TECHNOLOGY TRANSFER OF AQUATIC CHEMICAL SPECIATION MODELLING

REPORT TO THE
WATER RESEARCH COMMISSION

by

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WRC Report No 530
ISBN 1 86845 165 8

January 1995

INTRODUCTION

The motivation for a technology transfer project to promote the use of chemical speciation arose from a previous Water Research Commission project, No 319 *Phase Diagrams of Complex Precipitates (with special emphasis on the use of chemical speciation modeling)*. During that project the use of a computer model to obtain a speciated chemical analysis was introduced to a number of individuals and organisations concerned with the water industry. For many people the concept of chemical speciation was new, while others, although familiar with the principles of chemical speciation, lacked a practical tool to obtain speciation information. A need was thus identified to inform people about the benefits of having a fully speciated chemical analysis and to provide them with a tool to obtain such data.

A quantitative knowledge of the chemical composition of a water system and its interaction with its surroundings is essential for the understanding of phenomena as diverse as :- bioavailability and nutrient cycling, biotoxicity, scaling and corrosion, ground water quality, leachate attenuation, water treatment and chemical dosing, desalination and effluent treatment. The complexity of water systems is such that the use of basic chemical equilibrium theory is inhibited by the lack of complete equilibrium data and the ability to solve mathematically the individual equilibrium equations. In South Africa, PC-based computer models such as STASOFT (WRC/ESKOM), AQUACHEM (Chamber of Mines Research Organisation) have been written for specific and well defined situations. They can not be used to solve general speciation applications. JESS (CSIR) can be used for general applications but is a mainframe based program.

The U.S. EPA Centre for Exposure Assessment Modeling (CEAM) developed a PC-based general geochemical speciation program - MINTEQA2. This program can be used to calculate the equilibrium composition of laboratory solutions or natural aquatic systems. There are 91 chemical components currently available in MINTEQA2 and an additional 25 components that are specific to certain of the adsorption submodels. The chemical components include major ions commonly found in natural aqueous systems (Ca, Fe, S, etc.) as well as thirteen trace metals/metalloids of particular interest to environmental problems (Ag, As, Ba, Cd, Cr, Cu, Hg, Ni, Pb, Sb, Se, Tl, Zn) and other metals. Organic ligands of significant affinity for metal complexing are also included. MINTEQA2 is accompanied by a thermodynamic data base of over 1 400 species each involving two or more components. Additional components and equilibrium constants can be added. The program can be used to calculate the mass distribution at equilibrium among dissolved, adsorbed and solid phases under a variety of conditions. Specified values of pH, redox potential, partial pressure of gas phases and solid phases can be imposed on the system. The relative saturation indices of the possible solid phases are calculated and the total dissolved concentrations are corrected for the mass of precipitated solids.

The model can be used by persons possessing a scientific or engineering background with some exposure to inorganic chemistry and thermodynamics.

The Pollution Research Group had been using MINTEQA2 (and its precursor program MINEQL) for a number of years to analyse problems such as; fouling in reverse osmosis and evaporation systems; ground water pollution from vanadium pentoxide production; and sulphate and heavy metal removal using barium carbonate and calcium hydroxide.

MINTEQA2 was chosen as the best available vehicle to introduce the concept of using a computer program to obtain a fully speciated chemical analysis. The program was readily available at no cost and Pollution Research Group personnel possessed the expertise in use of the program to a level that would allow effective transfer of the methodology involved in using the program. It was envisaged that the ability to determine the chemical species present in water bodies, leachates and effluents would be of advantage to bodies such as government agencies, water authorities, mining houses, consultants, biologists, agriculturists and industrialists and would be useful in a wide range of applications **(Table 1)**

The aim of the project was to encourage and promote the use,in South Africa, of the chemical speciation program MINTEQA2. This was to be achieved by :

(i) the dissemination of the capabilities of the chemical equilibrium speciation program MINTEQA2.

(ii) holding workshops on the theoretical basis and practical use of MINTEQA2.

(iii) providing back-up support for MINTEQA2 users, through establishment of a help-desk or electronic bulletin board.

(iv) acting as a link between the United States Environmental Protection Agency (U.S. EPA) and South African users.

(v) supporting other WRC projects which require a knowledge of chemical speciation.

TABLE 1 : Possible areas of application for MINTEQA2

Areas of Application	Type of Information
Soil science and irrigation	The ability of different soil types to adsorb metals can be evaluated. This has implications for metal cycling and bio-uptake of potential pollutants.
Acid rain attenuation	The effects of acid rain on ground water composition or soil adsorbing capacity can be modelled enabling attenuation plumes to be delineated.
Solid waste disposal; ground water modeling; acid mine run-off	The interaction between ground waters and leachates from waste disposal sites or mine dumps can be evaluated.
Receiving water quality assessments and pollution risk assessment	The potential for pollution can be evaluated through a knowledge of dominant chemical species present. The effect of receiving water properties such as; pH, Eh and water hardness on the distribution of species can be modelled.
Water and waste water treatment	New treatment processes can be modelled and their effectiveness assessed. The effect of proposed changes to an existing treatment process can be evaluated.
Aquatic ecosystem modeling	Where sufficient data exists, the entire aquatic ecosystem can be modelled. Combined with areas such as plant physiology, zoology, epidemiology chemical speciation modeling would provide the means of establishing base line data for environmental monitoring.
Desalination	The effects of increasing ionic strength on species mobility, precipitation potential and osmotic pressure can be evaluated. Such information has implications for plant design and operation and can be used to assess priorities and courses of action.
Sewage treatment	The uptake of heavy metals on biomass and struvite precipitation can be modelled.

MINTEQA2 WORKSHOPS

Throughout the duration of the project, a number of workshops, varying in length from 1 to 3 days, were held. Where possible participants had sole access to a computer, or else two people shared a computer. One person to a computer was preferable, as when sharing, one participant generally tended to play a more passive role and did not derive the same hands-on benefit. Representatives of the following organisations or companies have attended a MINTEQA2 workshop.

Date	Organisation
March 1993	Rand Mines (Gold, Coal and Exploration Divisions)
May 1993	Water Institute of Southern Africa Conference Workshop
August 1993	Waites, Meiring and Barnard INC. (Consulting Engineers)
August 1993	Pulles, Howard and De Lange (PHD) (Consulting Engineers)
August 1993	Department of Water Affairs and Forestry - Natal Pollution Control Directorate
September 1993	Umgeni Water (Water Quality and Process Services Sections)
September 1993	Rand Water Board (Water Planning and Process Services Sections)
September, 1993	South African Hydrological Symposium Workshop
May 1994	Rhodes University (Institute for Water Research)
June 1994	Afriwater Conference Workshop
August 1994	Amcoal and JCI (Geohydrologists)
September 1994	Department of Water Affairs (Institute for Water Quality Studies)
September 1994	Goldfields and Anglo American Research Laboratories (Corporate Services)

A full list of delegates who have attended these workshops is given in **Appendix 1**. Instruction at the workshops was given through specially prepared manuals. **(Appendix 2 and 3)** For a 1 day workshop an introductory manual was used but for longer courses, an additional manual, comprising more advanced problems and case histories was compiled. The background to the problems was changed to match the potential use of speciation by the different participants. The layout of the manuals was such that a basic chemical problem was presented. Instructions and hints on how to present the problem to the computer model were given and generally some questions were required to be answered. The aim in providing set tasks was to ensure that delegates developed an interactive role with the program and became familiar with the output files and where to obtain information in them. Guidance was given in translating the numerical chemical solution to the problem back into the real world situation.
The need to evaluate whether, in the participants experience, the predicted solution was sensible and meaningful was emphasised. As experience in conducting the workshops was gained, this aspect became of increasing importance. This situation reaffirmed for course leaders that the philosophy of helping people to solve problems of which they had a detailed knowledge and understanding was the correct approach. At the end of a workshop,

participants were given the EPA's MINTEQA2 User's Manual and a copy of the MINTEQA2 program.

DISTRIBUTION OF MINTEQA2

In addition to holding MINTEQA2 workshops, copies of the program and User's Manual, together with the prepared manuals and relevant literature, were distributed on request to a wide variety of potential users. A list of people to whom MINTEQA2 was distributed is given in **Appendix 4**. In several cases, recipients later requested attendance at a workshop. The main reason for this was that in their work situation, potential users often did not have sufficient uninterrupted time to spend becoming familiar with the program and that they felt that attendance at a one-off workshop would leapfrog their skills in using the program to a level that they could competently make use of the program in their work.

The program and User's Manual was also made available through the Computing Centre for Water Research at the University of Natal, Pietermaritzburg (See **Electronic Communications**).

ELECTRONIC COMMUNICATIONS

During 1993, an Internet File Transfer Protocol (FTP) site was established on the mainframe computer of the Computing Centre for Water Research (CCWR) at the University of Natal, Pietermaritzburg. Personnel from the CCWR modified the computer code to enable the program to be run on their computer. Through this facility, MINTEQA2 can be accessed by users in remote centres. CCWR records show that this facility was used 11 times during the duration of the project. Users obtaining copies of or using MINTEQA2 through the CCWR came from Germany, France, Puerto Rica, United States of America and South Africa. It would appear that this facility has not yet reached its full potential, mostly because, apart from academic institutions, electronic communications are only now becoming more readily available to potential industrial users. Company security regulations regarding computer access have also hampered free flow and usage of this facility. This situation should improve with the current explosion in electronic communications and the availability of user-friendly software to access remote nodes. The structure for future expansion and development of this facility has been set in place.

PROJECT SUPPORT AND CONSULTING

Project support was given to several other WRC projects where chemical speciation was required. These included :-

- WRC Project No 325, *Research on the Modelling of Tubular Reverse Osmosis Systems.*
- WRC Project No 308, *Research into the Recovery of Water and Chemicals from Ion Exchange Regeneration Effluents*

This co-operation and interaction has been productive and resulted in the following preliminary reports :-

- *How to add* Cl_2 *(g),* Cl_2 *(aq), HOCL and* OCl^- *to the MINTEQA2 Thermodynamic Database* (**Appendix 5**)
- *Prediction of Conductivity from Equilibrium Ionic Speciation* (**Appendix 6**)

Assistance was also given to an Eskom funded project, undertaken by the PRG, entitled *On-site Evaluation of Anion-free Flocculants for Industrial Cooling Systems.* Mrs Jenny Reeves, Eskom, Technology Research Investigations (TRI), is currently using MINTEQA2 to model the cooling water circuit at Matla Power station. This work is part of a corporate project and will be included in Mrs Reeves' MSc Eng thesis (University of Natal). Mr Donald Vinnecombe, also from Eskom TRI has used MINTEQA2 to model ettringite precipitation as part of a corporate project on sulphate removal from cooling waters. A Sasol bursar, Mr Peter Gordon, is currently using chemical speciation to examine potential scalants in process cooling water at Secunda. This work will be presented as part of an MSc Eng thesis at the University of Natal. Postgraduate students from the Department of Chemistry, University of Natal, Durban were assisted in their study of the speciation of chelating chemicals.

In 1993, a course in Water Pollution Studies was given to Geology honours students at the University of Natal, Durban. The use of chemical speciation and in particular the program, MINTEQA2, formed the practical component of this course

Specialist consulting was undertaken on a number of industrial problems. Debex Desalination requested that chemical modeling of the predicted composition of effluent streams which will be generated at Columbus Stainless Steel plant be undertaken. Simulation of the effect of water softening on mine water from Kleinkoppie Colliery was also evaluated for Debex

Desalination. The feed to a new reverse osmosis plant at Secunda was modelled for Sasol to predict any potential scalants and to evaluate the effectiveness of proposed pretreatment schemes. This work was encouraging and indicated that success had been achieved in addressing one of the project aims, notably to create an awareness of the benefits of chemical speciation and in particular of the capabilities of the chemical equilibrium speciation program MINTEQA2.

FEEDBACK

Participants at initial MINTEQA2 workshops were asked to complete a questionnaire relating to the content and presentation of the workshop. The aim was to gather information which could be used to improve workshop material. A copy of the questionnaire is given in **Appendix** 7. Analysis of the answers received showed that, particularly for one day workshops, results were often ambiguous, with answers from different sections of the questionnaire contradicting each other, for example, replies often indicated that participants found the workshop too intensive, yet more examples were requested. A possible explanation for this is that the questionnaire was not scientifically structured. For future technology transfer projects of this nature, a professionally constructed questionnaire should be considered, if reliable feedback data is required. In general, feedback was positive and the workshops were well received. Many of the course participants were senior managers and stated that they attended the course to obtain an appreciation of the technique and its relevance to their activities. They envisaged that while they would not personally run the program, they would use the results and that they would require a more junior person to become the organisation's specialist.

ACHIEVEMENTS

The success of any technology transfer project is difficult to assess as the benefits of the skills taught to people may not become apparent for some time. Perhaps the best indicator of the success of the project lies in the number and in the varied backgrounds of participants in the MINTEQA2 workshops. Many of the participants were key personnel and decision makers in their jobs and generally felt that chemical speciation of their chemical data would be of considerable benefit to them in understanding the behaviour of the various water and effluent streams they dealt with. It will be some time before it can be assessed whether the initial enthusiasm has been translated into the workplace. However indications are that an appreciation of the insight provided by a speciated water analysis has been created.

Dr Kühn from the Department of Water Affairs and Forestry's Institute for Water Quality Studies (IWQS) has indicated that she perceives an increasing need for quantitative aquatic chemistry to be applied as a tool in data processing and characterising quality of water resources, in water resource management, and possible extension of the technique into the area of establishing water quality guidelines and permit allocation. Dr Carolyn Palmer from Rhodes University's Institute for Water Research has indicated that she considers specialist input and training on quantitative aquatic chemistry will be necessary to understand the relationship between sulphate chemistry and metal speciation in the Kruger National Park Rivers project. Both these organisations have indicated that they would be initiating projects to extend their use of chemical speciation.

Water consultants who attended the courses realised, that in view of the U.S. EPA's recommendation that MINTEQA2 be used to evaluate the fate of pollutants and for risk assessment, MINTEQA2 would become an essential tool for their consulting work.

Mr Gravelet-Blondin, Department of Water Affairs, Durban has an appreciation of the capabilities of MINTEQA2 and its potential for assessing future permit applications.

Mr Martin Prior and Mrs Sue Freese, Umgeni Water, are using MINTEQA2 to model adsorption of taste and odour compounds onto activated carbon

Eskom are considering using chemical speciation for quality assurance as it provides a reliable check on the cation/anion balance of their water analysis and envisage that the provision of a speciated water analysis would become part of their Laboratory Information Management System (LIMS). It is proposed that Mrs Jenny Reeves will provide technology transfer of the technique to all the power station chemists by 1996.

Chemical speciation modeling will form part of the Water Utilisation Engineering postgraduate course at the University of Pretoria and part of the Honours Environmental Geology course at the University of Natal, Durban in 1995. It is being considered for inclusion in the proposed Water Pollution Master of Science course at the University of Durban-Westville

RECOMMENDATIONS

Enhanced User Interface

A frequent comment by people who have attended the courses (and those that received the MINTEQA2 program and manuals up to a year in advance) was the difficulty in using the program without prior training. Compared to other general purpose chemical speciation models, MINTEQA2 is easy to use. The perception that MINTEQA2 is *user-unfriendly* arises from the fact that most people have become comfortable working within a Windows environment. While MINTEQA2 can be run through Windows, it does not lend itself easily to the cut/paste facilities of programs designed to work within the Windows framework and which people have come to expect as norm. In order to make MINTEQA2 more acceptable to users it is recommended that :-

- MINTEQA2 be rewritten in a PC Windows environment and that the needs of aquatic scientists be taken into account in designing the user interface
- provision is made for the incorporation of experimental results into its database. This aspect is important for aquatic scientists to enable calibration of the model to site specific conditions.
- modifications to the program should be undertaken in consultation with organisations such as the Department of Water Affairs and Forestry's Institute for Water Quality Studies (IWQS), so that the product meets the needs of future users.

These recommendations have been made because there is an indication from the U.S. EPA that further support and development of the program is unlikely. Thus it falls to the users of the program to develop it further. The undertaking of this task would result in considerable capacity and resource building for the aquatic scientific community.

Enhancing the Value of Chemical Data

Current environmental resource management research projects, such as the Kruger National Park Rivers Project, involve chemical analysis of natural water sources. Frequently an overview of the chemistry of these waters is lost because there is no integration of chemical data, or researchers are not aware of which chemical parameters are significant to a particular water system. The use of MINTEQA2 to provide speciated chemical analyses would highlight which chemical parameters and which physico-chemical mechanisms control a given water system and provide a tool to unify chemical results and turn raw chemical data into useful information. This information is essential to set discharge limits and to identify the necessary determinands for water quality monitoring. Areas where chemical data is lacking would also be highlighted. The use of MINTEQA2 to enhance the value of chemical data should be encouraged.

Extended Application of MINTEQA2

It is recommended that support and specialist input in the field of chemical speciation be given to as wide a range of aquatic problems as possible. Some specific areas of research to extend the application of MINTEQA2 are :-

- calibration of the speciation model to represent high priority South African waters. If calibration for South African waters is unsuccessful this would generate a further area of investigation.
- the role of chemical speciation in toxicity studies
- aquatic chemistry of natural and artificial wetlands
- immobilisation of heavy metals in the aquatic environment
- fate of phosphate in impoundments. The results from WRC Project No 465, *Detergent Phosphorous in South Africa : Impact on Eutrophication with Specific Reference to the Umgeni Catchment* illustrated that MINTEQA2 could be used successfully to study the fate of phosphate in a fresh water impoundment (Inanda Dam). Extension of this work, particularly the role of sediment adsorption, would provide a model for other impoundments.

Aspects of these topics are already the subject of ongoing research in South Africa. The use of computer chemical modeling would enrich existing research programes and ensure continuity in modeling skills.

Production of a Self Study Guide

Many participants at the MINTEQA2 workshops were high level managers who envisaged that in-house expertise in chemical modeling would be required, probably from more junior members of their organisation. The MINTEQA2 User's Manual is unsatisfactory as a teaching tool, being largely concerned with the *how to* of entering data and running the program. A self study guide containing examples where MINTEQA2 has been used to solve real world problems, would not only have a teaching role but would broaden the potential areas of application of MINTEQA2. Such a guide would allow a planned phasing out of WRC involvement in promoting chemical modeling while ensuring that the expertise gained in the use of MINTEQA2 would be available for the next generation of potential users.

Maintenance of an Internet FTP Site

The current explosion in the use of electronic communications should be exploited. It is recommended that a MINTEQA2 page or Chemical Speciation User Group be maintained and housed on the CCWR computer. Much in the same way as the Electronic Menbrane Information Library (EMILY) has demonstrated the power and benefits to the membrane community of a collective repository for information, a Chemical Speciation User Group FTP site could be used to hold various chemical speciation models, manuals, and worked examples. A list of researchers engaged in chemical speciation studies could be developed and future researchers on WRC projects could be encouraged to use the FTP site and to develop and extend the information stored there. Through this site the manuals currently stored there, could be upgraded and made more relevant to South African conditions by the inclusion of case histories. The site would eventually become self sustaining and become an interactive problem solving forum. It is recommended that all WRC projects using speciation archive their speciation results on the CCWR site.

Distribution of Available Software

MINTEQA2 has been used in several WRC projects. In addition, several new computer programs have resulted from research funded by the WRC. They include, STASOFT, IMPULSE and PREMSEP. It is recommended that copies of these programs be distributed at local conferences for the water community at a WRC stall This would ensure continued technology transfer at minimal cost

ACKNOWLEDGEMENTS

Thanks are extended to personnel from the Computing Centre for Water Research for their assistance in setting up the FTP site and for modifying the program code.

WATER RESEARCH COMMISSION PROJECT NO 530
TECHNOLOGY TRANSFER OF AQUATIC CHEMICAL
SPECIATION MODELING

APPENDIX 1

Attendance List at Minteqa2 Workshops
January 1993 - December 1994

Pollution Research Group
University of Natal
Durban
December 1994

Attendance at MINTEQA2 Workshops

The following people have attended a MINTEQA2 Workshop.

Name	Contact Address
Rand Mines, Randgold House, March, 1993	
Ms Elizabeth Roberts	Rand Mines (Douglas)
Mr Trevor Ochtman	Rand Mines (Douglas)
Mr Brian Cook	Rand Gold & Exploration
Mr Chris Theart	Rand Mines (Duvha)
Mr John Barnett	Rand Mines (ERPM)
Mr Brett du Toit	Rand Mines (ERPM)
Mr Ken McVey	Rand Mines Milling and Mining
Mr Wayne Hatton-Jones	Rand Mines (Harmony)
Mr Graham Trusler	Rand Mines Environmental Officer
WISA Conference, May 1993	
Mr F J du Toit	SASTECH Navorsing, P O Box 1, Sasolburg, 9570
Mr W D Saunders	SASTECH Navorsing, P O Box 1, Sasolburg, 9570
Mr G. H. du Plessis	SASTECH Navorsing, P O Box 1, Sasolburg, 9570
Dr S J J Geldenhuis	SRK
Ms Karen Pearce	CSIR
Mr Milos Peric	Energy Laboratory,Rand Afrikaans University
Mr Jurgen Menge	Municipality of Windoek, PO Box 59, Windoek, Namabia
Prof Paul Coetzee	Department of Chemistry, Rand Afrikaans University
Dr Herman Wiechers	Steward Scott
Mr Chris Swart	WaterTek
Mr Mark Graham	Umgeni Water
Waites, Meiring and Barnard INC., August 1993	
Mr Tony Leske	Waites Meiring and Barnard, PO Box 74397, Lynwood Ridge, 0040
Mr A.M. van Niekerk	Waites Meiring and Barnard
Mr Steve Wilkens	Waites Meiring and Barnard
Ms Praveshini Rajendra	Dept of Water Affairs, Private Bag X313, Pretoria 0001
Mr R. Naidoo	Dept of Water Affairs, Private Bag X313, Pretoria 0001
Department of Water Affairs, Durban office, August 1993	
Ms Fiona McCory	
Ms Angela Rankin	
Ms Georgina King	
Mr Carl Beath	
Mr Ashwin Seetal	
Mr Hasoon Karodia	
Mr Cedric Boarchards	

Mr Pat Reddy	
6th South African National Hydrological Symposium, September, 1993	
Dr Chris Dickens	Umgeni Water
Mr John Howard	Umgeni Water
Ms Sue Freese	Umgeni Water
Ms Brigetta Voights	Umgeni Water
Ms Manu Pillay	Umgeni Water
Post graduate Student	Centre for Waste Africa, University of Natal, Pietermaritzburg
Post Graduate Student	Centre for Waste Africa, University of Natal, Pietermaritzburg
Mr Faroz Swalaha	Department of Microbiology, University of Durban Westville
Mr Alfred Netshivhumbe	Department of Agronomy,University of Natal, Pietermaritzburg
Pulles, Howard and DeLange, September 1993	
Mr Graham Trussler	
Dr Herman Weichers	
Mr Louis DeLange	
Rand Water Board, September 1993	
Mr Norman Acton	Rand Water Board
Mr Tony Bailey	Rand Water Board
Dr Casie Brits	Rand Water Board
Ms Bettina Chale	Rand Water Board
Ms Elfriede Giard	Rand Water Board
Mr Machiel Steynberg	Rand Water Board
Rhodes University, May 1994	
Dr C Palmer	Rhodes University
5 postgraduate students	Rhodes University
Afriwater Conference, June 1994	
Mr E. Hardwick	IONCHEM, PO Box 446, Isando, 1600
Mr J. Lass	PHD, PO BOx 961, Auckland Park, 2006
Mrs A. Fowles	MINTEK, Private Bag X3015, Randburg, 2125
Ms S Lee	MINTEK, Private Bag X3015, Randburg, 2125
Dr K. Sole	MINTEK, Private Bag X3015, Randburg, 2125
Mr N de Beer	MINTEK, Private Bag X3015, Randburg, 2125
Dr M Wentzel	Water Research Group, Dept of Civil Engineering, University of Cape Town, Rondebosch, 7700
Dr. T.D. Wickins	Impala Platinum Mines, Brackpan
AMCOAL, 30th August - 1st September 1994	
Mr Richard Smart	
Mr Brent Baxter	
Mr Stuart Timm	
Mr Daniel Limpitlaw	
Mr Edward Nefale	
Mr Mark Surman	Johannesburg Consolidated (JCI)

Institute for Water Quality Studies, 6th - 8th September 1994	
Mr Sebastian Jooste	
Ms Tharina Seymore	
Ms Fia Swart	
Ms Vicky van der Merwe	
Anglo American Research Laboratories, 20th -21st September 1994	
Mr Jake Pressly	
Goldfields, 20th - 21st September 1994	
Mr Andrew McLaren	

In addition MINTEQA2 courses have been given to postgraduate students from the Department of Geography and Environmental Sciences, the Department of Geology and Applied Geology, and the Department of Chemical Engineering, University of Natal, Durban.

