STUDIES ON THE GROWTH, DISSOLUTION AND EQUILIBRIUM SOLUBILITY OF Ba, Pb AND Ra SULFATES IN AQUEOUS SULFATE MEDIA: WITH APPLICATIONS TO THE SULFURIC ACID LEACHING PROCESS FOR URANIUM MILLING.

By

CHRISTOPHER ROBIN PAIGE, B.Sc., M.Sc.

A Thesis

submitted to the School of Graduate Studies in partial fulfilment of the requirements for the degree Doctor of Philosophy

0

C

McMaster University

Copyright Christopher Robin Paige June 1990

.4

10

 $E_{\rm c}$

STUDIES ON THE GROWTH, DISSOLUTION AND EQUILIBRIUM SOLUBILITY OF Ba, Pb AND Ra SULFATES IN AQUEOUS SULFATE MEDIA

0

D

0

C

0

0

0

c

c

٠Ļ:

C

STUDIES ON THE GROWTH, DISSOLUTION AND EQUILIBRIUM SOLUBILITY OF Ba, Pb AND Ra SULFATES IN AQUEOUS SULFATE MEDIA: WITH APPLICATIONS TO THE SULFURIC ACID LEACHING PROCESS FOR URANIUM MILLING.

By

CHRISTOPHER ROBIN PAIGE, B.Sc., M.Sc.

с.

à

i

A Thesis

submitted to the Department of Chemistry in partial fulfilment of the requirements for the degree

Doctor of Philosophy

 $\hat{\mathbb{O}}$

McMaster UniversityCopyright Christopher Robin Paige June 1990

Û)

Ş.,

DOCTOR OF PHILOSOPHY (1990)

McMASTER UNIVERSITY Hamilton, Ontario

¢,

TITLE: Studies on the growth, dissolution and equilibrium solubility of Ba, Pb and Ra sulfates in aqueous sulfate media: with applications to the sulfuric acid leaching process for uranium milling

e.

ii

AUTHOR: Christopher Robin Paige, B. Sc. (London) M. Sc. (Brock) SUPERVISOR: Professor O. E. Hileman, Jr.

NUMBER OF PAGES: 217, xxix.

€**C**

ċ

 $\bar{\mathbb{C}}^{n}$

53 25

۲ ا

Abstract

The formation of hetero-epitaxial deposits of Ba, Pb and mixed Ba/Pb and Ba/Ra sulfates on quartz and mica surfaces has been demonstrated. The kinetics of their growth and dissolution has been established. The importance of the formation and dissolution of these deposits is found in the observation that they are all host solids for the formation of solid solutions of 228-radium (and by extension 226-radium).

Desorption studies caried out on Ba^{2+} , Ca^{2+} and SO_4^{2-} from quartz and mica surfaces into water indicate that these ions are strongly retained by mica surfaces, with retention times which are of sufficient duration to permit the formation of the potential host solids required by the National Uranium Mine Tailings model.

The equilibrium solubility of PbSO₄ in Na₂SO₄ solutions and in H₂SO₄ solutions from 0 to 6m has been measured experimentally at 60° C with subsequent modelling by means of the Pitzer formulation for ion activities at high ionic strength. The equilibrium solubility of BaSO₄ in H₂SO₄ solutions from 0 to 6m has been measured experimentally at both 25^oC and 60° C with subsequent modelling. Such data are a necessary

iii

requirement for the modelling of the evolution of uranium mill wastes by the National Uranium Mine Tailings model and for understanding the fate of radium during the milling and leaching processes.

ċ.

Э

iv

ė

 $\langle \cdot \rangle$

11 m

ţ,

e

Č)

С

2

-

1

e

12

Acknowledgements

P

-

1)

The author would like to express his thanks and appreciation to Professor O. E. Hileman, Jr. for his supervision, sense of humor, enthusiasm for chemistry and for creating the atmosphere of **shared** learning which is so important for **true** learning.

In addition, thanks are offered to all the other members of the department for their invaluable assistance and attention, especially for the wide ranging discussions which are so valuable a part of the activities of a University.

Finally, the greatest thanks are due to my wife, Valerie Elizabeth (Freeman) Paige, who for many years has accepted this rather curious person, who has such a persistent scientific interest, as a husband !

0

v

Never let success hide its emptiness from you, achievement its nothingness, toil its desolation. And so keep alive the incentive to push on further, that pain in the soul which drives us beyond ourselves.

Whither? That I don't know. That I don't ask to know.

Dag Hammarskjold

Youth, to live, must have some great aspiration.

?

5

Gaston Rebuffat

Table of Contents

.

	-	-	1.1
	-	~	
_	•		
•	_		-

2

Abstra	ctiii
Acknow	vledgementsv
Table c	of Contentsvii
List of	Figuresxii
List of	Tablesxxv
Symbol	Tablexxvii
x.*	
Chapte	er 1. Introduction1
1.1	Outline of the milling and processing of
	uranium ore1
1.2	Fate of radium during ore processing
1.3	Laboratory work on radium precipitation
	in the leach tanks
1.4	The Hileman-Snodgrass model of leach
	tank processes6
1.5	The Hileman-Snodgrass model of
	uranium mill waste tailings6
1.6	Components of the precipitation/dissolution
	model
1.7	Purpose of this research12

7.

Ċ

C

vii

	Chapte	er 2. Bad	ckground information 15
	2.1	Review of	Activity Coefficient Modelling
		using the	Pitzer equations15
	2.2	Supersatu	ration and Activity19
	2.3	Nucleation	
	2.4	Growth of	crystals24
	4	2.4.(i)	Growth by two-dimensional
	1		nucleation29
		2.4.(ii)	Growth by a spiral growth
			mechanism31
		2.4. (iii)	Growth in the presence of
			Impurities34
	2.5	Perfection	of crystals
			-
	Chapt	er 3. Sol	ubility of sparingly soluble
	sulpha	ites in H ₂	SO ₄
а с	3.1	Solubility of	of PbSO4 in H2SO4 and Na2SO4
	° o'	from 0 to	6m at 60 ^{.0} C by ICP/MS analytical
	25	methods	
2		3.1.1	Experimental procedure used
			for the determination of the
	л		equilibrium solubility of PbSO ₄
			in both Na ₂ SO ₄ - H ₂ O and
			H2SO4 - H2O mixtures
		3.1.2	Modelling of solubility equilibria
			using the Pitzer equations for
			activity coefficients

C

.

5

2

8 ÷

o O

*,*1

.1

С

С

0

\$2

.

. •

6 :

	3.1.3	Modelling of the available literature
	т. <u>1</u>	data for the solubility of PbSO ₄ in
		H ₂ SO ₄ and Na ₂ SO ₄ along with the
		experimental data obtained
		in this research
3.2	Solubility of	of BaSO ₄ in H ₂ SO ₄ and Na ₂ SO ₄
	from 0 to	6m at 25 ⁰ C and 60 ⁰ C52
	3.2.1	Experimental procedure53
	3.2.1.i	Preparation of mixed ¹³³ Ba/BaSO ₄
		crystals53
	3.2.1.ii	Solubility Measurements54
	3.2.2	Discussion arising from the
• ,		experimental procedures used for the
		determination of the solubility of
		PbSO ₄ and BaSO ₄ in sulfate media 56
	3.2.2.i	The effect of labelling on the
		solubility of the barium sulfate
	3.2.2 .ii	The effect of particle size on the
		solubility of substances
	3.2.2.iii	The nature of the filters used for
		the radio-labelled material
3.3	Results of	f the modelling of the available
	literature	data for the solubility of RaSO ₄
	in H2SO4	at 298K and the prediction of the
э.:	solubility	at 333K60

¢

ix

.

Chapte	er 4. Kinetics of the exchange process at the
faces	of large single crystals of barium
sulpha	ite and lead sulphate90
4.1	Introduction90
4.2	Kinetics of isotope exchange limited by the
	rate of surface reactions
4.3	Experimental procedure96
4.4.i	Experimental results and data analysis98
4.4.ii	Calculation of jump frequencies
4.4.iii	Comparison with data obtained from crystal
	growth and exchange experiments105
4.4.iv	Exchange for 133Ba on BaSO4 at 298K106
4.4.v	Exchange for ¹³³ Ba on BaSO ₄ at 333K107
4.4.vi	Exchange for ¹³³ Ba on BaSO ₄ at 298K in
	the presence of Pb ²⁺ ions107

Chapter 5. Kinetics of growth and dissolution of epitaxial films on quartz and mica surfaces. 129

	5.1	Objectives	of this phase of the research129
	5.2	Kinetics of	desorption of ions, involved in
		the Hilema	an-Snodgrass model, from quartz
		and mica	surfaces130
2.17 f.		5.2.i	Introduction130
		5.2.ii	Design and construction of the
			desorptio/dissolution cell131
		5.2.iii	Results and discussion133
	5.3	Growth of	potential host solids on quartz
		and mica	surfaces136

Page

X

 \mathbf{v}_{i}^{*}

0

G

. .

e

7

	5.3.i	Experimental procedure136
	5.3.ii	Results137
5.4	Kinetics of	of the growth of potential host
	solids on	model surfaces as a function of
	solution (concentration139
	5.4.i	Experimental140
	5.4.ii	Results and discussion141
5.5	Kinetics of	of the dissolution of potential host
	solids, in	cluding 228Ra as a mico-component,
	from mod	el surfaces143
	5.5.i	The preparation of carrier-free
**	à 8	228Ra from thorium, using cation
-		exchange columns144
	5.5.ii	Discussion146
æ	5.5.iii	Dissolution of the host matrix, as
		followed by radiotracer techniques148
	5.5.iv	Results and discussion148
	5.5.v	Dissolution of BaSO ₄ labelled with
		228 _{Ra} 149
	5.5.vi	Results of the dissolution of BaSO ₄
		labelled with 228Ra150

ľ,

.

Chapte	er 6 Summary and Conclusion for	
Entire	Thesis	188
6.i	Contributions to knowledge	.188
6.ii	Contributions to the literature	.191
6 .iii	Suggestions for further research	.193

Appendix	l	196
Appendix	11	198

2

xii[°]

:

~

e

Table of Figure Captions

1

Figure 1 Uranium mill process streams for the
sulfuric acid leach process14
Figure 2 Variation of the ionic strength I and the
ion and complex concentrations in a solution
containing 50mmol/L (NH4)2SO4 and NaH2PO4. The
pH is adjusted by ammonia, [N] _t being the total
ammonia (NH ₃ + NH ₄ +) in the system; calculations
based on data from (21) and (22)40
Figure 3 Activation free energy for nucleation as
a function of the nucleus size. The critical value
ΔG^* must be reached for creating a nucleus of
critical radius r [*] 41
Figure 4 Cap shaped nucleus of radius r forming
on a solid substrate, with which it forms the
contact angle a42
Figure 5 Schematic representation of a crystal
exhibiting flat (F), stepped (S) and kinked (K)
faces. Front face exhibits a polygonized growth
spiral, whereas the top face exhibits a two-
dimensional nucleus43
Figure 6 Birth and spread model; several two-
dimensional nuclei spread across the crystal face
(taken from 39)

Page

 \hat{y}

Page

Figure 7 Profile of a face growing by a spiral	
growth mechanism4	5
Figure 8 Schematic representation of the solute	
transfer from the smallest to the largest crystal	
during Ostwald ripening. The crystals are	
separated by the distance X and their concentration	
spheres interact through the cross-section A4	6
Figure 9 Comparison of the data for the	
solubility of PbSO ₄ in H ₂ SO ₄ at 298K by Crockford	
et al.(50), with the data of Danel and Plichon (54)	
at 293K7	7
Figure 10 Comparison of experimental solubility	
(+) and fitted values (solid line), using the Pitzer	
model, for PbSO ₄ in Na ₂ SO ₄ at 333K7	8`
Figure 11 Comparison of experimental solubility	
(+) and fitted values (solid line), using the Pitzer	
model, for PDSO4 in H2SO4 at $333K$ 7	9
Figure 12 Comparison of experimental solubility	
(+) and fitted values (solid line), using the Pitzer	
model, for PDSO4 in H2SO4 at $2/3K$ 8	10
Figure 13 Comparison of experimental solubility	
(+, taken from 54) and fitted values (solid line),	
using the Pitzer model, for PoSO4 in H2SO4 at	
293K	;1
Figure 14 Comparison of experimental solubility	
(+, taken from 53) and fitted values (solid line),	
	12

C

xiv

Figure 15 Scanning electron micro-photographs of BaSO4. Specimen A is a freshly prepared specimen while specimen B was "aged" in the mother liquor for 18 hours prior to the photography. The bar = $10\mu m$ in length......83 Figure 16 Comparison of experimental solubility (+) and fitted values (solid line), using the Pitzer model, for BaSO₄ in H₂SO₄ at 298K......84 Figure 17 Comparison of experimental solubility (+) and fitted values (solid line), using the Pitzer model, for BaSO₄ in H₂SO₄ at 333K......85 Figure 18 Comparison of experimental solubility (+, taken from 80) and fitted values (solid line), using the Pitzer model, for RaSO₄ in H₂SO₄ at Figure 19 Predicted solubility (solid line) for RaSO₄ in H₂SO₄-H₂O solutions at 308K. The only available experimental data (+) are shown at Predicted solubility (solid line) for Figure 20 RaSO₄ in H₂SO₄-H₂O solutions at 318K. The only available experimental datum (+) is shown at Predicted solubility (solid line) for Figure 21 RaSO₄ in H₂SO₄-H₂O solutions at 333K. No Figure 22 Crystal/solution interface with various possible positions for a growth unit: (1) in the solution; (2) at a flat surface; (3) at a step site and (4) at a kink site.....114

1<u>.</u> 1 Page

Page

Figure 23 Different hypothetical routes for transport from the solution to the crystal, utilizing the concept of compartment models......115 Figure 24 Plot of In (1-F) as a function of time for 133-Ba exchanging on the (001) face of a single crystal of barite at 298K. F is the exchange fraction......116 Figure 25 Plot of In (1-F) as a function of time .~ for 133-Ba exchanging on the (110) face of a single crystal of barite at 298K. F is the exchange fraction......117 Figure 26 Plot of In(1-F) as a function of time for 133-Ba exchanging on the (001) face of a single crystal of barite at 333K. F is the exchange fraction......118 Figure 27 Plot of In (1-F) as a function of time for 133-Ba exchanging on the (001) face of a single $\overline{\mathbf{v}}$ crystal of barite, in the presence of 0.75mM Pb2+ at 298K. F is the exchange fraction......119 Figure 28 Plot of In (1-F) as a function of time for 133-Ba exchanging on the (001) face of a single crystal of barite, in the presence of 75µM Pb2+ at 298K. F is the exchange fraction.....120 Figure 29 Plot of In (1-F) as a function of time for 210-Pb being sorbed on the (001) face of a single crystal of barite at 298K. F is the exchange fraction......121 6)

Figure 30 Plot of In (1-F) as a function of time for 210-Pb exchanging on the (001) face of a single crystal of anglesite at 298K. The regression equation is In (1-F)=-6.58299t+0.578468. The correlation coefficient=0.943196.....122 Figure 31 Comparison of experimental values of F and fitted values, for 133-Ba exchanging on the (001) face of a single crystal of barite at 298K. F is the exchange fraction.....123 Figure 32 Comparison of experimental values of F and fitted values, for 133-Ba exchanging on the (110) face of a single crystal of barite at 298K. F is the exchange fraction.....124 Figure 33 Comparison of experimental values of F and fitted values, for 133-Ba exchanging on the (001) face of a single crystal of barite at 333K. F is the exchange fraction......125 Figure 34 Comparison of experimental values of F and fitted values, for 210-Pb being sorbed on the (001) face of a single crystal of barite at 298K. F is the exchange fraction......126 Figure 35 Comparison of experimental values of F and fitted values, for 133-Ba exchanging on the (001) face of a single crystal of barite, in the presence of $75\mu M Pb^{2+}$ at 298K. F is the exchange fraction......127 Figure 36 Comparison of experimental values of F and fitted values, for 133-Ba exchanging on the (001) face of a single crystal of barite, in the presence of 0.75mM Pb2+ at 298K. F is the exchange fraction......128

ð

ÿ,

xvii

Figure 37 Drawing of desorption/dissolution cell used in order to study (i) desorption of ions and (ii) dissolution of BaSO₄ and (Ba/Ra)SO₄ heteroepitaxial deposits, from mica model surfaces......156 Figure 38 showing the arrangement of the cell with the solution reservoir and receiver. The flow rate is controlled by (i) the pump speed and (ii) the internal diameter of the pump tubing......157 Figure 39 Plot of fraction of 35SO4 retained on a specimen of muscovite mica. The 35SO₄ is desorbing into distilled, demineralized water which has been deaerated by means of nitrogen......158 Figure 40 Plot of log (desorption factor) as a 1 . function of log (time of desorption) for 35SO4 desorbing from mica into distilled water. The line fitted by regression analysis has an equation: log(DF)=0.213570*log(time)-0.00782. The correlation coefficient was 0.9942.159 Plot of fraction of 133Ba retained on a Figure 41 specimen of muscovite mica. The 133Ba is desorbing into distilled, demineralized water which has been deaerated by means of nitrogen......160 Figure 42 Plot of log (desorption factor) as a function of log (time of desorption) for 133Ba desorbing from mica into distilled water. The line . . fitted by regression analysis has an equation: log(DF)=0.38146*log(time)-0.49777. The correlation coefficient was 0.9676.161

Page

Figure 43 Plot of fraction of ⁴⁵Ca retained on a specimen of muscovite mica. The ⁴⁵Ca is desorbing into distilled, demineralized water which has been deaerated by means of nitrogen......162 Figure 44 Plot of log (desorption factor) as a function of log (time of desorption) for 45Ca desorbing from mica into distilled water. The line fitted by regression analysis has an equation: log(DF)=0.36451*log(time)-0.04032. The correlation coefficient was 0.9697.163 Figure 45 Plot of fraction of ¹³³Ba retained on a specimen of quartz. The 133Ba is desorbing into distilled, demineralized water which has been deaerated by means of nitrogen......164 Figure 46 Plot of log (desorption factor) as a function of log (time of desorption) for 133Ba desorbing from quartz into distilled water. The line fitted by regression analysis has an equation: log(DF)=1.26407*log(time)+0.59768 The correlation coefficient was 0.9894.165 Figure 47 Scanning electron micro-photographs of hetero-epitaxial deposits on muscovite mica, grown from aqueous solution: (a) BaSO₄ (b) PbSO₄ (c) mixed (Ba/Pb)SO4.166 Figure 48 Scanning electron micro-photographs of hetero-epitaxial deposits on quartz, grown from aqueous solution: (a) BaSO₄ (b) PbSO₄ (c) mixed

Ó

-

Figure 49 Scanning electron micro-photographs of hetero-epitaxial deposits on muscovite mica, grown from aqueous solution: (a) SrSO₄ at 6500x (b) SrSO₄ at 3540x.....168 Figure 50 Apparatus used to pass solution through ion exchange columns at reduced pressure. Column shown is 3-cm long of Dowex 50W-X12......169 Figure 51 Plot of rate of growth of BaSO₄ on mica. The concentration of the Ba(NO₃)₂ solution used as a source of Ba2+ag ions was 0.1M; the sulfuric acid concentration was 6m. The regression line drawn for the mean behaviour has an equation: Mean mass/cm²=2.09652e-5*Number of cycles+1.27753e-4. The correlation coefficient was 0.9874.....170 Figure 52 Rate of growth of BaSO₄ on mica from 0.1M barium nitrate solution and various concentrations of sulfuric acid. The four sets of points correspond to: #1 $[H_2SO_4]=9.9\times10^{-3}M$; the regression equation for these data is: g/cm².cycle=9.1258e-6*Number of cycles-7.53100e-6. The correlation coefficient=0.983. #2 [H2SO4]=0.504M; the regression equation for these data is: g/cm².cycle=3.257200e-5*Number of cycles-1.7900e-6. The correlation

coefficient=0.978.

