0000767</td>
<td>0.0000958</td>
<td>0.001464</td>
</tr>
<tr>
<td>24</td>
<td>0.0000767</td>
<td>0.0000958</td>
<td>0.001531</td>
</tr>
<tr>
<td>25</td>
<td>0.0000767</td>
<td>0.0000958</td>
<td>0.001597</td>
</tr>
<tr>
<td>26</td>
<td>0.0000767</td>
<td>0.0000958</td>
<td>0.001663</td>
</tr>
<tr>
<td>27</td>
<td>0.0000767</td>
<td>0.0000958</td>
<td>0.001730</td>
</tr>
</tbody>
</table>

$p$–nitrophenol is the total p-nitrophenol concentration in mol/dm³; 
Cl is the total hydrochloric acid concentration in mol/dm³; 
Na is the total sodium concentration in mol/dm³;
Table B.18.: Compositions of 12 experimental solutions used for p-nitrophenol dissociation validation from 100 to 300°C

<table>
<thead>
<tr>
<th>solution</th>
<th>$p$-nitrophenol</th>
<th>Cl</th>
<th>Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.000125</td>
<td>0.000095</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>0.000071</td>
<td>0.000100</td>
<td>0.000046</td>
</tr>
<tr>
<td>3</td>
<td>0.000071</td>
<td>0.000100</td>
<td>0.000073</td>
</tr>
<tr>
<td>4</td>
<td>0.000071</td>
<td>0.000100</td>
<td>0.000093</td>
</tr>
<tr>
<td>5</td>
<td>0.000058</td>
<td>0.000086</td>
<td>0.000085</td>
</tr>
<tr>
<td>6</td>
<td>0.000058</td>
<td>0.000086</td>
<td>0.000107</td>
</tr>
<tr>
<td>7</td>
<td>0.000058</td>
<td>0.000086</td>
<td>0.000116</td>
</tr>
<tr>
<td>8</td>
<td>0.000066</td>
<td>0.000093</td>
<td>0.000123</td>
</tr>
<tr>
<td>9</td>
<td>0.000066</td>
<td>0.000093</td>
<td>0.000173</td>
</tr>
<tr>
<td>10</td>
<td>0.000052</td>
<td>0.000092</td>
<td>0.000185</td>
</tr>
<tr>
<td>11</td>
<td>0.000051</td>
<td>0.000092</td>
<td>0.000294</td>
</tr>
<tr>
<td>12</td>
<td>0.000051</td>
<td>0.000092</td>
<td>0.000590</td>
</tr>
</tbody>
</table>

$p$-nitrophenol is the total p-nitrophenol concentration in $mol/dm^3$; Cl is the total hydrochloric acid concentration in $mol/dm^3$; Na is the total sodium concentration in $mol/dm^3$. 
C. Computational programs

for As - OH system

------------------------------------------------------------------
%FUNCTION : TO CALCULATE RANK OF ABSORBANCE MATRIX
------------------------------------------------------------------

function [r]=rank_int(A,g,t,lambda1,lambda2,k,d);
% A is Absorbance Matrix,
% g is tolerance with a step, example[0.001:0.001:0.2]
% parameters only for plotting:
% t is temperature
% lambda1 is from which wavelength
% lambda2 is to which wavelength
% k is which solutions number
% d is a solutions set number
% d eto nomer serii rastvorov
n=size(g);
a=n(2);
r=rank(A, g(1));
for i=2:a
    r2=rank(A, g(i));
    r=[r; r2];
end
figure
hold on
plot(g, r)
xlabel('tolerance')
ylabel('rank')
title([num2str(t) '°C;' ' seria N: ' num2str(d)])
gtext(['Wavelength interval : ' num2str(lambda1) ' - ' num2str(lambda2) ' nm'])
%to use gtext:click on a picture and press enter,only then text will appear
%gtext(['solutions : ' num2str(k)])
------------------------------------------------------------------
APPENDIX C. COMPUTATIONAL PROGRAMS

%GENERAL SCRIPT FOR ABSORBANCE DATA TREATMENT ->
%STABILITY CONSTANT EVALUATION /As-Na system
%--------------------------------------------------------