WATER RESEARCH COMMISSION PROJECT NO 530
TECHNOLOGY TRANSFER OF AQUATIC CHEMICAL
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APPENDIX 2

Introduction to MINTEQA2
Manual Prepared for Introductory MINTEQA2 Workshops

Pollution Research Group
University of Natal
Durban

December 1994

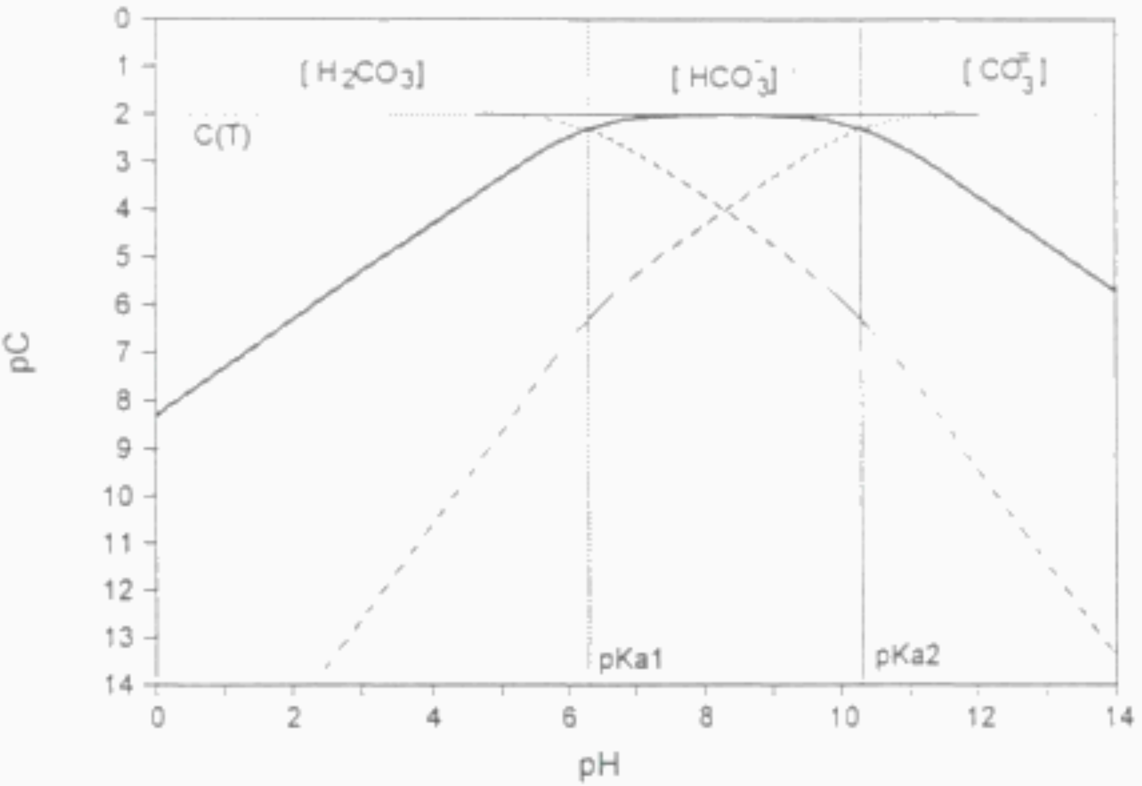
Introduction to MINTEQA2

V3.11

A geochemical equilibrium speciation program developed by
the U.S. Environmental Protection Agency

A WORKSHOP HELD AT AFRIWATER
JUNE 1994
POLLUTION RESEARCH GROUP,
DEPARTMENT OF CHEMICAL ENGINEERING
UNIVERSITY OF NATAL, DURBAN

FAX : 031 260-1118
E-MAIL : BUCKLEY@CHE.UND.AC.ZA
KERR@CHE.UND.AC.ZA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C(T)
pKa1
pKa2
pC
pH
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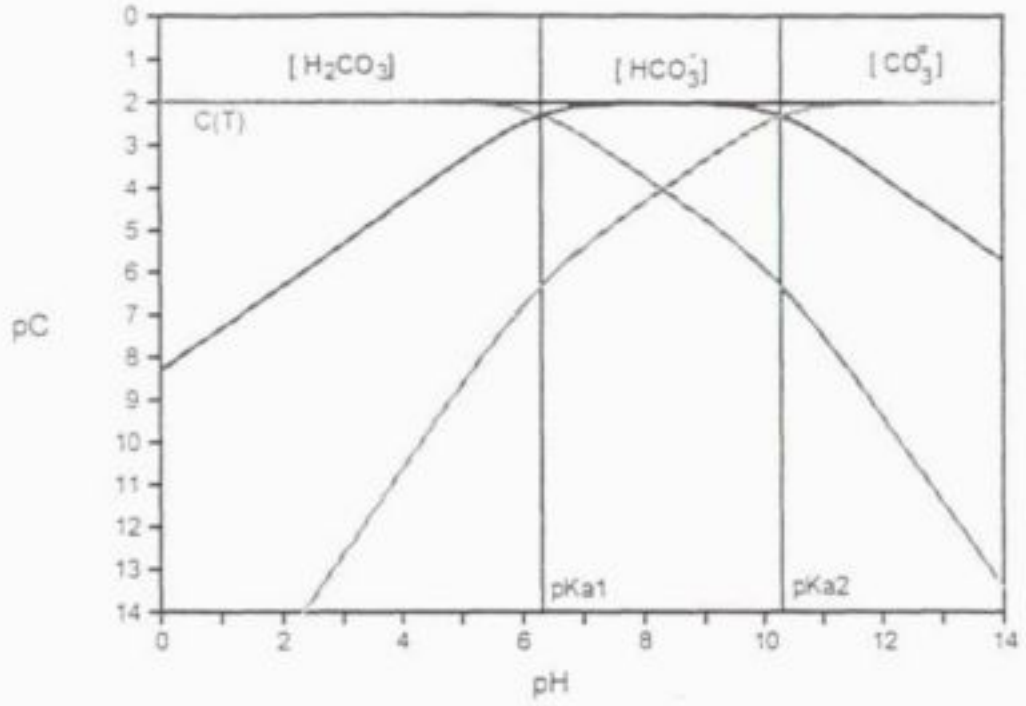
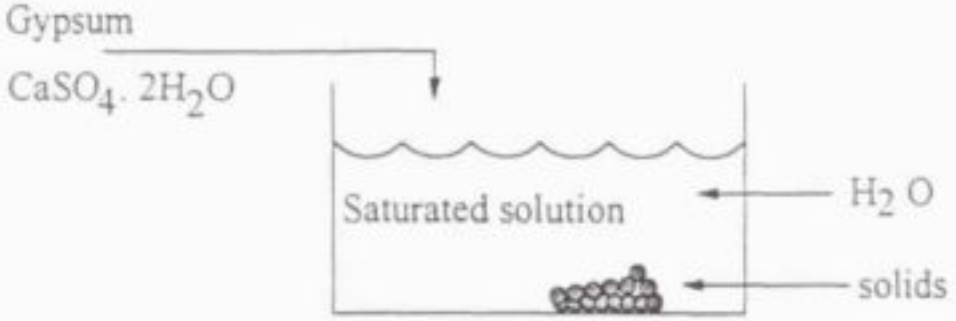


$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

$$k_{a1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = 10^{-6.3}$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$$

$$k_{a2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = 10^{-10.3}$$



Species present

Free ionic species	Ionic complex	Ion pair	Solid
H^+ OH^- Ca^{2+} SO_4^{2-}	HSO_4^- $CaOH^+$	$CaSO_4(aq)$	$CaSO_4 . 2H_2O$

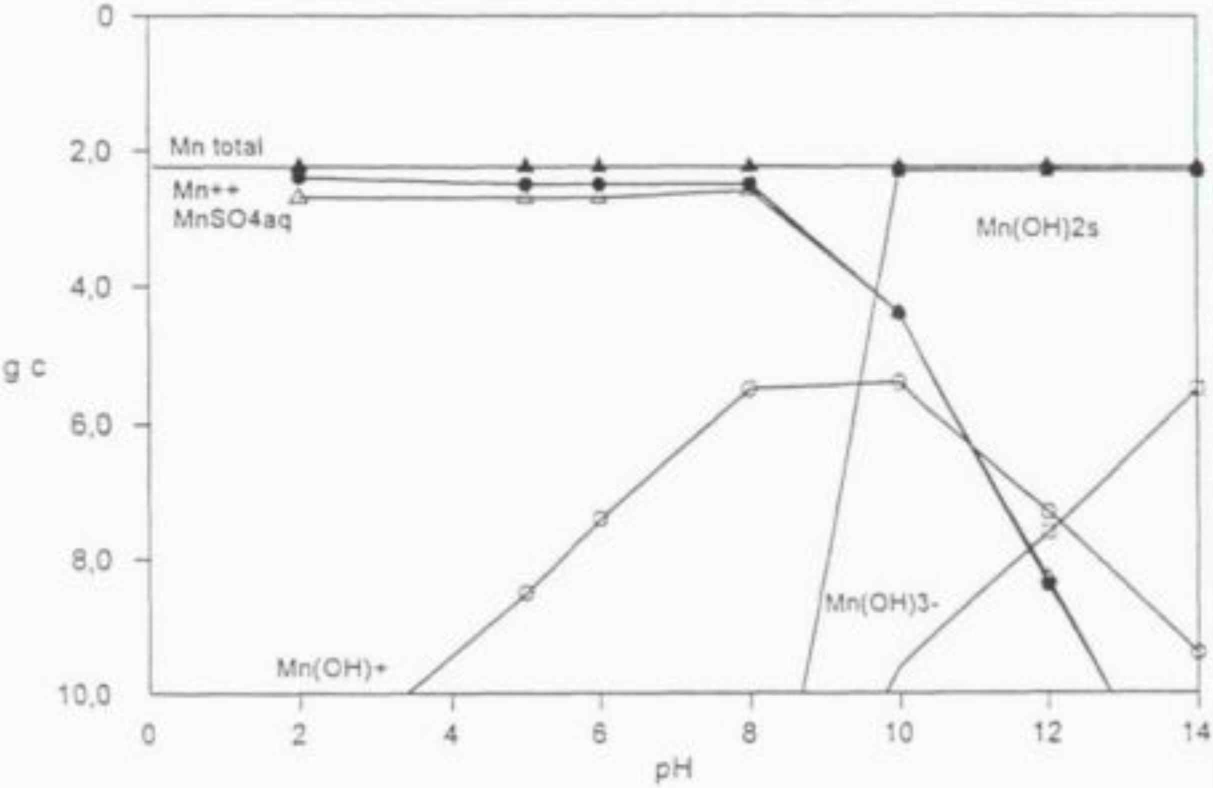
Mine effluent

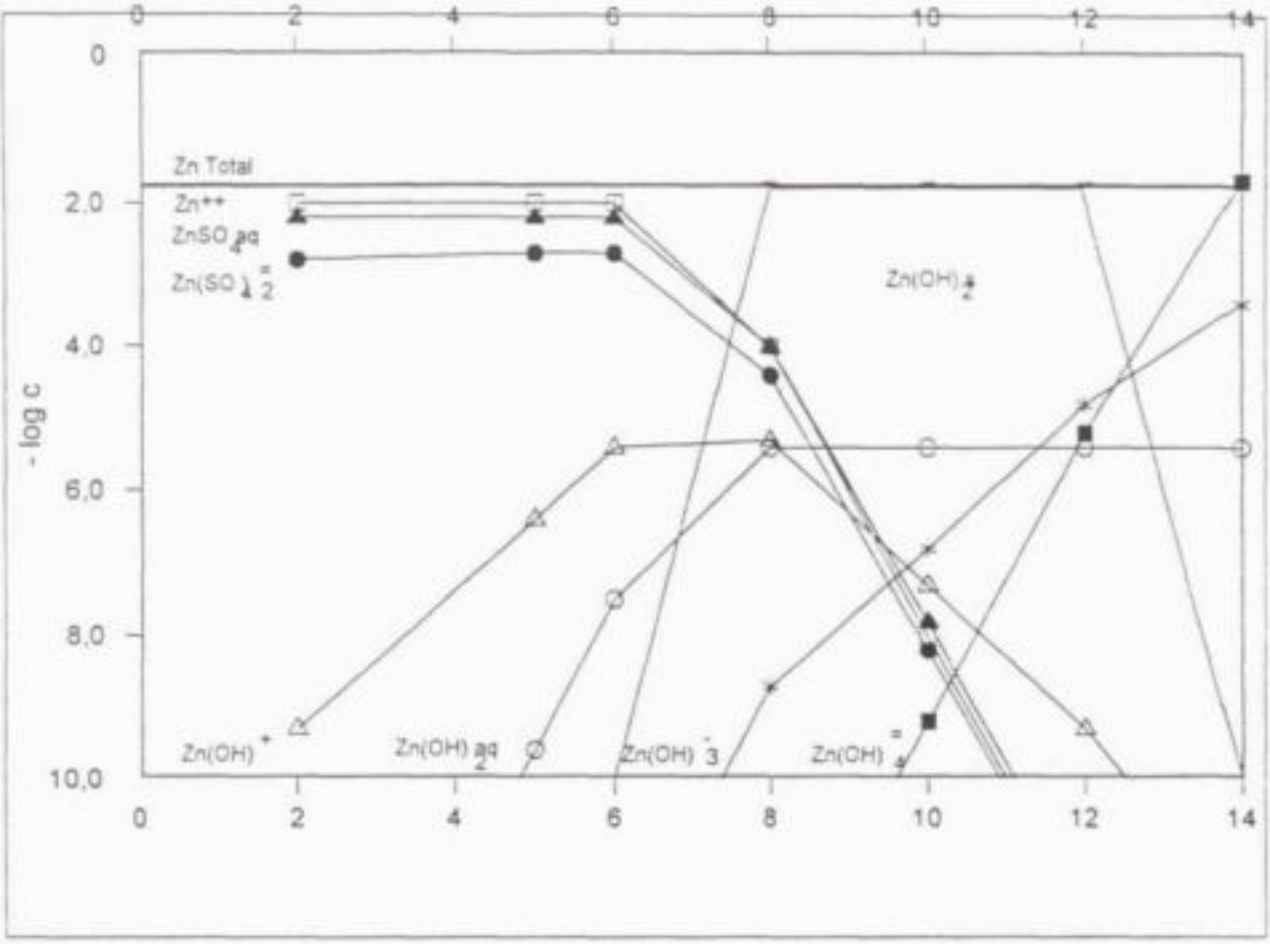
Sodium	112	Manganese	18
Magnesium	78	Zinc	5
Aluminium	308	Sulphate	4 345
Potassium	7	Phosphate	0,2
Calcium	191	Chloride	104
Iron	661	Silicate	305
Ammonia	37	pH	2,55

mg/l

Mine effluent

Determinands	14
Free ionic species	14
Other soluble species	74
Ion pairs	23
Possible solid precipitates	98




0
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4
6
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- log c
Zn Total
Zn++
$ZnSO_4$ aq
$Zn(SO_4)_2^=$
$Zn(OH)_2$ s
$Zn(OH)^+$
$Zn(OH)_2$ aq
$Zn(OH)_3^-$
$Zn(OH)_4^=$
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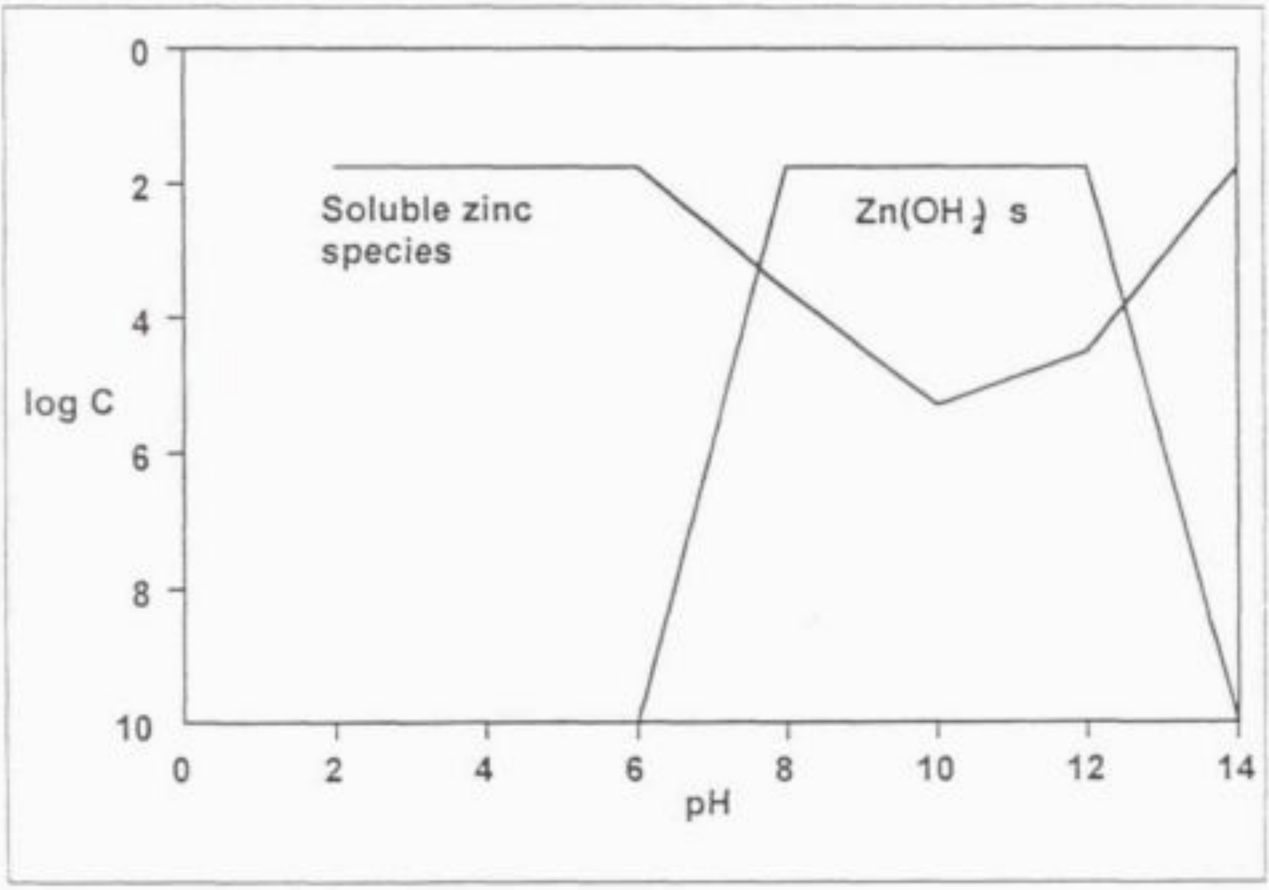
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log C
Soluble zinc species
$Zn(OH)_2$ s
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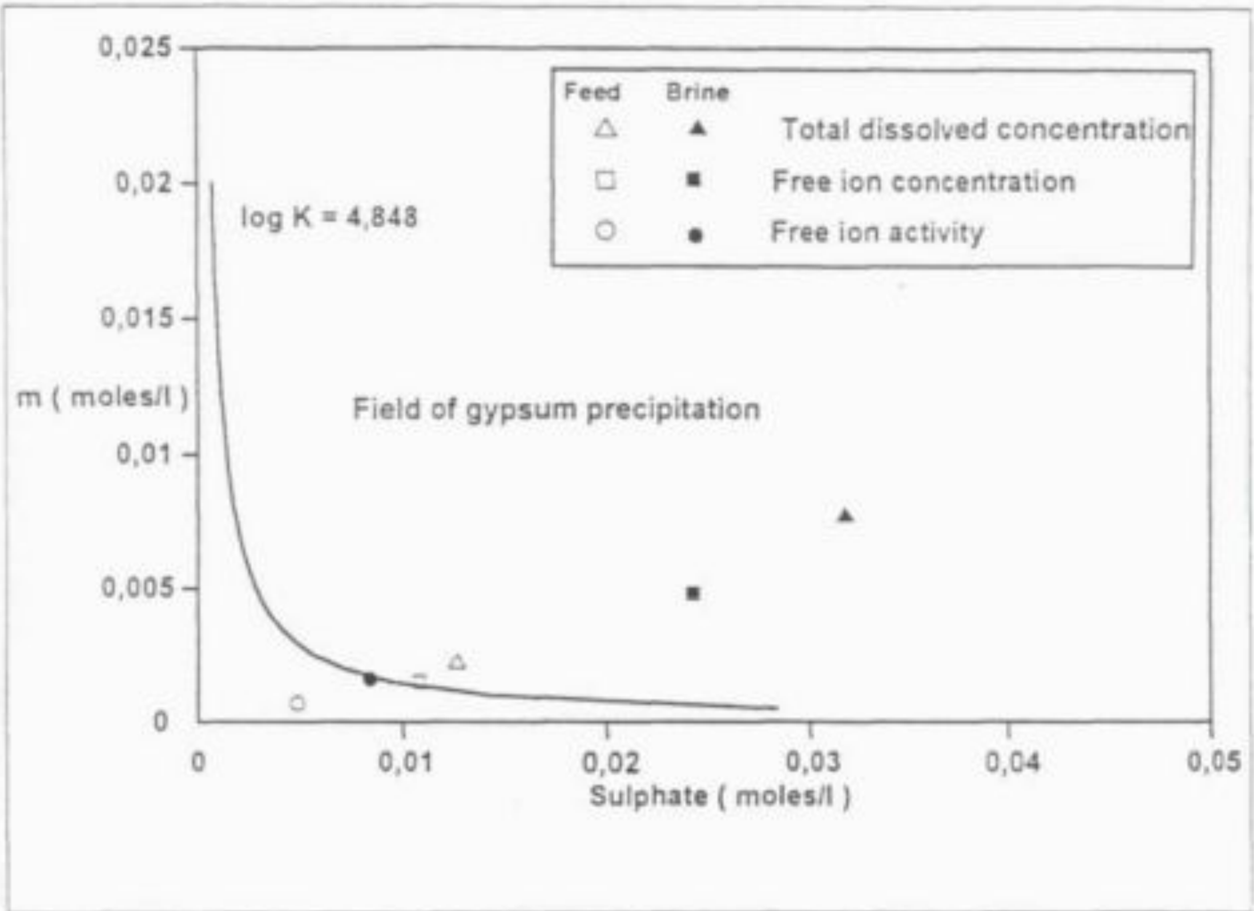
12
14
pH