ç.

Page

#3 [H2SO4]=0.99M; the regression equation for these data is: g/cm².cycle=5.22620e-5*Number of cycles+3.82600e-5. The correlation ÷ coefficient=0.992. #4 [H2SO4]=5.994M; the regression equation for these data is: g/cm².cycle=8.4156e-5*Number of 1 cycles+1.23380e-4. The correlation coefficient=0.970.171 Figure 53 Rate of growth of BaSO₄ on mica as a function of concentration of sulfuric acid. Concentration of Ba2+ is constant at 0.1M......172 Figure 54 Rate of growth of BaSO₄ on mica as a function of √concentration of sulfuric acid. Concentration of Ba2+ is constant at 0.1M. The regression equation is: Rate of growth=3.11436e-05*[H2SO4]0.5+1.14178e-05. The correlation coefficient is 0.977......173 Figure 55 Rate of growth of BaSO₄ on mica as a function of concentration of barium nitrate. Concentration of sulfuric acid is constant at 6m. The regression equation for the line is: Rate of growth=4.510442e-04*[Ba]+2.093576e-05. The correlation coefficient is 0.995.174

Page

Figure 56 Plot of rate of growth of PbSO4 on mica. The concentration of the Pb(NO3)2 solution used as a source of $Pb^{2+}aq$ ions was 0.1M; the sulfuric acid concentration was 6m. The regression line drawn for the mean behaviour has an equation: Mean change in mass/cm²=8.65688e-5*Number of cycles+1.7976e-4. The correlation coefficient was 0.9769.....175 Figure 57 Rate of growth of PbSO4 on mica from 0.1M lead nitrate solution and various concentrations of sulfuric acid. The four sets of points correspond to: #1 [H₂SO₄]=9.9x10⁻³ M; the regression equation for these data is: g/cm².cycle=9.924e-6*Number of cycles-6.972e-6. The correlation coefficient=0.98. #2 [H2SO4]=0.504M; the regression equation for these data is: g/cm².cycle=2.017e-5*Number of cycles+8.886e-6. The correlation coefficient=0.976. #3 [H2SO4]=0.99M; the regression equation for these data is: g/cm².cycle=3.441e-5*Number of cycles-6.920e-6. The correlation coefficient=1.00. #4 [H2SO4]=5.994M; the regression equation for these data is: g/cm².cycle=1.663e-4*Number of cycles+9.662e-6 The correlation coefficient=1.00.....176

Page

xxii

Figure 58 Rate of growth of PbSO₄ on mica as a function of concentration of sulfuric acid. Concentration of Pb2+ is constant at 0.1M. The regression equation is: Rate=2.63331e-05*[H2SO4]+8.3402e-06. The correlation coefficient=0.999......177 Figure 59 Rate of growth of PbSO4 on mica as a function of concentration of lead. Concentration of H₂SO₄ is constant at 6M. Equation of the regression line: Rate=7.79522e-04*[Pb]+2.38414e-05. Correlation coefficient=0.9982.....178 Figure 60 Plot of concentration of SO42- and HSO₄- species in H₂SO₄ as a function of [H₂SO₄].....179 Figure 61 Plot of net counts per minute against mass change per cm² for (133-Ba/Ba)SO₄ growing on mica. Three replicates are shown. The deposits were grown from 0.1M Ba(NO3)2 solution and 6M H2SO4 solution......180 Figure 62 Plot of mean net counts per minute against mean mass change per cm² for (133-Ba/Ba)SO4 growing on mica. The deposits were grown from C.1M Ba(NO3)2 solution and 6M H2SO4 solution. The regression equation is: Mean net counts/minute=1.01462e06*Mean change in mass/cm²+2.07473e01.The correlation coefficient is 0.987......181

Page

 \dot{t}

么

Figure 63 Dissolution of 133-Ba labelled BaSO₄ into 1.0x10-3MH2SO4 at 2.8mL/minute flow rate. The equation of the line is: (A0- A_t)/ A_0 =0.055516*Time of flow+0.001050. The Figure 64 Dissolution of 133-Ba labelled BaSO4 into 1.0x10⁻³MH₂SO₄ at 10mL/minute flow rate. The equation of the line is: (A0- A_t)/A₀=0.072684*Time of flow+0.007543. The correlation coefficient is 0.990......183 Figure 65 Dissolution of 133-Ba labelled BaSO4 into 1.0x10-3MH2SO4 at 19.5mL/minute flow rate. The equation of the line is: (An- $A_t)/A_0=8.15e-02*Time of flow-0.0015$. The correlation coefficient is 0.999......184 Figure 66 Rate of dissolution of 133-Ba labelled BaSO₄ into 1.0x10⁻³MH₂SO₄ as a function of flow rate. Each datum represents the slope of the graph in the previous three Figures......185 Figure 67 Growth of (228-Ra/Ba)So₄ on mica. The count rate was determined using a gas-flow proportional counter, with the mica specimen resting on the desorption/dissolution cell window. The equation of the line is: Counts/minute=1.772128e05*Mass+7.167618. The correlation coefficient is 0.9946......186 Sof

Figure 68 Rate of dissolution of $(228-Ra/Ba)SO_4$ solid solution into $1.0x10^{-3}MH_2SO_4$ at 298K. Flow rate =19.5mL/minute. The equation of the line is: Normalized rate of dissolution=8.28e-02*Time-3.422604e-02.

The correlation coefficient is 0.988......187

C

Φ

ë

c,

Ċ.

c

C

Ľ,

XXV

ø

Page

\$

List of Tables

13

Page Data available for the solubility of Table 1 PbSO₄ in solutions of H₂SO₄ and Na₂SO₄......64 Measured solubilities of lead sulfate Table 2 in sodium sulfate solutions at 60⁰C......65 Measured solubilities of lead sulfate in Table 3 sulfuric acid solutions at 60⁰C......66 Ion interaction parameters for Pb2+-Table 4 Ion interaction parameters for Pb2+-Table 5 Solubility of barium sulfate in sodium Table 6 Measured solubilities of barium sulfate in Table 7 sulfuric acid solutions at 250C......70 Table 8 Solubility of barium sulfate in sulfuric acid at 60⁰C......71 Ion interaction parameters for Ba2+-Table 9 Table 10 Ion interaction parameters for Ba2+-Ion interaction parameters for Ra2+-Table 11 Table 12 Ion interaction parameters for Ra2+-HSO₄²-.....75 Comparison of parameters for 2:2 Table 13

xxvi

Ę

Literature review of experimental Table 14 investigations of isotope exchange......108 Table 15 Parameter values ri and residence times τ_i for different single crystals of BaSO₄ under equilibrium conditions with respect to the macrocomponent......109 Table 16 Parameter values r; and residence times au_i for single crystals of BaSO₄ under equilibrium Parameter values \boldsymbol{r}_i and residence times Table 17 म for a single crystal of PbSO4 under equilibrium conditions with respect to the macro-component......111 Table 18 Calculated jump frequencies and the corresponding activation free energies AG† for some elementary transport processes in the systems PbSO₄/aqueous solution and BaSO₄/aqueous solution.....112 Table 19 Experimental jump frequencies and the corresponding activation free energies AG† for the system BaSO₄/aqueous solution.113 Table 20 Selected peaks from the gamma ray spectrum of the eluent (Canberra Series 90 system with an intrinsic Ge detector)152 Table 21 Decay scheme for 232-Thorium......153 Regression equations for the Table 22 radioactive decay constants of the daughter products of radium-228154 Comparison of experimental and Table 23 literature values for half-life155

Ċ

xxvii

SYMBOLS AND NOTATION

A - Debye-Huckel constant, log base10

A^{\$\phi\$} - Debye-Huckel constant for osmotic coefficients, log
base e

A? - Debye-Huckel constant for activity coefficients, log base e

ai - activity of species i

aw - activity of water

BY – parameter in Pitzer's activity coefficient equation

C^o - Pitzer parameter

I - ionic strength

K_{sp} -solubility product

M - solute molecular mass

m - molality

ν

n; - number of moles of i

 β_0 , β_1 , β_2 - Pitzer interaction coefficient; β_2 only used for 2:2 electrolytes

molal activity coefficient

- θ_{ij} Pitzer's coefficient for like charged ion interactions
 - sum of cation and anion stoichiometric numbers

xxviii

- vi stoichiometric number of ion i
- φ osmotic coefficient
- ψ_{ijk} Pitzer triple ion interaction parameter

J.

Subscripts:

- A anion
- a anion
- C cation
- c cation

¢

1

- i any species
- j any species

ß

 $(\mathbf{i}$

¢

Ţ,

CHAPTER 1 INTRODUCTION

1.1 Outline of the milling and processing of uranium ore.

Uranium-238 and its decay daughter radium-226 occur together in uranium ores. Examples of typical ores found in Ontario uranium ore bodies include brannerite (uranium titanium dioxide) and uraninite (uranium thorium oxide). The minerals are dispersed in a quartz pebble conglomerate matrix at Elliot Lake, while at Cluff Lake the host matrix is sandstone and clay. Pyrite is also found in the ores. Details of the milling processes for Quirke, Cluff Lake and Key Lake mills are given in (1). A simplified process flowchart (1) for a typical sulfuric acid leach mill is given in Figure 1. Commonly, the ores are crushed to some small size (e.g. 50% minus 200 mesh for the ore from Quirke Lake) and then leached using hot (60°C) sulfuric acid of 1 to 6M concentration to win the uranium. The leaching conditions are determined by the mineralogy of the

1

 $i^{(s)}$

v

ore, with refractory minerals such as brannerite and monazite requiring stronger oxidizing conditions, higher temperature and longer leaching time than minerals such as uraninite and pitchblende. Unlike the sulphate compounds of uranium, radium sulphate is essentially insoluble; thus it deposits on the finely mica fragments). quartz or (e.g. around gangue solids Essentially the entire radium content of the uranium ore ends up in the solid mill wastes (the mill tailings). The presence of radium-226 in these materials and the amount of mill waste produced makes mine backfilling or deep burial in geologically stable vaults impractical. Current practice is to place the solid and liquid mill wastes, after final neutralization, in a contained area known as the tailings pond. Radium contained in the tailings is slowly leached from these solids and enters the biosphere.

~

The leaching of radium-226 (half-life=1620a) from the to prime concern (tailings) is of mill waste uranium This source is the major influence environmental managers. upon the radiological dose to human beings resulting from Despite many laboratory and field uranium mill tailings (2). mechanism which controls the geochemical the studies, leaching (dissolution) behaviour of radium-226 has remained It is essential that the mechanism which controls the unclear. the understood order that in behaviour be leaching

ç

environmental and engineering management of uranium tailings be accomplished.

1.2 Fate of radium during Ore processing

Ċ

Previous research by Skeaff (3) has established that Ra-226 essentially remains with the solid phase in the leaching tanks of the mill. whereas other radionuclides of the U-238 chain (i. e., U-238, Th-230, Pb-210) are dissolved by sulfuric acid leaching. Using the chemical concept that sulfuric acid attack upon the uranium minerals should break uranium and all of its daughters out of the crystal structures, it would be expected that Ra-22 δ_{χ} should enter the solution in proportion to that in the uranium mineral; for radionuclides in secular an activity equivalent to that of the parent is equilibrium, expected. The work of Skeaff (3) showed that much of the Ra-226 is dissolved from coarser material and redistributed to the finer material, indicating that it must enter solution.

The most plausible explanations for this behaviour are that the radium is either on the surface of the leached solids in a reversibly adsorbed state, or that it is present as a coprecipitate with a metal sulfate precipitate. Previous work (4, 5) that included an analysis of solids from different parts of the mill chain (leaching tanks, neutralization tanks) using scanning electron microscopic-X-ray emission techniques (SEM-XRE) demonstrated that a small quantity of surface

 \sim

precipitates is found on solids from the leaching tanks and that a substantial quantity of precipitates is found after the neutralization tanks. These precipitates could contain Ra-226 as a coprecipitate. The SEM-XRE analysis suggested that such a surface precipitate must be quite small (< 1 μ m on the surface of 0.5mm solids).

Ĉ

work (6-13) using chemical Previous laboratory picture of confusing demonstrated а techniques has geochemical controls upon Ra-226 behaviour during dissolution Variables examined include liquid to solid and precipitation. ratio, concentration of cations and anions and leaching agents, ionic size and charge, and surface area. More recent work (14, 15) has systematically examined these mechanisms but does not permit general conclusions to be drawn concerning which mechanism is dominant. Another recent literature review (16) sulfate (radium/barium) dissolution of а that suggests coprecipitate may control much of the Ra-226 found in The adsorption of Ra-226 onto quartz and kaolinite tailings. and its coprecipitation have been investigated experimentally and theoretically by Langmuir and Reise (17, 18). Their results suggest a hypothesis that radium sorption behaviour can be explained by coprecipitation at low pH (<4) and by reversible adsorption behaviour in the neutral pH range. This would imply that a coprecipitate would be \mathcal{P} lausible for explaining Ra-226 behaviour in the leaching tanks.

1.3 Laboratory work on radium precipitation in the leach tanks.

Previous work by Snodgrass and Constable (4, 5) has suggested that Ra-226 coprecipitation with barium sulfate is the controlling mechanism for radium precipitation in the leach tanks. The work of Steger and Legeyt (19) on sulfuric acid leached uranium ore led to the suggestion that radium-226 is in the form of a mixed crystal with lead sulfate, with subsequent attainment of equilibrium conditions in the pore water of the leached ore allowing a re-proportioning of the radium between solid lead and barium sulfates. in a nuclear emulsion study on leaching tank solids, locations of high alpha activity were examined using SEM; small microcrystalline barium sulfate crystals which had precipitated on the surface of a silicate mineral were identified (20). The barite crystals were the likely source of the radium radiation and contained small quantities of lead. No lead sulfate particles were identified. Consequently for the National Uranium Tailings Program (NUTP) source term model, it is suggested that Ra-226 dissolution be modelled as controlled by barium sulfate and by lead sulfate host crystals.

()
1.4 The Snodgrass and Hileman model of leach tank processes.

 $\left(\right)$

(21) have hypothesised that the Snodgrass et al. following steps are involved in the leach tank processes. "Proton attack on the uranium and thorium minerals liberates the parent and daughter radionuclides into solution. Proton liberates stable also lead from the uranium-238 attack mineral along with barium, strontium and calcium from other minerals containing them in trace amounts. If conditions are appropriate, the metal ions and/or sulfate ion will adsorb onto a surface such as silica. If the local geometry (of the order of a few square Ångstroms) is suitable, crystal growth will be Consequently, systems of potential interest in the initiated". development of an overall predictive model for the purpose of describing solution and mineral equilibria in uranium mill leaching tanks include BaSO4-H2SO4-H2O, PbSO4-H2SO4-H2O and solid solutions involving these sulfates in addition to RaSO₄.

1.5 The Snodgrass and Hileman model of uranium mill waste tailings.

A conceptual model of the evolution of uranium mill waste tailings as a function of time has been proposed by Snodgrass et al. (21) and is quoted here, in part, from their Report:

"When milled solids leave the mill they are coated with three different forms of precipitates (or layers). These precipitates are formed in the leaching tanks, the partial neutralization tank and the final neutralization tank. In the leaching tanks, uranium, thorium, Ra-226 and Pb-210 are leached along with various metal sulphides. The reduced metals are oxidized and metal sulphates SO₄ precipitate. The (Ba/Ra) precipitate is believed to occur as part of the first (inner-most) layer. Ra²⁺ forms RaSO₄⁰ complexes and is rapidly incorporated into a BaSO₄ (s) structure. Because the sizes of Ra^{2+} and Ba^{2+} are quite similar, significant effects upon crystal growth would occur only when the molar ratio of Ra-226/Ba2+ is large.

Thorium species released in the leaching tanks are expected to be carried through the mill until the final neutralization tank. Thus, they are expected to be in the outer layer. Pb-210 will form sulphate complexes and may coprecipitate with PbSO₄ (s) in the leaching tanks. A (Ca/Pb)SO₄ coprecipitate may also form. Some thorium is expected to precipitate or adsorb in the partial neutralization tank because of the increase in pH.

Most of the thorium species are postulated to precipitate in the final neutralization tanks as hydroxides, or to become enmeshed in the gypsumettringite (6CaO.Al₂O₃.3SO₃.33H₂O) precipitates.

On placement in the tailings pile, available data suggests that the leaching waters remain basic for a period of time. The main constituent of dissolved solids during this period is gypsum. Dissolution of gypsum should give a pH of about 7. Because the observed pH is often higher, residual buffering from mill-added lime influences the pH. During the time period of gypsum dissolution, Ra-226 enmeshed with the CaSO₄ precipitates is the plausible source for Ra-226 in the leachates.

process, it is dissolution During this solids originally postulated that the Th(OH)4 in the final enmeshed within the gypsum neutralization tank remain on the particles until the pH decreases sufficiently to initiate their dissolution.