% 1. Model description: "in general script"
% 2. Constants used (water dissociation constant, densities):
% "water_constants_densities"
% 3. Parameters (total concentrations, Absorbance, density correction)
% "in general script"
% 4. Activities coefficients calculation:
% "[I]=ion_str(C104)"; "Debye_Huckel2"; Pitzer_Agamma_derivD_H;
% "activity_calculation"
% 5. Equilibrium concentrations calculation at a known Kt-d:
% "balance.."
% 6. Molar absorptivity calculation using Lagrange multiplier,
% constrained optimisation: "eps=nonnegative_ls(Abs,c,m):"
% 7. Absorbance theoretical calculation, sum of squares Aobs-Acalc:
% "object_absorbance" (5,6,7 in this separate program)
% 8. Minimisation of this sum: "in general script"
% 9. Figures: "figures"
%10. Uncertainty calculation using Gaussian propagation: "uncertainty"
%11. Workspace saving: "in general script, save..." in the name
% which system and temperature
%--------------------------------------------------------

%1. HA=H+ + A-; k=H*A/HA; pH varied by NaOH addition

clear all; close all
run water_constants_densities
lgkw=lgkw25;%! change when temperature is changed
d=d25;% density ! change when temperature is changed

%3. Parameters:
load E:\matlab_files\Data\data_25_300_As_NaOH.mat
load E:\As_OH_system\AS_final_data\eps_OH.mat% OH molar absorptivity
%corrected for density, but not for path length

kk=Ik_order(1:8)];% which chemical solutions to use
ll=find(lambda==250):1:find(lambda==196);% which wavelength interval
As=As(kk)'
Na=Na(kk)'
Abs=A(ll,kk)'/d;
eps_OH=ka(ll);%! change when temperature is changed
APPENDIX C. COMPUTATIONAL PROGRAMS

%run activity_calculation; Ion strength is less than $10^{-3}$, %effect on stability constant is negligible

\[ n = \text{length}(\text{As}); \]
\[ m = 3; \text{%number of absorbing species} \]
\[ \text{options} = \text{optimset}('\text{Display}', 'iter', '\text{TolX}', '1e-9); \]

if 1
\[ \text{lgx}_{\text{min}} = \text{fminbnd}(@\text{object_abs_As_Na}, -10, -7, \text{options}, \text{lgkw}, \text{As}, \text{Na}, \text{Abs}, \text{eps}_{\text{OH}}); \]
end

\[ [\text{F}_{\text{min}}, \text{eps}, \text{C}_{\text{abs}}, \text{pH}, \text{oh}] = \text{object_abs_As_Na}(\text{lgx}_{\text{min}}, \text{lgkw}, \text{As}, \text{Na}, \text{Abs}, \text{eps}_{\text{OH}}); \]

run Figures_As_Na %important to correct eps for path length of the cell
run uncertainties_As_Na %pm-is confidence level

\text{cd E:\matlab_files\Results}
\text{save result_25_As_NaOH lgx}_{\text{min}} \text{pm F}_{\text{min}} \text{eps} \text{C}_{\text{abs}} \text{pH} \text{kk 11 lambda As Na Abs}
\%
% !change the name when temperature is changed!!!!!
%SCRIPT FOR PLOTTING FIGURES:

figure1
plot(lambda(ll), Abs)
xlabel('Wavelength / nm')
ylabel('Absorbance')
title(['Spectra of arsenic containing solutions; Solutions: ' num2str(kk)])

figure#2
[T,P] = orthog_plot(Abs,3,lambda(ll));
title(['Orthogonal vectors, number of species'])

figure%3
plot(lambda(ll),[eps; eps_OH])
legend('undissociated species','deprotonated species')
xlabel('Wavelength / nm') ylabel('/epsilon')
title('Molar absorptivities of HAsO_2 and AsO_2^-')

figure%4
plot(lambda(ll), C_abs'*eps+oh'*eps_OH,'o')
hold on; plot(lambda(ll), Abs)
xlabel('Wavelength / nm')
ylabel('Absorbance')
title(['Comparison between calculated (o) and observed (line) absorbance; lgx_1=' num2str(lgx_min) '; resn='num2str(F_min)])