Chemical Speciation

gives better understanding of chemistry of system

- which species control system

  eg proton concentration
  partial pressure $CO_{2(g)}$

- which processes control system

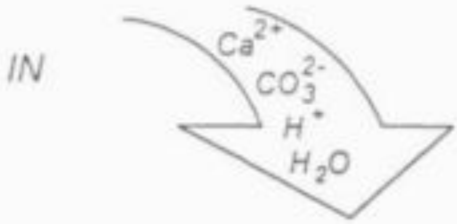
  eg dissolution/precipitation
  oxidation/reduction

chemical analysis → chemical speciation → chemical controls and processes

MINTEQA2 / PRODEFA2

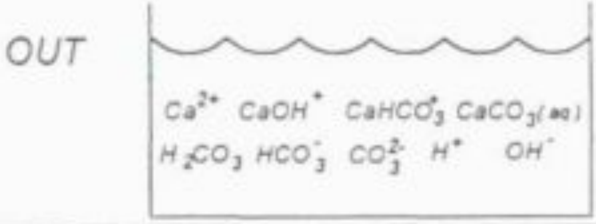
PRODEFA2

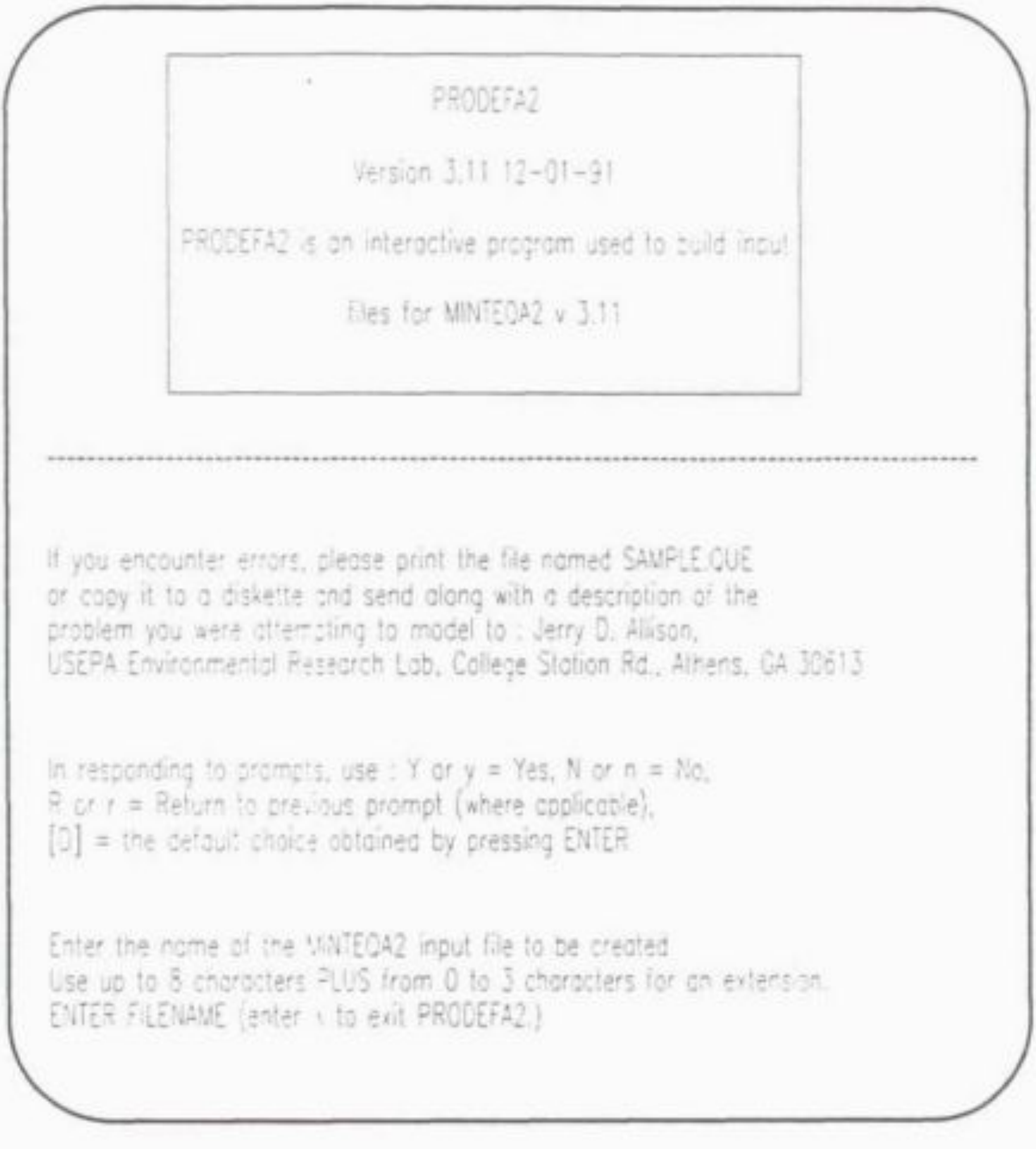
- creates input files



MINTEQA2

- **calculates concentration of species at equilibrium**
- **creates output files**





```
                          PRODEFA2

                  Version 3.11 12-01-91

       PRODEFA2 is an interactive program used to build input

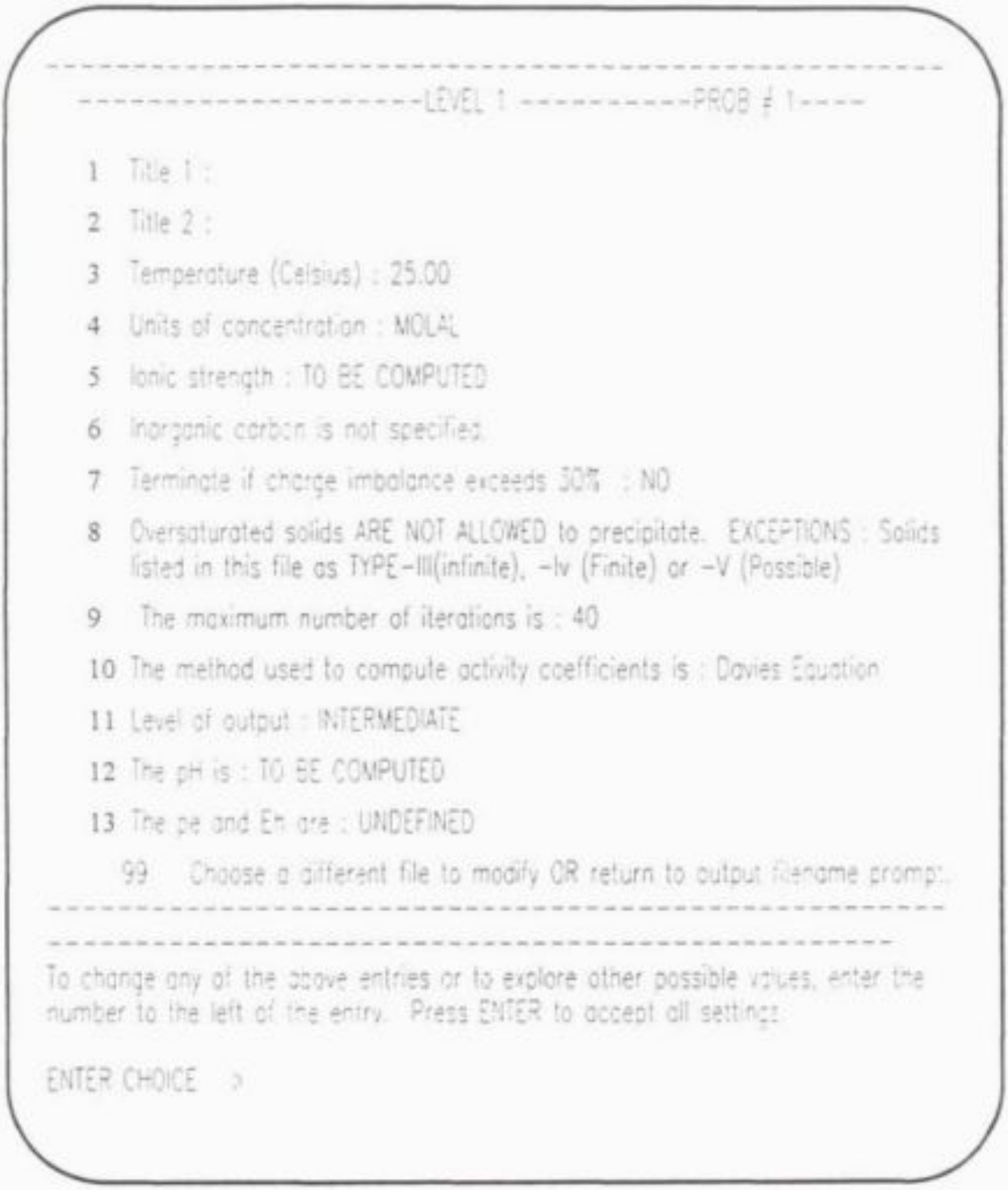
                   files for MINTEQA2 v 3.11

-------------------------------------------------------------------------


If you encounter errors, please print the file named SAMPLE.QUE
or copy it to a diskette and send along with a description of the
problem you were attempting to model to : Jerry D. Allison,
USEPA Environmental Research Lab, College Station Rd., Athens, GA 30613


In responding to prompts, use : Y or y = Yes, N or n = No,
R or r = Return to previous prompt (where applicable),
[D] = the default choice obtained by pressing ENTER


Enter the name of the MINTEQA2 input file to be created
Use up to 8 characters PLUS from 0 to 3 characters for an extension.
ENTER FILENAME (enter x to exit PRODEFA2.)
```



```
---------------------------------------------------------
 -------------------LEVEL 1 ----------PROB # 1----

   1  Title 1 :

   2  Title 2 :

   3  Temperature (Celsius) : 25.00

   4  Units of concentration : MOLAL

   5  Ionic strength : TO BE COMPUTED

   6  Inorganic carbon is not specified

   7  Terminate if charge imbalance exceeds 30%  : NO

   8  Oversaturated solids ARE NOT ALLOWED to precipitate.  EXCEPTIONS : Solids
      listed in this file as TYPE-III(infinite), -Iv (Finite) or -V (Possible)

   9   The maximum number of iterations is : 40

   10 The method used to compute activity coefficients is : Davies Equation

   11 Level of output : INTERMEDIATE

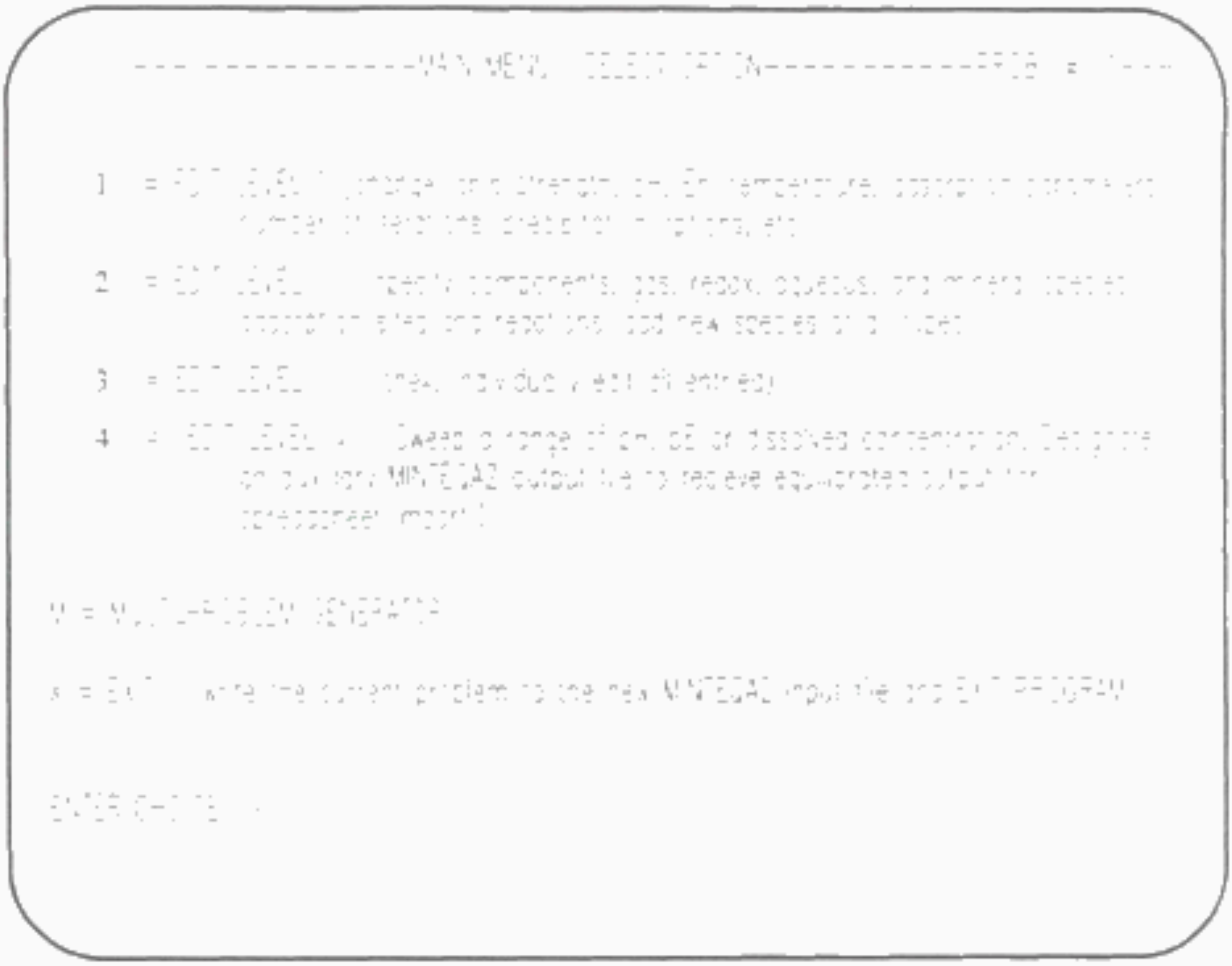
   12 The pH is : TO BE COMPUTED

   13 The pe and Eh are : UNDEFINED

      99   Choose a different file to modify OR return to output filename prompt.
---------------------------------------------------------

---------------------------------------------------------
To change any of the above entries or to explore other possible values, enter the
number to the left of the entry.  Press ENTER to accept all settings

ENTER CHOICE  >
```



```
---------------------MAIN MENU: SELECT OPTION-----------------PROB # 1 ---

  1  = EDIT LEVEL I  (Change: units, ionic strength, pH, Eh, temperature, carbonate as
           number of iterations, precision of output, etc)

  2  = EDIT LEVEL II   (Specify components, gas, redox, aqueous, and mineral species;
           sorption sites and reactions; add new species to d-base)

  3  = EDIT LEVEL III    (View individual d-base entries)

  4  = EDIT LEVEL IV   (Sweep a range of pH, pE or dissolved concentration; Designate
           an auxiliary MINTEQA2 output file to receive equilibrated output for
           spreadsheet import)

M = MULTI-PROBLEM GENERATOR

X = EXIT - write the current problem to the new MINTEQA2 input file and EXIT PROGRAM


ENTER CHOICE >
```

```
-----------------------------------------------------------------------------------------
    ------------- EDIT LEVEL I ------------------------PROB # 1
---------------- SELECT OPTION ----------------------------------

   1   = Specify AQUEOUS COMPONENTS - TOTAL CONCENTRATIONS or FIXED ACTIVITIES

   2   = Specify AQUEOUS SPECIES not in the database, search the database, or change a
              database AQUEOUS SPECIES equilibrium constant

   3   = Specify an ADSORPTION MODEL and REACTIONS

   4   = Specify GASES at FIXED partial pressures

   5   = Specify REDOX COUPLES with FIXED activity ratios

   6   = Specify INFINITE SOLID phases

   7   = Specify FINITE SOLID phases

   8   = Specify POSSIBLE SOLID phases

   9   = Specify EXCLUDED SPECIES of any type

R = RETURN to MAIN MENU

All choices allow you to browse and return without changing anything.
Most allow you to search or view a directory of the relevant database

ENTER CHOICE ([C] =R) :
```

Exercise 1 : add 0.01 M of sulphuric acid to water

Objectives

- introduction to **PRODEFA2**, default options
- introduction to **MINTEQA2**, output
- calculate pH of a solution

Hints

- Create an input file called **EX1** in Prodefa2
- Edit level 1 screen will appear
- Browse through the options even if you want to select the default value. For this problem:
  - Temperature 25 °C
  - Concentration units, molar
  - Solids are not allowed to precipitate
  - Select **Intermediate** output option
- After you have set up the conditions for the problem,
- press enter to proceed to next screen, which is the MAIN MENU
- Select EDIT LEVEL II
- Select AQUEOUS COMPONENTS

Specify components with known TOTAL DISSOLVED CONCENTRATIONS.

The components for this problem are:

$H^+ = 0.02$

$SO^{=}_4 = 0.01$ and

H_2O. **DO NOT** enter water. It will be added automatically.

- Return to EDIT LEVEL II and enter R to return to MAIN MENU
- Select EDIT LEVEL III and check your entry. Correct any errors and enter R to return to MAIN MENU
- X to exit **PRODEFA2** and enter **MINRUN**
- Input file name **EX1**
- Output file name **EX1.OUT**

Output

View the output file, **X1.OUT**, with **EDITOR-E** or other suitable program such as **PCTOOLS** The output files import easily into Wordperfect.

1 List the species present in the water, together with their concentrations

Species	Concentration

2 What is the pH of the solution?

Note: The pH is given in Part 5 of the output file. It can also be found in Part 3, Type 1 - COMPONENTS AS SPECIES IN SOLUTION, as the log activity of the component H^+. Type 1 species refers to those components which are present as free ions in solution

3. What is the sulphuric acid concentration in g/*l*

```
 ____________________________ PART 1 of OUTPUT FILE ________________________
  PC MINTEQA2 v3.10   DATE OF CALCULATIONS: 10-MAR-93  TIME:  8:28:37


Add 0.01 moles of sulphuric acid to water   (RM4)

-------------------------------------------------------------------------------
 Temperature (Celsius):  25.00
 Units of concentration: MOLAL
 Ionic strength to be computed.
 If specified, carbonate concentration represents total inorganic carbon.
 Do not automatically terminate if charge imbalance exceeds 30%
 Precipitation is allowed only for those solids specified as ALLOWED
   in the input file (if any).
 The maximum number of iterations is: 200
 The method used to compute activity coefficients is: Davies equation
 Intermediate output file
-------------------------------------------------------------------------------
    330  2.000E-02   -1.70 y
    732  1.000E-02   -2.00 y
 H2O has been inserted as a COMPONENT
INPUT DATA BEFORE TYPE MODIFICATIONS
   ID        NAME       ACTIVITY GUESS    LOG GUESS   ANAL TOTAL
    330  H+1                1.995E-02       -1.700   2.000E-02
    732  SO4-2              1.000E-02       -2.000   1.000E-02
      2  H2O                1.000E+00        0.000   0.000E-01

     Charge Balance: UNSPECIATED
       Sum of CATIONS=  2.000E-02 Sum of ANIONS =  2.000E-02
       PERCENT DIFFERENCE =  0.000E-01  (ANIONS - CATIONS)/(ANIONS + CATIONS)


               ------------------------------------------------------
              |  IMPROVED ACTIVITY GUESSES PRIOR TO FIRST ITERATION: |
              |       SO4-2       Log activity guess:    -2.47       |
              |                                                      |
               ------------------------------------------------------

 ____________________________ PART 3 of OUTPUT FILE ________________________
  PC MINTEQA2 v3.10   DATE OF CALCULATIONS: 10-MAR-93  TIME:  8:28:44


 PARAMETERS OF THE COMPONENT MOST OUT OF BALANCE:
      ITER      NAME        TOTAL MOL    DIFF FXN    LOG ACTVTY     RESIDUAL
        0   H+1             2.000E-02   6.547E-03    -1.70000    6.545E-03
        1   SO4-2           1.000E-02  -3.784E-04    -2.39067    3.774E-04
        2   SO4-2           1.000E-02   3.862E-03    -2.37627    3.861E-03
        3   SO4-2           1.000E-02   2.800E-04    -2.50300    2.790E-04
  ID        NAME        ANAL MOL   CALC MOL  LOG ACTVTY      GAMMA      DIFF FXN
  330  H+1            2.000E-02  1.542E-02    -1.87389    0.867202   4.666E-07
```

```
 732  SO4-2          1.000E-02  5.416E-03    -2.51381    0.565564   4.013E-07
   2  H2O            0.000E-01 -8.661E-13    -0.00022    1.000000   0.000E-01
-------------------------------------------------------------------------------
 Type I - COMPONENTS AS SPECIES IN SOLUTION
   ID        NAME        CALC MOL    ACTIVITY    LOG ACTVTY    GAMMA     NEW LOGK
    330  H+1             1.542E-02  1.337E-02    -1.87389   0.86720      0.062
    732  SO4-2           5.416E-03  3.063E-03    -2.51381   0.56556      0.248
-------------------------------------------------------------------------------
 Type II - OTHER SPECIES IN SOLUTION OR ADSORBED
   ID        NAME        CALC MOL    ACTIVITY    LOG ACTVTY    GAMMA     NEW LOGK
3307320  HSO4 -          4.584E-03  3.975E-03    -2.40064   0.86720      2.049
3300020  OH-             8.661E-13  7.511E-13   -12.12433   0.86720    -13.936
-------------------------------------------------------------------------------
 Type III - SPECIES WITH FIXED ACTIVITY
   ID        NAME        CALC MOL        LOG MOL    NEW LOGK     DH
      2  H2O            -8.661E-13     -12.062      0.000      0.000^L
______________________________________________________________________________
_____________________________ PART 4 of OUTPUT FILE ___________________________
  PC MINTEQA2 v3.10    DATE OF CALCULATIONS: 10-MAR-93   TIME:  8:28:44


                  PERCENTAGE DISTRIBUTION OF COMPONENTS AMONG
                TYPE I and TYPE II (dissolved and adsorbed) species
H+1              77.1      PERCENT BOUND IN SPECIES #     330   H+1
                 22.9      PERCENT BOUND IN SPECIES #3307320   HSO4 -
SO4-2            54.2      PERCENT BOUND IN SPECIES #     732   SO4-2
                 45.8      PERCENT BOUND IN SPECIES #3307320   HSO4 -
H2O             100.0      PERCENT BOUND IN SPECIES #3300020   OH-
^L
______________________________________________________________________________
_____________________________ PART 5 of OUTPUT FILE ___________________________
  PC MINTEQA2 v3.10    DATE OF CALCULATIONS: 10-MAR-93   TIME:  8:28:44


                 ------------------------------------------------------
                 ----------- EQUILIBRATED MASS DISTRIBUTION -----------

IDX     NAME           DISSOLVED             SORBED            PRECIPITATED
                    MOL/KG    PERCENT    MOL/KG    PERCENT    MOL/KG    PERCENT
330  H+1          2.000E-02   100.0   0.000E-01      0.0   0.000E-01      0.0
732  SO4-2        1.000E-02   100.0   0.000E-01      0.0   0.000E-01      0.0
  2  H2O          8.661E-13   100.0   0.000E-01      0.0   0.000E-01      0.0

     Charge Balance: SPECIATED
       Sum of CATIONS =  1.542E-02 Sum of ANIONS   1.542E-02
       PERCENT DIFFERENCE =   1.089E-03  (ANIONS - CATIONS)/(ANIONS + CATIONS)
     EQUILIBRIUM IONIC STRENGTH (m) =   2.083E-02
      EQUILIBRIUM pH                    =    1.874
      DATE ID NUMBER:              930310
      TIME ID NUMBER:             8284470^L
______________________________________________________________________________
```

```
_____________________________ PART 6 of OUTPUT FILE ____________________________
PC MINTEQA2 v3.10   DATE OF CALCULATIONS: 10-MAR-93  TIME:  8:28:45
```

Exercise 2: Add lime (portlandite) to water (RM2)

Objectives

- \- impose an infinite solid
- \- determine how much of an infinite solid dissolves in attaining equilibrium with water

Hints

- \- create an input file called EX2
- \- select INFINITE SOLID option from Edit Level 2
- \- choose the solid Portlandite ($Ca(OH)_2$) to represent lime
- \- change log K? **N**
- \- change enthalpy? **N**
- \- check entry in Edit Level 3
- \- exit Prodefa2

Output

1 What is the chemical formula of a) portlandite b) lime

Portlandite	
Lime	

2 How many moles of portlandite dissolved per kg of water?

3 Verify this by finding all the soluble Ca species and adding up their concentrations

ID	Species	Concentration
		Total

4 Verify that the solution is saturated with portlandite.

MINTEQA2 reports the Saturation Index (SI)

SI = log IAP - log K_{sp} (where IAP is Ion Activity Product)

If SI < 0, then the solution is undersaturated

If SI > 0, then the solution is oversaturated

If SI = 0, then the solution is in equilibrium with the solid.