When sufficient gypsum has dissolved, pyrite grains are exposed to oxygen and to the organisms in the film of water covering the solids. Also, some pyrite grains may be bare because final neutralization precipitates did not cover their

surface. Atmospheric oxygen penetrating to various depths of the unsaturated zone between rainfall events is the main source for oxygen in the tailings waters. Biofilms containing Thiobacillus ferrooxidans develop. The actual origins of such bacteria are not clear but microbiological work (e. g. 4) demonstrate that pyrite oxidizers develop both in tailings fresh from the mill and in old tailings which are dried and then leached.

As pyrite oxidation develops, the pH starts to decrease. It is suggested that pH is maintained in the 5-7 range as the pyrite-oxidizer community develops and as residual buffering minerals are attacked. As the pH decreases, the concentration of sulphate increases and minimizes the dissolution of gypsum. This sequence maintains the presence of gypsum in the solid phase of the unsaturated zone until the completion of pyrite oxidation.

When pyrite oxidation is nearly complete, the pore water sulphate concentration will decrease because the rate of sulphate production decreases. This allows the host crystal containing Ra-226 on the mineral particles to begin to dissolve due to the low sulphate concentration in the pore water." 1.6 Components of the precipitation/dissolution model

The source model for the control of Ra-226 release proposed for the National Uranium Tailings Project includes the following hypotheses:

(i) Radium-226 dissolution behaviour in uranium tailings formed from sulfuric acid leaching is controlled by the dissolution of a parent crystal with which it is coprecipitated.

(ii) That this coprecipitate is formed in the first several leaching tanks.

(iii) That a coprecipitation mechanism rather than a reversible adsorption in the leaching tanks controls the partitioning of Ra-226 onto the solid phase after dissolution of the parent U-238 mineral.

(iv) That the host crystal may be composed of sulfates of Ca. Ba, Sr, Fe and/or Pb.

(v) That this coprecipitate remains chemically stable in tailings piles until the porewater concentrations of sulfate are low enough to allow the dissolution of the mixed crystals containing Ra-226.

In order to evaluate this model, several pieces of information have been identified by Snodgrass and Hileman

(21) as being required. These include (among others) the following:

The identification of the surface precipitate (host (i) crvstal) Ra-228 containing Ra-226 and with direct observational techniques the identification of the and crystallization site.

2

((

(ii) The evaluation and quantification of the kinetics of dissolution of mono-minerals containing Ra-226, Ra-228, Ba, Pb, Ca, Fe and Sr.

(iii) The validation of the hypothesis that the same host solid controlling Ra-226 in the leaching tank solids also controls its dissolution behaviour in old tailings.

A major obstacle to the evaluation of this model is the existence of significant data gaps in the current literature. These missing data include:

(i) The solubility of potential host solids such as $BaSO_4$ and $PbSO_4$ in H_2SO_4 solutions from 0 to 6M in concentration and at $60^{\circ}C$, required in order to trace the fate of each of the solids and soluble species in the mill processing streams from the leaching tanks until placement in the tailings ponds and subsequent evolution has occurred.

(ii) Appropriate thermodynamic parameters for the modelling of such data in sulfuric acid according to one of the modern activity coefficient models.

÷

(iii) Positive identification of potential host crystals on the surface of substrates similar to those found in the process stream.

(iv) A knowledge of the kinetics of the exchange and adsorption of cations implicated in the model.

(v) Data to validate the assumption that adsorption onto the surface of substrates likely to be found in the process stream does occur for the appropriate anions and cations, with a time scale for retention sufficiently long to allow growth of surface deposits.

(vi) Kinetic data for the dissolution of some, at least, of the potential host solids into dilute sulfuric acid.

(vii) Data to demonstrate that the dissolution of potential host solids controls the release of Ra-226 from a solid solution.

1.7 Purpose of this research

Consideration of the gaps in the data required to evaluate the Snodgrass and Hileman model led to the definition of the goals for this research. These goals are:

ļ.

(i) To determine the solubility of potential host solids such as BaSO₄ and PbSO₄ in H₂SO₄-H₂O solutions from 0 to 6M in concentration and at 25^{0} C and 60^{0} C.

(ii) To model such data for solubility in sulfuric acid using the Pitzer activity coefficient model. Where parameters

12

9 Q

required for the model are not available in the literature, these parameters will be estimated using appropriate numerical techniques.

(iii) Data will be obtained for the rate of desorption of anions and cations implicated in the model, from model surfaces.

(iv) The kinetics of the exchange and adsorption of cations implicated in the model will be investigated and modelled.

(v) Attempts will be made to grow potential host solids on model surfaces.

(vi) The kinetics of the growth of these potential host solids on the model surfaces will be examined as a function of solution concentrations.

 \mathcal{O}

D

Ű

£

(vii) The dissolution kinetics of these surface deposits will be determined using radio-tracer techniques. Surface deposits will then be grown which incorporate radium in the host matrix. The dissolution kinetics of the radium microcomponent, followed by counting, will subsequently be related to the rate of dissolution of the host matrix.

Each of these components of the research is treated in detail in the following chapters of this work.

4331

 $\{$

Figure 1 Uranium mill process streams for the sulfuric acid leach process

 \mathcal{O}

С

. •

<u>(</u>)

 $^{\circ}$



Chapter 2 Background Information

 \mathbb{C}

0

2

The aim of this survey is to provide an overview of the background information required in order to desian the experiments needed to meet the objectives of the study and to evaluate and interpret the data obtained. This will include alkaline earth sulfate solubility measurements in sulfuric acid solutions (0 to 6M), requiring the modelling of activity coefficients using the Pitzer formalism; crystal growth investigations which require an understanding of models for nucleation and crystal growth from solutions and onto preformed surfaces; and dissolution of crystals and of crystals deposited on substrates, which requires a knowledge of models of dissolution processes.

2.1 Review of Activity Coefficient Modelling using the Pitzer Equations.

of thermodynamic models activity Advances in coefficients - for example, the work of Pitzer and his school have proven invaluable to researchers dealing with species in The application of these models to systems aqueous systems. of geochemical interest has largely been due to the efforts of researchers such as Harvie and Weare (22) and Harvie et al. The use of the Pitzer equations to describe solution (23).equilibria in mixed-salt systems of high ionic strength demands data for the interaction parameters of ions. While an

extensive database of ion interaction parameters currently is in existence (see, for example, 24), in many cases, such as the PbSO₄-H₂SO₄-H₂O and BaSO₄-H₂SO₄-H₂O systems, the required ion interaction parameters of interest are unavailable. These obtained data must be through the regression analysis of published data based mineral on solubility, E.M.F. isopiestic, activity, osmotic and measurements in single and mixed salt systems.

The Pitzer expressions, as formulated by Harvie et al. (23), are given by:

$$\ln \gamma_{M} = z_{M}^{2} F_{+} \sum_{a=1}^{N_{a}} m_{a} (2B_{Ma} + ZC_{Ma})$$

$$+ \sum_{c=1}^{N_c} m_c (2\Phi_{Mc} + \sum_{a=1}^{N_a} m_a \psi_{Mca})$$

+ $\sum_{a=1}^{N_{e}} \sum_{a'=a+1}^{N_{a}} m_{a'} \psi_{aa'M} + |z_{M}| \sum_{c=1}^{N_{c}} \sum_{a=1}^{N_{a}} m_{c} m_{a} C_{ca} + \sum_{n=1}^{N_{n}} m_{n} (2\lambda_{nM})$ (1)

Ç

(2)

0

$$\ln \gamma_{X} = z_{X}^{2} F + \sum_{c=1}^{N_{c}} m_{c} (2B_{cX} + ZC_{cX})$$

$$+\sum_{a=1}^{N_{a}} m_{a}(2\Phi_{Xa} + \sum_{c=1}^{N_{c}} m_{c}\psi_{Xac}) + \sum_{c=1}^{N_{c}-1} \sum_{c'=c+1}^{N_{c}} m_{c} m_{c'}\psi_{cc'} x$$

+
$$|Z_X| \sum_{c=1}^{N_c} \sum_{a=1}^{N_a} m_c m_a C_{ca} + \sum_{n=1}^{N_n} m_n (2\lambda_{nX})$$

In the expression for individual ion activity coefficients, m_c and z_c are the molality and charge of cation c, respectively. N_c is the total number of cations. Similar symbolism is used for anions, a, and neutrals, n. The parameter λ accounts for the interactions between neutral species and ionic species in the solution. The subscripts M, X, and n refer to cations, anions, and neutral species respectively. The remaining terms are defined as follows:

F=-A^{$$\phi$$} $\left(\frac{I^{1/2}}{1+1.2I^{1/2}} + \frac{2}{1.2} \ln (1+1.2I^{1/2}) \right) + \sum_{c=1}^{N_c} \sum_{a=1}^{N_a} m_c m_a B_{ca}$

 $\mathbf{\hat{z}}$

$$c + \sum_{c=1}^{N_{c}-1} \sum_{c'=c+1}^{N_{c}} m_{c} m_{c'} \phi_{cc'} + \sum_{a=1}^{N_{a}-1} \sum_{a'=a+1}^{N_{a}} m_{a} m_{a'} \phi_{aa'}$$
(3)

where the variation in A^{φ} with temperature was computed from the equation :

$$A\phi = 0.377 + 4.684 \times 10^{-4} \times (T-273.15) + 3.74 \times 10^{-6} \times (T-273.15)^2$$

obtained by fitting to the data of Bradley and Pitzer (25).

Ũ

 \odot

$$\mathbf{F} = -\mathbf{A}^{\phi} \left(\frac{\mathbf{I}^{1/2}}{\mathbf{I} + 1.2 \mathbf{I}^{1/2}} + \frac{2}{1.2} \ln \left(1 + 1.2 \mathbf{I}^{1/2} \right) \right) + \sum_{c=1}^{N_c} \sum_{a=1}^{N_a} m_c m_a B_{ca}$$

$$+ \sum_{c=1}^{N_{c}-1} \sum_{c'=c+1}^{N_{c}} m_{c} m_{c'} \phi_{cc'} + \sum_{a=1}^{N_{a}-1} \sum_{a'=a+1}^{N_{a}} m_{a} m_{a'} \phi_{aa'}$$

$$C_{MX} = C_{MX}^{\phi} \left| Z_{M} Z_{X} \right|^{1/2}$$
(4)

where:

2.0

Ċ

Ģ

$$Z = \sum_{i} |z_{i}| m_{i}$$
⁽⁵⁾

The second term, B, in equations (3) and (4) is given the following ionic strength dependence:

$$B_{MX} = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} g(\alpha_{MX} \sqrt{I}) + \beta_{MX}^{(2)} g(12\sqrt{I})$$
(6)

and its first derivative with respect to I, used in equation (5), is:

$$B_{MX} = \beta_{MX}^{(1)} g(\alpha_{MX} \sqrt{I}) + \beta_{MX}^{(2)} g(12\sqrt{I}) / I$$
(7)

The β_{MX} and C_{MX} are adjustable parameters specific to each solute.

The functions g and g^t are defined by the equations:

$$g(x) = 2(1-(1+x)e^{-x})/x^2$$
(8)

 $g'(x) = -2(1-(1+x+x^2/2))e^{-x})/x^2$ (9)

(3)

e

with $x = \alpha_{MX}\sqrt{1}$ or $12\sqrt{1}$. When either cation M or anion X is univalent $\alpha_{MX} = 2.0$. For 2-2 or higher valence pairs $\alpha_{MX} = 1.4$. In most cases $\beta(2)$ equals zero for univalent pairs. For 2-2 electrolytes a non-zero $\beta(2)$ is more common.

It was decided to omit the term for neutral species and Given the extremely low the Φ and ψ components. concentration of the metal cations it seems likely that the contribution made by these terms would be very small. As noted by Pitzer (26) it is the β and C^{φ} terms that have the greatest effect on activity coefficient calculations, so that the Φ and ψ terms may contribute little or nothing to the The electrostatic terms implicit in the Φ calculations. coefficient, which are dependent only on the ion charges and the total ionic strength, account for the electrostatic effects of unsymmetrical mixing and are equal to zero when the ions Details of the computational are of the same charge. techniques adopted and the results of the modelling will be given in a subsequent section of this text.

2.2 Supersaturation and activity

Supersaturation within a system may be generated in a number of different ways. The most common methods are:

(i) cooling or heating the solution, according to whether solubility increases or decreases with increasing temperature.

(ii) solvent removal.

<u>(</u>-

(iii) mixing solutions containing soluble species giving rise to the precipitation of sparingly soluble ones.

(iv) changing the pH.

0

(v) dialyzing the solution.

(vi) precipitation from homogeneous solution.

There are many variants of these methods.

The driving force for nucleation and growth is the difference between the chemical potential of a molecule in the supersaturated and saturated solution, respectively. If C is the actual concentration before any crystallization and C_s the concentration at equilibrium, i.e. the solubility, the driving force per molecule can be written as (27):

 $\Delta \mu = k_B T \ln (C/C_S)$

1

(10)

where $k_{\rm B}$ is the Boltzmann constant and T the kelvin temperature.

Several quantities are used for defining the supersaturation. The most common ones are:

(i) the ratios $\beta = C/C_s$ and $\sigma = (C-C_s)/C_s$

(ii) the difference $C - C_S$.

The two former quantities are dimensionless since they are normalized with respect to solubility. However, their values depend on the units chosen for the concentrations. On the other hand, C-Cs, which represents the amount of solute which may precipitate, is much more dependent on the concentration units (molar fractions, molarities, gram per litre, etc.). In most cases, it is preferable to use β or σ , the subsequent comparison between supersaturations in different systems being simpler. It is noteworthy that the same values of B can be obtained for different values of C-Cs. This occurs, for example, when different temperature or pH ranges are available for crystallization. In some cases, it is $\Delta \mu / k_B T =$ Inß which is taken as the definition of supersaturation. Since in many solutions the supersaturation is small, it is also possible to approximate In β by σ . However, the discrepancy becomes important as soon as the supersaturation exceeds 15%.

In electrolytic solutions where the solute is more or less dissociated, activities are preferred to concentrations for calculating the supersaturation. In order to illustrate this point, consider an imaginary substance RX in an aqueous solution. When dissolution takes place :

RX ---> R²⁺ + X²⁻

(11)

(12)

When equilibrium is achieved, the thermodynamic solubility constant K_S of the substance is:

 $K_{S} = \gamma [R^{2+}]_{eq} \gamma [X^{2-}]_{eq}$

where the symbol γ refers to the activities of the free divalent ions R²⁺ and X²⁻.

Then, the supersaturation must be defined as:

 $\beta = \gamma [R^{2+}] \gamma [X^{2-}]/K_s$

(13)

The ionic product in the numerator relates the actual activities of the ions in solution. For any chemical species, i, activity and concentration are related by:

 $a_{i_{i_{j}}} = \gamma_i C_i$,

Ċ

e F G

(14)

 γ_i is the activity coefficient, which may defined by an appropriate activity coefficient model (e. g. the Pitzer model; the Davies equation; the Debye-Huckel equation , etc.). For example the Debye-Huckel model may be used at low ionic strengths:

$$\log \gamma_i = Az_i^2 |1/2| / (1+Br_i^2 |1/2)$$

(15)

"I" is defined by equation (16).

 $I=1/2 \sum C_i z_i$

(16)

In the Debye-Hückel equation (equation 15). the constants A and B are 0.5317 and 0.3334 at 25° C when r is expressed in Å; C_i , z_i and r_i are the concentrations, charges and radii in solution of the species i under consideration. Values of ri have been tabulated (28) for many different substances. All uncharged species have z=0 and r=0, so that they do not contribute in increasing the ionic strength, I, of the solution, their activity coefficient γ_i being equal to 1 as can be seen in eq. (16). When there are several, or many, dissolved species in solution, the calculation of the activities must be made by an iterative procedure. In the simple example, there is no particular reason why the substance RX must be fully dissociated in solution and why R2+ and X2- do not form any complexes with H⁺ or OH⁻. To simplify the problem, only one soluble complex RX and only one complex with the solvent has been allowed. In that case, the following equilibria HXand mass balances must be taken into account:

 $[OH^{-}][H^{+}] = K_{1c}$ $[HX^{-}]/[H^{+}][X^{2^{-}}] = K_{2c}$ $[RX]/[R^{2^{+}}][X^{2^{-}}] = K_{3c}$

(17a) (17b) (17c)

(18a)

0

Mass balances:

C_R = [R²⁺] + [RX]

 $C_{X} = [X^{2}^{-}] + [RX] + [HX^{-}]$ (18b) $C_{H} = [H^{+}] + [HX^{-}] - [OH^{-}]$ (18c)

eqs. (18) is solved for the the set of When concentrations, the resulting expressions are inserted in the set of eqs. (17) which is solved by iteration, taking as initial values the dissociation constants ${\rm K}_{\rm C}$ and the thermodynamic stability constants Ka. Once the concentrations of the different species are known, it is possible to calculate activities and supersaturation.

In real systems, the solution is rarely pure as in the example given above and consideration must be given to whether the supersaturation changes in the presence of impurities. Two main cases are possible: the impurity only increases the ionic strength, I, of the solution without forming complexes with the solute or it increases I and simultaneously forms soluble complexes with the solute (by trapping R^{2+} or χ^{2-} in the example described above). Since the concentrations and consequently the activities of the free ions decrease, the supersaturation (eq. (13)) must decrease proportionally.

÷

c

ų,

Instead of calculating the variation in supersaturation of a given substance, the variation of the concentrations in a solution containing only two salts will be shown here. The pH will be assumed to be adjusted by the addition of ammonia. When 50 mmol/L of $(NH_4)_2SO_4$ and NaH_2PO_4 are dissolved in water, the pH of the solution is about 4.50. Several ions and complexes form. The dissociation constants of the chemical species involved can be found from (29). **Figure 2** shows the concentration curves of the ions and complexes as a function of pH. Some concentrations change by several orders of magnitude. Others, like that of SO_4^2 -, not given in **Figure 2**, change by only a small amount: $4.7x10^{-2}$ to $6.1x10^{-3}$ for pH=4.5 and 10, respectively. The total ammonia concentration $[N]_t$ which includes all species containing NH₃ or NH₄⁺, changes slowly between pH=4.5 and 8, but the amount required to raise the pH to 10 increases drastically above this value. Despite this fact, the ionic strength of the solution varies significantly only between pH=6 and 8. Indeed, above the latter value, there is no contribution of [NH₃] to I, since NH₃ is an uncharged species. Now, if any solute is added to the solution and if it dissociates and associates with the components of the solution, all equilibria are shifted and the concentrations modified.