figure%5
path=1.8 %for example % plot(lambda(ll),[eps]/path)
legend('HAsO_2','AsO_2^-')
xlabel('Wavelength / nm')
ylabel('/epsilon')
title('Molar absorptivities of HAsO_2 and AsO_2^- corrected for the path length of the cell')
%SCRIPT: WATER CONSTANTS AND DENSITIES:

\[ \begin{align*} 
\lgkw25 &= -14; 
\lgkw50 &= -13.276; 
\% \ lgkw75 \\
\% \ lgkw80 \\
\% \ lgkw90 \\
\lgkw100 &= -12.266; 
\lgkw150 &= -11.644; 
\lgkw200 &= -11.302; 
\lgkw250 &= -11.196; 
\lgkw300 &= -11.301; \\
d25 &= 1; 
\text{d}50 &= 1; 
\text{d}100 &= 0.9625; 
\text{d}150 &= 0.9217; 
\text{d}200 &= 0.8703; 
\text{d}250 &= 0.8058; 
\text{d}300 &= 0.7153; 
\end{align*} \]
%%FUNCTION: ORTHOGONALISATION OF MATRIX, written by O. Suleimenov

function [T,P] = orthog_plot(A,n,lambda);

% orthogonalization
[Y,I]=sort(sum(A));
tmp=size(I);
startvector=I(1,tmp(2));

for I = 1:n
    t1 = A(:,startvector);
    t2 = 0;
    while sum(abs(t2-t1)) > 0.00001
        t2 = t1;
        p1 = t2'*A/(t2'*t2);
        p1 = p1/sqrt(p1*(p1'));
        t1 = A*p1';
    end
    if I == 1
        P = p1;
        T = t1;
    else
        P = [P; p1];
        T = [T, t1];
    end
    A = A-t1*p1;
end
figure plot(lambda, P)
APPENDIX C. COMPUTATIONAL PROGRAMS

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%FUNCTION : OBJECTIVE
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

function [F,eps,C_abs,pH,oh]=object_abs_As_Na(lgx,lgkw,As,Na,Abs,eps_OH);
n=length(As);
    for j=1:n
        [h(j),oh(j),haso2(j),aso2(j)]=balance_As_Na(lgx,lgkw,As(j),Na(j));
    end

C_abs=[haso2;aso2]; pH=-log10(h);

Abs_OHcorr=Abs-oh.'*eps_OH;

eps=nonnegative_ls(Abs_OHcorr,C_abs,2);

A_cal=C_abs.'*eps;

F=sum(sum((Abs-A_cal).^2));
function eps=nonnegative_ls(Abs,c,m);

%m-number of absorbing species
[m1,n1]=size(Abs);
[m2,n2]=size(c);
eps=zeros(m2,n1);

for j=1:n1;
    eps(:,j)=inv(c*c')*c*Abs(:,j);
    c_new=[];
    index=0;
    for i=1:m
        if eps(i,j)<0
            index=1;
            eps(i,j)=0;
        else
            c_new=[c_new;c(i,:)];
        end
    end

    if index>0
        eps_new=inv(c_new*c_new')*c_new*Abs(:,j);
        l=1;
        for i=1:m
            if (eps(i,j)>0)
                eps(i,j)=eps_new(l,:);
                l=l+1;
            end
        end
    end
end
APPENDIX C. COMPUTATIONAL PROGRAMS

-------------------------------------------------------------------------------------------------------------------------------------------------------------------
%FUNCTION : OBJECTIVE
-------------------------------------------------------------------------------------------------------------------------------------------------------------------

function [F,eps,C_abs,pH,oh]=object_abs_As_Na(lgx,lgkw,As,Na,Abs,eps_OH);

n=length(As);

for j=1:n
    [h(j),oh(j),haso2(j),aso2(j)]=balance_As_Na(lgx,lgkw,As(j),Na(j));
end

C_abs=[haso2;aso2]; pH=-log10(h);

Abs_OHcorr=Abs-oh.'*eps_OH;

eps=nonnegative_ls(Abs_OHcorr,C_abs,2);