5 What is the pH of water saturated with lime?

```
_____________________________________________________________________________
______________________________ PART 1 of OUTPUT FILE _________________________
 PC MINTEQA2 v3.10   DATE OF CALCULATIONS:  9-MAR-93  TIME: 14: 0:52


Adding lime (portlandite) to water to make a saturated solution


-----------------------------------------------------------------------------
 Temperature (Celsius):  25.00
 Units of concentration: MOLAL
 Ionic strength to be computed.
 If specified, carbonate concentration represents total inorganic carbon.
 Do not automatically terminate if charge imbalance exceeds 30%
 Precipitation is allowed only for those solids specified as ALLOWED
   in the input file (if any).
 The maximum number of iterations is: 200
 The method used to compute activity coefficients is: Davies equation
 Intermediate output file
----------------------------------------------------------------------------
    330  0.000E-01   -7.00 y
    150  0.000E-01  -16.00 y
 H2O has been inserted as a COMPONENT
  3   1
2015001   -22.6750    30.6900
INPUT DATA BEFORE TYPE MODIFICATIONS
   ID        NAME        ACTIVITY GUESS    LOG GUESS   ANAL TOTAL
    330  H+1                  1.000E-07        -7.000   0.000E-01
    150  Ca+2                 1.000E-16       -16.000   0.000E-01
      2  H2O                  1.000E+00         0.000   0.000E-01

     Charge Balance: UNSPECIATED
       Sum of CATIONS=  0.000E-01 Sum of ANIONS =  0.000E-01
       PERCENT DIFFERENCE =  0.000E-01  (ANIONS - CATIONS)/(ANIONS + CATIONS)*L
_____________________________________________________________________________
______________________________ PART 3 of OUTPUT FILE _________________________
  PC MINTEQA2 v3.10   DATE OF CALCULATIONS:  9-MAR-93  TIME: 14: 1: 0



PARAMETERS OF THE COMPONENT MOST OUT OF BALANCE:
      ITER       NAME         TOTAL MOL    DIFF FXN    LOG ACTVTY     RESIDUAL
        0   H+1               0.000E-01   9.463E+08    -7.00000     9.462E+08
        1   H+1               0.000E-01   2.366E+08    -7.30103     2.366E+08
        2   H+1               0.000E-01   5.914E+07    -7.60206     5.914E+07
        3   H+1               0.000E-01   1.479E+07    -7.90309     1.478E+07
        4   H+1               0.000E-01   3.696E+06    -8.20412     3.696E+06
        5   H+1               0.000E-01   9.241E+05    -8.50516     9.240E+05
        6   H+1               0.000E-01   2.310E+05    -8.80620     2.310E+05
        7   H+1               0.000E-01   5.776E+04    -9.10724     5.775E+04
        8   H+1               0.000E-01   1.444E+04    -9.40831     1.444E+04
        9   H+1               0.000E-01   3.610E+03    -9.70941     3.610E+03
       10   H+1               0.000E-01   9.025E+02   -10.01058     9.024E+02
       11   H+1               0.000E-01   2.256E+02   -10.31189     2.256E+02
```

```
    12   H+1              0.000E-01  5.640E+01  -10.61348   5.640E+01
    13   H+1              0.000E-01  1.410E+01  -10.91563   1.410E+01
    14   H+1              0.000E-01  3.524E+00  -11.21887   3.524E+00
    15   H+1              0.000E-01  8.793E-01  -11.52410   8.792E-01
    16   H+1              0.000E-01  2.163E-01  -11.83160   2.163E-01
    17   H+1              0.000E-01  4.736E-02  -12.12979   4.736E-02
    18   H+1              0.000E-01  4.261E-03  -12.33349   4.259E-03
    19   H+1              0.000E-01 -1.073E-05  -12.36162   8.421E-06
    21   H+1              0.000E-01  1.406E-02  -12.36155   1.406E-02
    22   H+1              0.000E-01  2.031E-03  -12.42461   2.027E-03
    23   H+1              0.000E-01  2.768E-04  -12.43391   2.735E-04
    24   H+1              0.000E-01  4.044E-05  -12.43518   3.711E-05
    25   H+1              0.000E-01  5.870E-06  -12.43537   2.537E-06
ID        NAME       ANAL MOL   CALC MOL  LOG ACTVTY     GAMMA      DIFF FXN
 330  H+1            0.000E-01  4.468E-13  -12.43539   0.821342   8.511E-07
 150  Ca+2           0.000E-01  1.400E-02   -2.19579   0.455088   0.000E-01
   2  H2O            0.000E-01  8.511E-07    0.00000   1.000000   0.000E-01
--------------------------------------------------------------------------

Type I - COMPONENTS AS SPECIES IN SOLUTION
  ID         NAME        CALC MOL   ACTIVITY   LOG ACTVTY    GAMMA     NEW LOGK
   330  H+1              4.468E-13  3.669E-13  -12.43539   0.82134      0.085
   150  Ca+2             1.400E-02  6.371E-03   -2.19579   0.45509      0.342
--------------------------------------------------------------------------

Type II - OTHER SPECIES IN SOLUTION OR ADSORBED
  ID         NAME        CALC MOL   ACTIVITY   LOG ACTVTY    GAMMA     NEW LOGK
1503300  CaOH +          5.334E-03  4.381E-03   -2.35839   0.82134    -12.513
3300020  OH-             3.333E-02  2.738E-02   -1.56261   0.82134    -13.913
--------------------------------------------------------------------------

Type III - SPECIES WITH FIXED ACTIVITY
  ID         NAME        CALC MOL         LOG MOL   NEW LOGK     DH
      2  H2O             8.511E-07        -6.070     0.000      0.000
2015001  PORTLANDITE    -1.933E-02        -1.714   -22.675     30.690'L
__________________________________________________________________________
____________________________ PART 4 of OUTPUT FILE ________________________
  PC MINTEQA2 v3.10   DATE OF CALCULATIONS:  9-MAR-93  TIME: 14: 1: 2


                 PERCENTAGE DISTRIBUTION OF COMPONENTS AMONG
              TYPE I and TYPE II (dissolved and adsorbed) species
H+1             13.8     PERCENT BOUND IN SPECIES #1503300   CaOH +
                86.2     PERCENT BOUND IN SPECIES #3300020   OH-
Ca+2            72.4     PERCENT BOUND IN SPECIES #     150   Ca+2
                27.6     PERCENT BOUND IN SPECIES #1503300   CaOH +
H2O             13.8     PERCENT BOUND IN SPECIES #1503300   CaOH +
                86.2     PERCENT BOUND IN SPECIES #3300020   OH-
'L
__________________________________________________________________________
____________________________ PART 5 of OUTPUT FILE ________________________
  PC MINTEQA2 v3.10   DATE OF CALCULATIONS:  9-MAR-93  TIME: 14: 1: 2
```

```
              ----------------------------------------------------------
              ----------- EQUILIBRATED MASS DISTRIBUTION -----------

IDX    NAME            DISSOLVED             SORBED              PRECIPITATED
                    MOL/KG    PERCENT    MOL/KG    PERCENT     MOL/KG    PERCENT
330  H+1         -3.867E-02    100.0   0.000E-01      0.0   0.000E-01      0.0
150  Ca+2         1.933E-02    100.0   0.000E-01      0.0   0.000E-01      0.0
  2  H2O          3.867E-02    100.0   0.000E-01      0.0   0.000E-01      0.0

     Charge Balance: SPECIATED
       Sum of CATIONS =  3.333E-02 Sum of ANIONS   3.333E-02
       PERCENT DIFFERENCE =   1.277E-03  (ANIONS - CATIONS)/(ANIONS + CATIONS)
     EQUILIBRIUM IONIC STRENGTH (m) =   4.733E-02
     EQUILIBRIUM pH                   =  12.435
     DATE ID NUMBER:           930309
     TIME ID NUMBER:         14010296'L
_____________________________________________________________________________
_____________________________ PART 6 of OUTPUT FILE __________________________
  PC MINTEQA2 v3.10   DATE OF CALCULATIONS:  9-MAR-93  TIME: 14: 1: 3

Saturation indices and stoichiometry of all minerals
    ID #     NAME      Sat. Index        Stoichiometry in [brackets]
  2015000 LIME          -10.122    [ -2.000] 330  [  1.000] 150  [  1.000]   2
   2015001 PORTLANDITE     0.000    [ -2.000] 330  [  1.000] 150  [  2.000]   2
```

Exercise 3: Make a 0.01M sulphuric acid saturated with lime (Portlandite)

Objectives

- this exercise is a combination of Ex1 and Ex2 It illustrates the use of a seed file

Hints

- create an input file called EX3
- call EX1 as a seed file
- you should be able to proceed from here

Output

1 How many moles of portlandite dissolved per *l*(kg) of water?

2 List the species present as Type 1 (components as species in solution). These are essentially free ions in solution.

ID	Type 1	Concentration

3 List the species present as Type II (other species in solution). This category includes ionic complexes and ion pairs

ID	Type II	Concentration

4 Verify that the total dissolved calcium concentration is equal to the amount of portlandite dissolved

5 What mineral would you expect to precipitate from this solution?

6 In Part 5 of the output file, why does the concentration of H^+ have a minus sign? Verify your answer from part 3 of the output

```
_______________________________________________________________________________
___________________________ PART 1 of OUTPUT FILE _____________________________
 PC MINTEQA2 v3.10   DATE OF CALCULATIONS: 10-MAR-93  TIME:  8:49: 1


sulphuric acid add lime


-------------------------------------------------------------------------------
 Temperature (Celsius):  25.00
 Units of concentration: MOLAL
 Ionic strength to be computed.
 If specified, carbonate concentration represents total inorganic carbon.
 Do not automatically terminate if charge imbalance exceeds 30%
 Precipitation is allowed only for those solids specified as ALLOWED
   in the input file (if any).
 The maximum number of iterations is: 200
 The method used to compute activity coefficients is: Davies equation
 Intermediate output file
-------------------------------------------------------------------------------
    330  2.000E-02   -1.70 y
    732  1.000E-02   -2.00 y
    150  0.000E-01  -16.00
 H2O has been inserted as a COMPONENT
  3   1
2015001   -22.6750    30.6900
INPUT DATA BEFORE TYPE MODIFICATIONS
   ID        NAME       ACTIVITY GUESS    LOG GUESS   ANAL TOTAL
    330  H+1                 1.995E-02       -1.700   2.000E-02
    732  SO4-2               1.000E-02       -2.000   1.000E-02
    150  Ca+2                1.000E-16      -16.000   0.000E-01
      2  H2O                 1.000E+00        0.000   0.000E-01


      Charge Balance: UNSPECIATED
        Sum of CATIONS=  2.000E-02 Sum of ANIONS =  2.000E-02
        PERCENT DIFFERENCE =  0.000E-01  (ANIONS - CATIONS)/(ANIONS + CATIONS)



              --------------------------------------------------------
             |  IMPROVED ACTIVITY GUESSES PRIOR TO FIRST ITERATION: |
             |       SO4-2       Log activity guess:    -2.47        |
             |                                                       |
              --------------------------------------------------------'L
_______________________________________________________________________________
___________________________ PART 3 of OUTPUT FILE _____________________________
 PC MINTEQA2 v3.10   DATE OF CALCULATIONS: 10-MAR-93  TIME:  8:49:10



PARAMETERS OF THE COMPONENT MOST OUT OF BALANCE:
     ITER      NAME         TOTAL MOL    DIFF FXN    LOG ACTVTY     RESIDUAL
      0   SO4-2             1.000E-02   1.308E+19    -2.46786     1.308E+19
      1   SO4-2             1.000E-02   3.270E+18    -2.46786     3.269E+18
```

```
    2   SO4-2           1.000E-02   8.118E+17    -2.46786   8.117E+17
    3   SO4-2           1.000E-02   2.030E+17    -2.46786   2.029E+17
    4   SO4-2           1.000E-02   5.074E+16    -2.46786   5.073E+16
    5   SO4-2           1.000E-02   1.268E+16    -2.46786   1.268E+16
    6   SO4-2           1.000E-02   3.171E+15    -2.46786   3.171E+15
    7   SO4-2           1.000E-02   7.928E+14    -2.46786   7.927E+14
    8   SO4-2           1.000E-02   1.982E+14    -2.46786   1.982E+14
    9   SO4-2           1.000E-02   4.955E+13    -2.46786   4.955E+13
   10   SO4-2           1.000E-02   1.239E+13    -2.46786   1.239E+13
   11   SO4-2           1.000E-02   3.097E+12    -2.46786   3.097E+12
   12   SO4-2           1.000E-02   7.742E+11    -2.46786   7.741E+11
   13   SO4-2           1.000E-02   1.936E+11    -2.46786   1.935E+11
   14   SO4-2           1.000E-02   4.839E+10    -2.46786   4.838E+10
   15   SO4-2           1.000E-02   1.210E+10    -2.46786   1.210E+10
   16   SO4-2           1.000E-02   3.024E+09    -2.46786   3.024E+09
   17   SO4-2           1.000E-02   7.561E+08    -2.46786   7.560E+08
   18   SO4-2           1.000E-02   1.890E+08    -2.46786   1.890E+08
   19   SO4-2           1.000E-02   4.725E+07    -2.46786   4.725E+07
   20   SO4-2           1.000E-02   1.181E+07    -2.46786   1.181E+07
   21   SO4-2           1.000E-02   2.953E+06    -2.46786   2.953E+06
   22   SO4-2           1.000E-02   7.383E+05    -2.46786   7.383E+05
   23   SO4-2           1.000E-02   1.846E+05    -2.46785   1.846E+05
   24   SO4-2           1.000E-02   4.615E+04    -2.46785   4.614E+04
   25   SO4-2           1.000E-02   1.154E+04    -2.46783   1.153E+04
   26   SO4-2           1.000E-02   2.884E+03    -2.46780   2.884E+03
   27   SO4-2           1.000E-02   7.209E+02    -2.46775   7.208E+02
   28   SO4-2           1.000E-02   1.802E+02    -2.46763   1.801E+02
   29   SO4-2           1.000E-02   4.502E+01    -2.46741   4.501E+01
   30   SO4-2           1.000E-02   1.124E+01    -2.46695   1.124E+01
   31   SO4-2           1.000E-02   2.804E+00    -2.46602   2.803E+00
   32   SO4-2           1.000E-02   6.970E-01    -2.46413   6.969E-01
   33   SO4-2           1.000E-02   1.719E-01    -2.46042   1.719E-01
   34   SO4-2           1.000E-02   4.164E-02    -2.45477   4.163E-02
   35   SO4-2           1.000E-02   9.726E-03    -2.45816   9.725E-03
   36   SO4-2           1.000E-02   1.807E-03    -2.51028   1.806E-03
   37   SO4-2           1.000E-02   7.048E-05    -2.55904   6.948E-05
   39   SO4-2           1.000E-02   1.136E-03    -2.56174   1.135E-03
   40   SO4-2           1.000E-02   2.292E-04    -2.59260   2.282E-04
   41   SO4-2           1.000E-02   3.151E-05    -2.59985   3.051E-05
   42   SO4-2           1.000E-02   4.862E-06    -2.60084   3.862E-06
   43   H+1             2.000E-02   4.043E-06   -12.39590   2.847E-07
ID        NAME        ANAL MOL   CALC MOL  LOG ACTVTY     GAMMA     DIFF FXN
 330  H+1           2.000E-02  5.031E-13   -12.39591   0.798752  6.527E-07
 732  SO4-2         1.000E-02  6.156E-03    -2.60102   0.407051  1.260E-07
 150  Ca+2          0.000E-01  1.879E-02    -2.11638   0.407051  0.000E-01
   2  H2O           0.000E-01  2.000E-02    -0.00022   1.000000  0.000E-01
------------------------------------------------------------------------

Type I - COMPONENTS AS SPECIES IN SOLUTION
  ID         NAME         CALC MOL   ACTIVITY   LOG ACTVTY    GAMMA      NEW LOCK
   330  H+1              5.031E-13  4.019E-13   -12.39591   0.79875       0.098
   732  SO4-2            6.156E-03  2.506E-03    -2.60102   0.40705       0.390
```

```
   150  Ca+2            1.879E-02  7.649E-03    -2.11638  0.40705      0.390
-------------------------------------------------------------------------------
 Type II - OTHER SPECIES IN SOLUTION OR ADSORBED
   ID        NAME       CALC MOL   ACTIVITY   LOG ACTVTY   GAMMA     NEW LOGK
3307320  HSO4 -         1.224E-13  9.775E-14   -13.00987  0.79875      2.085
3300020  OH-            3.128E-02  2.499E-02    -1.60231  0.79875    -13.900
1503300  CaOH +         6.010E-03  4.801E-03    -2.31869  0.79875    -12.500
1507320  CaSO4 AQ       3.844E-03  3.905E-03    -2.40840  1.01591      2.302
-------------------------------------------------------------------------------
 Type III - SPECIES WITH FIXED ACTIVITY
   ID        NAME       CALC MOL        LOG MOL   NEW LOGK    DH
      2  H2O            2.000E-02        -1.699     0.000     0.000
2015001  PORTLANDITE   -2.865E-02        -1.543   -22.675    30.690'L
_______________________________________________________________________________
___________________________ PART 4 of OUTPUT FILE _____________________________
 PC MINTEQA2 v3.10   DATE OF CALCULATIONS: 10-MAR-93  TIME:  8:49:14


                     PERCENTAGE DISTRIBUTION OF COMPONENTS AMONG
                   TYPE I and TYPE II (dissolved and adsorbed) species
H+1                 83.9     PERCENT BOUND IN SPECIES #3300020   OH-
                    16.1     PERCENT BOUND IN SPECIES #1503300   CaOH +
SO4-2               61.6     PERCENT BOUND IN SPECIES #    732   SO4-2
                    38.4     PERCENT BOUND IN SPECIES #1507320   CaSO4 AQ
Ca+2                65.6     PERCENT BOUND IN SPECIES #    150   Ca+2
                    21.0     PERCENT BOUND IN SPECIES #1503300   CaOH +
                    13.4     PERCENT BOUND IN SPECIES #1507320   CaSO4 AQ
H2O                 83.9     PERCENT BOUND IN SPECIES #3300020   OH-
                    16.1     PERCENT BOUND IN SPECIES #1503300   CaOH +
'L
_______________________________________________________________________________
___________________________ PART 5 of OUTPUT FILE _____________________________
 PC MINTEQA2 v3.10   DATE OF CALCULATIONS: 10-MAR-93  TIME:  8:49:14


                    ----------------------------------------------------
                    ----------- EQUILIBRATED MASS DISTRIBUTION -----------

IDX     NAME           DISSOLVED            SORBED            PRECIPITATED
                    MOL/KG    PERCENT   MOL/KG   PERCENT    MOL/KG   PERCENT
330  H+1          -3.729E-02   100.0  0.000E-01     0.0  0.000E-01     0.0
732  SO4-2         1.000E-02   100.0  0.000E-01     0.0  0.000E-01     0.0
150  Ca+2          2.865E-02   100.0  0.000E-01     0.0  0.000E-01     0.0
  2  H2O           3.729E-02   100.0  0.000E-01     0.0  0.000E-01     0.0

    Charge Balance: SPECIATED
      Sum of CATIONS =  4.359E-02 Sum of ANIONS   4.359E-02
      PERCENT DIFFERENCE =   4.595E-04  (ANIONS - CATIONS)/(ANIONS + CATIONS)
    EQUILIBRIUM IONIC STRENGTH (m) =   6.854E-02
    EQUILIBRIUM pH                   =  12.396
```

```
   DATE ID NUMBER:          930310
   TIME ID NUMBER:         8491424'L

______________________________________________________________________________
_____________________________ PART 6 of OUTPUT FILE __________________________
 PC MINTEQA2 v3.10   DATE OF CALCULATIONS: 10-MAR-93  TIME:  8:49:14


Saturation indices and stoichiometry of all minerals
    ID #      NAME       Sat. Index        Stoichiometry in [brackets]
 6015000 ANHYDRITE       -0.080     [  1.000] 150  [  1.000] 732
 6015001 GYPSUM           0.130     [  1.000] 150  [  1.000] 732  [  2.000]   2
 2015000 LIME           -10.122     [ -2.000] 330  [  1.000] 150  [  1.000]   2
 2015001 PORTLANDITE      0.000     [ -2.000] 330  [  1.000] 150  [  2.000]   2
```

Ex3b. An extension of EX3 to confirm that gypsum ($CaSO_4.2H_2O$) will precipitate from 0.01M solution of sulphuric acid saturated with lime.

Objectives

- use of precipitation option

Hints

- create an input file called EX3b
- call EX3 as a seed file
- allow precipitation, (Edit Level 1, Option 8),

Output

1 How many moles of gypsum are precipitated per *l*(kg) of water?

2 The only source of calcium is from the portlandite added. What should the total dissolved concentration of calcium be in the equilibrium solution?

	Concentration
Total Ca conc at start of problem	
Ca in gypsum precipitated	
Total dissolved Ca conc in equilibrium solution	

Verify your answer in Part 5 of output file.

```
______________________________________________________________________________
_____________________________ PART 1 of OUTPUT FILE __________________________
  PC MINTEQA2 v3.10   DATE OF CALCULATIONS: 11-MAR-93  TIME: 12: 7:55


sulphuric acid add lime
allow ppt
------------------------------------------------------------------------------
 Temperature (Celsius):  25.00
 Units of concentration: MOLAL
 Ionic strength to be computed.
 If specified, carbonate concentration represents total inorganic carbon.
 Do not automatically terminate if charge imbalance exceeds 30%
 Precipitation is allowed for all solids in the thermodynamic database and
   the print option for solids is set to: 1
 The maximum number of iterations is: 200
 The method used to compute activity coefficients is: Davies equation
 Intermediate output file
-----------------------------------------------------------------------------
    330  2.000E-02   -1.70 y
    732  1.000E-02   -2.00 y
    150  0.000E-01  -16.00
 H2O has been inserted as a COMPONENT
  3   1
2015001   -22.6750    30.6900
INPUT DATA BEFORE TYPE MODIFICATIONS
   ID        NAME       ACTIVITY GUESS    LOG GUESS   ANAL TOTAL
    330  H+1                1.995E-02        -1.700   2.000E-02
    732  SO4-2              1.000E-02        -2.000   1.000E-02
    150  Ca+2               1.000E-16       -16.000   0.000E-01
      2  H2O                1.000E+00         0.000   0.000E-01


     Charge Balance: UNSPECIATED
       Sum of CATIONS=  2.000E-02 Sum of ANIONS =  2.000E-02
       PERCENT DIFFERENCE =  0.000E-01  (ANIONS - CATIONS)/(ANIONS + CATIONS)



             ----------------------------------------------------
            |  IMPROVED ACTIVITY GUESSES PRIOR TO FIRST ITERATION: |
            |       SO4-2       Log activity guess:    -2.47       |
            |                                                      |
             ----------------------------------------------------
______________________________________________________________________________
_____________________________ PART 3 of OUTPUT FILE __________________________
  PC MINTEQA2 v3.10   DATE OF CALCULATIONS: 11-MAR-93  TIME: 12: 8: 2



PARAMETERS OF THE COMPONENT MOST OUT OF BALANCE:
     ITER       NAME        TOTAL MOL    DIFF FXN    LOG ACTVTY     RESIDUAL
       0   SO4-2            1.000E-02   1.308E+19   -2.46786     1.308E+19
       1   SO4-2            1.000E-02   3.270E+18   -2.46786     3.269E+18
```

```
  2   SO4-2               1.000E-02  8.118E+17   -2.46786    8.117E+17
  3   SO4-2               1.000E-02  2.030E+17   -2.46786    2.029E+17
  4   SO4-2               1.000E-02  5.074E+16   -2.46786    5.073E+16
  5   SO4-2               1.000E-02  1.268E+16   -2.46786    1.268E+16
  6   SO4-2               1.000E-02  3.171E+15   -2.46786    3.171E+15
  7   SO4-2               1.000E-02  7.928E+14   -2.46786    7.927E+14
  8   SO4-2               1.000E-02  1.982E+14   -2.46786    1.982E+14
  9   SO4-2               1.000E-02  4.955E+13   -2.46786    4.955E+13
 10   SO4-2               1.000E-02  1.239E+13   -2.46786    1.239E+13
 11   SO4-2               1.000E-02  3.097E+12   -2.46786    3.097E+12
 12   SO4-2               1.000E-02  7.742E+11   -2.46786    7.741E+11
 13   SO4-2               1.000E-02  1.936E+11   -2.46786    1.935E+11
 14   SO4-2               1.000E-02  4.839E+10   -2.46786    4.838E+10
 15   SO4-2               1.000E-02  1.210E+10   -2.46786    1.210E+10
 16   SO4-2               1.000E-02  3.024E+09   -2.46786    3.024E+09
 17   SO4-2               1.000E-02  7.561E+08   -2.46786    7.560E+08
 18   SO4-2               1.000E-02  1.890E+08   -2.46786    1.890E+08
 19   SO4-2               1.000E-02  4.725E+07   -2.46786    4.725E+07
 20   SO4-2               1.000E-02  1.181E+07   -2.46786    1.181E+07
 21   SO4-2               1.000E-02  2.953E+06   -2.46786    2.953E+06
 22   SO4-2               1.000E-02  7.383E+05   -2.46786    7.383E+05
 23   SO4-2               1.000E-02  1.846E+05   -2.46785    1.846E+05
 24   SO4-2               1.000E-02  4.615E+04   -2.46785    4.614E+04
 25   SO4-2               1.000E-02  1.154E+04   -2.46783    1.153E+04
 26   SO4-2               1.000E-02  2.884E+03   -2.46780    2.884E+03
 27   SO4-2               1.000E-02  7.209E+02   -2.46775    7.208E+02
 28   SO4-2               1.000E-02  1.802E+02   -2.46763    1.801E+02
 29   SO4-2               1.000E-02  4.502E+01   -2.46741    4.501E+01
 30   SO4-2               1.000E-02  1.124E+01   -2.46695    1.124E+01
 31   SO4-2               1.000E-02  2.804E+00   -2.46602    2.803E+00
 32   SO4-2               1.000E-02  6.970E-01   -2.46413    6.969E-01
 33   SO4-2               1.000E-02  1.719E-01   -2.46042    1.719E-01
 34   SO4-2               1.000E-02  4.164E-02   -2.45477    4.163E-02
 35   SO4-2               1.000E-02  9.726E-03   -2.45816    9.725E-03
 36   SO4-2               1.000E-02  1.807E-03   -2.51028    1.806E-03
 37   SO4-2               1.000E-02  7.048E-05   -2.55904    6.948E-05
 39   SO4-2               1.000E-02  1.136E-03   -2.56174    1.135E-03
 40   SO4-2               1.000E-02  2.292E-04   -2.59260    2.282E-04
 41   SO4-2               1.000E-02  3.151E-05   -2.59985    3.051E-05
 42   SO4-2               1.000E-02  4.862E-06   -2.60084    3.862E-06
 43   H+1                 2.000E-02  4.043E-06  -12.39590    2.847E-07
PC MINTEQA2 v3.10   DATE OF CALCULATIONS: 11-MAR-93  TIME: 12: 8: 6

ITERATIONS= 44:  SOLID GYPSUM       PRECIPITATES'L
______________________________________________________________________
____________________________ PART 3 of OUTPUT FILE ___________________
PC MINTEQA2 v3.10   DATE OF CALCULATIONS: 11-MAR-93  TIME: 12: 8: 6


PARAMETERS OF THE COMPONENT MOST OUT OF BALANCE:
    ITER      NAME        TOTAL MOL   DIFF FXN   LOG ACTVTY   RESIDUAL
```

```
     44   H+1             0.000E-01  -8.600E-03   -12.39591    8.598E-03
     45   H+1             0.000E-01   1.356E-02   -12.34405    1.356E-02
     46   H+1             0.000E-01   2.379E-03   -12.39439    2.375E-03
     47   H+1             0.000E-01   5.095E-04   -12.40272    5.060E-04
     48   H+1             0.000E-01   1.075E-04   -12.40448    1.039E-04
     49   H+1             0.000E-01   2.253E-05   -12.40485    1.901E-05
     50   H+1             0.000E-01   4.714E-06   -12.40493    1.197E-06
  ID        NAME       ANAL MOL   CALC MOL  LOG ACTVTY      GAMMA      DIFF FXN
  330  H+1           2.000E-02  4.897E-13   -12.40494     0.803714   9.862E-07
  150  Ca+2          0.000E-01  1.759E-02    -2.13444     0.417260   0.000E-01
  732  SO4-2         1.000E-02  4.640E-03    -2.71312     0.417260   0.000E-01
    2  H2O           0.000E-01  1.498E-02    -0.00022     1.000000   0.000E-01
-----------------------------------------------------------------------------

 Type I - COMPONENTS AS SPECIES IN SOLUTION
   ID        NAME        CALC MOL   ACTIVITY   LOG ACTVTY    GAMMA      NEW LOGK
    330  H+1            4.897E-13  3.936E-13   -12.40494   0.80371       0.095
    732  SO4-2          4.640E-03  1.936E-03    -2.71312   0.41726       0.380
    150  Ca+2           1.759E-02  7.338E-03    -2.13444   0.41726       0.380
-----------------------------------------------------------------------------

 Type II - OTHER SPECIES IN SOLUTION OR ADSORBED
   ID        NAME        CALC MOL   ACTIVITY   LOG ACTVTY    GAMMA      NEW LOGK
3307320  HSO4 -         9.202E-14  7.396E-14   -13.13100   0.80371       2.082
3300020  OH-            3.174E-02  2.551E-02    -1.59328   0.80371     -13.903
1503300  CaOH +         5.850E-03  4.702E-03    -2.32772   0.80371     -12.503
1507320  CaSO4 AQ       2.852E-03  2.894E-03    -2.53856   1.01467       2.303
-----------------------------------------------------------------------------

 Type III - SPECIES WITH FIXED ACTIVITY
   ID        NAME        CALC MOL        LOG MOL    NEW LOGK     DH
      2  H2O            1.498E-02       -1.824      0.000      0.000
2015001  PORTLANDITE   -2.880E-02       -1.541    -22.675     30.690
-----------------------------------------------------------------------------

 Type IV - FINITE SOLIDS (present at equilibrium)
   ID        NAME        CALC MOL        LOG MOL    NEW LOGK     DH
6015001  GYPSUM         2.509E-03       -2.601      4.848     -0.261
-----------------------------------------------------------------------------

 Type V - UNDERSATURATED SOLIDS (not present at equilibrium)
   ID        NAME        CALC MOL        LOG MOL    NEW LOGK     DH
2015000  LIME           7.555E-11      -10.122    -32.797     46.265
6015000  ANHYDRITE      6.158E-01       -0.211      4.637      3.769'L

_______________________________________________________________________________
____________________________ PART 4 of OUTPUT FILE ____________________________
  PC MINTEQA2 v3.10   DATE OF CALCULATIONS: 11-MAR-93  TIME: 12: 8: 7



                   PERCENTAGE DISTRIBUTION OF COMPONENTS AMONG
                 TYPE I and TYPE II (dissolved and adsorbed) species
H+1               84.4     PERCENT BOUND IN SPECIES #3300020   OH-
                  15.6     PERCENT BOUND IN SPECIES #1503300   CaOH +
Ca+2              66.9     PERCENT BOUND IN SPECIES #     150   Ca+2
                  22.3     PERCENT BOUND IN SPECIES #1503300   CaOH +
                  10.8     PERCENT BOUND IN SPECIES #1507320   CaSO4 AQ
```

```
SO4-2          61.9     PERCENT BOUND IN SPECIES #    732   SO4-2
               38.1     PERCENT BOUND IN SPECIES #1507320   CaSO4 AQ
H2O            84.4     PERCENT BOUND IN SPECIES #3300020   OH-
               15.6     PERCENT BOUND IN SPECIES #1503300   CaOH +
^L
_______________________________________________________________________
___________________________ PART 5 of OUTPUT FILE _____________________
  PC MINTEQA2 v3.10   DATE OF CALCULATIONS: 11-MAR-93  TIME: 12: 8: 7


              -----------------------------------------------------
              ----------- EQUILIBRATED MASS DISTRIBUTION -----------

IDX     NAME            DISSOLVED           SORBED          PRECIPITATED
                     MOL/KG   PERCENT   MOL/KG  PERCENT    MOL/KG  PERCENT
330  H+1          -3.759E-02   100.0  0.000E-01     0.0  0.000E-01     0.0
150  Ca+2          2.629E-02    91.3  0.000E-01     0.0  2.509E-03     8.7
732  SO4-2         7.491E-03    74.9  0.000E-01     0.0  2.509E-03    25.1
  2  H2O           3.759E-02   100.0  0.000E-01     0.0  0.000E-01     0.0

     Charge Balance: SPECIATED
       Sum of CATIONS =  4.102E-02 Sum of ANIONS   4.102E-02
       PERCENT DIFFERENCE =   1.202E-03  (ANIONS - CATIONS)/(ANIONS + CATIONS)
     EQUILIBRIUM IONIC STRENGTH (m) =   6.324E-02
     EQUILIBRIUM pH                   =  12.405
     DATE ID NUMBER:           930311
     TIME ID NUMBER:         12080762^L
_________________________________________________________________________
___________________________ PART 6 of OUTPUT FILE _______________________
  PC MINTEQA2 v3.10   DATE OF CALCULATIONS: 11-MAR-93  TIME: 12: 8: 7


Saturation indices and stoichiometry of all minerals
   ID #     NAME       Sat. Index        Stoichiometry in [brackets]
  6015000 ANHYDRITE      -0.211    [  1.000] 150  [  1.000] 732
  6015001 GYPSUM          0.000    [  1.000] 150  [  1.000] 732  [  2.000]   2
  2015000 LIME          -10.122    [ -2.000] 330  [  1.000] 150  [  1.000]   2
  2015001 PORTLANDITE     0.000    [ -2.000] 330  [  1.000] 150  [  2.000]   2
```