This example, which describes a very simple system, perfectly illustrates how difficult it is to adjust the ionic strength and the other paramters such as supersaturation without knowing precisely what happens in the solution.

2.3 Nucleation

c

Đ

When a sufficient degree of supersaturation is attained, nuclei form according to two principal mechanisms. When the nuclei occur in the bulk of the solution, nucleation is termed homogeneous. On the other hand, when nuclei form onto solid substrates, nucleation is called heterogeneous. The nucleation theories for vapor or solution are presented elsewhere in detail (27, 30). For this reason, only some essential points will be emphasized here.

In a solution where the mean energy provided by the supersaturation is constant, there must be some energy fluctuations in order to obtain embryos which then transform into nuclei and crystals. In the first step of the process, the molecules, which randomly diffuse through the solution, meet and coalesce in the form of small aggregates. Hence, the formation of embryos is most often the result of the addition

2.3.2 Structural Assignments; Adducts of 1 with DMAD

Huisman *et. al.* assigned the structures of \underline{X} and \underline{II} based on the ¹H N.M.R. spectra of the adducts and by chemical degradation techniques.

i, Proton N.M.R. Spectra; Adducts X and II



Figure 2.2. Structures of adducts \underline{X} and \underline{II} .

Huisman found that the low field regions of the proton spectra of each adduct show two vinyl proton signals between 5 and 6 ppm. These vinyl resonances consist of a sirglet and a doublet. This precludes the possibility that they are Diels-Alder products which would give a characteristic doublet of doublets in the vinyl region.

Catalytic hydrogenation of the ester activated double bond resulted in loss of the vinyl singlet, indicating that only one vinyl proton existed on the steroidal skeletons. This is consistent with ene addition at C_6 or C_7 . However, addition at C_6 can be excluded because the resulting adducts would contain 3 vinyl protons. This indicates that \underline{X} and \underline{II} are the result of ene addition at C_7 .

Huisman also reported ¹H N.M.R. evidence for the assignments of the sites of unsaturation within the rings. Adduct \underline{X} has distinct singlet resonances for methyl

The corresponding critical activation free energy for nucleation is given by equations 22 and 23.

$$\Delta G^* = (16\pi \Omega^2 \Gamma^3) / 3(k_B T \ln \beta)$$
(22)

$$\Delta G^* = 1/3 \ (4\pi r^{*2} \Gamma) \tag{23}$$

The latter equations show that the energy required to produce a nucleus, stable at the supersaturation β , is one third the energy required to create its surface. At the critical value, r^* , the nucleus is stable (Figure 3). If one molecule is withdrawn from it ($r < r^*$), it dissolves spontaneously. On the other hand, if one molecule is added to it ($r > r^*$), it grows spontaneously, both processes taking place with an energy gain.

Equation (22) shows that the activation energy for nucleation decreases with increasing supersaturation and temperature, and with decreasing interfacial free energy. In other words, it may be expected that a larger nucleation rate will occur at larger β and T, and smaller Γ values. Finally, in eq. (22) the dimensionless quantity $16\pi/3$ is the so-called "shape factor" of the nucleus. For a cubic-shaped nucleus, the shape factor is 32 with V=8r³ and S=24r² in eq. (19).

 \mathcal{L}

Homogeneous nucleation arises mainly in clean solutions when the supersaturation is rather high. In contrast, heterogeneous nucleation occurs most frequently when the supersaturation is low and when the solute molecules have some affinity for solid substrates. which may be а deliberately introduced solid or the walls of the crystallization vessel, the surface of the stirrer or any other solid e. g. dust and particles. With such a nucleation

· ·

 \sim

mechanism, the nucleus develops onto the substrate with which it makes a contact angle α . Figure 4 shows this special situation for a cap-shaped nucleus, a situation which involves three areas and surface free energies (substrate/nucleus, substrate/solution and nucleus/solution). Solution of the equations for the nucleus size and activation energy for nucleation implies that the critical radius for heterogeneous nucleation is the same as that for homogeneous nucleation (eq. (21)). However, since the nucleus develops onto the substrate, the sphere is incomplete and less molecules are required to form it (Figure 4). On the other hand, the critical activation energy for heterogeneous nucleation is now the product of the activation energy for homogeneous nucleation and a term depending on the value of α . This is shown in equation 24.

 $\Delta G^{*}_{het} = \Delta G^{*} (1/2 - 3/4\cos\alpha + 1/4\cos^{3}\alpha)$ (24)

The influence of α is easy to demonstrate, using three particular values. For $\alpha = 180^{\circ}$, the term in parentheses is unity, and $\Delta G^*_{het} = \Delta G^*$. The nucleus has no affinity for the substrate. For $\alpha = 90^{\circ}$, $\Delta G^*_{het} = \Delta G^*/2$ and for $\alpha \Rightarrow 0$, $\Delta G^*_{het} \Rightarrow 0$. The smaller α , the smaller the energy required for forming the nucleus. Thus, the substrate catalyzes the nucleation and the nucleus may form at very low supersaturation. In some cases, the nuclei never form in the bulk of the solution but always on a surface (e.g. the walls of a crystallizer or on a piece of a crushed solid), especially when the surface exhibits a certain surface texture or is activated, perhaps by grinding as in a mill.

There are also some special cases of heterogeneous nucleation where the nuclei which transform later into crystals are more or less oriented on the substrate. There may be a textural orientation: the nuclei all have the same contact

المرير

-

\$

plane with respect to the substrate but are not oriented with respect to each other. In other cases there is also an azimuthal orientation which generates a perfect orientation of all nuclei: i. e. there is an epitaxial relationship between deposit and substrate.

2.4 Crystal Growth.

0

C

...

When a nucleus develops and transforms into a crystal, it exhibits different faces, the growth mechanisms and growth rates of which depend not only on external factors (such as supersaturation, impurities, etc.), but also on internal factors (such as structure, bonds and defects). Therefore, before discussing the growth of crystals, it is important to first consider the influence of the crystal structure on the growth mechanisms.

In order to carry out this task the Periodic Bond Chain theory (PBC) (31) is summarized here. This theory is based on the assumption that growth is the result of the consecutive formation of strong bonds between growth units. A PBC is an uninterrupted chain of strong bonds which repeat periodically through the crystal. For complicated structures there are three types of PBC, the complete PBC being the one that has the same composition as the crystal and no electrostatic dipole moment perpendicular to the direction along which it runs. According to this concept, three types of faces may be found in a crystal (**Figure 5**):

-**F** faces (flat): They have PBCs in at least two different directions in a slice of thickness d_{hkl} (interplanar distance).

- S faces (stepped): They contain only one PBC in the slice d_{hkl} .

- K faces (kinked): They contain no PBC in the slice dhkl.

Since K faces contain only kinks, i. e., growth sites, they grow by direct incorporation of atoms or molecules. Since F

faces are flat, the number of kinks is very small in contrast with the K faces. Such F faces grow either by a twodimensional nucleation mechanism or by a spiral-growth mechanism. The layers spread parallel to the crystal face. Finally, the S faces grow by a one-dimensional nucleation mechanism. Accordingly, one may predict that the growth rate of the F faces should be much smaller than the growth rate of the K faces. The S faces are intermediate between these two limiting cases.

Since it is only necessary to know the relative values of the bond energies for finding the PBCs and classifying the faces, it should be possible to determine the relative growth This was shown (32) by introducing the rates of the faces. concept of reduced growth rate. This is an expression of the growth rate where all factors which are independent of the crystal face are not considered. In short, the growth rate of any face is supposed to be proportional to the attachment energy of a growth unit deposited on a terrace of the face Implicitly, it is understood that the under consideration. higher this energy , the greater the relaxation time for desorption of the growth unit, and consequently the larger the rate of growth of the face.

2.4 (i) Growth by two-dimensional nucleation.

 \mathcal{L}

6

In the case of perfect crystals, or when there are no a crystal face, growth takes place by twodefects in create а two-In order to dimensional nucleation (33). molecules, or more adsorbed the dimensional nucleus. generally the growth units, must diffuse to the face and cluster. Once the nucleus has exceeded a critical size it becomes stable and exhibits some kink positions where the growth units can then be more readily incorporated. Such a situation is depicted in the upper part of Figure 5. In further

steps, the two-dimensional nucleus spreads across the surface. When a complete layer has formed, the crystal has grown by one monomolecular layer. Two models are likely for such a mechanism. In the mononuclear model there is only one nucleus which spreads across the surface at the same time. It is supposed that the whole crystal face is covered before the next nucleus forms. In such a case, the growth rate, R, of the face is given by equation (25). R = J₂dS (25)

 J_2 is the two dimensional nucleation rate, d the height of the layer, and S the area of the face.

In the polynuclear mechanism (illustrated in Figure 6) several nuclei spread on the face at the same time. Each nucleus expands until it encounters another nucleus or the edges of the faces.

Equations (25-27), describing the growth models by two dimensional nucleation, are somewhat different according to the theory from which they are derived. For the mononuclear mechanism, for instance, the rate of growth is given by equation 26.

 $R = k\beta^{1/2} \exp(-\Delta G/k_{B}T)$ (26)

In the case of the polynuclear mechanism, the rate of growth is given by either equation 27 or 28.

R	=	kB1/6[exp(B)-1]]2/3 ex	p(-∆G/3k _B T)	(27)
R	=	kB1/3(B-1)2/3	Inß1/2	exp(-∆G/k _B T)	(28)

where k is a kinetic constant depending on temperature and ΔG is the activation free energy for creating the two dimensional

nucleus. If the nucleus is a square, then the activation free energy is given by equation 23.

 $\Delta G = 4\lambda^2/k_BT \ln \beta$

(29)

where λ is the edge free energy (per molecule) of the nucleus.

Growth by a two-dimensional nucleation mechanism is rather rare. Moreover, when it occurs, it is often difficult to control and adjust the growth rate at a given value. As in the case of three-dimensional nucleation, there is a critical value of the supersaturation, typically 30% to 50% below which there is no growth at all and above which growth becomes very rapid.

2.4 (ii) Growth by a spiral growth mechanism

When a screw dislocation emerges on a crystal face, it provides a step or a sequence of steps which can spread over the surface. Since the steps are always present, adsorbed solute molecules are more easily trapped than in the previous case. Growth is much more regular. The steps expand by rotating around the emergence point of the dislocation and when a step reaches the face edges, the crystal thickness has increased by one monolayer. Actually, the height of the step is often greater than **d**, the thickness of a monolayer, especially in impure solutions where step bunching is often observed.

The spiral growth mechanism was first developed in the so-called Burton, Cabrera and Frank (BCF) theory (34) and later generalized and adapted to solution growth (35-37). Some relevant equations have been presented in a review of crystal growth from non-aqueous solutions (38), the theories being fully described in (39), with special attention to diffusion

problems (40). Here only some important points will be described.

Because the steps of the growth spirals are equidistant and move with a lateral velocity v (Figure 7), the growth rate of the face is given by equation 30.

$$R = vd/y \tag{30}$$

The distance, y, between the steps is strongly dependent on supersaturation. This dependence is shown by equation 31.

$$y = f\lambda a/k_BT \ln\beta$$
 (31)

where a is the length of a growth unit and f the dimensionless shape factor of the spiral (f=9 for a circular spiral). The expression of v is much more cumbersome than that of y.

The most general equation for R is of the form shown in equation 32.

$$R = N_0 \Lambda D_V \sigma \times \{\Lambda + \delta + \Lambda \Lambda_S \ y/x_S^2 + \Lambda[y/2x_S \ \text{coth}(y/2x_S) \ -1]\}^{-1}$$
(32)

where D_V is the coefficient for volume diffusion, λ the length for entering the crystal surface from the solution, and λ_S the length for exchanging growth units between step and surface. Accordingly, the four terms in the denominator are lengths. They represent a kind of impedance for the adsorption reaction, the impedance in the unstirred layer of thickness δ , the impedance for entering the steps, and finally the impedance for surface diffusion (x_S being the mean free path of the adsorbed molecules). It is impossible to solve such an equation and only the limiting cases can be considered. As an example, consider the normal cases $\Lambda * x_S$, since the mean free path of surface diffusion is probably small in solution. We may also imagine that $\Lambda * \delta$ since the thickness of the boundary layer in supersaturated solutions is rather limited. Finally, if $\Lambda_S * x_S$, then eq. (32) reduces to relatively simple expressions. If the supersaturation is small, $y * x_S$, and the rate of growth is given by equation 33.

$$R = \frac{2 n_{so} D_s \Omega K_B T \sigma^2}{X_s f \lambda a}$$

 n_{s0} is the number of adsorbed growth units, per unit area, at crystal-solution equilibrium, and D_s is the surface coefficient. At high supersaturation, $y \ll x_s$ and the rate of growth is now given by equation 34.

(34)

(33)

$$R = \frac{n_{so} D_s \Omega \sigma}{x_s^2}$$

These two equations are often oversimplified and reduced to $R = b \sigma^2$ or $R = b \sigma$. The kinetic coefficients b depend on temperature. From a plot of ln b versus 1/T it is possible to estimate the growth enthalpy. It is sometimes possible to rule out some growth mechanisms by comparison of the experimental values with those associated with the different mechanisms, when it is possible to estimate the latter enthalpies with the required accuracy.

Finally, it is noteworthy that eq. (32) contains N_0 , the solubility, a parameter included in n_{s0} in eqs. (33) and (34). Here, it is also found that, all other things being equal (driving force included), the growth rate of a crystal is much larger in solutions where the solubility is high. For example, is about 80 octacosane, which times more soluble than hexatriacontane, grows about 80 times faster (41).

2.4 (iii) Growth in the presence of impurities

When growth takes place in the presence of impurities, the growth rates of the crystal can be greatly affected. More precisely, each face is affected in a specific way according to the affinity of the impurity for the face. Several parameters in the growth rate equations are modified by impurity adsorption (39) according to whether adsorption takes place in the kinks, the steps or on the flat surfaces between the steps. The corresponding adsorption models have been reviewed and discussed several times (42, 43). Here only the general trends are described.

At least theoretically, impurity adsorption eshould increase the growth rate of a face since adsorption decreases the edge free energy, λ (eq. (31)). But, as in the case of threedimensional nucleation, the kinetic factor is affected by the impurity to a greater degree than the thermodynamic factor. It is sufficient to block a few kinks in order to slow down the growth rate by several orders of magnitude. Impurities or additives may be active at very low concentration and the general trend is that their efficiency increases with increasing concentration. In general, when adsorption is reversible and desorption rapid, the shape of the growth rate curve is not appreciably modified from that obtained in a pure solution. The shifted curves toward are higher

 \mathcal{L}^{\dagger}

supersaturations, but remain linear, quadratic or exponential as a function of supersaturation.

2.5 Perfection of Crystals.

Ĥ

ĊX.

In most systems, especially in closed systems, there is a when supersaturation decrease of the continuous The term phase is used to designate crystallization occurs. several types of solids. When the phases have exactly the same chemical composition but different crystal structures they are/ \gtrsim called polymorphs. From mineralogical and crystallographic or polymorphic polymorph the term of view points modification should be employed only in this case. Graphite and diamonds are probably the most famous polymorphs since both are built up by carbon atoms and only carbon atoms. In some cases, the crystal composition differs only by the number of solvent molecules present. Solvates are phases where the ratio of solute over solvent molecules is a constant. Hydrates are the most common solvates. In some cases, especially when an solvent number of the precipitates, phase amorphous molecules in the precipitate is not clearly defined and changes when the crystallinity increases with time.

1:

In solution, when several phases coexist, the only stable phase is the one which has the lowest solubility. However, according to Ostwald's rule of stages (44), it is rarely the most stable phase which nucleates first. On the contrary, if a solution is supersaturated with respect to two phases at the same time, it is often the phase of highest solubility, i.e the less supersaturated one, which crystallizes first. When growth proceeds, the solute concentration decreases until it reaches the solubility curve of the crystallized phase. At this point the solution is supersaturated only with respect to the phase of lowest solubility. If no crystals of this latter phase form, then the first precipitated phase remains in a metastable state. On the other hand, when a crystal of the new phase forms, the solute concentration decreases once more and the first phase becomes unstable. It dissolves more or less rapidly, then generates solute molecules contributing to the growth of the stable phase. The transformation kinetics of these so-called solution-mediated phase transformations have been discussed in a recent paper (45). In some special cases, there are epitactic relationships between the new stable phase and the old metastable phase onto which it grows (46).

Another consequence of the decrease of supersaturation in a closed system is Ostwald ripening. In contrast with phase transitions. it occurs between crystals of the same composition and structure, i.e. crystals of the same phase. As was pointed out in the section devoted to nucleation, a nucleus-a crystal here-is stable only if it has a critical size which depends on the supersaturation of the solution. In a system where there are several or many crystals, these crystals have different sizes according to the time at which they formed and the velocity at which they grew. Consequently, only one class of crystals obeys eq. (12), with $r=r^*$ for the mean residual supersaturation β . Replacing the volume Ω by the ratio m/p (molecular weight over density), equation (12) may be rewritten to give equation 35.

 $ln(C_r/C_s) = 2m\Gamma/k_BTpr$

171

 \overline{U}

Ð

 α

(35)

This is the Gibbs-Thomson-Freundlich equation-where the subscript r indicates that the equality is fulfilled only for crystals of radius r. C_S is therefore the solubility of a large crystal of "infinite" size: a few tens of micrometers on the laboratory scale. If the crystal is not too small, then the solubility is given by equation 36.

This is another way to show that the solubility of a small crystal is larger than the solubility of a large one. If the crystal which has the critical radius r^* is now considered, the difference in solubility between this crystal and any other is given by equation 37.

$$C_{r} - C_{r^{*}} = \frac{2 m_{\gamma} C_{s}}{K_{B} T \rho} \left(\frac{1}{r} - \frac{1}{r^{*}}\right)$$
(37)

A crystal of size $r < r^*$ must dissolve whereas a crystal of size $r > r^*$ must grow, since neither of them is in equilibrium with the solution. According to the theories (47-49), the rate-determining step of Ostwald ripening is often (but not only) volume diffusion, assuming that dissolution and growth kinetics are greater than diffusion kinetics.