A_cal=C_abs.'*eps;

F=sum(sum((Abs-A_cal).^2));

-------------------------------------------------------------------------------------------------------------------------------------------------------------------
APPENDIX C. COMPUTATIONAL PROGRAMS

%FUNCTION : SPECIATION PROGRAM, idea from O. Suleimenov

function [h,oh,haso2,aso2]=balance_As_Na(lgx,lgkw,As,Na);
    na=Na;
    astot=As;
    k=10^(lgx);
    kw=10^(lgkw);
    C(1)=1;
    C(2)=k+na;
    C(3)=-k*astot+k*na-kw;
    C(4)=-k*kw;
    a=roots(C);  %everything is OK
    k=0; in=1; for i=1:3
        if isreal(a(i))
            if a(i)>0 & a(i)<astot
                h=a(i);
                oh=kw/h;
                haso2=(astot*h+kw-h*na-h^2)/h;
                aso2=-(kw-h*na-h^2)/h;

                if oh>0 & haso2>0 & aso2>0
                    in=i;
                end
            end
        end
    end
    h=a(in);
    oh=kw/h;
    haso2=(astot*h+kw-h*na-h^2)/h;
    aso2=-(kw-h*na-h^2)/h;

    if (k==0)
        error('No real roots between 0 and astot!!!')
    end
APPENDIX C. COMPUTATIONAL PROGRAMS

%FUNCTION : SPECIATION PROGRAM WITH NaOH ASSOCIATION

function [h, oh, haso2, aso2, na, naoh] = balance_As_Na_assoc(lgk, lgkw, As, NA, lgkam);

AS = As;
NA = Na;
kw = 10^lgkw;
k1 = 10^lgk;
kam = 10^lgkam;

c(1) = kw * kam^2 - k1 * kam;
c(2) = kw^2 * km^3 + k1 - k1 * km^2 * k1 * km - NA + 2 * k1 * km * NA - k1 * AS * km;
c(3) = -3 * kw^2 * km^3 * NA + k1 * AS * km + NA^3 * kw * km^2 * NA - 2 * kw * km * NA^2 + k1 * km^2 * NA - k1 * NA^2 * km;
c(4) = -kw * km^2 * NA^3 + 3 * kw^2 * km^3 * NA^2 - km^2 * NA - 2 * km^2 * NA^2;
c(5) = -kw^2 * km^3 * NA^3;

g = roots(c);
k1 = 0;
t = 1;
for u = 1:4
    if isreal(g(u))
        if g(u) > 0 & g(u) < AS
            naoh = g(u);
            oh = -naoh / (km * (naoh - NA));
            na = -naoh + NA;
            h = -(naoh - NA) * kw * km / naoh;
            haso2 = (-naoh^2 + kw * km^2 * naoh^2 - 2 * kw * km^2 * naoh * NA + kw * km^2 * NA^2 +
                      naoh^3 * km - 2 * NA * naoh^2 * km + NA^2 * naoh * km + AS * naoh^2 * km -
                      AS * naoh * km + NA) / (naoh * km * (naoh - NA));
            aso2 = -(-naoh^2 + kw * km^2 * naoh^2 - 2 * kw * km^2 * naoh * NA + kw * km^2 * NA^2 +
                      naoh^3 * km - 2 * NA * naoh^2 * km + NA^2 * naoh * km) / (naoh * km * (naoh - NA));

            if na > 0 & oh > 0 & haso2 > 0 & h > 0 & aso2 > 0
                t = u;
            end
        end
    end
end
end
APPENDIX C. COMPUTATIONAL PROGRAMS