Exercise 4 : To find the amount of lime needed to raise the pH of a sulphuric acid solution to pH 8.

Objectives

- to fix the pH of a solution

Hints

- create an input file called EX4
- call EX1 as a seed file
- set equilibrium pH to 8, (Edit Level 1, Option 12)

Output

By fixing the pH of the solution at pH 8, you have now asked MINTEQA2 to predict what the speciation of the solution would be at pH 8. Think about what would have to happen for the solution to come to pH 8, and try the following questions.

1 If the pH value of the solution was 8, what would be the total concentration of hydroxyl ions at pH 8?

2 How much portlandite (Ca(OH)$_2$ needs to be added to raise the pH value to 8?

Think about this carefully. You have started with an acid solution and want to turn it into an alkaline solution. The correct (best) answer you can get is that 1.0e-2 moles of Ca(OH)$_2$ need to be added. Adjusting solutions to required pH values is a common chemistry problem. Make sure you understand the modeling technique.

```
 ___________________________________________________________________________
 ____________________________ PART 1 of OUTPUT FILE ________________________
  PC MINTEQA2 v3.00   DATE OF CALCULATIONS: 11-MAR-93  TIME: 14:50:41


h2so4 fix pH at 8


-----------------------------------------------------------------------------
 Temperature (Celsius):  25.00
 Units of concentration: MOLAL
 Ionic strength to be computed.
 If specified, total carbonate concentration represents total inorganic carbon.
 Do not automatically terminate if charge imbalance exceeds 30%
 Precipitation is allowed only for those solids specified as ALLOWED
   in the input file (if any).
 The maximum number of iterations is: 200
 The method used to compute activity coefficients is: Davies equation
 Intermediate output file
-----------------------------------------------------------------------------
    330  2.000E-02   -1.70
    732  1.000E-02   -2.00
 H2O has been inserted as a COMPONENT
  3   1
    330     8.0000      0.0000
INPUT DATA BEFORE TYPE MODIFICATIONS
   ID         NAME        ACTIVITY GUESS    LOG GUESS   ANAL TOTAL
    330  H+1                  1.995E-02        -1.700   2.000E-02
    732  SO4-2                1.000E-02        -2.000   1.000E-02
      2  H2O                  1.000E+00         0.000   0.000E-01

    CHARGE BALANCE: UNSPECIATED
          SUM OF CATIONS=  2.000E-02 SUM OF ANIONS =  2.000E-02
          PERCENT DIFFERENCE =  0.000E-01   (ANIONS - CATIONS)/(ANIONS + CATIONS)^L
 ___________________________________________________________________________
 ____________________________ PART 3 of OUTPUT FILE ________________________
  PC MINTEQA2 v3.00   DATE OF CALCULATIONS: 11-MAR-93  TIME: 14:50:49



PARAMETERS OF THE COMPONENT MOST OUT OF BALANCE:
     ITER       NAME        TOTAL MOL     DIFF FXN     LOG ACTVTY
       2   SO4-2            1.000E-02   7.513E-03     -2.00000
   ID         NAME        ANAL MOL   CALC MOL   ACTIVITY    LOG ACTVTY     GAMMA      NEW LOGK    DIFF FXN
    732  SO4-2           1.000E-02  1.000E-02 5.710E-03    -2.24337    0.570997      0.2434   9.456E-09
      2  H2O             0.000E-01 -1.155E-06 9.995E-01    -0.00022    1.000000      0.0002   0.000E-01
    330  H+1             2.000E-02  1.150E-08 1.000E-08    -8.00000    0.869278      0.0608   0.000E-01
-----------------------------------------------------------------------------
  Type I - COMPONENTS AS SPECIES IN SOLUTION
   ID         NAME         CALC MOL   ACTIVITY    LOG ACTVTY     GAMMA     NEW LOGK       DH
    330  H+1              1.150E-08  0.0000000     -8.00000    0.869278      0.061      0.000
    732  SO4-2            1.000E-02  0.0057100     -2.24337    0.570997      0.243      0.000
-----------------------------------------------------------------------------
```

```
 Type II - OTHER SPECIES IN SOLUTION OR ADSORBED
   ID        NAME         CALC MOL   ACTIVITY    LOG ACTVTY     GAMMA     NEW LOGK        DH
3300020  OH-              1.155E-06  0.0000010    -5.99822    0.869278    -13.937     13.345
3307320  HSO4 -           6.376E-09  0.0000000    -8.25630    0.869278      2.048      4.910
----------------------------------------------------------------------------------------
 Type III - SPECIES WITH FIXED ACTIVITY (fixed pH, fixed pe, infinite solids, gases, etc.)
   ID        NAME         CALC MOL        LOG MOL      NEW LOGK       DH
      2  H2O             -1.155E-06       -5.937       0.000       0.000
    330  H+1              2.000E-02       -1.699       8.000       0.000¯L
________________________________________________________________________________________
_________________________________ PART 4 of OUTPUT FILE _______________________________
  PC MINTEQA2 v3.00   DATE OF CALCULATIONS: 11-MAR-93  TIME: 14:50:49


PERCENTAGE DISTRIBUTION OF COMPONENTS AMONG TYPE I and TYPE II (dissolved and adsorbed) species
SO4-2               100.0     PERCENT BOUND IN SPECIES #    732   SO4-2
H2O                 100.0     PERCENT BOUND IN SPECIES #3300020   OH-
H+1                 101.6     PERCENT BOUND IN SPECIES #3300020   OH-
¯L
________________________________________________________________________________________
_________________________________ PART 5 of OUTPUT FILE _______________________________
  PC MINTEQA2 v3.00   DATE OF CALCULATIONS: 11-MAR-93  TIME: 14:50:50



                  ------------------------------------------------------------
                  ----------- EQUILIBRATED MASS DISTRIBUTION -----------

IDX     NAME              DISSOLVED              SORBED               PRECIPITATED
                      MOL/KG    PERCENT     MOL/KG    PERCENT      MOL/KG    PERCENT
732  SO4-2          1.000E-02    100.0   0.000E-01      0.0    0.000E-01      0.0
  2  H2O            1.155E-06    100.0   0.000E-01      0.0    0.000E-01      0.0
330  H+1           -1.137E-06    100.0   0.000E-01      0.0    0.000E-01      0.0

    CHARGE BALANCE: SPECIATED
          SUM OF CATIONS =  1.150E-08 SUM OF ANIONS   2.000E-02
          PERCENT DIFFERENCE =   1.000E+02   (ANIONS - CATIONS)/(ANIONS + CATIONS)
     EQUILIBRIUM IONIC STRENGTH (m) =   2.000E-02
     EQUILIBRIUM pH                 =   8.000
     DATE ID NUMBER:           930311
     TIME ID NUMBER:         14505002¯L
________________________________________________________________________________________
_________________________________ PART 6 of OUTPUT FILE _______________________________
  PC MINTEQA2 v3.00   DATE OF CALCULATIONS: 11-MAR-93  TIME: 14:50:50


Saturation indices and stoichiometry of all minerals
    ID #     NAME       Sat. Index         Stoichiometry (in parentheses) of each component
```

Exercise 5: Check that addition of the lime concentration reached in Ex 4 will raise the pH of the acid solution to a value of 8.0

Objectives

- to add a finite solid
- to add a solid as soluble components

Hints

Before you attempt this problem make sure you totally understand how you arrived at the required concentration of lime.

There are two methods to tackle this problem. The safest one is to use the finite solid option

Method 1 : finite solid option

- create an input file called EX5
- call EX1 as a seed file
- pH to be computed
- add finite solid ; enter the lime concentration from Exercise 4

Method 2: add solid as soluble components

The lime could also be added as soluble components. This is equivalent to dissolving the lime in a beaker and adding it to the acid solution. Before attempting this method do a mass balance calculation of the components in your starting solution and the final solution you require.

From the output file of exercice 4

- add calcium as a component at required concentration
- add hydroxyl as a component at required concentration. Be careful here. The only way to add hydroxyl ions is to adjust the proton concentration. Your mass balance calculation will help you here.

Output

1 What is the pH of the solution.

2 Was your answer to Ex 4 correct or not?

```
______________________________________________________________________

finite solid option lime to 8


..................................................................................
 Temperature (Celsius):  25.00
 Units of concentration: MOLAL
 Ionic strength to be computed.
 If specified, carbonate concentration represents total inorganic carbon.___________
_____________________________ PART 1 of OUTPUT FILE __________________________
  PC MINTEQA2 v3.10   DATE OF CALCULATIONS: 17-MAY-94  TIME: 10:22:37

 Do not automatically terminate if charge imbalance exceeds 30%
 Precipitation is allowed only for those solids specified as ALLOWED
   in the input file (if any).
 The maximum number of iterations is: 200
 The method used to compute activity coefficients is: Davies equation
 Intermediate output file

..................................................................................
    330  2.000E-02   -1.70 y
    732  1.000E-02   -2.00 y
    150  0.000E-01  -16.00

 H2O has been inserted as a COMPONENT
  4   1
2015001   -22.6750    30.6900   1.000E-02

INPUT DATA BEFORE TYPE MODIFICATIONS

   ID       NAME       ACTIVITY GUESS    LOG GUESS   ANAL TOTAL
   330  H+1                 1.995E-02       -1.700   2.000E-02
   732  SO4-2               1.000E-02       -2.000   1.000E-02
   150  Ca+2                1.000E-16      -16.000   0.000E-01
     2  H2O                 1.000E+00        0.000   0.000E-01


      Charge Balance: UNSPECIATED

        Sum of CATIONS=  2.000E-02 Sum of ANIONS =  2.000E-02

        PERCENT DIFFERENCE =  0.000E-01  (ANIONS - CATIONS)/(ANIONS + CATIONS)


              ......................................................
             |  IMPROVED ACTIVITY GUESSES PRIOR TO FIRST ITERATION: |
             |       SO4-2       Log activity guess:    -2.47        |
             |                                                       |
              ......................................................
```

```
_______________________________ PART 3 of OUTPUT FILE ___________________________
 PC MINTEQA2 v3.10   DATE OF CALCULATIONS: 17-MAY-94  TIME: 10:22:41



PARAMETERS OF THE COMPONENT MOST OUT OF BALANCE:

     ITER      NAME         TOTAL MOL    DIFF FXN    LOG ACTVTY    RESIDUAL
       0   SO4-2            1.000E-02   1.308E+19    -2.46786     1.308E+19
       1   SO4-2            1.000E-02   3.270E+18    -2.46786     3.269E+18
       2   SO4-2            1.000E-02   8.118E+17    -2.46786     8.117E+17
       3   SO4-2            1.000E-02   2.030E+17    -2.46786     2.029E+17
       4   SO4-2            1.000E-02   5.074E+16    -2.46786     5.073E+16
       5   SO4-2            1.000E-02   1.268E+16    -2.46786     1.268E+16
       6   SO4-2            1.000E-02   3.171E+15    -2.46786     3.171E+15
       7   SO4-2            1.000E-02   7.928E+14    -2.46786     7.927E+14
       8   SO4-2            1.000E-02   1.982E+14    -2.46786     1.982E+14
       9   SO4-2            1.000E-02   4.955E+13    -2.46786     4.955E+13
      10   SO4-2            1.000E-02   1.239E+13    -2.46786     1.239E+13
      11   SO4-2            1.000E-02   3.097E+12    -2.46786     3.097E+12
      12   SO4-2            1.000E-02   7.742E+11    -2.46786     7.741E+11
      13   SO4-2            1.000E-02   1.936E+11    -2.46786     1.935E+11
      14   SO4-2            1.000E-02   4.839E+10    -2.46786     4.838E+10
      15   SO4-2            1.000E-02   1.210E+10    -2.46786     1.210E+10
      16   SO4-2            1.000E-02   3.024E+09    -2.46786     3.024E+09
      17   SO4-2            1.000E-02   7.561E+08    -2.46786     7.560E+08
      18   SO4-2            1.000E-02   1.890E+08    -2.46786     1.890E+08
      19   SO4-2            1.000E-02   4.725E+07    -2.46786     4.725E+07
      20   SO4-2            1.000E-02   1.181E+07    -2.46786     1.181E+07
      21   SO4-2            1.000E-02   2.953E+06    -2.46786     2.953E+06
      22   SO4-2            1.000E-02   7.383E+05    -2.46786     7.383E+05
      23   SO4-2            1.000E-02   1.846E+05    -2.46785     1.846E+05
      24   SO4-2            1.000E-02   4.615E+04    -2.46785     4.614E+04
      25   SO4-2            1.000E-02   1.154E+04    -2.46783     1.153E+04
      26   SO4-2            1.000E-02   2.884E+03    -2.46780     2.884E+03
      27   SO4-2            1.000E-02   7.209E+02    -2.46775     7.208E+02
      28   SO4-2            1.000E-02   1.802E+02    -2.46763     1.801E+02
      29   SO4-2            1.000E-02   4.502E+01    -2.46741     4.501E+01
      30   SO4-2            1.000E-02   1.124E+01    -2.46695     1.124E+01
      31   SO4-2            1.000E-02   2.804E+00    -2.46602     2.803E+00
      32   SO4-2            1.000E-02   6.970E-01    -2.46413     6.969E-01
      33   SO4-2            1.000E-02   1.719E-01    -2.46042     1.719E-01
      34   SO4-2            1.000E-02   4.164E-02    -2.45477     4.163E-02
      35   SO4-2            1.000E-02   9.726E-03    -2.45816     9.725E-03
      36   SO4-2            1.000E-02   1.807E-03    -2.51028     1.806E-03
      37   SO4-2            1.000E-02   7.048E-05    -2.55904     6.948E-05
      39   SO4-2            1.000E-02   1.136E-03    -2.56174     1.135E-03
      40   SO4-2            1.000E-02   2.292E-04    -2.59260     2.282E-04
      41   SO4-2            1.000E-02   3.151E-05    -2.59985     3.051E-05
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    42   SO4-2           1.000E-02  4.862E-06   -2.60084   3.862E-06
    43   H+1             2.000E-02  4.043E-06  -12.39590   2.847E-07

ID       NAME        ANAL MOL   CALC MOL  LOG ACTVTY    GAMMA     DIFF FXN
 330  H+1            2.000E-02 5.031E-13  -12.39591   0.798752  6.527E-07
 732  SO4-2          1.000E-02 6.156E-03   -2.60102   0.407051  1.260E-07
 150  Ca+2           0.000E-01 1.879E-02   -2.11638   0.407051  0.000E-01
   2  H2O            0.000E-01 2.000E-02   -0.00022   1.000000  0.000E-01


-------------------------------------------------------------------------


Type I - COMPONENTS AS SPECIES IN SOLUTION

  ID       NAME        CALC MOL  ACTIVITY   LOG ACTVTY   GAMMA    NEW LOGK
   330  H+1            5.031E-13 4.019E-13  -12.39591  0.79875     0.098
   732  SO4-2          6.156E-03 2.506E-03   -2.60102  0.40705     0.390
   150  Ca+2           1.879E-02 7.649E-03   -2.11638  0.40705     0.390


-------------------------------------------------------------------------


Type II - OTHER SPECIES IN SOLUTION OR ADSORBED

  ID       NAME        CALC MOL  ACTIVITY   LOG ACTVTY   GAMMA    NEW LOGK
3307320  HSO4 -        1.224E-13 9.775E-14  -13.00987  0.79875     2.085
3300020  OH-           3.128E-02 2.499E-02   -1.60231  0.79875   -13.900
1503300  CaOH +        6.010E-03 4.801E-03   -2.31869  0.79875   -12.500
1507320  CaSO4 AQ      3.844E-03 3.905E-03   -2.40840  1.01591     2.302


-------------------------------------------------------------------------
Type III - SPECIES WITH FIXED ACTIVITY

  ID       NAME        CALC MOL       LOG MOL   NEW LOGK     DH
     2  H2O            2.000E-02      -1.699     0.000     0.000


-------------------------------------------------------------------------
Type IV - FINITE SOLIDS (presumed present at equilibrium)

  ID       NAME        CALC MOL       LOG MOL   NEW LOGK     DH
2015001  PORTLANDITE   0.000E-01      -1.543    -22.675    30.690


__________________________________________________________________________
____________________________ PART 4 of OUTPUT FILE _______________________
  PC MINTEQA2 v3.10   DATE OF CALCULATIONS: 17-MAY-94  TIME: 10:22:42



                 PERCENTAGE DISTRIBUTION OF COMPONENTS AMONG
               TYPE I and TYPE II (dissolved and adsorbed) specie
H+1             83.9     PERCENT BOUND IN SPECIES #3300020   OH-
                16.1     PERCENT BOUND IN SPECIES #1503300   CaOH +
SO4-2           61.6     PERCENT BOUND IN SPECIES #    732   SO4-2
```

```
               38.4     PERCENT BOUND IN SPECIES #1507320   CaSO4 AQ

Ca+2           65.6     PERCENT BOUND IN SPECIES #    150   Ca+2
               21.0     PERCENT BOUND IN SPECIES #1503300   CaOH +
               13.4     PERCENT BOUND IN SPECIES #1507320   CaSO4 AQ

H2O            83.9     PERCENT BOUND IN SPECIES #3300020   OH-
               16.1     PERCENT BOUND IN SPECIES #1503300   CaOH +


______________________________________________________________________
___________________________ PART 5 of OUTPUT FILE ____________________
 PC MINTEQA2 v3.10   DATE OF CALCULATIONS: 17-MAY-94  TIME: 10:22:42


               --------------------------------------------------
               ----------- PROVISIONAL MASS DISTRIBUTION -----------


IDX    NAME            DISSOLVED             SORBED             PRECIPITATED
                    MOL/KG   PERCENT    MOL/KG   PERCENT     MOL/KG   PERCENT

330  H+1         -3.729E-02   100.0   0.000E-01     0.0   0.000E-01     0.0
732  SO4-2        1.000E-02   100.0   0.000E-01     0.0   0.000E-01     0.0
150  Ca+2         2.865E-02   100.0   0.000E-01     0.0   0.000E-01     0.0
  2  H2O          3.729E-02   100.0   0.000E-01     0.0   0.000E-01     0.0

      Charge Balance: SPECIATED

       Sum of CATIONS =  4.359E-02 Sum of ANIONS   4.359E-02

       PERCENT DIFFERENCE =   4.595E-04  (ANIONS - CATIONS)/(ANIONS + CATIONS)

     PROVISIONAL IONIC STRENGTH (m) =   6.854E-02

______________________________________________________________________
___________________________ PART 6 of OUTPUT FILE ____________________
 PC MINTEQA2 v3.10   DATE OF CALCULATIONS: 17-MAY-94  TIME: 10:22:42


Saturation indices and stoichiometry of all undersaturated minerals

   ID #     NAME       Sat. Index       Stoichiometry in [brackets]
 6015000 ANHYDRITE       -0.080    [  1.000] 150  [  1.000] 732
 2015000 LIME           -10.122    [ -2.000] 330  [  1.000] 150  [  1.000]   2
 2015001 PORTLANDITE      0.000    [ -2.000] 330  [  1.000] 150  [  2.000]   2

 ITERATIONS=  44:  SOLID PORTLANDITE  DISSOLVES

______________________________________________________________________
___________________________ PART 3 of OUTPUT FILE ____________________
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PC MINTEQA2 v3.10   DATE OF CALCULATIONS: 17-MAY-94  TIME: 10:22:43



PARAMETERS OF THE COMPONENT MOST OUT OF BALANCE:

   ITER       NAME           TOTAL MOL     DIFF FXN    LOG ACTVTY     RESIDUAL
    44    Ca+2               1.000E-02    6.355E-03    -2.11638     6.354E-03
    45    Ca+2               1.000E-02    7.203E-03    -2.26104     7.202E-03
    46    Ca+2               1.000E-02    1.876E-03    -2.39520     1.875E-03
    47    Ca+2               1.000E-02    2.971E-04    -2.43371     2.961E-04
    48    Ca+2               1.000E-02    9.340E-05    -2.43247     9.240E-05
    49    Ca+2               1.000E-02    4.620E-05    -2.42961     4.520E-05
    50    Ca+2               1.000E-02    2.324E-05    -2.42813     2.224E-05
    51    Ca+2               1.000E-02    1.162E-05    -2.42739     1.062E-05
    52    Ca+2               1.000E-02    5.807E-06    -2.42702     4.807E-06
    53    Ca+2               1.000E-02    2.902E-06    -2.42684     1.902E-06
    54    Ca+2               1.000E-02    1.450E-06    -2.42674     4.504E-07
    55    H+1                0.000E-01   -1.638E-05    -9.10306     1.638E-05
    56    H+1                0.000E-01   -8.188E-06    -8.80206     8.187E-06
    57    H+1                0.000E-01   -4.092E-06    -8.50117     4.091E-06
    58    H+1                0.000E-01   -2.041E-06    -8.20067     2.041E-06
    59    H+1                0.000E-01   -1.010E-06    -7.90178     1.010E-06
    60    H+1                0.000E-01   -4.858E-07    -7.60914     4.858E-07
    61    H+1                0.000E-01   -2.090E-07    -7.33955     2.090E-07
    62    H+1                0.000E-01   -6.139E-08    -7.13884     6.137E-08
    63    H+1                0.000E-01   -6.402E-09    -7.05656     6.389E-09
    64    H+1                0.000E-01   -7.117E-11    -7.04701     5.802E-11

 ID         NAME          ANAL MOL   CALC MOL  LOG ACTVTY     GAMMA      DIFF FXN
  330  H+1              0.000E-01  1.056E-07    -7.04691    0.850276   6.882E-22
  732  SO4-2            1.000E-02  7.163E-03    -2.42666    0.522684  -1.455E-07
  150  Ca+2             1.000E-02  7.163E-03    -2.42666    0.522684  -1.455E-07
    2  H2O              2.000E-02  2.000E-02    -0.00022    1.000000   0.000E-01


------------------------------------------------------------------------------


 Type I - COMPONENTS AS SPECIES IN SOLUTION

    ID          NAME          CALC MOL   ACTIVITY    LOG ACTVTY    GAMMA      NEW LOGK
    330  H+1                1.056E-07  8.976E-08    -7.04691    0.85028       0.070
    732  SO4-2              7.163E-03  3.744E-03    -2.42666    0.52268       0.282
    150  Ca+2               7.163E-03  3.744E-03    -2.42666    0.52268       0.282


------------------------------------------------------------------------------


 Type II - OTHER SPECIES IN SOLUTION OR ADSORBED

    ID          NAME          CALC MOL   ACTIVITY    LOG ACTVTY    GAMMA      NEW LOGK
 3307320  HSO4 -            3.837E-08  3.262E-08    -7.48650    0.85028       2.058
 3300020  OH-               1.316E-07  1.119E-07    -6.95131    0.85028     -13.928
```