Let us consider two crystals of radii r_1 and r in a solution at constant temperature T and bulk concentration C_s . Since they are not of infinite size and since equilibrium must be achieved, the crystals must (slightly) dissolve in order to restore the proper concentrations. At the end of this process they are surrounded by spherical zones of concentration C_{r1} and C_r respectively (**Figure 8**). When the distance X between the crystals is not too large, the two concentration spheres intersect with a cross section of area A. Since there is a concentration difference around the crystals, there is also a concentration gradient. According to Fick's law the mass q of solution transferred per unit time from the smallest to the largest crystal is described by equations 38 and 39.

 $dq/dt = D_V (A/X) (C_{r1}-C_r),$

9

(38)

c

c

$$\frac{dq}{dt} = D_{v} \left(A/X \right) \frac{2 m_{\gamma} C_{s}}{K_{B} T \rho} \left(\frac{1}{r_{1}} - \frac{1}{r} \right)$$
(39)

where D_V is the coefficient for volume diffusion. Since the crystal of radius r has a surface area $4\pi r^2$, upon replacing q by r we finally obtain equation 40.

$$\frac{dr}{dt} = \frac{D_{v} m_{v} C_{s}}{2 \pi \rho^{2} K_{B} T} (A/X) (\frac{1}{r^{2}}) (\frac{1}{r_{1}} - \frac{1}{r})$$
(40)

This equation gives the rate of growth of the crystal of size r.

Actually, in a real system, where there are many crystals, several diffusion lengths and crystal radii must be taken into account and eq. (40) is difficult to solve explicitly. With some important simplications (47,48) and assuming that the critical size r^* corresponds to the average size r^- of the crystals in the system, then the highest possible growth rate of the crystals which ripen is:

$$(\frac{dr}{dt})_{max} = \frac{D_v m_\gamma C_s}{2 K_B T \rho^2 r^2}$$
 (41)

Integration of eq. (41) yields equation 42.

$$\frac{1}{r} - \frac{1}{r_0} = \frac{3 D_v m_\gamma C_s}{4 K_B T \rho^2} (t - t_o)$$

0

(42)

Since r_0 , the crystal radius at time zero, is often negligible, it may be said as an approximation that the crystal radius increases proportional to the cube root of time.

It is noteworthy that, in general, Ostwald ripening is very fast for crystals of radius less than 1 μ m, fast for crystals around 1 μ m, but very slow as soon as the crystal reach about 100 μ m. Here, however, only the case of a true isothermal ripening has been discussed. When temperature fluctuations (49) are applied to the system the ripening kinetics increase drastically, since dissolution and growth rates are accelerated.

The main consequence of Ostwald ripening is the disappearance of most crystals, especially the smallest ones. The number of crystals decreases while the mean size increases. With increasing time, only one crystal should remain in the system. Another consequence of this process is habit modification. During growth, supersaturation is generally large as compared to that which exists when ripening takes place. The growth shape slowly transforms into an equilibrium shape which may be completely different.

5

£.

Figure 2 Variation of the ionic strength I and the ion and complex concentrations in a solution containing 50mmol/L $(NH_4)_2SO_4$ and NaH_2PO_4 . The pH is adjusted by ammonia, $[N]_t$ being the total ammonia $(NH_3 + NH_4^+)$ in the system; calculations based on data from (21) and (22).

Ū

ß

-

С

Ċ

j.

ir,

c

ρ


Ċ,

1

c

O

C 0

°o

Figure 3 Activation free energy for nucleation as a function of the nucleus size. The critical value ΔG^* must be reached for creating a nucleus of critical radius r^* .

- C

:(5)

-

З

÷.

Ċ,

(>

مترسي.

C

v

ູ

41

 ${\boldsymbol{\mu}}$

1

 i^{\pm}



с

3 2

Ç ÷

2----

Ŧſ

1

Ċ,

Figure 4 Cap shaped nucleus of radius r forming on a solid substrate, with which it forms the contact angle α .

ρ

-

5

 \sim

칅

Ľ

¢

c

c

÷.,

Э

c

 $\mathcal{S}^{(p)}$

2

÷

с

0

c

42

11:

¢ _____

Ċ,

Ċ

 \mathbb{C}^{2}

e

,**,** ċ Ģ

q, ...



\$ ÷

;=; ; Ø





<u>)</u>]

Figure 5 Schematic representation of a crystal exhibiting flat (**F**), stepped (**S**) and kinked (**K**) faces. Front face exhibits a polygonized growth spiral, whereas the top face exhibits a two-dimensional nucleus.

o

S

Ċ

-277

Ċ

 \mathbb{C}

32

: ۲

;: °))



C T

. . .

Figure 6 Birth and spread model; several two-dimensional nuclei spread across the crystal face (taken from 39).

5 (Ö

2

<u>آليست</u>

Ð

10

ċ

 \odot

ø

2

0

,`

 \odot

C

e

2

÷

7

τ

æ

e

Э

Ç

d

Ċ

2 0 ≥ 0 .



°

Ę

Figure 7 Profile of a face growing by a spiral growth mechanism.

Č.

Ξ. C

R

2 d Y \$

 $\overline{}$ 0 Ċ

~ Q e C ĕ

C Ç 0 ŵ

C

0 \sim

Figure 8 Schematic representation of the solute transfer from the smallest to the largest crystal during Ostwald ripening. The crystals are separated by the distance X and their concentration spheres interact through the cross-section A.

> . .

> > ç.

5 11

Ŕ

0

z,

775

5

5

r.

.

ſť

 \mathbf{v}^{1}

ð

¢

 \mathcal{O}

С

C

Ŀ

-

 $\boldsymbol{\zeta}_{2}$

c

٦

è \tilde{U} ſ?

-C

0



X

:C'L

Chapter 3. Solubility of sparingly soluble sulfates in H_2SO_4

As indicated in Chapter 1 of this thesis, systems of interest in the development of an overall predictive model for the purpose of describing solution and mineral equilibria in uranium mill leaching tanks and mill waste drainage waters include PbSO₄-H₂SO₄-H₂O and BaSO₄-H₂SO₄-H₂O. A review of the literature of aqueous based electrolyte systems at high ionic strength led to the conclusion that the best method to employ for the purpose of predicting or modelling electrolyte solubilities would include the Pitzer model for calculating the μ_i activity coefficients of ions. The use of this method requires values for the interaction parameters for lead and barium with sulfate ions, and for lead, and barium with hydrogen sulfate ions. Such information is not available in the current literature. Thus, a major objective of this portion of the investigation was the estimate these parameters and their variation with temperature, over the range from 0°C to 60°C. Where the experimental data required for the parameter estimation were judged to be inadequate, the necessary information^a was generated in the laboratory.

3.1 Solubility of PbSO₄ in H_2SO_4 and Na_2SO_4 from 0 to 6m at 60⁰C by ICP/MS analytical methods.

The solubility of PbSO4 in H2SO4 has been determined from 0° C to 55° C by Crockford and Brawley (50, 51) and by Comparison of the values Crockford and Addlestone (52). obtained by these workers at 25°C with the values obtained by Craig and Vinal (53) or Danel and Plichon (54) leads to the conclusion that there are difficulties with the data of This is illustrated in Figure 9. Crockford and coworkers. Reliable data for the PbSO4-H2SO4-H2O solubility reduces to that of Craig and Vinal at 25°C and Danel and Plichon at 20°C. The acceptable data for the solubility of PbSO4 in solutions of H_2SO_4 and Na_2SO_4 are summarized in Table 1. In the modelling it is essential to have data available to 60° C, the temperature at which leaching of the uranium ore is carried out. Consequently, it was decided to accept the literature data at 200C and 250C and to measure the solubility of PbSO4 in both Na₂SO₄ - H₂O and H₂SO₄ - H₂O mixtures at 60^{0} C.

2

c

0

٦

3.1.1 Experimental procedure used for the determination of the equilibrium solubility of PbSO₄ in both Na₂SO₄ - H₂O and H₂SO₄ - H₂O mixtures.

Individual masses of lead sulfate ('Baker Analyzed' Reagent) greater than the expected total solubility were placed in clean, dry, screw-cap polycarbonate centrifuge tubes (previously washed in10% v/v HNO₃ for 24h) and 15mL of sulfuric acid or sodium sulfate of the selected concentration were added. The tubes were capped, with the threads of the tubes being wrapped with Teflon tape, then placed in a thermostat at 70° C. The temperature was measured by a mercury-in-glass thermometer to the nearest 0.1° C. Gentle shaking was provided by means of a stirring motor running at low speed. The temperature was lowered over a period of two

2

1.

davs to 60⁰C. After one week of shaking, a 3-mL aliquot of each solution was decanted into a pre-heated plastic syringe then quickly filtered through a 0.2µm P.T.F.E. filter membrane. The first 10 drops of the filtrate were rejected; then it was delivered into a plastic scintillation vial. Using an Eppendorf pipette, a 100-µL aliquot was removed and delivered into a The tube contained a known mass of 1% centrifuge tube. sulfuric acid or sodium sulfate sufficient to bring the concentrations of Pb into the 0-200ppb range along with 500ppb rhodium as an internal standard. Available data for the solubility of PbSO₄ in H₂SO₄ at 20⁰C (54) enabled calculations to be performed which confirmed that the solutions of PbSOA in 1% sulfuric acid were undersaturated. The tubes were sealed and the total mass was determined. Standards were prepared from an AAS lead standard made up in 1% sulfuric acid or sodium sulfate with 500ppb rhodium as internal standard. The samples and standards were then subjected to Inductively coupled plasma mass spectrometry analysis using an Elan Instruments ICP/MS system.

3.1.2 Modeliing of Solubility equilibria using the Pitzer equations for Activity Coefficients.

)). == `

~

Advances in models of activity coefficients for example, the work of Pitzer and his school have proven invaluable to researchers dealing with species in aqueous systems. The application of these models to systems of geochemical interest has largely been due to the efforts of researchers such as Harvie and Weare (22) and Harvie et al. (23). As previously mentioned, the use of the Pitzer equations to describe solution equilibria in mixed-salt systems of high ionic strength demands data for the interaction parameters of ions. While extensive an database of ion interaction parameters currently is in existence (see for example.

Zemaitis et al. 24), in many cases, such as the $PbSO_4-H_2SO_4-H_2O$ system, the required ion interaction parameters of interest are unavailable. These data must be obtained through the regression analysis of published data based on mineral solubility, isopiestic, activity, osmotic and E.M.F. measurements in single and mixed salt systems.

· .--

2

The binary interaction parameters β_{MSO4}^0 , β^1_{MSO4} β^2_{MSO4} and C^{ϕ} can, in principle, be determined from the properties of a binary solution of MSO₄ measured as a function of the concentration of the MSO₄ (see Section 2.1 Chapter 2). For sparingly soluble compounds, such a measurement is There is, however, a small database of clearly very difficult. common ion solubility measurements in Na2SO4 available for PbSO₄. From this database it is possible to estimate the interaction parameters of Pb^{2+} and SO_4^{2-} . In addition to the present study, there is a collection of solubility data available for $PbSO_4-H_2SO_4-H_2O$ from which $Pb^{2+}-HSO_4^-$ interaction parameters may be estimated to a degree capable of providing an adequate predictive model of the solubility of PbSO4 in sulfuric acid up to 6m-the highest sulfuric acid concentration recommended by Pitzer et al. (58) for the application of their reported parameters for the sulfuric acid-water system.

The regression model used for the analysis of the solubility data had the form shown in equation 43.

 $\ln K^{0} - \ln m \operatorname{Pb} - \ln m \operatorname{SO}_{4} = \ln \gamma_{\operatorname{Pb}} + \ln \gamma_{\operatorname{SO}_{4}}$ (43)

 \cap

The K^0 was treated as a parameter of the model in the regression analysis which was performed. The Pitzer expressions, as formulated by Harvie et al. (23) and as presented in chapter 2 of this document, were substituted for the individual ion activity terms in equation (43). Following the analysis of the data for BaSO₄ in Na₂SO₄ presented by

Monnin et al.(59), it was decided to omit any consideration of the mixing parameters ψ and ϕ . It was felt that these would contribute very little to the calculations.

The temperature dependent expressions for the Pitzer parameters, $\beta^{(0)}$, $\beta^{(1)}$ and C ϕ , for the Na₂SO₄ system given by De Lima and Pitzer (60) and Rogers and Pitzer (61) were used. In addition, the parameterization of the sulfuric acid system as presented by Reardon and Beckie (62) was accepted, including their temperature dependent expressions for the values of β^0_{H-HSO4} , β^1_{H-HSO4} and C ϕ_{H-HSO4} .

The regression analyses were performed using the nonlinear least squares subroutine "GAUSHAUS" (63), adapted for use on an I. B. M. microcomputer. The parameter values for each system were determined by minimizing a weighted least squares fit to the experimental solubility data. Initially, the PbSO₄ - Na₂SO₄ solubility data were analysed in order to estimate the Pb2+-SO₄2- interaction parameters. The resulting values of the Pb2+-SO42- parameters were then used as an initial estimate to carry out the evaluation of the Pb2+-HSO₄⁻ parameters. The HSO₄⁻ equilibrium was allowed for in the computations by estimating the concentrations of HSO4and SO_4^{2-} , computing the activity coefficients. then performing the regression analysis in order to estimate the unknown parameters. The values so obtained were then used to refine the estimates of the concentrations of HSO_4^- and SO_4^{2-} and the process repeated until convergence was attained. Generally, for the sparingly soluble sulfates, four such iterations were required for convergence to the third significant figure in the parameters. In every case the solubility data for PbSO4 in water were included in the regression analysis.

2

.

المرازية التي ال

3.1.3 Modelling of the available literature data for the solubility of PbSO₄ in H_2SO_4 and Na_2SO_4 along with the experimental data obtained in this research.

The results of the determination of the solubility of PbSO₄ in sodium sulfate and sulfuric acid are presented in Tables 2 and 3, together with appropriate statistical indices of precision. Plots of these experimental solubility data are shown in **Figures 10** and **11** respectively.

The results of the modelling of the experimental data obtained in this study are also presented in Figures 10 and 11. The results of the modelling of the remaining literature data for PbSO₄ in sulfuric acid are shown in Figures 12 to 14. The results of the modelling of the literature data for the solubility of PbSO₄ in Na₂SO₄ at various temperatures is to be found in Appendix 1 in the form of plots of the solubility.

Values for the ion interaction parameters of $Pb^{2+}-SO_4^{2-}$ and $Pb^{2+}-HSO_4^{-}$ at the different temperatures are presented in Tables 4 and 5 respectively, along with estimated 95% confidence intervals (on the basis of a linear approximation to the model in the neighbourhood of the estimate) for each parameter.

3.2 Solubility of BaSO₄ in H₂SO₄ and Na₂SO₄ from 0 to 6m at 25° C and 60° C.

There are two sets of solubility measurements reported in the literature for BaSO₄ in Na₂SO₄ solutions (63, 64). Both are in the form of a graph. These data were digitized using a McMaster developed FORTH program and a Hewlett-Packard plotter (65). The digitized data are presented in Table 6. There is a very small collection of solubility data available in the literature for BaSO₄-H₂SO₄-H₂O (von Weimarn, 66 ; Trenner and Taylor, 67); the concentration of sulfuric acid used in all of these studies, however, far exceeded 6m. There appears to be no literature data available for the solubility of $BaSO_4$ in H_2SO_4 at elevated temperatures.

It became evident from a consideration of literature values for the solubility of sparingly soluble sulfates in sulfuric acid that the only analytical methods likely to succeed in providing reliable data for the solubility of barium sulfate in sulfuric acid solutions to 6m in concentration would be either the radio-tracer method or ICP/MS. After careful consideration of the properties of readily available radio-isotopes it was decided to use barium-133 as a radio-tracer for the determination of the solubility of $BaSO_4$ in H_2SO_4 . The properties and production of this isotope are described in Brown and Firestone (68).

3.2.1 Experimental procedure.

.

3.2.1.i Preparation of mixed BaSO₄/133-BaSO₄ crystals

Barium sulfate was labelled with 133-Ba radiotracer by 18.537MBg of 133-Ba (NEN Products/DuPont) adding to 220.5mg±0.1mg of barium nitrate (Baker Analyzed Reagent) dissolved in 100mL of distilled, demineralized water filtered through 0.45µm membrane filters. The BaSO₄ was then prepared by the method of precipitation from homogeneous solution using the slow hydrolysis of sulfamic acid as the source of sulfate ions (Gordon et al., 69). The precipitate was allowed to ripen for 18h in the mother liquor and was then Non-radioactive specimens of the washed by decantation. fresh and aged precipitate prepared at the same time using this technique were examined using a scanning electron microscope in order to ensure that no very small particles remained in solution. The electron microphotographs are presented in Figure 15.

3.2.1.ii Solubility measurements

 \sim

Aliquots of the labelled BaSO₄ in the form of a slurry were pipetted into clean polypropylene snap-top tubes. The tubes and contents were centrifuged, the excess supernatant solution decanted and pairs of the tubes were then placed in the clips of a Labquake shaker. Finally 3-mL of the appropriate the tube. The distilled. into solvent were pipetted demineralized water used for the solubility determination in the absence of sulfuric acid was deaerated by passing nitrogen The solutions were allowed to through it from a cylinder. shake gently for 5 months at 250 C ±10 C before separation and counting was performed. The solution was separated from the precipitate before counting by centrifugation in an Eppendorf high-speed centrifuge, followed by filtration through 0.2µm Teflon filter media prewetted with methanol. The first 10 Counting was carried out drops of the filtrate being rejected. using a well-type Na(I)/TI scintillation counter with a Baird-Atomic amplifier-analyzer and a Baird-Atomic Scaler type 955-150. The system was tuned to the 133-Ba photo-peak at 355.9keV using an Advance Instruments OS250 dual-trace and the both the photo-peak to monitor oscilloscope As the half-life of 133-Ba is 10.543a instrument window. (68) a careful counting programme was designed and followed, with counting periods of 2 hours for each of the samples. Blank counts were performed on 2-mL samples of the solvents. These blanks were counted between samples. The total counts collected in all cases was greater than 100 000. The longterm stability of the system was monitored by the counting of a sealed tube containing a 2-mL sample of 133-Ba of fixed No significant drift in the performance of the concentration. system was detected.