\[ \text{naoh} = g(t); \]
\[ \text{oh} = -\text{naoh}/(\text{kam}*(\text{naoh}-\text{NA})); \]
\[ \text{na} = -\text{naoh}+\text{NA}; \]
\[ \text{h} = -(\text{naoh}-\text{NA})*\text{kw}\cdot\text{kam}/\text{naoh}; \]
\[ \text{haso}_2 = \frac{(-\text{naoh}^2+\text{kw}\cdot\text{kam}^2+\text{naoh}^2-2-\text{kw}\cdot\text{kam}^2+\text{naoh}^2+\text{kw}\cdot\text{NA}+\text{kw}\cdot\text{kam}^2+\text{NA}^2+\text{naoh}^3-3\cdot\text{kw}\cdot\text{kam}^2+\text{naoh}^2+\text{kw}\cdot\text{NA}+\text{kw}\cdot\text{kam}^2+\text{NA}^2+\text{naoh}^3-3\cdot\text{kw}\cdot\text{kam}^2+\text{naoh}^2+\text{kw}\cdot\text{NA}+\text{kw}\cdot\text{kam}^2+\text{NA}^2+\text{naoh}^3-3\cdot\text{kw}\cdot\text{kam}^2+\text{naoh}^2+\text{kw}\cdot\text{NA}+\text{kw}\cdot\text{kam}^2+\text{NA}^2)}{\text{naoh}\cdot\text{kam}*(\text{naoh}-\text{NA})}; \]
\[ \text{aso}_2 = -\frac{(-\text{naoh}^2+\text{kw}\cdot\text{kam}^2+\text{naoh}^2-2-\text{kw}\cdot\text{kam}^2+\text{naoh}^2+\text{kw}\cdot\text{NA}+\text{kw}\cdot\text{kam}^2+\text{NA}^2+\text{naoh}^3-3\cdot\text{kw}\cdot\text{kam}^2+\text{naoh}^2+\text{kw}\cdot\text{NA}+\text{kw}\cdot\text{kam}^2+\text{NA}^2+\text{naoh}^3-3\cdot\text{kw}\cdot\text{kam}^2+\text{naoh}^2+\text{kw}\cdot\text{NA}+\text{kw}\cdot\text{kam}^2+\text{NA}^2+\text{naoh}^3-3\cdot\text{kw}\cdot\text{kam}^2+\text{naoh}^2+\text{kw}\cdot\text{NA}+\text{kw}\cdot\text{kam}^2+\text{NA}^2+\text{naoh}^3-3\cdot\text{kw}\cdot\text{kam}^2+\text{naoh}^2+\text{kw}\cdot\text{NA}+\text{kw}\cdot\text{kam}^2+\text{NA}^2)}{\text{naoh}\cdot\text{kam}*(\text{naoh}-\text{NA})}; \]

if (k1==0)
    error('No real roots between 0 and astot!!!')
end
APPENDIX C. COMPUTATIONAL PROGRAMS

% SCRIPT HOW CALCULATE UNCERTAINTIES:

% dPhi-changing in constant when As is changed on hi
% input:
    k_min=10^((lgx_min);
sigma_Abs=0.001*Abs;%uncertainty of Abs;
sigma_As=0.03*As;
sigma_Na=0.03*Na;
sigma_lgkw= 1.1513e-016;%((10^(-14+0.005)-10^(-14-0.005))/2
    t_student=2;%Student coefficient
    hi=1e-9;%small number
    hi1=1e-5;
    hi2=1e-4;
%program:
    n=length(As);
    if 1
        dPhiSb=0; dPhiNa=0; dPhikw=0;
        for j=1:n
            options=optimset('Display','iter','TolX',1e-9);
            As_input1=[As(1:(j-1));As(j)+hi;As(j+1:n)];
            As_input2=[As(1:(j-1));As(j)-hi;As(j+1:n)];
            Na_input1=[Na(1:(j-1));Na(j)+hi1;Na(j+1:n)];
            Na_input2=[Na(1:(j-1));Na(j)-hi1;Na(j+1:n)];
            lgkw_input1=lgkw+hi2;
            lgkw_input2=lgkw-hi2;
            lgx_min1As = fminbnd(@object_abs_As_Na,-10,-7,options,
                        lgkw,As_input1,[Na],Abs,eps_OH);
            lgx_min2As = fminbnd(@object_abs_As_Na,-10,-7,options,
                        lgkw,As_input2,[Na],Abs,eps_OH);
            dPhiAs(j)=(10^lgx_min2As-10^lgx_min1As)/(2*hi);
            lgx_min1Na = fminbnd(@object_abs_As_Na,-10,-7,
                        options,lgkw,As,[Na_input1],Abs,eps_OH);
            lgx_min2Na = fminbnd(@object_abs_As_Na,-10,-7,
                        options,lgkw,As,[Na_input2],Abs,eps_OH);
            dPhiNa(j)=(10^lgx_min2Na-10^lgx_min1Na)/(2*hi1);
            lgx_min1kw = fminbnd(@object_abs_As_Na,-10,-7,
APPENDIX C. COMPUTATIONAL PROGRAMS

```matlab
options,lgkw_input1,[As],[Na],Abs,eps_OH);
lgx_min2kw = fminbnd(@object_abs_As_Na,-10,-7,
    options,lgkw_input2,[As],[Na],Abs,eps_OH);

dPhikw=(10^lgx_min2kw-10^lgx_min1kw)/(2*hi2);

end

dPhiNa_avg=sum(dPhiNa'.*sigma_Na)/n;
dPhiAs_avg=sum(dPhiAs'.*sigma_As)/n;
dPhikw_a=dPhikw*sigma_lgkw;
    K_sigma=sqrt(dPhiNa_avg^2+dPhiAs_avg^2+dPhikw_a^2);

pm=log10(1+K_sigma/k_min)*t_student;
%The same as: 0.5*(log10(k_min+K_sigma*2)-log10(k_min-K_sigma*2))
```
APPENDIX C. COMPUTATIONAL PROGRAMS