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1503300  CaOH +          1.237E-08  1.052E-08    -7.97797   0.85028    -12.528
1507320  CaSO4 AQ        2.837E-03  2.855E-03    -2.54432   1.00662      2.306

--------------------------------------------------------------------------------

 Type III - SPECIES WITH FIXED ACTIVITY

   ID        NAME        CALC MOL        LOG MOL   NEW LOGK     DH
     2  H2O              2.000E-02       -1.699      0.000      0.000

--------------------------------------------------------------------------------

 Type V - UNDERSATURATED SOLIDS (not present at equilibrium)

   ID        NAME        CALC MOL        LOG MOL   NEW LOGK     DH
2015001  PORTLANDITE     9.811E-12      -11.008    -22.675     30.690

__________________________________________________________________________________
______________________________ PART 4 of OUTPUT FILE ______________________________
  PC MINTEQA2 v3.10   DATE OF CALCULATIONS: 17-MAY-94  TIME: 10:22:43



                PERCENTAGE DISTRIBUTION OF COMPONENTS AMONG
             TYPE I and TYPE II (dissolved and adsorbed) species


H+1            >1000.     PERCENT BOUND IN SPECIES #    330   H+1
               >1000.     PERCENT BOUND IN SPECIES #3307320   HSO4 -
SO4-2            71.6     PERCENT BOUND IN SPECIES #    732   SO4-2
                 28.4     PERCENT BOUND IN SPECIES #1507320   CaSO4 AQ
Ca+2             71.6     PERCENT BOUND IN SPECIES #    150   Ca+2
                 28.4     PERCENT BOUND IN SPECIES #1507320   CaSO4 AQ

H2O              91.4     PERCENT BOUND IN SPECIES #3300020   OH-
                  8.6     PERCENT BOUND IN SPECIES #1503300   CaOH +

__________________________________________________________________________________
______________________________ PART 5 of OUTPUT FILE ______________________________
  PC MINTEQA2 v3.10   DATE OF CALCULATIONS: 17-MAY-94  TIME: 10:22:43



                -----------------------------------------------------
                ----------- EQUILIBRATED MASS DISTRIBUTION -----------


IDX     NAME                DISSOLVED            SORBED          PRECIPITATED
                       MOL/KG    PERCENT    MOL/KG    PERCENT    MOL/KG    PERCENT

330  H+1             6.882E-22   100.0   0.000E-01      0.0   0.000E-01      0.0
```

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732  SO4-2          1.000E-02   100.0   0.000E-01     0.0   0.000E-01     0.0
150  Ca+2           1.000E-02   100.0   0.000E-01     0.0   0.000E-01     0.0
  2  H2O            1.439E-07   100.0   0.000E-01     0.0   0.000E-01     0.0


     Charge Balance: SPECIATED

       Sum of CATIONS =  1.433E-02 Sum of ANIONS   1.433E-02

       PERCENT DIFFERENCE =   2.791E-09  (ANIONS - CATIONS)/(ANIONS + CATIONS)

     EQUILIBRIUM IONIC STRENGTH (m) =   2.865E-02

     EQUILIBRIUM pH                 =   7.047

     DATE ID NUMBER:          940517
     TIME ID NUMBER:        10224378

_____________________________________________________________________________
___________________________ PART 6 of OUTPUT FILE ___________________________
  PC MINTEQA2 v3.10   DATE OF CALCULATIONS: 17-MAY-94  TIME: 10:22:43


Saturation indices and stoichiometry of all minerals

   ID #     NAME      Sat. Index       Stoichiometry in [brackets]
  6015000 ANHYDRITE      -0.216    [  1.000] 150  [  1.000] 732
  6015001 GYPSUM         -0.006    [  1.000] 150  [  1.000] 732  [  2.000]   2
  2015000 LIME          -21.130    [ -2.000] 330  [  1.000] 150  [  1.000]   2
  2015001 PORTLANDITE   -11.008    [ -2.000] 330  [  1.000] 150  [  2.000]   2
```

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______________________________________________________________________________
________________________________ PART 1 of OUTPUT FILE _______________________
  PC MINTEQA2 v3.10   DATE OF CALCULATIONS: 19-MAY-94  TIME: 12:49:50


To add lime to sulphuric acid to adjust to pH 8.  Pre mix method



------------------------------------------------------------------------------
 Temperature (Celsius):  25.00
 Units of concentration: MOLAL
 Ionic strength to be computed.
 If specified, carbonate concentration represents total inorganic carbon.
 Do not automatically terminate if charge imbalance exceeds 30%
 Precipitation is allowed only for those solids specified as ALLOWED
   in the input file (if any).
 The maximum number of iterations is: 200
 The method used to compute activity coefficients is: Davies equation
 Intermediate output file

------------------------------------------------------------------------------
    330  0.000E-01    -1.70 y
    732  1.000E-02    -2.00 y
    150  1.000E-02    -2.00

 H2O has been inserted as a COMPONENT

INPUT DATA BEFORE TYPE MODIFICATIONS

   ID         NAME       ACTIVITY GUESS    LOG GUESS   ANAL TOTAL
    330  H+1                  1.995E-02       -1.700   0.000E-01
    732  SO4-2                1.000E-02       -2.000   1.000E-02
    150  Ca+2                 1.000E-02       -2.000   1.000E-02
      2  H2O                  1.000E+00        0.000   0.000E-01


     Charge Balance: UNSPECIATED

       Sum of CATIONS=  2.000E-02 Sum of ANIONS =  2.000E-02

       PERCENT DIFFERENCE =  0.000E-01  (ANIONS - CATIONS)/(ANIONS + CATIONS)



               -----------------------------------------------------
              |  IMPROVED ACTIVITY GUESSES PRIOR TO FIRST ITERATION: |
              |       SO4-2       Log activity guess:     -2.47       |
              |                                                       |
               -----------------------------------------------------
```

```
_______________________________________________________________________________
______________________________ PART 3 of OUTPUT FILE __________________________
  PC MINTEQA2 v3.10   DATE OF CALCULATIONS: 19-MAY-94  TIME: 12:49:53



PARAMETERS OF THE COMPONENT MOST OUT OF BALANCE:

     ITER       NAME        TOTAL MOL    DIFF FXN   LOG ACTVTY    RESIDUAL
       0   Ca+2             1.000E-02  6.937E-03   -2.00000   6.936E-03
       1   Ca+2             1.000E-02 -6.843E-04   -2.29390   6.833E-04
       2   Ca+2             1.000E-02  3.716E-03   -2.30081   3.715E-03
       3   Ca+2             1.000E-02  7.789E-04   -2.40000   7.779E-04
       4   Ca+2             1.000E-02  5.445E-05   -2.42468   5.345E-05
       5   Ca+2             1.000E-02  3.744E-06   -2.42651   2.744E-06
       6   H+1              0.000E-01 -9.383E-09   -7.06102   9.370E-09
       7   H+1              0.000E-01 -1.529E-10   -7.04710   1.397E-10

  ID        NAME         ANAL MOL   CALC MOL  LOG ACTVTY     GAMMA     DIFF FXN
   330  H+1            0.000E-01  1.056E-07    -7.04687   0.850276  -4.076E-14
   732  SO4-2          1.000E-02  7.163E-03    -2.42665   0.522686   5.608E-09
   150  Ca+2           1.000E-02  7.163E-03    -2.42665   0.522686   5.608E-09
     2  H2O            0.000E-01 -1.439E-07    -0.00015   1.000000   0.000E-01

--------------------------------------------------------------------------------


  Type I - COMPONENTS AS SPECIES IN SOLUTION

    ID        NAME         CALC MOL   ACTIVITY   LOG ACTVTY    GAMMA      NEW LOGK
     330  H+1            1.056E-07  8.977E-08    -7.04687   0.85028       0.070
     732  SO4-2          7.163E-03  3.744E-03    -2.42665   0.52269       0.282
     150  Ca+2           7.163E-03  3.744E-03    -2.42665   0.52269       0.282

--------------------------------------------------------------------------------


  Type II - OTHER SPECIES IN SOLUTION OR ADSORBED

    ID        NAME         CALC MOL   ACTIVITY   LOG ACTVTY    GAMMA      NEW LOGK
3307320  HSO4 -          3.837E-08  3.262E-08    -7.48646   0.85028       2.058
3300020  OH-             1.316E-07  1.119E-07    -6.95128   0.85028     -13.928
1503300  CaOH +          1.237E-08  1.052E-08    -7.97793   0.85028     -12.528
1507320  CaSO4 AQ        2.837E-03  2.856E-03    -2.54431   1.00662       2.306

--------------------------------------------------------------------------------


  Type III - SPECIES WITH FIXED ACTIVITY

    ID        NAME         CALC MOL        LOG MOL    NEW LOGK      DH
       2  H2O            -1.439E-07       -6.842       0.000      0.000

_______________________________________________________________________________
```

```
__________________________________ PART 4 of OUTPUT FILE ____________________________
 PC MINTEQA2 v3.10   DATE OF CALCULATIONS: 19-MAY-94  TIME: 12:49:53


               PERCENTAGE DISTRIBUTION OF COMPONENTS AMONG
             TYPE I and TYPE II (dissolved and adsorbed) species


H+1
             >1000.     PERCENT BOUND IN SPECIES #3300020   OH-

             >1000.     PERCENT BOUND IN SPECIES #1503300   CaOH +


SO4-2
               71.6     PERCENT BOUND IN SPECIES #    732   SO4-2

               28.4     PERCENT BOUND IN SPECIES #1507320   CaSO4 AQ


Ca+2
               71.6     PERCENT BOUND IN SPECIES #    150   Ca+2

               28.4     PERCENT BOUND IN SPECIES #1507320   CaSO4 AQ


H2O
               91.4     PERCENT BOUND IN SPECIES #3300020   OH-

                8.6     PERCENT BOUND IN SPECIES #1503300   CaOH +


_______________________________________________________________________________________
__________________________________ PART 5 of OUTPUT FILE ____________________________
 PC MINTEQA2 v3.10   DATE OF CALCULATIONS: 19-MAY-94  TIME: 12:49:53


              ---------------------------------------------------
              ----------- EQUILIBRATED MASS DISTRIBUTION -----------


IDX     NAME              DISSOLVED            SORBED            PRECIPITATED
                     MOL/KG   PERCENT     MOL/KG   PERCENT     MOL/KG   PERCENT

330  H+1           -4.076E-14   100.0   0.000E-01     0.0   0.000E-01     0.0
732  SO4-2          1.000E-02   100.0   0.000E-01     0.0   0.000E-01     0.0
150  Ca+2           1.000E-02   100.0   0.000E-01     0.0   0.000E-01     0.0
  2  H2O            1.439E-07   100.0   0.000E-01     0.0   0.000E-01     0.0
```

```
Charge Balance: SPECIATED

  Sum of CATIONS =  1.433E-02 Sum of ANIONS   1.433E-02

  PERCENT DIFFERENCE =   9.517E-12  (ANIONS - CATIONS)/(ANIONS + CATIONS)

EQUILIBRIUM IONIC STRENGTH (m) =   2.865E-02

EQUILIBRIUM pH                 =   7.047

DATE ID NUMBER:          940519
TIME ID NUMBER:        12495393

_____________________________________________________________________________
______________________________ PART 6 of OUTPUT FILE ________________________
 PC MINTEQA2 v3.10   DATE OF CALCULATIONS: 19-MAY-94  TIME: 12:49:54