Once the solutions at 25^{0} C had been filtered the solvent was replenished and the tubes placed in a thermostat at 70^{0} C

 $\pm 0.2^{0}$ C. The temperature was then reduced to 60^{0} C $\pm 0.2^{0}$ C over a period of 2 days and the solutions were allowed to reach equilibrium "from above ". During the separation procedure at 60^{0} C the syringe and filter holder, wrapped in aluminium foil, were allowed to attain the temperature of the thermostat before the filtration was carried out. The centifugation step was omitted. This cycle of operations was repeated 3 times in all, with pairs of replicate experiments being performed at both temperatures.

The sulfate concentration of the dilute solutions of sulfuric acid was verified by use of high-performance ion chromatography (H. P. I. C.) using sodium sulfate standard solutions for calibration.

specific The activity of the labelled solid was determined by filtering off the BaSO₄ from a sample using a Teflon pre-washed filter weighed on а Mettler M55 Microgramatic balance. The BaSO₄ was dissolved from the filter into alkaline E. D. T. A. with the use of an ultrasonic cleaner. The mass of the BaSO4 was determined by difference. A series of quantitative dilutions were made in a 5-mL volumetric flask, using alkaline E. D. T. A., until the count rate of a 2-mL aliquot was measurable with acceptable precision. A 2-mL blank of alkaline E. D. T. A. was also counted. This determination was performed in triplicate. The results of the experimental determination of the solubility of BaSO4 in H2SO4-H2O solutions at 298K are presented in Table 7 and those at 333K are found in Table 8. In each case 95% confidence intervals about the mean results are presented where replicate measurements are available. These data and the results of modelling these data are presented in the form graphs in Figures 16 and 17. of The Pitzer parameters estimated for the Ba2+-SO42- interactions are tabulated in

 \mathcal{E}

w

Table 9 for the two temperatures, while the parameters for $Ba^{2+}-HSO_4^{-}$ are summarized in Table 10.

3.2.2 Discussion arising from the experimental procedures used for determining the solubility of PbSO₄ and BaSO₄ in sulfate media.

The procedures followed for determining the solubility of $PbSO_4$ and $BaSO_4$ in sulfuric acid and sodium sulfate raise a number of questions which need to be discussed before leaving this phase of the research. These will be considered under the following headings: 3.2.2.i, the effect of labelling on the solubility of the barium sulfate; 3.2.2.ii, the effect of particle size on the solubility of substances; 3.2.2.iii, the nature of the filters used for the radio-labelled material.

3.2.2.i The effect of labelling on the solubility of the barium sulfate.

A series of papers (70) has been published in which it is contended that radioactive isotopes, incorporated at normal tracer levels into various systems involving measurement of rates of solution, exchange rates, solubility and sublimation cause changes in the behaviour being studied. A review of this work has been published (71). In contrast, evidence on the solubility of CaSO₄ labelled with ⁴⁵Ca and BaSO₄ labelled with 35S contradicts the findings in (70). The work of Bovington (72) on 35S labelled PbSO4 and BaSO4 suggested that in the case of BaSO₄ a 10% increase of solubility over accepted values for inactive material occurred. The effect was found to be independent of the specific activity. The enhancement of the solubility was attributed to radiation damage. In a careful investigation, Berdonosov (73) found that in the case of cerium oxalate-if allowance for adsorption and colloid formation was made-the radiochemical method of

0

02 -

determining solubility gave results which agreed with those obtained using other methods. He found that the specific activity of the samples used did not have an effect on the solubility values determined. In the paper due to Bovington (72), the enhanced solubility of radioactive $BaSO_{\Delta}$ is ascribed to the production of minute surface crystallites which probably arise as a result of self-irradiation damage in the crystals. This damage is produced by the β - particles of 35S, a proportion of which have energy in excess of the 0.1 MeV required to directly transfer sufficient energy to an atomic nucleus to result in an atomic displacement (74). The situation with respect to enhancement of solubility due to radio-labelling would thus appear to be open to debate. If such an effect occurs it appears to be: (i) mainly exhibited by very sparingly soluble substances, and (ii) due to radiation damage which is probably caused by displacement of atoms. The most effective particles in bringing about such displacements are "heavy particles" (e. g. protons, α -particles or fast neutrons). Direct displacement is much less likely in the case of irradiation by X-rays (74).

In conclusion, the study carried out in this research using radio-tracer labelling utilized a relatively low level of (approximately 2.39 mCi/g specific activity BaSO₄ as compared to the 30mCi/g used by Bovington) with a much higher level of efficiency for the detector system. And an Xray emitter (133-Ba) which appears unlikely to cause atomic The inclusion of pure water as a displacements was used. solvent was intended to act as a "quality control" on the The mean value determination of the solubility. of the solubility of BaSO₄ in pure water at 25⁰C determined in this study, $9.88 \times 10^{-6} \pm 0.9 \times 10^{-6}$ mol/kg, compares favourably with that given by Nancollas and Purdie, 1.040x10-5 M (75).

2

ŝ

3.2.2.ii The effect of particle size on the solubility of substances.

Many reported data for the solubility of sparingly soluble substances exhibit a wide variability in results at any particular temperature. For example the solubility of celestite in both water and solutions of NaCl-H₂O (76) exhibits such variation. The variability has been attributed to two major factors. The first is the well-documented effect of particle size on solubility. This has been extensively studied by Enustun and Turkevich (77) for the case of celestite. These researchers found, in a series of experiments using material of varying particle size distributions, that the smallest-sized particles present appeared to control the solubility. Thev reported the following expression relating the observed solubility enhancement to the minimum particle size present.

 $\log a / a_0 = 1.6/x$

(44)

where a is the observed activity of the solid phase; a_0 is the activity of the pure solid in macrocrystalline form; and x is the minimum particle size in nanometers. Use of this equation, in conjunction with a knowledge of the analytical uncertainty associated with the technique being used for the measurement of the solubility, enables an estimate to be made of the detectable enhancement in the solubility which would occur if a material were present of a given particle size. Typical particle sizes likely to give rise to significant enhancement of solubility would be approximately 0.4µm or less in diameter. The scanning electron microphotographs which are presented in Figure 15 give no indication of the presence of individual particles of this magnitude for the barium sulfate grown using the technique of precipitation from homogeneous solution (69). In addition, the mixing process for BaSO₄ with the sulfuric acid solutions was deliberately carried out in such a manner as to avoid crushing or breaking the crystals - processes which appear likely to produce fragments of a very small size.

The second factor which has been postulated to account for the variability in the published data for celestite relates to the susceptibility of this material to surface poisoning. A detailed study of this phenomenon was carried out by Campbell and Nancollas (78). They identified the source of this surface poisoning effect as the de-ionized water used in the When double-distilled water was used, all experiments. effects on dissolution and precipitation were inhibitory For this reason, all water used in the experiments removed. carried out in this research, including that used to prepare the solutions of Na₂SO₄ or H₂SO₄ was distilled, demineralized, filtered water of the highest obtainable quality with a measured conductance of less than 1.8 µS/cm. In the case of the solubility measurements in pure water, the water was deaerated by use of dry nitrogen from a cylinder in order to avoid the presence of any carbonate formation due to dissolved CO2. The polypropylene tubes used for the solubility determinations were all washed with H.P.L.C. grade methanol before use in order to remove any manufacturing residues likely to be present.

3.2.2.iii The nature of the filters used for the radiolabelled material.

The effect of adsorption and colloid formation on the measured values of the solubility of sparingly soluble substances has been discussed in the literature (79). In the case of the determination of the solubility of $RaSO_4$, for example, ignoring the adsorptive losses to the filter led to very low results (80, 81). It was found during the research described in this thesis that losses of activity of radio-labelled solutions to filters can be substantial. For example,

adsorption on cellulose acetate filters caused the loss of virtually all the activity of even highly active solutions of 133-Ba in water. Teflon filter media have been found to cause no loss of activity due to adsorption. Data to support these statements are available and are given in **Appendix I**. Consequently, during the course of this research all filtration was carried out using $0.2\mu m$ Teflon filter media pre-wetted with H.P.L.C. grade methanol.

The possible presence of extremely small particles was investigated by filtering duplicate specimens of unlabelled BaSO₄, gently shaken for 2 weeks in 0.1M and 1.0M H₂SO₄ solutions at 250C, through 0.1µm polycarbonate and 0.2µm Teflon membrane filter media, then subjecting these to analysis by ICP/MS in order to investigate the possibility of very small particles of BaSO4 passing through the pores of the filters. No statistically significant difference in the concentration of the solutions filtered through these different media was found. It was concluded that no very small particles were present in the filtered solutions that could lead to artificially high values for the solubility. This confirms the information with respect to the particle sizes given by the electron microphotographs in Figure 15.

3.3 Results of modelling the available literature data for the solubility of $RaSO_4$ in H_2SO_4 at 298K and the prediction of the solubility at 333K.

There is a single set of data available on the solubility of RaSO₄ in sulfuric acid (Lind et al. 80). The studies of Nikitin and Tolmatscheff (81) provided data on the solubility of RaSO₄ in aqueous solutions at 20° C. They measured the solubility at 20° C in water (5 determinations) and in Na₂SO₄ solutions (3 determinations). As noted in Seidel (59) the solubility data for water given by Lind et al. is 1870 times too

ġ

 ∇

low compared to that given by Nikitin. In their paper, Lind et al. state that the filters used in their investigations were 1 inch of closely packed cotton, or asbestos fibre for solutions containing more than 45% sulfuric acid. It would appear likely that the data obtained from the studies in water-and perhaps in low concentrations of sulfuric acid as solvent-are too low. This is almost certainly due to adsorption losses to the filters. It should also be noted here that the solubility data for RaSO₄ in H₂SO₄ given in Seidel is quoted as "g/25cc" but in the original paper of Lind et al. the data are in "g/cc". It would appear that there is an error in the data reported by Seidel.

The experimental data selected from those reported by Nikitin and Lind and the results of our modelling of them are shown in Figure 18. The parameters which appear to give a reasonable fit to the data are presented in Tables 11 and 12. Based on these parameters and the estimated temperature dependence of Pitzer parameters for 2:2 sulfates tabulated in (24) we estimated values for the parameters for RaSO4 at 35°C, 45°C and 60°C. The log Ksp in each case was calculated from the equation given by Langmuir and Reise (17). The values of these estimates are also presented in Tables 11 and without confidence intervals, while Figures 19, 20 and 12. 21 show the predicted solubility of RaSO₄ in H₂SO₄ at 35^{0} C, The paper of Lind et al. contains two 45⁰C and 60⁰C. measurements of the solubility of RaSO4 in sulfuric acid at 35°C and one measurement of the solubility at 45°C. These data permit a limited comparison to be made of the predicted solubility at 35⁰C, 45⁰C and 60⁰C with experimental data. As shown in Figure 19 the agreement between observed and solubility appears reasonable for the higher predicted concentration of sulfuric acid at 35⁰C. The datum at low significantly different from concentration of sulfuric acid is the predicted value. As the experimental value appears to be

.1

 \cdot

0

 \approx

Ð

low with respect to the predicted value, a plausible explanation of the difference would be adsorption losses to the filters. Of course with such a limited database, this explanation is purely speculative. At 45^{0} C the single datum agrees well with the predicted value, as seen in Figure 20. The agreement obtained at 35^{0} C and 45^{0} C suggests that the predicted solubility at 60^{0} C, shown in Figure 21, is probably reasonable.

Conclusion

U

17

The objectives originally defined for this phase of the research would appear to have been achieved: the solubility of PbSO₄ in Na₂SO₄ and H₂SO₄ at 60⁰C has been determined; the solubility of BaSO₄ in H₂SO₄ at 25⁰C and 60⁰C has been determined. These data have been modelled using the Pitzer formalism and parameters derived from them. Parameters for Ra²⁺⁻SO₄²⁻ and Ra²⁺⁻HSO₄⁻ interactions have been estimated.

For the PbSO₄ solubility the derived Pitzer parameters appear to give a good fit to the solubility of PbSO4 in both Na2SO4 and H2SO4. Confirmatory tests carried out using the modelling program PHRQPITZ give good agreement with the experimental data for Na2SO4 at 250C using our derived parameters, even though, as pointed out by Prof. Reardon (private communication) the value for β^2 is greater in magnitude than those found for other 2:2 sulfates. The position for the BaSO₄ is not quite so clear. The data provided by Leiser (63) and by Felmy et al. (64) require that the interaction parameters estimated for the $Ba^{2+}-SO_{4}^{2-}$ interactions be large and negative. Such parameters have, in fact, been reported by Monnin et al. (59) as a result of the regression analysis of the BaSO4-Na2SO4 data of Leiser and of the SrSO₄-Na₂SO₄ data of the same author. However a comparison of these $Ba^{2+}-SO_4^{2-}$ parameters with those available in the literature for other 2:2 sulfates indicates that such values are clearly anomalous. This is demonstrated in Table 13, kindly provided by Professor Reardon (private communication). Regression analysis of the data obtained in sulfuric acid at 25⁰C in this research appears to yield parameters similar to those of other 2:2 sulfates, if regressed without use of the Ba²⁺⁻SO₄²⁻ parameters derived from solubility data in Na2SO4. This, of course, creates the difficulty of a lack of data, generated external to the present investigation, for purposes of comparison,. It has been pointed out (Monnin, 58) that the binary parameters for slightly He points out that soluble salts are of limited influence. setting the B_{BaSO4} parameters to zero is a very satisfactory approximation.

÷c.

υ

TABLE 1Data available for the solubility of PbSO4 insolutions of H_2SO_4 and $Na_2SO_4^1$

SYSTEM	<u>TEMPERATURE (K)</u>	REFERENCE
H2SO4 -H2O	273	Craig & Vinal (53)
H2SO4 -H2O	293	Danel & Plichon (54)
H2SO4 -H2O	298	Craig & Vinal (53)
H2SO4 -H2O	298	Kolthoff et al (55)
H2SO4 -H2O	333	This study
Na ₂ SO ₄ -H ₂ O	288	Huybrechts et al (56)
Na ₂ SO ₄ -H ₂ O	303	Huybrechts et al (56)
Na ₂ SO ₄ -H ₂ O	298	Kolthoff et al (55)
Na ₂ SO ₄ -H ₂ O	333	This study

¹In addition, Seidel (57) lists a number of other sources containing a small amount of data of variable quality. These were not used in this study.

 $\langle \rangle$

 $_{\rm e} \odot$

e v

יי ב $\overline{\mathbb{C}}$

Ċ,

[Na2SO4] mol/kg	[Pb] mol/kg	95%Confidence
		Interval
	(3 replicates)	
1.00 x 10 ⁻⁴	1.06 x 10 ⁻⁴	±1.2 x 10 ⁻⁵
1.00 x 10 ⁻³	2.72 x 10 ⁻⁵	± 2.7 x 10 ⁻⁶
1.00 x 10 ⁻²	2.82 x 10 ⁻⁵	\pm 9.6 x 10 ⁻⁷
2.00 x 10 ⁻²	3.02 x 10 ⁻⁵	
4.00 x 10-2	3.05 x 10 ⁻⁵	
8.00 x 10 ⁻²	3.06 x 10 ⁻⁵	
1.00 x 10 ⁻¹	3.12 x 10 ⁻⁵	± 2.8 x 10 ⁻⁶
2.00 x 10 ⁻¹	3.32 x 10 ⁻⁵	
3.50 x 10 ⁻¹	4.47 x 10 ⁻⁵	
5.00 x 10 ⁻¹	5.54 x 10 ⁻⁵	
1.00	9.05 x 10 ⁻⁵	± 1.2 x 10 ⁻⁵
1.50	1.14 x 10 ⁻⁴	

Table 2 Measured solubilities of lead sulfate in sodium sulfate solutions at $60^{\circ}C$

Note: Replicate experiments were only carried out at the solution concentrations shown . The values in Table2 represent mean values for these cases.

Ċ

c

1Ş

0

÷

4

÷

Table 3 Measured solubilities of lead sulfate in sulfuric acid solutions at $60^{\circ}C$

[H2SO4] mol/kg	[Pb] mol/kg	95% Confidence Interval (3 replicates)
0 (water) 1.00 $\times 10^{-4}$ 1.00 $\times 10^{-3}$ 1.00 $\times 10^{-2}$ 2.00 $\times 10^{-2}$ 4.00 $\times 10^{-2}$ 5.00 $\times 10^{-2}$ 7.90 $\times 10^{-2}$ 4.47 $\times 10^{-1}$ 8.90 $\times 10^{-1}$ 1.84 2.89 3.95 6.19	1.42 X 10^{-4} 1.23 x 10^{-4} 3.10 x 10^{-5} 2.41 x 10^{-5} 2.27 x 10^{-5} 2.76 x 10^{-5} 2.74 x 10^{-5} 2.93 x 10^{-5} 3.64 x 10^{-5} 3.86 x 10^{-5} 3.86 x 10^{-5} 3.10 x 10^{-5} 3.10 x 10^{-5} 3.22 x 10^{-5} 3.22 x 10^{-5}	$\pm 5 \times 10^{-6}$ $\pm 7 \times 10^{-6}$ $\pm 4 \times 10^{-7}$

Note: Replicate experiments were only carried out at the solution concentrations shown. The values in Table 3 represent mean values for these cases. Fig. 10(a) shows all the experimental points.

ټ

S.

c

ð

12

÷,

e

c

୍ଟ : ୧

2

÷

Table 4 Ion interaction parameters	s for	Pb²+-SO₄²-
------------------------------------	-------	------------

т∘к	β°	β ¹	β ²	95% Conf Interval o β ⁰	idence n: β ¹	β ²
273	0.0377	3806	-97	±0.088	±0.55	±7
293	0.3424	1.608	-122	±0.346	±2.26	±24
298	0.1118	4.477	-119	±0.145	±0.84	±7
333	2.009	5.1E-05	-170	±2.00	±16	±56

Note: The fitting of the β^0 and β^1 parameters led to considerable apparent temperature variation. Following a review of the initial parameter set by Prof. C. Monnin, and discussion with Prof. E. J. Reardon the decision was made to constrain these parameters. This practice is common, as experience has shown that the values of these parameters do <u>not</u> exhibit a large temperature dependency over such small temperature intervals. This was also done for the Pb²⁺-HSO₄⁻ parameters. The values selected were those found from the regression analysis of the 25⁰C data of Craig and Vinal.