%FUNCTION: INTERPOLATION OF STABILITY CONSTANTS

function [x,a,b,c,d,e,f,A]=clarke_glew_TdependanceH(tettaC, t,lgK,H);
R=8.31451;
% tettaC v C
	eteta=273.15+tettaC;
T=273.15+t;
x1=[1/teteta 1/teteta 1/teteta 1/teteta 1/teteta 1/teteta 1/teteta];
x2=(1/teteta)-(1./T);
x3=(teteta./T)-1+log(T./teteta);
%log=natural
x4=(teteta/2)*((T./teteta)-(teteta./T)-2*log(T./teteta));
x5=(teteta^2/12)*((T./teteta).^2-6*(T./teteta)+3+2*((teteta./T)+
6*log(T./teteta)));
10-3*(teteta./T)-12*log(T./teteta));
x=[x1', x3', x4',x5',x6'];
% Ax=B;
%A=x'B;
%RlnK=ax(1)+bx(2)+cx(3)+dx(4)+ex(5)+fx(6)
lnK=lgK.*2.3026;
A=x\(lnK*R-H.*x2)'

a=A(1);
b=H;
c=A(2);
d=A(3);
e=A(4);
f=A(5);
% theolgK=A'*(x'/(2.3026*R));
xx=[x1',x2', x3', x4',x5',x6'];
RtheolnK=[a b c d e f]*xx';
theolgK=RtheolnK/(2.3026*R);
figure
plot(T,theolgK,'ks')
hold on
plot(T, lgK, 'ro')

% figure
% plot(1./T, theolgK, 'gs'); hold on; plot(1./T, lgK, 'ro')
APPENDIX C. COMPUTATIONAL PROGRAMS

%SCRIPT: TO DETERMINE THERMODYNAMIC FUNCTIONS OF THE REACTION OF ARSENOUS ACID DISSOCIATION:

%dH_298 for this reaction is taken from Sellers et al., 1964
%H=6.58kcal=27.537kJ/mol
H=27531;
tettaC=25;
t=[25 50 100 150 200 250 300];
lgK=[-9.25, -8.90, -8.25, -7.80, -7.40, -7.21, -7.11];
[x,a,b,c,d,e,f,A]=clarke_glew_TdependanceH(tettaC, t,lgK,H);
%FUNCTION: TO CONVERT nm -> cm⁻¹, eV, kJ/mol

function [obr_cm, eV, kJ_mol] = convert(nm)
%kJ_mol=kJ/mol
obr_cm=1./nm*10⁻⁷;
eV=0.000124*10000000./nm;

% E=hνNa (Na*h*c*v) Na*h*c=0.119 626 564 92 J m mol⁻¹
kJ_mol=0.11962656492.*obr_cm*100/1000;