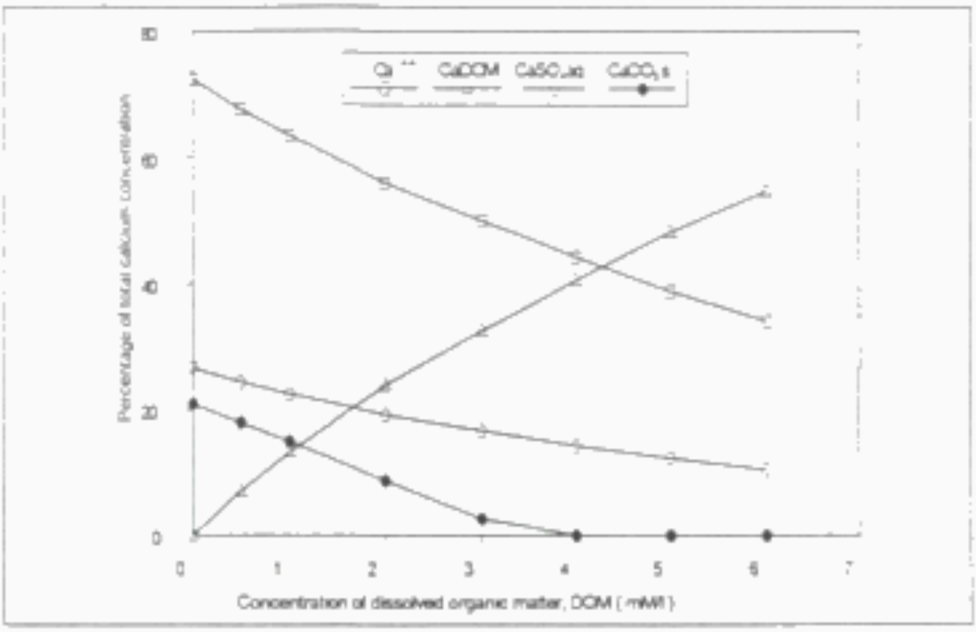

Saturation indices and stoichiometry of all minerals

   ID #     NAME      Sat. Index       Stoichiometry in [brackets]
 6015000 ANHYDRITE      -0.216    [  1.000] 150  [  1.000] 732
 6015001 GYPSUM         -0.006    [  1.000] 150  [  1.000] 732  [  2.000]   2
 2015000 LIME          -21.130    [ -2.000] 330  [  1.000] 150  [  1.000]   2
 2015001 PORTLANDITE   -11.008    [ -2.000] 330  [  1.000] 150  [  2.000]   2
```

Some advanced modeling features in MINTEQA2

Organic complexation

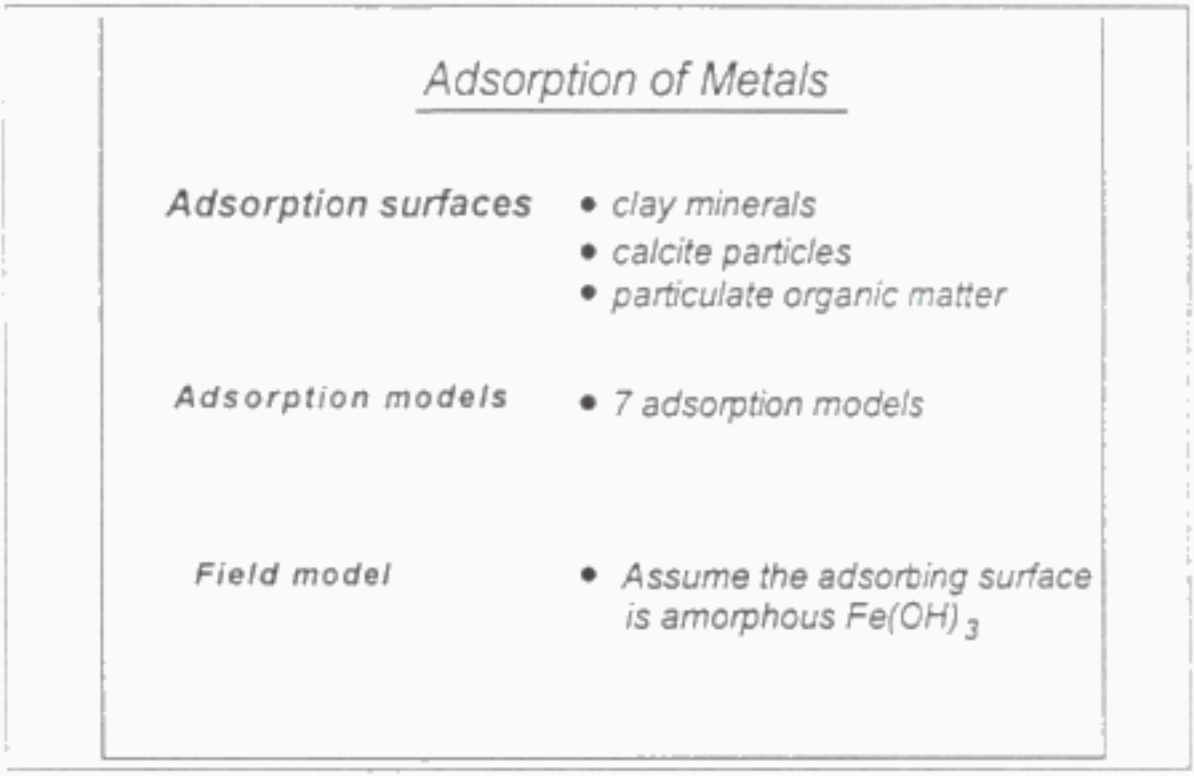
MINTEQA2 contains a composite organic ligand called DOM Constants for the complexation with a number of metals are provided in the MINTEQA2 data base DOM can be used to assess how significant organic complexation might be in your system The ligand is based on the dissolved organic concentrations found in the Suwannee River, Fargo Georgia,USA. When you use DOM you are assuming that the organic composition and concentration of your water is similar to that of the Suwannee River. The purists won't like that, but the chances are you know neither the organic components, their concentrations, nor the appropiate equilibrium constants for your water, so DOM is the best you can do.
DOM is entered in exactly the same way as any other component (edit level 2, option 1).
A useful exercise is to vary the organic concentration and see the effect on the disrtibution of the species



Variation in the concentration of calcium species with increasing concentration of dissolved organic matter. The concentration of the soluble calcium-organic complex increases at the expense of all other calcium species present, including the equilibrium solid phase, calcium carbonate.

Surface adsorption

In many aqueous environments the fate or distribution of metal ions is regulated by adsorption/desorption reactions occurring at the interface between the aqueous solution and particulate matter such as mineral particles, organic matter or living cells. Various mathematical models have been developed to describe ion adsorption. Seven such models are available in MINTEQA2. The choice of model to use depends on the depth of information available for the creation of input files.



Adsorption of Metals

Adsorption surfaces
- *clay minerals*
- *calcite particles*
- *particulate organic matter*

Adsorption models
- *7 adsorption models*

Field model
- *Assume the adsorbing surface is amorphous $Fe(OH)_3$*

For natural water systems there is evidence that the binding capacity of sediments is determined largely by amorphous ferric oxide which forms a coating on inorganic support particles (Luoma and Davies, 1983). MINTEQA2 provides a separate data base of surface complexation reactions with FeO (FEO-DBS). This data base is used with the Diffuse Layer Model. The database is compiled using sediments with the following characteristics

Characteristics of the amorphous iron oxide surface used to model the extent of surface adsorption, using the Diffuse Layer Model

Specific surface area (m^2 per g)	600
Concentration of solid (g/*l*)	3,422
Surface site density (moles/*l*)	
Type 1 (high energy)	$4,18 \times 10^{-2}$
Type 2 (low energy)	$7,69 \times 10^{-3}$

The chances of having site specific sediment data are small. By using the FEO-DBS data base you can get an idea of how important adsorption might be in your system, and by varying chemical parameters such as pH, you can examing desorption conditions.

The following table gives an indication of how important it might be to examine the extent of adsorption in your system

A comparison of the precentage distribution of dissolved, adsorbed and precipitated phosphate, calcium, sulphate and nickel, with and without adsorption modeling

	Dissolved		Adsorbed		Precipitated	
	No adsorption modeling	Adsorption modeling	No adsorption modeling	Adsorption modeling	No adsorption modeling	Adsorption modeling
PO_4	0,7	0,1	-	99,9	99,3	0,0
Ca	91,4	13.4	-	78,8	8,6	7,8
SO_4	100,0	98,2	-	1,0	0,0	0,0
Ni	100,0	0,4	-	99,6	0,0	0,0

WATER RESEARCH COMMISSION PROJECT NO 530
TECHNOLOGY TRANSFER OF AQUATIC CHEMICAL
SPECIATION MODELING

APPENDIX 3

MINTEQA2 : Additional Modeling Problems and Case Studies of Advanced Modeling Options

Manual Prepared for Advanced MINTEQA2 Workshops

Pollution Research Group
University of Natal
Durban
December 1994

MINTEQA2 :Additional Modeling Problems

AND CASE STUDIES OF ADVANCED MODELING OPTIONS

COMPILED BY CAROL KERR
POLLUTION RESEARCH GROUP
UNIVERSITY OF NATAL
DURBAN

Additional Minteqa2 Problems

These problems are no more difficult to do than those presented in the basic tutorial book. In some cases new PRODEFA2 options are used while in others some thought is required as to what information you actually want MINTEQA2 to give you, and what information you need to give the model to get meaningful predictions. This is probably the most difficult aspect of using MINTEQA2. It can not be taught. Familarity with the program will help but an overall grasp of the problem is the best aid of all. In dealing with real world problems, simplify down. Do not get bogged down in large files, with too many variables. Rather simplyify to the basic chemistry which is likely to be controlling the system. When a feel for the system behaviour has been gained, then additional inputs to the system can be added to the model and their effect on the basic chemistry noted.

Above all : READ YOUR USER'S MANUAL. The answers to most of the question you will ask can be found in the manual.

COMMENT : When running input files with only a few components, Phase Rule violations sometimes occur, especially if you are also bringing solids into the picture. A way to avoid these violations is to add extra components, such as sodium or potassium, nitrate etc, ie components that are generally not strong complex formers. Phase rule violations are common when learning to use MINTEQA2. Generally it means that you are trying to do too much at once, for example, fixed pH, fixed partial pressure of gases, add infinite solid, allow precipitation . Simplify the problem, take it one step at a time.

Exercise 1 : Simulating a titration

Add 1,0 x 10^{-3} M of sulphuric acid to 1*l* of water

- What is the pH of the solution?
- What is the total proton concentration?
- Do you understand why proton concentation is not the same as pH?
- You want to titrate the acid solution with sodium hydroxide. Can you set up an input file to do this?

> **HINTS** : There are several possibilities, you could add a known amount of sodium hydroxide as components, and repeat for increasing amounts of sodium hydroxide. Your cation and anion balance would be fine but this would be a tedious procedure. Rather forego an ion balance and use the sweep option (Edit Level 4). By adding sodium hydroxide you will be raising the pH. In MINTEQA2 terms this is identical to reducing the proton concentration, so in the sweep option, if you use incremental changes, your increment needs to be negative. For 20 sweeps a reasonable increment is -2.0e-4. This produces a long output file ; scroll through to see effects of alkali addition. You could plot up a titration curve from the output file

- How much sodium hydroxide do you need to add to raise the pH to 11,2?

Exercise 2 : Adding an alkali to water

Can you add 0,01 M of Potassium Hydroxide to water?

Remember that in MINTEQA2, OH^- is not a component; it is represented in terms of components H^+ and H_2O as (H_2O minus H^+)

- What is the pH of the solution?

Exercise 3 : Equilibration with a gas phase

Use the INFINITE SOLID option (Edit Level 2, Option6). If you want to add a **known** amount of a compound , it may be added through the FINITE SOLID option, (if it exists as a solid) or by adding it as COMPONENTS in the correct stoichiometric ratios

- How much calcite will dissolve in water to give a saturated solution?
- What is the pH of the solution?
- If the saturated calcite solution is in equilibrium with carbon dioxide in the atmosphere, how much calcite would dissolve? Use Edit Level 2, Option 4. The partial pressure of CO_2 (g) at normal atmospheric pressure is 0,0003 atm
- How much carbon dioxide gas had to dissolve so that equilibrium is attained?
- What is the equilibrium pH when the solution is in equilibrium with CO_2 in the atmosphere?

Exercise 4 : Dealing with alkalinity

This problem concerns the various ways carbonate is handled by MINTEQA2 and involves an understanding of what an alkalinity value actually means. Inorganic carbonate can be entered as a COMPONENT in Edit Level 2, Option 1 in the normal way. If the alkalinity of a water is known, it can be entered directly as alkalinity in Edit Level 1, Option 6. When entering alkalinity do not allow solids to precipitate (read the User's Manual- it does tell you this). If you need to consider solids in the problem together with alkalinity, then two runs are required. In the first, enter the alkalinity value and do **not** allow solids to precipitate. In the second run, enter the total carbonate concentration (found in the output from run 1- you should know where to find it) and allow solids to precipitate.

COMMENT : This double run technique can be very useful, for example it is often useful to know the total proton concentration rather than a pH value, especially when several solids are precipitating. By entering the total proton concentration or total carbonate concentration found in a preliminary run, then a degree of freedom is liberated, which may just be enough to allow the problem to run without a Phase Rule violation. (see earlier comment on Phase Rule violations

A cooling water with a pH of 7,7 has the following composition.

Determinand	Concentration (mg/l)	Concentration (molar)
Calcium	120	3,0e-3
Magnesium	22	9,16e-4
Sodium	373	1,62e-2
Sulphate	774	8,06e-3
Chloride	236	6,64e-3
Alkalinity mg/l $CaCO_3$	130	
mg/l CO_3	78	1,29e-3

For this water, enter carbonate both ways.

- Examine the total carbonate concentration for each method. Can you explain the results.

Exercise 5 : Changes in ground water composition

A ground water flow path is depicted in Figure 1. Groundwater flows from point A, through points B and C to discharge at the surface at Point D. Using MINTEQA2, model the changes in the equilibrium ground water chemistry along this flow path. Unless instructed otherwise, do not allow solids to precipitate. In order to avoid possible Phase Rule violations when modeling with a small number of components, add 1.0e-4 moles of sodium and nitrate to the water. These ions will not affect the chemical speciation of other ions and can be ignored thereafter. There is no transport component in this problem, you are simply trying to predict how the chemical composition of the ground water would change as it passed through various rock types.

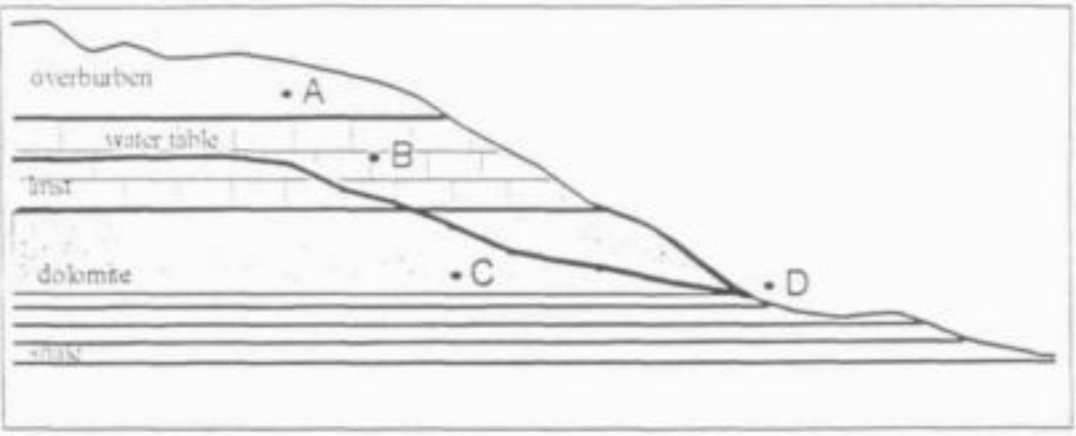


FIGURE 1 : Schematic diagram of groud water flow path

Point A : overburden horizion

The ground water is open to the atmosphere. The partial pressure of $CO_2(g)$ was found to be 0.003 atm. Normal $pCO_2(g)$ is 0.0003 atm.

- Why can $pCO_2(g)$ be greater than atmospheric?
- What is the pH of the ground water?

Point B : limestone horizion

The ground water has entered the limestone horizion but is above the water table.

- (i) What is the pH of the ground water?
- (ii) How much calcite dissolves, (a) in moles/l and (b) in mg/l?
- (iii) What is the total dissolved carbonate concentration ($CO_3^{=}$) of the water in moles/l?
- (iv) What is the total dissolved proton concentration (H^+) of the water in moles/l/
- (v) What is the total dissolved calcium concentration in moles/l?

Point C : dolomite horizion

The water is below the water table and is in contact with the dolomite horizion. Using the values from questions iii, iv and v above, create an appropiate new input file. Remember to add Na^+ and NO_3^- to avoid possible Phase Rule violations.

- (i) What is the pH of the water?

- (ii) How much dolomite dissolves in moles/l?

- (iii) What is the saturation state of the water with respect to calcite?

- (iv)Equilibrate the water with calcite by allowing solids to precipitate
    - (a) what is the pH of the water after equilibration with calcite?
    - (b) how much calcite precipitates?
    - (c) how much dolomite dissolves? Compare this amount to your answer in question ii in this section and briefly explain the result.
    - (d) list the total dissolved concentrations of ions in the water after equilibration with dolomite and calcite.

Point D : discharge point

The ground water has reached the discharge point D Using the total dissolved concentrations from iv(d) above create an appropiate new input file to model the water composition at this point. Allow oversaturated solids to precipitate.

- (i) What is the pH of the water?

- (ii) What minerals are predicted to precipitate? Give the amounts in moles/l.

- (iii) Are the minerals predictied to precipitate realistic in terms of the geological situation? Explain your answer. How could you improve the model parameters?

Advanced Modeling Options

MINTEQA2 contains a number of input options through which invarient measurements for a chemical system, such as pH, can be defined. There are some options which can be classed as advanced modeling options. These are :

- adsorption modeling
- modeling with a dissolved organic matter component
- modeling with redox equilibria

For many systems, the data required to model these aspects are ill-defined, either because routine chemical monitoring does not include their measurement or because the system has not been adequately characterised. Yet, particularly for natural systems, these three aspects, either individually or combined, are likely to be the controlling influences on the chemistry of a system. MINTEQA2 has provided for the situation where real field data is lacking, by providing options which allow for reasonable assumptions to be made. Based on these assumptions the program will calculate equilibrium concentrations. Results obtained using these advanced modeling options should be viewed as guides or trends for the system. In a dynamic natural system, processes such as precipitation and adsorption are likely to be governed by kinetic factors, such as diffusion or dissolution rates, rather than by equilibrium processes. Although the uncertainty factor in using these modeling options may be high, work conducted to date suggests that it is preferable to consider these influences on a given system, rather than to ignore them entirely.

Of the advanced modeling options, modeling to examine the effects of surface adsorption and modeling to examine the effects of organic complexation are fairly straight forward. Modeling with redox equilibria can be more difficult due to uncertainty in measurement.

CASE STUDY : Modeling the distribution and fate of phosphorous species in a fresh water impoundment

In the aquatic environment, phosphorus may be present in an organic or inorganic form. In both categories the individual phosphorus species may be present as either dissolved, precipitated or adsorbed phases. Interchange between the various categories is possible as a result of chemical and biological action. A knowledge of the various types of phosphorus species, and their relative distribution, is important in understanding the fate of phosphorus in the environment. In a study of the impact of phosphate reduction measures on eutrophication in a fresh water impoundment, chemical speciation data was used to interpret the interaction between the various physical, chemical and biological processes which governed the mass distribution of phosphorous in the system. Processes such as precipitation, adsorption, biological uptake and stratification, remove phosphorous from the aquatic system, while the formation of soluble ionic complexes, dissolution, desorption, mineralisation and turnover supply phosphorus to the system. The relative merits and contributions of these various physico-chemical processes can be assessed through a knowledge of chemical speciation.

A simplified fresh water composition is given in the table below. The total carbonate concentration was calculated from an alkalinity value, taking account of the carbonate speciation. Total Phosphate includes soluble orthophosphate (inorganic and organic) as well as particulate phosphate

Water Quality Determinand	**Summer surface water Simplified analysis**	
	mg/l	moles/l
Calcium	10.4	2.59e-4
Magnesium	10.4	2.30e-4
Sodium	20.9	9.09e-4
Potassium	2.4	6.13e-5
Total iron	0.48	8.59e-6
Chloride	26	7.39e-4
Fluoride	0.15	1.01e-6
Sulphate	12.2	1.27e-4
Total phosphate	1.28	1.34e-5
Total carbonate		9.58e-4
Temperature(°C)	29	
pH	8.3	

- Model the phosphorous speciation of the water.
- What solid phases are predicted to precipitate? Are these phases realistic?
- Describe the distribution of soluble phosphate species.
- What is the implication of the phosphorous speciation for bioavailibility?
- Using Edit Level 2, Option3, model the effect of surface adsorption on the distribution of phosphate species. Allow precipitation to occur if required by equilibrium conditions, so that the competive effect of adsorption versus precipitation processes can be evaluated. READ the block below carefully before attempting adsorption modeling.

SURFACE ADSORPTION

The effects of surface adsorption can be modelled by assuming that the properties of the adsorption surface, regardless of its original state, will be controlled by a surface layer of amorphous ferric hydroxide. There is considerable data in the literature to support this assumption. MINTEQA2 provides a separate database file, **FEO-DLM.DBS**, which contains surface reactions that are applicable to the **Diffuse Layer Model** for adsorption of some metals and ligands onto an amorphous iron oxide surface.

The properties of the iron hydroxide layer for which the FEO-DLM.DBS database can be attached to the Diffuse Layer Adsorption Model are:

Solids concentration of 3,422 g/l and with an amorphous iron concentration of 0,721 mg/g.

Specific surface area = 600 m^2/g

High energy site density = 1,922e-4 moles/l

Low energy site density = 7,690e-3 moles/l

These values are based on average porosity, dry density and amorphous iron concentrations of some aquifer materials encountered by the EPA in their work.

- You should be able to produce a diagram similar to that given in Figure 2.

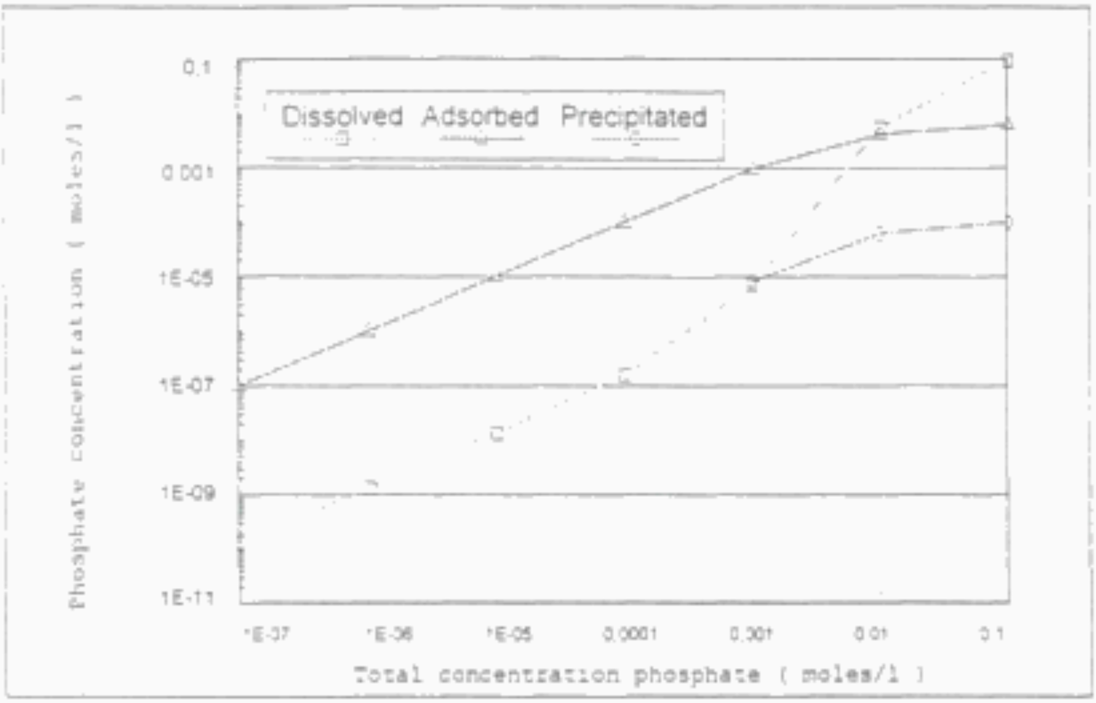


FIGURE 2 : Effect of surface adsorption on the distribution of phosphate species in a fresh water impoundment.

- Under what circumstances might desorption occur? How would you model these to examine the extent of possible desorption

CASE STUDY : Modeling to examine the effects of organic complexation

It is generally accepted that the presence of organic material, particularly humic substances, in an aqueous system, can influence the distribution of the inorganic species present. The organic material may be dissolved or particulate. Either of these categories offers different mechanisms of interaction with the inorganic ions present in the water, for example, dissolved organic material may form ionic complexes or ion pairs with inorganic ions, while particulate organic material may offer electrostatic adsorption surfaces on which the inorganic ions may bind. The nature of the organic material will depend on the environment of the water, for example, the organic material found in a lake water will be different from that in an esturine water, and even within a given body of water there may be seasonal or depth variations in the nature of the organic material present. This complexity of natural systems, is compounded by the analytical difficulties of identifying all the organic compounds present. Thus waters, whether natural or process streams, are rarely well characterised in terms of their organic content. As a result there are few thermodynamic data available for naturally occurring organic compounds. The lack of thermodynamic data restricts the use of chemical speciation computer models in studying the effect of organic complexation on the distribution of inorganic species.

Two approaches have been taken in attempts to resolve this difficulty :

- (i) the use of ***recipes*** representing common sources of organic material
- (ii) the use of ***composite organic ligands***, for which the complexing affinity with some metals has been determined

Use of Hypothetical Recipes to Model the Effect of Organic Material on Metal Complexation

A number of recipes for the organic component of several waters have been developed to enable the effect of the organic material on metal complexation to be considered. These include, a recipe representing the organic content of sewage, (Morel et al., 1975), a recipe representing the organic content of sludge derived soil leachate, (Mattigod and Sposito, 1978), and a recipe representing the organic composition of seawater, (Stumm and Brauner, 1975). These recipes, given in the table below, contain certain classes of organic acids whose proton dissociation constants fall into the same ranges observed for organic material in natural systems and which are expected to be present, or to simulate closely, the organic acids present in each system. The measured stability constants for trace metal complexes with these organic compounds are assumed to be good approximations to the unknown stability constants and are available in the MINTEQA2 database.

Recipes developed to represent organic ligands present in sewage, sludge-derived soil leachate and seawater

Recipe for Sewage		Recipe for sludge-derived soil leachate		Recipe for seawater	
Ligand	Conc (mM)	Ligand	Conc (μM)	Ligand	Conc (mM)
Acetate	0,500	Benzenesulphonate	54	Acetate	0,007
Glycinate	0,500	Salicylate	54	Citrate	0,007
Tartrate	0,025	Phthalate	107	Tartrate	0,007
Glutamate	0,200	Citrate	72	Glycinate	0,007
Salicylate	0,155	Maleate	107	Glutamate	0,007
Phthalate	0,125	Ornithine	44	Phthalate	0,007
		Lysine	44		
		Valine	44		
		Arginine	32		
TOTAL	6,0 mM carbon		2,2 mmol/g ΔH^-		2,3 mg *l* carbon

Use of a composite ligand to model the effect of organic matter on metal complexation

A recent addition to the MINTEQA2 database, December 1991, is a composite ligand representing dissolved organic material from the Suwannee River, Fargo, Georgia (**DOM** - component identification number, 145). There is no distinction between humic and fulvic fractions in this composite ligand. The thermodynamic constants relevant to this composite ligand are discussed here in some detail, as the MINTEQA2 User's Manual has not been updated to include this information. Further information can be found in the file **UPDATE.TXT** on the MINTEQA2 diskette.

Work by Perdue and Serkiz (1987, 1988) showed that for proton binding to ligands in humic substances in Suwannee River DOM, the formation constant, (mean log K_i value), was 3,87. Susetyo et al. (1990) determined that the average humic anion charge, Z_L, was -2,8 and that the mean log K value for metal binding was 6,4. Using a site density of 4,8 x 10-4 moles/g of organic matter, log K values for the complexation of some trace metals with Suwannee River DOM have been determined (Susetyo et al.; 1991). These are given in the table below. The organic matter contained 48,79 % carbon.

Mean log K values determined for the complexation of some trace metals with Suwannee River dissolved organic matter (DOM) (Susetyo et al.; 1991)

Cation	Mean log K
H^+	3,87
Al^{3+}	5,20
Fe^{3+}	6,20
$Cr(OH)_2$	15,32
Ba^{2+}	3,10
Be^{2+}	3,40
Cd^{2+}	3,00
Cu^{2+}	4,90
Ni^{2+}	3,30
Pb^{2+}	5,20
Zn^{2+}	3,50

These values, together with the appropriate reactions have been included in the thermodynamic data base of MINTEQA2, Version 3.11 as file **COMPLIG.DBS.** The incorporation of these reactions in standard equilibria calculations is accomplished by including a separate subroutine (COMPOSIT). This sub routine is initiated **automatically** by MINTEQA2 when DOM is included as a system component in the input file. PRODEFA2 has also been modified so that new composite ligand reactions, not included in COMPLIG.DBS, can be added by the user.

The concentration of the composite ligand component is always specified in moles of sites per litre (regardless of the setting for units of concentration).

The Effect Of Organic Material on Metal Complexation in Power Station Cooling Water

Modeling with a "sewage" recipe

Sewage effluent was returned as make-up water to a power station cooling water circuit. MINTEQA2 was used to examine whether the presence of dissolved organic matter had any effect on the chemical speciation, and hence precipitation potential, of the major cations in the cooling water.

In order to model this scenario a total carbon and inorganic carbon analysis of the water is required. By subtraction the dissolved organic concentration can be determined. This value is required to adjust the "sewage recipe" to match the organic carbon concentration of the water.

For the cooling water modelled, the total carbon content was 57 mg/ℓ as C and the inorganic carbon concentration was 32 mg/ℓ as C. The chemical composition of the cooling water was modelled with the components of the "sewage" recipe proportioned to the organic concentration of the cooling water. It was assumed that the water was not in equilibrium with the partial pressure of atmospheric carbon dioxide.

Without the addition of "sewage", the cooling water was predicted to be oversaturated with respect to calcium carbonate and to precipitate 62.7 mg/ℓ of calcite.

Of the various organic ligands contained in the sewage recipe, only acetate and phthalate showed any affinity to complex with the calcium, magnesium and sodium ions of the cooling water The overall effect of the formation of these complexes is negligible at the organic carbon concentration modelled The amount of calcite precipitated is predicted to be reduced by 1 mg/*l* (to 61,7 mg/*l*) due to the formation of the soluble calcium acetate and calcium phthalate complexes. Increasing the "sewage" total carbon to 72 mg/*l*, (approximating raw sewage, Morel et al, 1975) resulted in a 2 mg/*l* reduction in the mass of calcite precipitate (60,7 mg/*l*)

Modeling with DOM

The power station cooling circuit water was modelled with increasing amounts of dissolved organic material, represented by the composite organic DOM

Of the cations present in the water, only calcium and magnesium form soluble metal-organic complexes Figure 3 shows the changing concentration of calcium species with increasing concentration of dissolved organic material. As the concentration of dissolved organic matter increases, the metal-organic complex, (CaDOM), increases at the expense of all other calcium species ,including the equilibrium solid phase, calcium carbonate. At organic concentrations greater than approximately 4 mmoles/*l* (as C), the calcium-organic complex becomes the dominant calcium species present. The affinity of the dissolved organic material for calcium is sufficiently strong to compete with the precipitation process

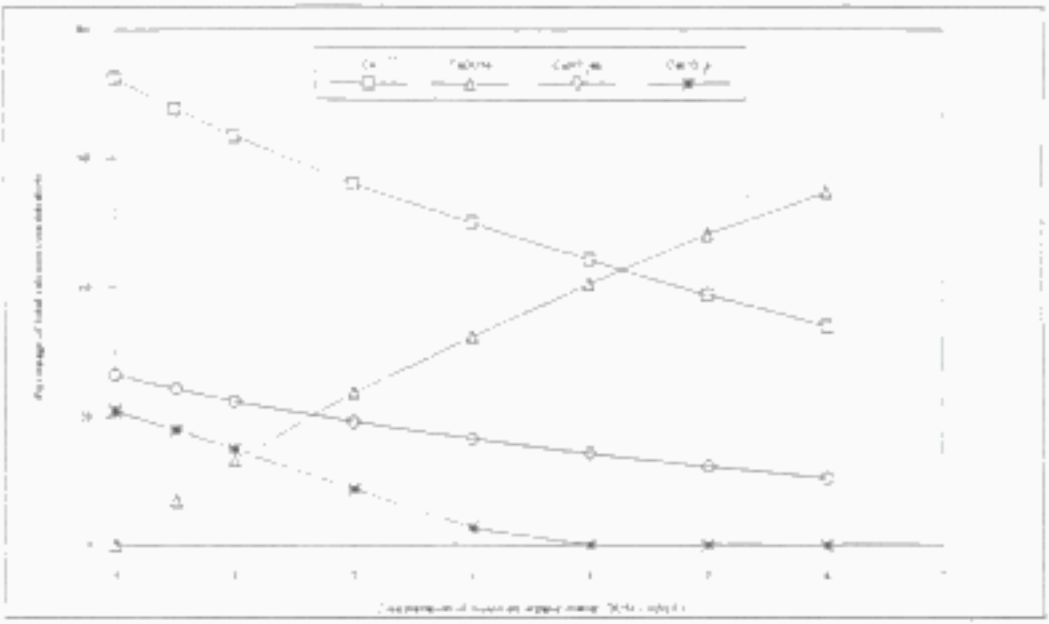


Figure 3 : Variation in the concentration of calcium species with increasing concentration of dissolved organic matter. The concentration of the soluble calcium-organic complex increases at the expense of all other calcium species present, including the equilibrium solid phase, calcium carbonate.

The formation of a calcium-organic complex, has implication for the efficient operation of any flocculation/clarification or water softening process used to treat this cooling water, and would result in less calcium being removed from the water than expected. This conclusion is similar to that reached when the cooling water was modelled with the sewage recipe, but in this case the model predicts that the amount of calcium carbonate precipitated would be reduced by 55 mg/l, compared to a reduction of only 1 mg/l when the sewage recipe was used.

CASE STUDY : modeling to examine the effect of redox conditions on the distribution of chemical species

The acid/base equilibria in an aqueous solution can be described by the quantity $pH = -\log \{H^+\}$ In a similar way the equilibrium position for redox pairs (ie, all oxidation/reduction pairs) in a given system can be described by the quantity $p\varepsilon = -\log \{\varepsilon\}$, where ε is an electron

In redox chemistry, by convention, the redox reaction is represented by the reduction half reaction, for example the redox half reaction of interest to many natural waters is the reduction of Fe^{3+} to Fe^{2+}

$$Fe^{3+} + \varepsilon^- = Fe^{2+}$$

The tendency for this reaction to proceed is measured by the half cell value, E. E measured relative to the standard hydrogen electrode is known as E_H values or as oxidation potential or redox potential The values are obtained by measurement with a Pt electrode and are commonly given the symbol Eh. Eh values may be positive or negative depending on the ratio of oxidised/reduced species in the redox pair being considered. Increasing Eh values indicate increasingly oxidising conditions and decreasing Eh values indicate increasingly reducing conditions The quantities Eh and are related by the equation

The measurement of redox potential in natural systems, although seemingly simple, is fraught with difficulties, and is complicated and controversial. Part of the difficulty stems from the fact that some of the reactions that determine redox potential are slow, so that instantaneous readings with a platinum electrode do not give the true equilibrium potential When Eh values for some redox pairs obtained from field measurements are plotted against calculated Eh values, the spread is so wide that most Eh measurements can only be used in a qualitative sense Pankow (1991) advocates that Eh measurements should be viewed only as providing guidance as to the direction of reactions within any given system, and as to the range of concentration values that are feasible in the system.

Within this framework MINTEQA2 can be used to determine the equilibrium Eh of a solution, provided concentrations of both the reduced and oxidised species are known Alternatively, if only the total concentration of a cation or anion likely to be involved in a redox equilibrium relationship, is known, a fixed redox ratio can be imposed and MINTEQA2 will calculate the concentration of species present in the reduced and in the oxidised state. If the user is unsure whether redox equilibria will apply, MINTEQA2 will provide a list of redox pairs, based on the chemical components of the system. In the following example the redox option, Edit Level 2, Option5 has been used.

The Distribution Of Chemical Species in Acid Mine Water

A mine effluent in the Witbank region had a pH value of 2,5. The composition of the water (Sampling station BSFB12, January 1991) is given below.

Chemical composition (*mg/l*) of acid mine water from the Witbank region

Na	Mg	K	Al	Ca	Mn	Fe	Ni	Zn	Si	NH_4	SO_4	Cl
112	78	7	308	191	18	661	1	5	89	37	4.345	104

The available chemical analysis was limited and the oxidation state of iron in the water was not indicated. A general treatment was being sought which would make the water more suitable for further treatment or for use as a source of low grade water. Because the chemical data was inexact, a general approach to the chemical speciation of the water was adopted. In a preliminary investigation, MINTEQA2 was used to examine iron speciation in the effluent by initially assuming that all iron was present in the ferrous state and then assuming that all iron was present in the ferric state. These two model scenarios gave the limiting conditions for iron speciation. Model predictions indicated that a possible treatment route would be to aerate the water, to an oxygen partial pressure of 0,21 atm and a carbon dioxide partial pressure of 0,0003 atm, to ensure that all iron was in the ferric state. Under these conditions it was predicted that 99 % of iron would be removed from solution as the solid phase hematite (Fe_2O3). More realistically the iron precipitate is likely to be some form of amorphous iron hydroxide. Exclusion of hematite (Edit Level 2, Option 9) comfirmed this. Saturation of this solution with lime, would result in the precipitation of several metal hydroxides, leaving a treated water consisting largely of sodium, potassium and chloride ions together with smaller amounts of calcium and sulphate ions. A comparison of the predicted total dissolved concentrations of the water after different treatment stages is given.

The TDS concentration of the water is reduced by aeration and saturation with lime. The high pH could be adjusted with sulphuric acid. This would result in the precipitation of an additional amount of gypsum and remove further calcium and sulphate ions from the water.

Predicted chemical composition of acid mine water under different modeling conditions. The data indicates that a possible treatment method would be aeration and saturation with lime, $Ca(OH)_2$. The TDS of the treated water is reduced.

	Untreated acid mine water (mg/l)	Acid mine water, all iron as Fe^{2+} (mg/l)	Acid mine water, all iron as Fe^{3+} (mg/l)	Acid mine water, aerated (mg/l)	Acid mine water, aerated and saturated with lime
Na	112	112	112	112	112
Mg	78	78	78	78	0
Al	308	186	308	308	308
Ca	191	191	191	191	804
Mn	18	18	18	18	18
K	7	7	7	7	7
Zn	5	5	5	5	3
Total Fe	661				
Fe^{2+}		661	-	0	0
Fe^{3+}		-	0	0	0
NH_4	37	37	37	37	37
NO_3	0.2	0.2	0.2	0.2	0
CO_3	-	-	-	0.5	0.4
Cl	104	104	104	104	104
SO_4	4 345	3 888	4 345	4 345	918
pH	2.5	2.5	1.7	1.9	12.5
Eh (mV)	-	-	-	1 105	1 105
TDS (mg/l)	5 666	5 287	5 215	5 205	2 010

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WATER RESEARCH COMMISSION PROJECT NO 530
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APPENDIX 4

Distribution List for MINTEQA2 Discs and Manuals

Pollution Research Group
University of Natal
Durban
December 1994

Distribution List for MINTEQA2 Discs and Manuals

A copy of the MINTEQA2 program and User's Manual, together with other appropiate literature, have been distributed to the following people:-

Name	Organisation
Prof Hudson	Groundwater Research
Andrew McLaren	Goldfields, PO Box 61525, Marshalltown,2107
Sebastian Jooster	Institute of Water Quality Studies, Private Bag X313, Pretoria, 0001
Mr Graham Trusler	Randgold and Exploration
Mr Andrew Swart	Anglo American
Prof H van Leuen	University of Pretoria
Dr G Renken	Debex Desalination
Dr Schaekers	Genmin
Prof R Loewenthal	University of Cape Town
Mr B Joubert	Eskom, Private Bag 6652, Newcastle, Natal, 2940
Mr H Potgieter	PPC, PO Box 40073, Cleveland, 2022
Ms J Barnett	AECI Research and Development Devpartment
Mr D Vinnecomb	Technology Research Investigations, Eskom
Mr M Ginster	Sastech Water Research
Dr H Steys	Department of Zoology, University of Pretoria
Dr H Kasan	Natal Technikon
Dr B Martinicgh	Department of Chemistry, University of Natal
Dr E Meintjies	Rand Water Board
Prof P Rose	Rhodes University
Ms R Timm	SRK
Dr Yves Chapron	C.E.N.G. , Grenoble, France
Mr A Mills	University of Cambridge
Mr. R Bell	SCI, Sasol
Mr. A L Carvello	Chemserve water Services
Mr. D M Johnson	BHT Water Treatment (PTY) LTD
Mr. R Moodley	East Rand Gold and Uranium
Mr E Otto	Sastech

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APPENDIX 5

Preliminary Report : How to Add Cl_2 (g), Cl_2 (aq), HOCl and OCl^- to the MINTEQA2 Thermodynamic Database

Pollution Research Group
University of Natal
Durban
December 1994

HOW TO ADD Cl_2 (g), Cl_2 (aq), HOCl AND OCl^- TO THE MINTEQA2 THERMODYNAMIC DATABASE

MINTEQA2 divides chemical species into two categories: components which are stored in COMP.DBS and other species defined in terms of these components and stored in the file THERMO.DBS.

Cl_2 (aq), Cl_2 (g), HOCl and ClO^- do not appear in any MINTEQA2 database because their presence would result in reactions which in practice do not occur in most groundwater problems. However, in problems involving industrial process and waste streams they may be necessary.

Additional aqueous species may usually be defined inside PRODEFA2 and this has the advantage of not tampering with the database. However, PRODEFA2 requires the major cation in the new species to be specified before one can proceed any further in the definition. Since defining Cl_2 (aq) in terms of the available components results in:

$$Cl_2\,(aq) = 2Cl^- - 2e^-$$

and neither Cl^- nor e^- appears in the list of options, it is not possible to add Cl_2 from inside PRODEFA2. Gases also have to be added directly to the database.

Explanation of the databases and instructions for modifications are given in Appendix A of the manual and the identical text is also available in the file DATABASE.TXT. Since it is not desirable to have these species available to MINTEQA2 for most problems, the original databases and the final working copies of the modified databases should be saved under different names.

The required thermodynamic data cannot be taken directly from the literature because MINTEQA2 adopts the convention of assigning $\Delta G^\circ_f = 0$ and $\Delta H^\circ_f = 0$ to the species regarded as components rather than to the chemical elements in their reference states.

For example, for the usual convention, Cl^- has $\Delta H^\circ_f = -39{,}9\,52$ kcal/mol at 25° C which implies:

$$1/2Cl_2\,(g) + e^- = Cl^- \qquad \Delta H^\circ_r = -39{,}9\,52 \text{ kcal/mol}$$

However, since MINTEQA2 assigns $\Delta H^\circ_f = 0$ to both Cl^- and e^- according to this convention Cl_2 (g) has $\Delta H^\circ_f = 2x(+39{,}9\,52)$ kcal/mol.

The appropriate ΔG°_f for Cl_2 (g) can be calculated in the same way and substituted into

$$\log K = -\Delta G^\circ_r/(2{,}303RT)$$

where $R = 1{,}98171x10^{-3}$ kcal/mol/K and T = 298,15 K.

Note that MINTEQA2 uses the 1 molar std state convention for aqueous species and all thermodynamic quantities are in kcal/mol.

Literature data for Cl_2 (aq) refers to the reaction:

$$Cl_2\,(g) = Cl_2\,(aq) \qquad \Delta H^\circ_f = -5{,}6 \text{ kcal/mol}$$

Therefore:

$$1/2Cl_2\,(aq) = Cl^- - e^- \quad \Delta H^\circ_f = (-39{,}952+5{,}6) \text{ kcal/mol}$$

Therefore in the MINTEQA2 convention $\Delta H^\circ_f = -2x(-39{,}952+5{,}6)$ kcal/mol for Cl_2 (aq).

Cl_2 (aq) dissociates in water as follows:

$$Cl_2\,(aq) + H_2O = HClO + H^+ + Cl^-$$
$$HClO = H^+ + ClO^-$$

H_2O, H^+ and Cl^- are all MINTEQA2 components. The other species may be defined as follows:

$$\begin{aligned} HClO &= Cl_2 + H_2O - H^+ - Cl^- \\ &= 2Cl^- - 2e^- + H_2O - H^+ - Cl^- \\ &= Cl^- + H_2O - H^+ - 2e^- \end{aligned}$$

and similarly:

$$ClO^- = Cl^- + H_2O - 2H^+ - 2e^-$$

The entries made in the database were as follows:

```
1800012 Cl2 AQ      74.3040 -47.2019  0.000  0.000 0.00 0.00 0.00  70.9060
0.00 2    2.000 180  -2.000  1
3301800 HOCl AQ      11.0520 -50.5779  0.000  0.000 0.00 0.00 0.00  52.4604
0.00 4    1.000 180   1.000  2   -1.000 330   -2.000  1
1800013 ClO -1      84.7630 -58.1325  0.000  0.000-1.00 0.00 0.00  51.4524
0.00 4    1.000 180   1.000  2   -2.000 330   -2.000  1
1800011 Cl2 (g)     79.9040 -46.0196  0.000  0.000 0.00 0.00 0.00  70.9060
0.00 2    2.000 180  -2.000  1
```

Note that:
1) ClO^- actually has non-zero Debye-Huckel parameters but no data was available
2) Cl_2 (g) has to be entered in the GASES.DBS as well as THERMO.DBS

Once the modifications are complete, the databases have to be unformatted for MINTEQA2 to be able to use them. First the old versions of THERMO.UNF and TYPE6.UNF are deleted and then the command UNFRMT is executed.

Once Cl_2 (g) is in the database its partial pressure can be specified in PRODEFA2. There is a slight difficulty, however. When a gaseous species is selected from the menu, PRODEFA2 checks if the components making up the gas have been specified as part of the problem yet. If not, it includes them and temporarily assigns them concentrations of zero. There seems to be some bug in the code so that if it has to do this for more than one component, it skips back to the previous menu before allowing one to specify a partial pressure, thereby terminating the entry. This can be overcome by initially specifying a Cl^- concentration which can be deleted in Edit Level 3 later if necessary.

It must be borne in mind that the MINTEQA2 database uses thermodynamic values determined in typical natural water systems while for example data from e.g. Weast [2] refers to pure components, resulting in some slight inconsistencies in the data.

HOW TO ADD DISSOLVED OXYGEN

O_2 (aq) can be defined as a species from inside PRODEFA2. Go to Edit Level 2 and select the options to define a new species. O_2 (aq) may be defined as:

$$O_2\ (aq) = 2H_2O - 4H^+ - 4e^-$$

so the major cation is H_2O. H^+ or e^- may be specified as the other major ion. The relevant log K is -85,9484 and the enthalpy of formation is 133,83 kcal/mol. The final component involved is selected after the thermodynamic data has been entered.

REDOX REACTIONS

MINTEQA2 deals with different oxidation states of the same element in one of two ways: it may either define one state as a component and the others as species with the redox reactions as their formation reactions, or it may define different components for each oxidation state. In the latter case, no mass transfer between oxidation states can occur unless the user specifically allows it.

The manual's explanation of the second method is slightly ambiguous which has caused some confusion. Recall that the reactions in the MINTEQA2 databases are formation reactions of species from components and that all components are defined to have $\Delta G^\circ_f = 0$. This means that writing a redox reaction between two components apparently results in $\Delta G^\circ_r = 0$ which is meaningless. MINTEQA2 overcomes this inconsistency by defining a mock species known as a redox couple with $\Delta G^\circ_f = \Delta G^\circ_r$ (and $\Delta H^\circ_f = \Delta H^\circ_r$) for the relevant reaction.

Note that introducing this species into the calculations fixes the equilibrium activity ratio for all the reactants as K for the reaction. In general, the ratio of the activities of the two oxidation states is not fixed as other components are also involved.

The redox couples are all assumed to be excluded species unless, they are selected for inclusion in Option 5 of Edit Level II.

For example, consider the redox reaction:

$$Cr(OH)_2^+ + 2H^+ + e^- = Cr^{2+} + 2H_2O \qquad \log K = 2{,}947$$

In MINTEQA2 this becomes:

$$Cr(OH)_2^+ + 2H^+ + e^- - Cr^{2+} - 2H_2O = Cr^{2+}/Cr(OH)_2^+$$

where $Cr^{2+}/Cr(OH)_2^+$ is a mock species with $\Delta G^\circ_f = -2{,}303 \times RT \times 2{,}947$

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APPENDIX 6

Preliminary Report : Prediction of Conductivity from Equilibrium Ionic Speciation

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December 1994

PREDICTION OF CONDUCTIVITY FROM EQUILIBRIUM SPECIATION

Introduction

Conductivity is often used as an overall indicator of concentration of ionic solutes in the streams associated with reverse osmosis plants. Frequently it is the only such indicator available for a particular stream. While it is not possible to recover the underlying solution composition from the conductivity alone, it may be possible to estimate composition from the conductivity together with information on other streams through modelling of the RO process. This requires the relationship between composition and conductivity to be known. An investigation is being undertaken to establish a means of predicting conductivity from solution composition, using data on the conductivities of various solutions. Since conductivity is some product of ionic mobility in solution and the ionic charge, it was apparent that the speciation of ions in a solution should be taken into account.

Theoretical background

The theory of ionic conductivity has been reviewed by Erdey-Grūz (1974). Equivalent conductivity Λ is the conductivity of the solution divided by the number of molar equivalents of ions dissolved in it. For a dissociated electrolyte, the limiting value of equivalent conductivity for an extremely dilute solution is

$$\Lambda^0 = \lambda_c^0 + \lambda_a^0 \qquad (1)$$

where λ_c^0 and λ_a^0 are the limiting conductivities of the individual cation and anion separately. In this limit, the conductivity of each ion is independent of that of other ions present in the solution. Because of interactions between ions, the mobility of a given ion depends on the nature and concentrations of other ions present, and in a solution of finite dilution the law of independent migration is not valid.

For very dilute solutions the empirical *square root law of Kolrausch* is valid:

$$\Lambda = \Lambda^0 - k\sqrt{c} \qquad (2)$$

Here Λ is the equivalent conductivity of a solution with concentration c, and k is a constant which is dependent only on the valence of the ion, being larger the higher the valence.

Note that Kolrausch's law does not use the speciation of the actual solution: it assumes that the ions are completely dissociated and independently mobile and then uses an empirical term to account for all deviations from this hypothetical situation.

At higher concentrations, the square root dependence on composition no longer holds and empirical corrections involving other functions of concentration have been developed for single solute solutions.

For solutions containing more than two ions, these relationships are generalized as

$$\kappa = \sum c_i \, |z_i| \, \lambda_i \qquad (3)$$

where κ is the specific conductivity of the solution, c_i is the concentration of ion i and z_i is its ionic charge.

For mixed electrolytes at higher concentrations the theory is inadequate to predict conductivity accurately.

Basis of the present correlation

The correlation developed here makes use of four basic ideas :

a) equilibrium speciation to obtain the distribution of ions actually present in the solution.

b) a limiting specific solution conductivity calculated from the distribution of ions and the limiting equivalent conductivities of the original ions.

c) a correction for concentration of similar form to the Kolrausch law.

d) a correct for temperature of the form $\kappa(T) = \kappa(20^oC)\left[\frac{\mu(20^oC)}{\mu(T)}\right]^{0,896}$ (Talbot, House and Pethybridge, 1990).

One very important ionic interaction at finite dilution is the association of ions to form ion pairs. Neutral ion pairs do not contribute directly to the conductivity of the solution and are explicitly excluded from the speciation based correlation. However, charged ion pairs e.g. $NaCO_3^-$ do contribute to the solution conductivity and must be accounted for when ion pairs form a significant proportion of the charged species present. Since the concept of limiting ionic conductivity is based on the idea that there is no association of ions at infinite dilution, there are no λ_i^0 in the literature (with the exception of the bicarbonate and bisulphate ion pairs).

For single solute solutions, ion pair formation can be accounted for by the empirical terms in the correlation since the degree of association is directly related to the concentration. However, in mixed solute solutions the degree of association between two ions depends on the other species present. For the present correlation it would be most convenient to have average molar conductivities for key ion pairs which would allow them to be handled like other charged species.

Procedure

1) The MINTEQA2 program (Allison, Brown and Novo-Gradac, 1990) was used to speciate single solute solutions of $CaCl_2$, KNO_3 , $MgCl_2$, $MgSO_4$, Na_2SO_4 and K_2SO_4 at 20°C. The limiting solution conductivity was calculated by:

$$\kappa^0 = \sum c_i \, |z_i| \, \lambda_i^0 \qquad (4)$$

Data from Weast was then fitted to the expression:

$$\kappa = \kappa^0 - A I^n \qquad (5)$$

Here $I = \frac{1}{2}\sum z_i^2 c_i$ is the ionic strength, while A and n are constants which gave the best fit. Solute concentrations up to 0,7M ionic strength were considered.

2) Stock solutions of Na_2CO_3, $NaHCO_3$, Na_2SO_4, KCl, $MgCl_2$ and $CaCl_2$ were made up and used to make up multisolute solutions. Conductivities were measured at 25°C and compared with predictions calculated by equation (5). Initially, the species $NaCO_3^-$ was not included in the calculation.

Results and discussion

1) The best fit values of A and n at 20°C were found to be 27,606 and 1,28 respectively. A graphical comparison of measured and fitted values for these solutions at 20° C is presented in Figure 1.

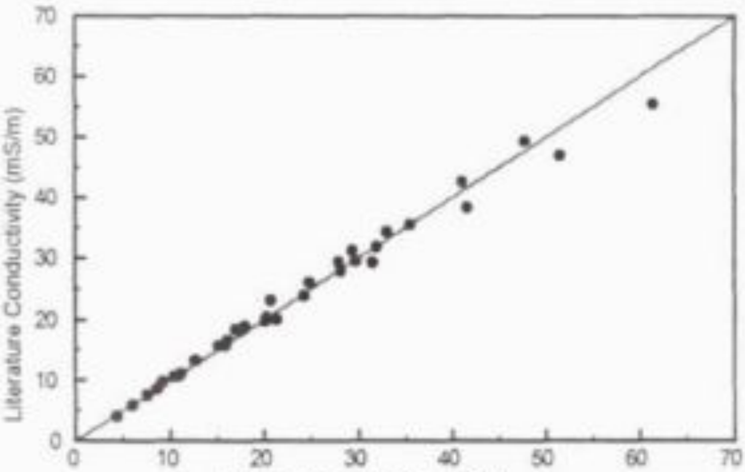

Figure 1. Comparison of conductivity predictions with literature data at 20°C

2) The measured vs. predicted values of conductivity at 25°C are presented in Figure 2. The same values of A and n as in 1 were used in the predictions. It was found that all the predictions were higher than the measured conductivities with the exception of those solutions with significant concentrations of $NaCO_3^-$ where the predictions were too low. Clearly, the presence of this particular ion pair must be taken into account.

significant concentrations of $NaCO_3^-$ where the predictions were too low. Clearly, the presence of this particular ion pair must be taken into account.

Best fit values of A and n for the data at 25°C excluding the data points involving significant amounts of $NaCO_3^-$ were found to be 32,623 and 1,21 respectively. It would appear that the empirical correction is temperature dependent and this point needs further investigation.

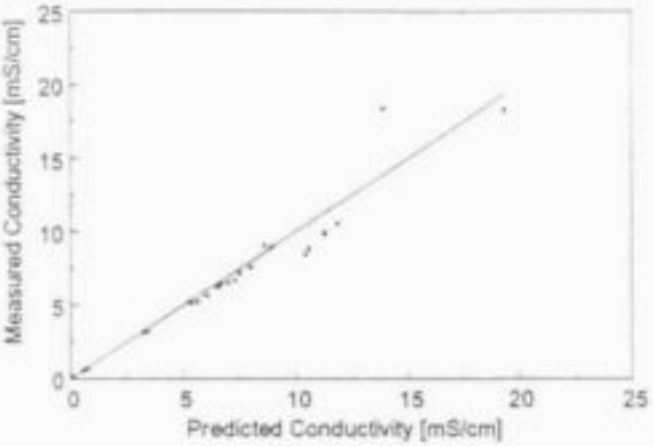

Figure 2. Comparison of conductivity predictions with measured data at 25°C

Further work required

1) It is proposed that an average molar conductivity of the ion pair $NaCO_3^-$ be determined as follows.

a) MINTEQA2 will be used to speciate solutions of pure Na_2CO_3 and mixtures of Na_2CO_3 and NaCl.

b) Predicted conductivities will be calculated as above and the difference between the prediction and the literature or measured value divided by the concentration of $NaCO_3^-$ to determine its molar conductivity.

If this approach proves successful, it could be used to determine suitable values for other ion pairs.

2) The validity of the temperature correction is yet to be determined. This will be investigated using single solute solutions from the literature and multisolute solutions made up in the laboratory. One problem is the lack of data on limiting ionic conductivities at different temperatures and these may also have to be estimated. Alternatively, it may be acceptable to predict the conductivity that would be measured for a given actual speciation at 25° C and then use the viscosity correction to get the final answer.

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SPECIATION MODELING

APPENDIX 7

Questionnaire on MINTEQA2 Workshop

Pollution Research Group
University of Natal
Durban
December 1994

USER PROFILE

1. What is your highest educational qualification in chemistry?

2. Indicate how many years ago you last studied chemistry formally

1	2	3	4	5
0-5	5-10	10-15	15-20	over 20

3. How would you rate your knowledge of inorganic chemistry

1	2	3	4	5
Poor				Very good

4. How would you rate your computational ability

1	2	3	4	5
Poor				Very good

5. Is chemistry an important aspect of your job?

1	2	3	4	5
No				Very important

COURSE CONTENT

1. Rate the amount of theory in the course

1	2	3	4	5
Too much				Too little

2. If you would have liked more theory, briefly indicate which aspects you would have liked covered.

3 Would you have liked more worked examples?

1	2	3	4	5
No				Yes

4. Would you have liked more group work?

1	2	3	4	5
No				Yes

COURSE PRESENTATION

1. Rate the pace of the course.

1	2	3	4	5
Too slow				Too fast

2. Would you have preferred the course to be spread over 1, 2 or 3 days?

3. Where the worked examples clearly set out?

1	2	3	4	5
No				Yes

4. Rate the clarity of the overhead projections

1	2	3	4	5
Illegible				Easily read

5. Rate the relevance of the overhead projections

1	2	3	4	5
Not relevant				Totally relevant

6. How could the presentation of the course be improved?

7. How could the content of the course be improved?

COURSE EXPECTATION

1. How did you hear about MINTEQA2?

2. Why did you attend the course?

3. Do you feel the program will be useful to you?

1	2	3	4	5
Not at all				Definitely

4. How many hours per week do you see yourself using MINTEQA2?

5. Would you recommend the use of the program to any one else in your organisation?

1	2	3	4	5
No				Yes

6. If so, to whom

7. Should the course be run in Afrikaans?

1	2	3	4	5
Not necessary				Essential

FOLLOW-UP

1. If you intend using MINTEQA2, do you feel you would require further assistance?

1	2	3	4	5
No				Yes

2. Should the assistance take the form of:

a) a user workshop?

1	2	3	4	5
No				Yes

b) a telephone help desk?

1	2	3	4	5
No				Yes

c) a fax help desk

1	2	3	4	5
No				Yes

d) a modem helpdesk

1	2	3	4	5
No				Yes

e) by correspondence

1	2	3	4	5
No				Yes

3. Do you feel on-site assistance would be useful?

1	2	3	4	5
No				Yes

4. If so, what would you be willing to pay? (R0 - R1000/day)