T⁰ K	βο	β1	Value of pKsp
273	0.1886 ± 0.05	1.721 ± 0.5	7.975 ± 0.02
293	0.1805 ± 0.09	2.105 ± 1	7.734 ± 0.04
298	0.2568 ± 0.03	1.617 ± 0.3	7.754 ± 0.01
333	0.2536 ± 0.2	2.783 ± 2	7.768 ± 0.04

Table 5
Ion interaction parameters for Pb²⁺⁻HSO₄

The electrostatic coefficient for lead-hydrogen was found to be approximately 0 when estimated by regression.

.

÷.

С

è

ĺ

e

ි. - ර - ර

 \rangle

Ċ

С

15

 $\overline{\mathcal{A}}$

c

c

Table 6Solubility of barium sulfate in sodium sulfateat 200C1,2

[Na ₂ SO ₄]_mol/kg	¹ [Ba] mol/kg	[Na ₂ SO ₄] mol/kg	2 [Ba] mol/kg
5.1 x 10 ⁻⁴	4.9 x 10 ⁻⁷	5.45 x 10 ⁻⁴	1.53 x 10 ⁻⁷
1.0 x 10 ⁻³	3.4 x 10 ⁻⁷	8.79 x 10 ⁻⁴	1.20 x 10 ⁻⁷
2.1 x 10 ⁻³	2.2 x 10 ⁻⁷	1.18 x 10 ⁻³	9.73 x 10 ⁻⁸
5.4 x 10 ⁻³	1.4 x 10 ⁻⁷	2.00 x 10 ⁻³	6.70 x 10 ⁻⁸
1.1 x 10 ⁻²	9.5 x 10 ⁻⁸	3.15 x 10 ⁻³	5.11 x 10 ⁻⁸
2.2 x 10 ⁻²	7.2 x 10 ⁻⁸	3.94 x 10 ⁻³	5.11 x 10 ⁻⁸
5.5 x 10 ⁻²	5.0 x 10 ⁻⁸	4.94 x 10 ⁻³	3.67 x 10 ⁻⁸
1.1 x 10 ⁻¹	4.2 x 10 ⁻⁸	6.15 x 10 ⁻³	3.67 x 10 ⁻⁸
2.3 x 10 ⁻¹	2.9 x 10 ⁻⁸	7.18 x 10 ⁻³	5.74 x 10 ⁻⁸
0.56	2.3 x 10 ⁻⁸	7.94 x 10 ⁻³	5.43 x 10 ⁻⁸
0.91	2.1 x 10 ⁻⁸	8.00 x 10 ⁻³	4.79 x 10 ⁻⁸
1.1	1.9 x 10 ⁻⁸	8.06 x 10 ⁻³	4.15 x∍10 ⁻⁸

¹These data were presented in the form of a graph (Lieser, 1965) from which these values were obtained by digitizing the graph. The work of Monnin *et al.* has called these data into question.

² Taken from Felmy et al. (64). These data were obtained from the graph presented in their paper.

. m

 \mathcal{O}

ំ ព

69

0

ç c

ų
Table 7 Measured solubilities of barium sulfate in sulfuric acid solutions at $25^{\circ}C$

[H ₂ SO ₄] mol/kg	[Ba] mol/kg	95% Confidence Interval (3 replicates)
0 (water) 3.00×10^{-4} 1.00×10^{-3} 3.00×10^{-3} 7.92×10^{-2} 4.50×10^{-1} 8.90×10^{-1} 1.84 2.89 3.95 6.19	9.88 x10-6 4.80 x10-7 2.14 x 10-7 1.32 x 10-7 9.20 x 10-8 8.86 x 10-8 9. 57 x 10-8 1.13 x 10-7 1.14 x 10-7 1.11 x 10-7 1.28 x 10-7	$\pm 9 \times 10^{-7}$ $\pm 9 \times 10^{-10}$ $\pm 2 \times 10^{-9}$ $\pm 2 \times 10^{-9}$ $\pm 6 \times 10^{-9}$ $\pm 5 \times 10^{-9}$ $\pm 2 \times 10^{-9}$ $\pm 7 \times 10^{-9}$

Note: The values at 7.92 x 10^{-2} m and 8.90 x 10^{-1} m were checked in a separate experiment using ICP/MS and non-radioactive BaSO₄. The values obtained for these data were 7.65 x 10^{-8} m and 1.29 x 10^{-7} m for a single determination, respectively.

 ∂

Table 8Solubility of barium sulfate in sulfuric acid at 60^0C

[H ₂ SO ₄] mol/kg	[Ba] mol/kg	95% Confidence
		Interval
		(based on # of replicates
		shown in parentheses)
0 (water)	1.56 x 10 ⁻⁵	± 1 x 10 ⁻⁶ (6)
1.00 x 10-3	5.64 x 10 ⁻⁷	$\pm 2 \times 10^{-9}$ (3)
3.00 x 10 ⁻³	3.84 x 10 ⁻⁷	
7.92 x 10 ⁻²	3.33 x 10 ⁻⁷	
4.50 x 10 ⁻¹	3.55 x 10 ⁻⁷	
8.90 x 10 ⁻¹	4.87 x 10 ⁻⁷	·
1.84	5.21 x 10 ⁻⁷	
2.89	7.25 x 10 ⁻⁷	
3.95	8.25 x 10 ⁻⁷	± 2 x 10 ⁻⁸ (4)
6.19	7.67 x 10 ⁻⁷	±5 x 10 ⁻⁸ (3)

v

e.

-

 $^{\circ}$

C

e

0

8

o .

-1

ļį

ń

ı'

e

T⁰ K	βο	β ¹	β 2	95% Coni Interval	idence	
				on β ^o	β 1	β2
293	-1.00	6.60	-154.3			±5.0
				(data fr	om Lieser	in Na ₂ SO ₄)
293	-1.00	+12.6	-153.4 (F	Parameters take	n from M	onnin, 58)
298	0.000	4.181	-157.9	±1.8	±12	±93
333	0.000	6.955	-156.5	±1.8	±12	±80
2						(This study)

12

 Table 9
 Ion interaction parameters for Ba²⁺-SO4²⁻

2

б

3

а О

Table 10	ion interacti	ion parameters for	Bact-HSU4

ć

्

.,

G

÷

.

T₀ K	βο	β ¹	Value of pK _{sp}
298	0.0412 ± 0.4	2.283 ± 5	9.980 ± 0.02
333	0.0420 ± 0.1	2.696 ± 2	9.718 ± 0.04
The electr	ostatic coefficient	for barium-h	nydrogen was found
to be appro	ximately 0.100 who	en estimated	by regression.

£

110

ţ

Ċ

г

ç.

e

Second a grade

JE

C

¢

т ⁰ К	βο	β 1	β ²
298	0.0000	4.115	-156 ±61
308	0.0000	4.115	-161 (predicted)
318	0.0000	4.115	-166 (predicted)
333	0.0000	4.115	-174 (predicted)

Table 11 Ion interaction parameters for Ra²⁺⁻SO₄²⁻

95% confidence intervals are not quoted as: (i) The very small amount of data (8 values) produced very wide confidence intervals for the 6 parameters regressed. (ii) At 35^{0} C, 45^{0} C and 60^{0} C the parameters were not obtained by regression, but were estimated using the temperature coefficients of variation for the parameters of CaSO₄ in place of those for RaSO₄. As was found in the case of barium sulfate, many of the parameters may be set equal to zero.

fi

e

ß

15.	-			
ΤºΚ	βο	β ¹	Value of pK _{sp}	
298	0.2240	1.460	10.408(regressed)	
308	0.2240	1.460	9.9618	
318	0.2240	1.460	9.8610	
333	0.2240	1.460	9.6512	

Table 12 Ion interaction parameters for Ra²⁺⁻HSO₄-

The electrostatic coefficient for radium-hydrogen was set at 0.100 by analogy with barium-hydrogen.

95% confidence intervals are not quoted as: (i) The very small amount of data (8 values) at 25° C produced very wide confidence intervals for the parameters. (ii) At 35° C , 45° C and 60° C the parameters were not obtained by regression, but were estimated using the temperature coefficients of variation for the parameters of CaSO₄ in place of those for RaSO₄.

÷

÷

÷

2

ç,

Compound	βο	β 1	β ²	
<u>_</u>	·			
CaSO ₄	0.200	3.1973	-52.24	÷
MgSO ₄	0.2210	3.3430	-37.23	
FeSO ₄	0.2568	3.0630	-42.00	
MnSO ₄	0.2130	2.9380	-41.91	
SrSO ₄	0.2000	3.1973	-78.00	
NiSO4	0.1594	2.9260	-42.76	
ZnSO4	0.1949	2.8830	-32.81	
CoSO4	0.2000	2.7000	-30.71	
CuSO ₄	0.2340	2.5270	-48.33	
BaSO ₄	-1.0	6.6	-154.0	ت 0

 Table 13
 Comparison of parameters for 2:2 sulfates

Note: These data were supplied by courtesy of Prof. E. J. Reardon. The parameters for BaSO₄ reported are essentially the same as those of Monnin *et al.*

0

Ċ,

ଡି

р

0

S

Ċ.

J

Figure 9 Comparison of the data for the solubility of $PbSO_4$ in H_2SO_4 at 298K by Crockford et al.(50), with the data of Danel and Plichon (54) at 293K. At <u>low</u> concentrations, 1mol/L is approximately 1mol/kg, for purposes of comparison.

Ϋ́,

F.E. 2 5

h

7)

° 0



 ≤ 1

Figure 10 Comparison of experimental solubility (+) and fitted values (solid line), using the Pitzer model, for PbSO₄ in Na₂SO₄ at 333K.

c

 \bigcirc

 θ

ø

C



Figure 11 Comparison of experimental solubility (+) and fitted values (solid line), using the Pitzer model, for PbSO₄ in H₂SO₄ at 333K.

o

¢

0

ł,

e

Ģ

С

÷

 \mathcal{O}



 \circ

log [P504] mol/kg.

 $\hat{\mathbf{O}}$

Figure 12 Comparison of experimental solubility (+), taken from 53) and fitted values (solid line), using the Pitzer model, for PbSO₄ in H_2SO_4 at 273K.

Û



ċ

iog [PbS04] mol/kg.

{!

Figure 13 Comparison of experimental solubility (+) and fitted values (solid line), using the Pitzer model, for PbSO₄ in H_2SO_4 at 293K.

C

्यम

G

 \cdot t

c

C

ķ

С

С





log [P5204] mol/kg.

С

\$î

Figure 14 Comparison of experimental solubility (+) and fitted values (solid line), using the Pitzer model, for PbSO₄ in H₂SO₄ at 298K.

c

ŝ

\$





log [P504] mol/kg.

\$

Figure 15 Scanning electron micro-photographs of BaSO4 . Specimen A is a Lashly prepared specimen while specimen B was "aged" in the mother liquor for 18 hours prior to the photography. The bar = $10\mu m$ in length.

0

Û

5

¢

e

S

2

9

Q

c

5

¢

S

2

Ð

...



Figure 16 Comparison of experimental solubility (+) and fitted values (solid line), using the Pitzer model, for BaSO₄ in H₂SO₄ at 298K.

С

c

e

J

e

1.

\$

 \mathfrak{G}

¢

راني. سي آ

....

c

ç,

(



log [BaSO4] mol/kg.

e

Figure 17 Comparison of experimental solubility (+) and fitted values (solid line), using the Pitzer model, for BaSO₄ in H₂SO₄ at 333K.

c

С

2

í.

 \odot

z`

0

ψ

E.

÷

Ċ

¢

J

Ś



¢

ų,

Figure 18 Comparison of experimental solubility (+) and fitted values (solid line), using the Pitzer model, for RaSO₄ in H_2SO_4 at 298K.

0.1



Ģ



log [RaSO4] mol/kg.

-

»."

Figure 19 Predicted solubility (solid line) for $RaSO_4$ in H_2SO_4 - H_2O solutions at 308K. The only available experimental data (+) are shown at 0.005M and 3.02M; taken from (76).

ē.

 \hat{n}



.

Figure 20 Predicted solubility (solid line) for $RaSO_4$ in $H_2SO_4-H_2O$ solutions at 318K. The only available experimental datum (+) is shown at 3.02M; taken from (76).

¢

Ċ,

 \odot

C

þ

 \mathcal{O}

 \mathcal{J}^{\dagger}



C

ŗ

on [40264] اسما/ل

ļ

Figure 21 Predicted solubility (solid line) for $RaSO_4$ in H_2SO_4 - H_2O solutions at 333K. No experimental data are known to exist.

æ

`

C?

r

1.

\$

¢

0

æ,

c

Ş:

Ţ.

ς,

9

С

0.0



Į)



È

الام204] mol/L

c

Q

Chapter 4

Kinetics of the exchange process at the faces of large single crystals of barium sulfate and lead sulfate.

4.1 Introduction

ς.

÷

Mass transport at the solid-liquid interface and, in particular at the solid-aqueous electrolyte interface, is an important consideration during studies on crystal growth and dissolution. Under such circumstances a driving force is present which results in a net transport of material toward or away from the crystal. During growth or dissolution, attention is focussed on the dependence of the net transport on factors such as super- or undersaturation, temperature and interfacial investigations on properties. In performing growth or dissolution, however, it must be kept in mind that the net transport is the result of oppositely directed fluxes of material. These fluxes provide for the attainment of the dynamic state between crystal and solution at equilibrium.

ر ا Transport kinetics in systems at equilibrium have been in which experimental studies the subject of manv radiotracers were used to follow the transport of material in one or both of the subsystems -the solution or the crystal. The results published in the period 1915-1949 are summarized in a In many cases monograph by Myers and Prestwood (82). reported in the literature, isotope exchange which occurred simultaneously with the transport of some macrocomponent was studied rather than pure isotope exchange. In the majority of experimental studies, equilibriation, with respect to the macrocomponent, was neglected.

4.2 Kinetics of isotope exchange limited by the rate of surface reactions

When the rate of isotope exchange is limited only by the rate of reaction I shown below, the rate of isotope exchange equals the rate of the reaction.

Т

(47)

 $A_{b}^{*} + A_{s} \xleftarrow{} A_{b} + A_{s}^{*}$

In this scheme, A and A* denote the exchangeable species, b denotes the bulk solution and s the solid phase.

The net rate of reaction I is defined by equation 45.

$$\frac{dC_{A_{S}}}{dt} = k(c_{A_{b}} c_{A_{S}} c_{A_{b}} c_{A_{S}})$$
(45)

The results of the integration of Equation 45 under the boundary conditions of material balance and the initial condition (namely, the whole of the radioactivity is in the solution at the initial moment) are shown as equation 46 and equation 47.

$$\ln(1 - F) = -k(c_{A_{b}} + (\sigma/V)c_{A_{s}})t$$
(46)

 $\ln(1-F) = -R_{M}t(Q_{b} + Q_{s})/(Q_{b}Q_{s})$

С

The symbols are defined in the symbol table. The latter is known as the "McKay equation" (83) and is often applied to the interpretation of experimental results.

When the exchangeable ions in the system under study are present only in the solution and on a solid surface that is easily accessible (e. g. a non-porous solid), reaction I is the the of isotope exchange. process limiting rate only Surprisingly, for many real systems a linear dependence of In(1-F) on t is observed. The value of R_M in eq. (47) may then be easily evaluated from such a dependence with no regard for the mechanism of the isotope exchange in the system studied. Therefore, such a formal equation has been used even for those systems in which the rate of isotope exchange is controlled by diffusion (84). Strictly, it is not applicable in such situations.

The McKay equation may be applied only to the systems in which the dependence of In (1-F) on t is rectilinear. A curvilinear dependence is obtained when the heterogeneous isotope exchange is described by more than a single surface reaction. Some examples of such systems are given below (85). Note that in these schemes a shortened form of each reaction is used. For example, reaction I is written as:

2

П

Ċ,

b ks
In the solid, some layers may be identified which undergo exchange reactions with neighbouring layers; for example, the first layer with the second one and with the solution. In such a system, the process of isotope exchange is described by the reactions shown in III.

Here s_i denotes the consecutive layers of the solid with i=1,2,...,n. There are solutions to rate equations reported in the literature (86) corresponding to the reaction sequence III which may be transformed in order to describe surface reactions with isotope exchange.

On the other hand, one may assume that there are some kinds of surface sites with different rate constants of reaction I type, such as that shown in scheme IV, where the exchangeable ions are sorbed on the solid surface; or as in scheme V where the exchangeable ions are built into the crystalline lattice of the solid.

$$b \xleftarrow{k_{a_i}}$$

a_i

5

i=1,2,....,n

IV -

 $b \stackrel{ks_i}{=} s_i$ i=1,2,....,n

One may also assume some more complex models of isotope exchange in the systems comprising a solid and an interacting solution. Some possible schemes are illustrated in VI to VIII. For example:

(a) A gradual exchange with a uniform adsorption layer, as shown schematically in VI.

(b) A gradual exchange with non-uniform both 'a' and 's' phases, as in VII.

(c) Parallel exchange with 'a' and 's' phases, shown in VIII.

 $b \xleftarrow{k_a} a \xleftarrow{k_{s_i}} s_i i=1,2,...,n$ VI

$$\stackrel{\mathsf{K}_{a_i}}{\longleftarrow} \hat{a}_i \stackrel{\mathsf{K}_{s_i}}{\longleftarrow} s_i$$

b

0

i=1,2,.....jn

VII-

- V



÷

c

Some similar schemes for small values of m and n were considered by Campbell and O'Connor (87). For each scheme the rate equation shown in equation: 48 was obtained.

 $1 - F = \sum_{i=1}^{m+n} h_i e^{-r_i t}$ (48)

In equation 48 r_i and h_i are, respectively, coefficients dependent on the amounts and concentrations of macrocomponent in the appropriate states and the rate constants describing the isotope exchange among these states.

With the aid of tracer kinetics, the tracer experiments may lead to a description of the exchange in terms of subsystems or "compartments" and measurements of transport rates between these compartments. The term compartment has also been used in a more physical sense in the description of the crystal/solution interface, namely as a region with a specific environment for the building unit(s) (e.g. ions or molecules) of the crystal. For instance, the Gouy-Chapman layer, the Stern layer, the outer crystal layer and the inner (bulk) crystal might be considered as such compartments. Also, the different positions (surface, step and kink) for building units at a crystal interface (see **Figure 22**), often used in ĥ.

VIII

describing crystal growth processes, may be thought to constitute different compartments.

Different possible routes for transport from the solution to surface, step or kink sites are shown in **Figure 23**. The compartments are distinguished by the different numbers of building units which they contain and by their specific bonding for the building units. Thus, each will have a distinct exchange rate and residence time.