%nm=1/30000*10⁻⁷(iz obr.cm)
function [q, pH] = raspred_AS_plot1(lkw, lgk, As, Na);

[h, oh, haso2, aso2] = balance_As_Na(lgx, lgkw, As, Na(1));

[q] = [haso2, aso2, h, oh];
pH = -log10(h); u = size(Na);

for i = 2:u
    [h, oh, haso2, aso2] = balance_As_Na(lgx, lgkw, As, Na(i));
    q = [q; haso2, aso2, h, oh];
end

pH = -log10(q(:, 3));

% переводим в %, кол-во % с большой буквы
Haso2 = q(:, 1) * 100 / astot;
Aso2 = q(:, 2) * 100 / astot;

figure
plot(pH, Haso2, 'm', pH, Aso2, 'g')

plot(pH, q(:, 1), 'r', pH, q(:, 2), 'g', pH, q(:, 3), 'y')
xlabel('pH')
function [c, lambda, A] = read_data1(data)

m = size(data); c1 = data - 14; c = 10.^(c1); c = c';
    a = num2str(data(1));
    a = strrep(a, '.', '_');
    file = strcat(a, '.txt');
    fid = fopen(file, 'rt');
    T = fscanf(fid, '%f %f', [2, inf]);
    fclose(fid);
    lambda = T(:, 1);
    A = T(:, 2);
for i = 2:m(2)
    a = num2str(data(i));
    a = strrep(a, '.', '_');
    file = strcat(a, '.txt');
    fid = fopen(file, 'rt');
    T = fscanf(fid, '%f %f', [2, inf]);
    fclose(fid);
    A = [A T(:, 2)];
end
fclose(fid);
APPENDIX C. COMPUTATIONAL PROGRAMS

----------------------------------
%FUNCTION : SPECIATION PROGRAM FOR KHP, NAOH AND ARSENOUS ACID
----------------------------------

function [h, oh, h2aso3, h3aso3, hp, phtal]=KHPtitr(pkw, pk1, pKa, NA, K, P, AS);
kw=10^(~(-pkw));
k1=10^(~(-pk1));
Ka=10^(~(-pKa));
c(1)=Ka^2-k1*Ka;
c(2)=k1*KA+NA-kw*Ka-k1*Ka^2+K1*Ka*K-P*Ka^2-k1*AS*Ka+k1*Ka*Na^3-Ka^2*Na-Ka^2*K;
c(3)=2*Ka^2*K*K^2-P*Ka^2+2+2*Ka^2*K^2-P-k1*Ka*K*P+k1*Ka*K^2+kw*Ka*K+
k1*AS*Ka*P^-3*Ka^-3+2*Ka^-2*Na*P-k1*Ka*Na*P;
c(5)=-Ka^-3*P^-3;
a=roots(c);
t=0;
for i=1:4
  if isreal(a(i))
    if a(i)>0
      phtal=a(i);
      hp=P-phtal;
      h=-Ka*(-P+phtal)/phtal;
      h2aso3 = -(-kw*phtal^2+Ka*K*phtal*P-Ka*K*phtal^2+Ka*Na*phtal*P-
                 Ka*Na*phtal^2+Ka^2*P^2-2*ka^2*phtal+ka^2*phtal^2-ka*P^2*phtal+ka^-3)/phtal/Ka/(-P+phtal);
      oh=kw/h;
      h3aso3 = -(AS*Ka*phtal*P+AS*Ka*phtal^2-2*Ka*K*phtal^2+2*ka*K*phtal^-2+ka*K*phtal^2+ka*Na*phtal^2+2*ka^2*P^2-2*ka^2*P*phtal+
                 ka^2*phtal^2-ka*P^2*phtal+ka^-2*phtal^2-ka*phtal^3)/phtal/Ka/(-P+phtal);
      if hp>0 & h2aso3>0 & h3aso3>0 & h>0
        t=i;
      end;
    end
  end
end

phtal=a(t);
hp = P-phtal;
h = -Ka*(-P+phtal)/phtal;
h2aso3 = -(-kw*phtal^2+Ka*K*phtal*P-Ka*K*phtal^2+2*ka*Na*phtal*P-

133
APPENDIX C. COMPUTATIONAL PROGRAMS

\[
\begin{align*}
&\frac{K_a N_A \text{phtal}^2 + K_a^2 \text{P}^2 - 2K_a \text{P} \text{phtal} + K_a^2 \text{phtal}^2 - K_a \text{P}^2 \text{phtal} + K_a \text{phtal}^3}{\text{phtal} / K_a / (-\text{P} + \text{phtal})} \\
oh &= \frac{kw}{h} \\
&\text{h3aso3} = \frac{(-A_S K_a \text{phtal} \text{P} + A_S K_a \text{phtal}^2 - kw \text{phtal}^2 + K_a K \text{phtal} \text{P} - K_a K \text{phtal}^2 + K_a N_A \text{phtal} \text{P} - K_a N_A \text{phtal}^2 + K_a^2 \text{P}^2 - 2K_a \text{P}^2 \text{phtal} + K_a^2 \text{phtal}^2 - K_a \text{P}^2 \text{phtal} + K_a \text{phtal}^3)}{\text{phtal} / K_a / (-\text{P} + \text{phtal})};
\end{align*}
\]
APPENDIX C. COMPUTATIONAL PROGRAMS

%FUNCTION: SPECIATION AT EACH POINT OF TITRATION

function [Q] = matal(pkw, pk1, pKa, NA1, AS1, K1, P1, Vn, Vd);
%Vn=solution volume on the titration start
%Vd=added solution volume example [0.01:0.5:10] in ml
[NA, AS, K, P] = OHdelutKHP(NA1, AS1, K1, P1, Vn, Vd);

[h, oh, h2aso3, h3aso3, hp, phtal] = KHPtitr(pkw, pk1, pKa,
    NA(1), K(1), P(1), AS(1));
Q = [h oh h2aso3 h3aso3 hp phtal];
y = size(Vd);
for i = 2:y
    [h, oh, h2aso3, h3aso3, hp, phtal] = KHPtitr(pkw, pk1, pKa,
        NA(i), K(i), P(i), AS(i));
    Q = [Q; h oh h2aso3 h3aso3 hp phtal];
end
function \[G\]=perl(NA1, pkw, pk1, pKa, AS1, K1, P1, Vn, Vd, X);

\[Q\]=mata1(pkw, pk1, pKa, NA1, AS1, K1, P1, Vn, Vd);

\[W\]=\text{diff}\left(\text{log10}(Q(:, 1))\right);

\[a\]=\text{size}(Vd');

\[f\]=\text{a}(:, 2)-1;

\[v\]=\text{size}(\text{Vd}(1:f));

\[u\]=\text{size}(\text{W});

\[S\]=\text{[Vd}(1:f) W];

\[s\]=\text{size}(S);

\[y, m\]=\text{min}(S);

\[x=S(m(2), 1);

\[G\]=(X-x)^2;

%primer resheniya v \text{from Cary5\matlab26_05_99_calk.txt.}
%pKa konstanta dlya KHP, X-min v diriviate exp, Vn-m sol s As,
%Vd, skol'ko dobavlyala, K-C(K)...

136
%FUNCTION : TO CALCULATE DILUTED CONCENTRATIONS FOR TITRATION

function [NA, AS, K, P]=OHdelutKHP(NA1, AS1, K1, P1, Vn, Vd);
    %Vn=solution volume on the titration start
    %Vd=added solution volume example [0.01:0.5:10] in ml
AS=AS1*Vn/(Vn+Vd(1));
NA=NA1*Vn/(Vn+Vd(1));
P=P1*Vd(1)/(Vn+Vd(1));
K=K1*Vd(1)/(Vn+Vd(1));
d=size(Vd);
for i=2:d
    as=AS1*Vn/(Vn+Vd(i));
    na=NA1*Vn/(Vn+Vd(i));
    p=P1*Vd(i)/(Vn+Vd(i));
    k=K1*Vd(i)/(Vn+Vd(i));
    AS=[AS;as];
    NA=[NA;na];
    P=[P;p];
    K=[K;k];
end
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Bibliography


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