The growth units may diffuse (very slowly) from their position at the interface to inner crystal layers or, more likely, they may be buried. These layers can also be included in models and will constitute а fifth the compartment compartment really becomes compartment. Whether а important in an experiment depends on the magnitude of the exchange rate constants and on the amount of material in each compartment (the compartment size). The exchange rates may be influenced by various factors such as the crystallographic structure of the outer solid layer, the surface morphology and presence of impurities which can be preferentially 🥏 the adsorbed at the interface.

The aim of this phase of the study is to gain a more detailed insight into the transport of ions implicated in the Hileman-Snodgrass model. These include the $BaSO_4/aqueous$ solution and $PbSO_4/aqueous$ solution systems. The elaboration of the data acquired by these experiments will be divided into two stages, namely the description of the tracer-system interrelations and the interpretation of the system behaviour in terms of the elementary transport processes at the molecular level.

4.3 Experimental Procedure

1.1

...

 ℓ

ē

The experimental procedure followed was similar for all the experiments. The description will be given for the case of BaSO₄. Large natural crystals of BaSO₄ were obtained from

BaSO₄ crystals of typical size 10 x10 x Wards Scientific. 5mm were cleaved from the specimens described. The crystallographic orientation of the faces ({001} and {110}) was determined by comparison with diagrams of cleavage specimens in a mineralogical text (88). Some of the fragments of the natural crystal were ground in an agate mortar and then used to prepare a saturated solution of BaSO4 in distilled demineralized filtered water.

Ę.

After 25⁰C for equilibration at one week the solid/solution mixture was separated by filtration through a 0.2µm Teflon filter. The crystal was then added to this liquid contained in a screw-top polypropylene vial. This was sealed and, after two weeks of equilibration time, 20µL of an aqueous solution of 133BaCl2 was added. The crystal was taken out of the solution at intervals ranging from 1 minute at the start of the experiment to several days at the end. The liquid clinging to the crystal was removed by washing once with distilled demineralized water and twice with H. P. L. C. grade methanol.

The activity present at each of the two faces was determined by means of a thin-end window Geiger-Muller tube and scaler, counting in a fixed geometry. A total of 10.000 counts was collected for each stage of the experiment. In order to avoid the inclusion of the edges of the crystal in the counting, a thick lead diaphragm with a small hole bored in it was used to restrict counting to the central region of each face. In order to avoid the presence of activity on a face opposite to that under study contributing to the total count rate, the face opposite to each experimental face was coated/7 with paraffin wax before the activity added. was Exchange experiments were carried out, using 133Ba2+, on: (i) Two different crystallographic faces of BaSO₄ at 25⁰C in order to investigate the effect (if any) of crystallographic orientation on the attainment of equilibrium.

(ii) the $\{001\}$ face of BaSO₄ at 60° C.

(iii) the {001} face of BaSO₄ in the presence of two different low concentrations of Pb^{2+} .

(iv) the {001} face of PbSO₄ using ²¹⁰Pb.

Sorption experiments were carried out on: (v) $210Pb^{2+}$ on the {001} face of BaSO4.

In the case of PbSO₄ the radio-tracer used was 210-Pb (Amersham). For the 210Pb exchange and sorption experiments care was taken to ensure that the radio-tracer was in radioactive equilibrium with its 210Po daughter when counting was carried out.

Once the data indicated that equilibrium had been attained, the crystals were placed in "cold" solutions of their ions. The re-exchange process was examined qualitatively by counting the crystal faces after a period equal to the time required for the initial equilibration.

The surface area of each of the faces was then calculated after measuring the length of the edges of each crystal using a Bausch and Lomb magnifying eyepiece with a scale divided into 1/100mm intervals. Interfacial angles for the crystals, required in order to complete the calculations of the facial areas, were measured with a protractor scale using the same eyepiece.

4.4 i Experimental results and data analysis.

The large natural crystals of BaSO₄ used for the exchange studies were subjected to neutron activation analysis (kindly performed by Mr. A. Kabir of the McMaster Nuclear Reactor). It was found that the principal impurities were Sn, Sr and K. The concentrations were not determined in this study. Tests carried out separately from the exchange studies assured the author that the use of a coating of paraffin wax was an effective method of avoiding the presence of

activity at faces of the crystal other than those under investigation.

Qualitatively, it was found that for all crystals used for the investigations, the re-exchange experiments allowed about 30% of the activity to remain in the crystals. It appears unlikely that this can be explained by diffusion in the solids, due to the extremely slow rate of solid diffusion at low temperatures. A more likely explanation for this residual activity may be found in a burial process during the course of the exchange. It was found that the crystallographic nature of the face undergoing exchange affected the rate of approach to equilibrium. However the final specific activity of the crystal faces was the same.

The exchange reaction of the system barium sulfate/barium ions (among others) was studied by Lieser et al. (97). They reported that the surface mass reaction was the rate determining step in this reaction. Their results also indicated that the activation energy was greatly influenced by the pretreatment of the crystals.

The initial presentation of the quantitative results for the exchange experiments for $133Ba^{2+}/BaSO_4$ and $210Pb^{2+}/PbSO_4$ is in the form of a McKay plot or plot of ln (1-F) as a function of time, where the exchange fraction, F is defined as:

$$F = A(t) - A(0)/A(\infty) - A(0)$$

÷

(49)

÷.,

where: A(0) is the initial activity of the crystal face; A(t) is the activity at some instant, t; and $A(\infty)$ is the final equilibrium value attained.

The exchange fraction is a measure of the progress of the surface reaction. These plots are shown in **Figures 24-30**.

The linear or curvilinear nature of these plots indicates whether the heterogeneous isotope exchange is described by more than a single surface reaction. When the exchange was believed to be described by more than a single surface reaction, subsequent analysis was carried out by fitting the model described by equation 48. Since this model is non-linear in the parameters, the technique of non-linear regression was used. The approach used was to minimize the residual sum of squares between the model described in equation (48) and the experimental data. The adequacy of the fit was initially assessed by a plot of the fitted values overlaid with the observed responses. These plots of the fitted values overlaid with the observed responses are shown in Figures 31 to 36. The approach used in order to judge the adequacy of the model follows: terms were added or removed; the effect on the residual sum of squares was examined; then, a decision was made regarding the necessity of these terms. The use of the extra sum of squares analysis commended itself to us by virtue of the fact that it is unaffected by nonlinear parametereffects and is therefore more exact than the t -test in the In addition, examination of plots of the nonlinear case. residuals was used, with the criterion of random distribution of the residuals as a requirement for entertaining a given Such plots of the residuals versus, for example, the model. fitted values may reveal outliers or general inadequacy in the A plot of the residuals form of the expectation function. against the predictor variable (in this case the ionic strength $_{\rm e}$ or the concentration of the major electrolyte) may identify an effect due to that variable which has not been accounted for. The values of the parameters obtained by the regression analyses for these systems are tabulated in Tables 15, 16 and 17.

<u>е</u>р., ".

- ()

Examination of equation 48 shows that the values of the parameters r_i given in that equation are estimates of the rate

constants for the isotope exchange process between the states, the compartments. The rate constants are equal to the fraction of ions which leave а compartment under consideration each second. The shape of the initial plots of In(1-F) versus t, or the number of terms in the summation, equation 47, enables the number of compartments involved in the exchange process to be identified. For example, if the data presented in Figure 24 are considered, two distinct portions can be discerned. This means that three different states or compartments are probably involved, one of which must be the saturated solution (of BaSO₄ in this case). The two other compartments can only correspond to 133Ba2+ ions occupying different types of site in, or on, the crystal because only the activity of the bulk crystal was measured. If these two compartments have no exchange between each other and both communicate with the much larger central compariment individually, then the parameters r_1 and r_2 correspond to the rate constants k1 and k2 for transport between the central compartment and the two crystal ones. The residence times. τ_i , of the appropriate ions in the crystal compartments may then be calculated from $\tau_i = k_i^{-1} = r_i^{-1}$, i=1,2. In Tables 15, 16 and 17 the residence times, τ_i , calculated on the basis of this assumption, are tabulated for the different crystals, crystal faces, temperatures and concentrations of co-solute ions.

If we relate the rate constant to the behavior of individual ions, it may be considered as the jump frequency of a single ion for some given elementary process. The jump frequencies for various elementary transport processes will be calculated from theoretical concepts outlined by Neilsen (89). The calculated values may then be compared with values obtained from crystal growth experiments (89) and from the exchange experiments performed in this research.

c

÷

4.4.ii Calculation of jump frequencies.

As demonstrated by a number of workers (89, 90, 91) it may be useful to relate the jump frequency, v, to the Gibbs activation free energy of an elementary transport process, ΔG^{\dagger} , by means of Eyring's Transition State Theory:

 $v = v_0 e^- \Delta G^{\dagger}/kT$

(50)

where $v_0 = kT/h$ (6.21 x 10¹²s⁻¹ at 298K).

The jump frequency for diffusion of ions in the aqueous solution, v_D , is given by equation (51).

 $v_{D}=D/a^2$

5

(51)

The symbol "D" represents the diffusion coefficient and "a" some "unified" molecular diameter; say the diameter of a water molecule (300pm or 3Å). The diffusion coefficient for Pb²⁺ and Ba²⁺ respectively are 1.07 x 10^{-5} and 1.15 x 10^{-5} (92,93) at the cation concentration of the appropriate saturated solution. The calculated diffusion frequency and equivalent activation free energy are tabulated in Table 18.

The integration frequency v_{in} for incorporation into a crystal lattice position at a kink site appears to be related to the cation dehydration frequency according to equation (52) taken from (89).

 $v_{in} = 10^{-3} v_{dh}$

(52)

The calculated integration frequency and the equivalent activation free energy are tabulated in Table 18.

The jump frequencies for the transition of ions from the solution to the adsorption layer at the crystal surface and vice versa can not be calculated independently, in contrast to the

jump frequencies of the processes described in the previous discussion. The adsorption and desorption jump frequencies can be calculated, however, under the assumption that they are rate determining. In this case the adsorption frequency v_{ad} is related to the flux of ions by equation (53).

 $F = Q v_{ad} = Vc_s v_{ad} = Aac_s v_{ad}$ (53) where: F is the flux of ions as determined from the previous exchange experiments, A is the area of the crystal in contact with the solution and the other symbols are defined in the symbol table. It is presumed that adsorption in one jump is possible from a layer of thickness "a" adjacent to the crystal surface. The desorption frequency may be calculated from the microscopic equilibrium condition expressed in equation (54).

 $c_s v_{ad} = c_{ad} v_{ds}$

+

In this equation c_{ad} represents the concentration of cations in the adsorption layer and v_{ds} the frequency for desorption of ions from this layer into the solution. The concentration of cations in the adsorption layer, c_{ad} , follows from the adsorption equilibrium described in equation (55).

 $K_{ad} = c_{ad} / c_s$ (55)

 K_{ad} is the adsorption equilibrium constant. K_{ad} may be estimated from the ion pair association constant K_{I} , K_{ad} being 200 K_I for 2:2 electrolytes (89). In this work, use will be made of the fact that the parameter β^2 , estimated in chapter 3 of this thesis and involved in the modelling of the solubility of Pb²⁺ and Ba²⁺ in sulfate systems, may be related to K_I by the relationship (94) shown in equation (56).

(54)

Ç,

 $K_1 = -2 \beta^{(2)}$

(56)

The jump frequency for the detachment of ions from kink positions to the adsorption layer, v_{de} , may be evaluated from the microscopic equilibrium at kink sites. This equilibrium is described by equation (57).

vde Ckink = VinCad

0

5

(57)

(59)

The quantity c_{kink} is the concentration of cations at kink sites. If this factor c_{kink} is written in terms of the fraction, x, of surface sites of the kink type and the total concentration of ions in the solid, c_t , then equation (57) is the result.

 $c_{kink} = xc_t$ (58)

The total concentration of ions in the solid, c_t , is 19.2 mol dm⁻³ for BaSO₄ and 20.9 mol dm⁻³ for PbSO₄. Using equation (56) and the computed values for v_{in} and c_{ad} previously found v_{de} is found to be given by equation 59.

 $v_{de} = (v_{in} c_{ad}/c_t) x^{-1}$

The misorientation of the crystal faces is assumed to be about 1^0 (95), resulting in the introduction of approximately two monomolecular steps per surface area of 100 sites in square. As at a step, about one kink is found for every five sites (34), this misorientation of 1^0 results in a fraction of kink sites, x, of approximately 1%.

The jump frequency for surface diffusion can not be calculated independently, as it depends on the frequency for desorption (89). This is not measurable if the ad- and desorption processes are not rate determining. It may be deduced, however, that surface diffusion is very rapid except for very soluble substances with a low interfacial energy (89). Because both $PbSO_4$ and $BaSO_4$ are only slightly soluble and possess a high interfacial energy, surface diffusion will not be rate limiting in the present case.

, **1**4

. 1

c

4.4.iii Comparison with data obtained from crystal growth and exchange experiments.

The experimental rate constants (jump frequencies) obtained from crystal growth experiments and the exchange experiments carried out during our studies are compared in Table 19. From crystal growth experiments on BaSO4 in aqueous solution a transport rate constant of 1.9 x 10⁵ s⁻¹ has been reported by Neilsen (89). This rate constant was obtained by fitting growth data to the parabolic rate law which belongs to the surface spiral growth mechanism. The results of crystal growth experiments for the majority of the ionic crystals growing by a parabolic rate law have been interpreted by assuming that the rate-determining integration part consists of the two simultaneous steps: (i) release of a molecule of water of hydration from a cation and (ii) the diffusion of the cation into the lattice site from а neighbouring position. Because of the large difference between the rate constants obtained in the exchange experiments it is clear that the latter must be attributed to different processes. The jump frequencies for exchange are to be correlated with the detachment of ions which must pass a higher activation barrier than kink ions, as may be concluded on the basis of the rather high activation energy for the exchange processes. This would be in agreement with the numerical simulations carried out by Gilmer and Bennema in which it was found that a very low kink density and flat surfaces occurred at equilibrium (96).

In conclusion, it has been demonstrated that equilibrium (exchange) and non-equilibrium (crystal growth) experiments vield different information about the interfacial kinetics. The rate constants which play the key role in crystal growth are believed to be largely determined by the solute-solvent interaction (the dehydration of cations), whereas the rate constants for exchange are perhaps a measure of the activation energy needed in order to break bonds in the solid phase. There appear to be at least two different types of bonding for Ba2+ and Pb^{2+} ions within the crystals or at their surfaces. This different behaviour of one type of ion could be explained by the fact that these ions differ in type of bonding at the crystal For example Ba²⁺ (or Pb²⁺) in kink- and step-like surfaces. Another explanation of the existence of two positions. different compartments for the ions would be that the ions having the larger rate constants are situated in the first crystal layer and those having the smaller rate constants correspond to ions in the bulk of the crystal.

The precision of the counting component of the experiments was probably better than 1%, due to the total number of counts collected. It was found that the positioning of the crystals being counted was not critical, probably due to the penetrating nature of the radiations being counted. It is clear that these data require replication, in order to permit the precision of the computed values to be evaluated.

4.4 iv Exchange for 133-Ba on BaSO4 at 298K.

 \odot

с. С

> The present study has demonstrated that there are at least two different types of bonding for Ba2+ ions either within the crystal or at its surface. Different rate constants are found for these two types of Ba2+ ions, which if they may which are only be resident at sites considered to be solution compartment, the larger communicating with 6x10⁴ and correspond to residence times at 298K of -

 -8×10^{5} s, respectively. This different behaviour of a single type of ion may be due to differences in the bonding of the Ba²⁺ ions at the crystal surface: for example, Ba²⁺ in kinkand step-type positions. Ions in the kink sites possess half the number of bonds of ions inside the crystal and ions in step positions one bond less. Another plausible explanation of the existence of two different compartments for the Ba²⁺ ions would be that the ions with the larger rate constants are situated in the outer crystal layer and those with the smaller rate constants are to be found in the inner layers of the crystal.

4.4 v Exchange for the 133-Ba on BaSO₄ at 333K

The effect of an increase in the temperature is clear from inspection of the rate constants shown in Table 15. An increase in temperature of 35° C has increased the rate constants for the exchange reaction with both sites by a factor of about 8-10 times. An increase for the rate constant of this order is reasonable, based on the very approximate rule of a doubling in the rate for every 10° C increase in temperature.

4.4 vi Exchange for the 133-Ba on BaSO₄ at 298K in the presence of Pb^{2+} ions.

The influence of the impurity ions, Pb^{2+} , on the exchange rate is evident from an inspection of the entries for BaSO₄ at 298K in Table 15 and the same system in the presence of 0.075mM Pb²⁺, shown in Table 16. The presence of the lead ions retards the exchange processes appreciably, possibly due to preferential adsorption at the BaSO₄/solution interface. In the case of the 0.75mM Pb²⁺ the fast exchange process appears to disappear completely.

CONTRACTOR OF STREET

Labelled Element	Solution	Solid	Proposed Mechanism	Reference	
Ba	Ba ²⁺	BaSO ₄	S, R	Lieser et al.	(97)
S	s045-	BaSO ₄			
Sr	Sr ²⁺	SrSO4			
CI	CI	AgCl			
Sr	Sr ²⁺	SrSO ₄	S, R	Lieser	(98)
Ca	CaCl2	CaCO3	. 9		
		Ca ₃ (PO ₄) ₂	· 2, •		
		CaSO4.2H2O	R	Abdel Salam	(99)
Ca	CaCl ₂	CaCO3	S	Huang et al.	(100)
Ca	CaCl2	CaC ₂ O ₄	S, D	Huang et al.	(101)
Ca	Ca ²⁺	CaCO3	S	Moller et al.((102)
Ca	Ca ²⁺	CaCO3	S	Binsma et al	.(103)

Table 14Literature review of experimental investigations ofisotopeexchange

Key: S=surface reaction; R=recrystallization; D=diffusion in the solid phase.

Note: Studies involving ion exchange resins have not been included. These are examined in (104).

¢

e

4

í'

 \bigcirc

e.

12

0

ς

C

Table 15Parameter values r_i and residence times τ_i fordifferentsinglecrystalsofBaSO4underequilibriumconditionswithrespect to themacro-component..

Crystal(face)	BaSO ₄ (001)	BaSO ₄ (110)	BaSO ₄ (001)
Temp ⁰ K	298	298	333
Exchanging sorbing ion	133 _{Ba} 2+	133 _{Ba} 2+	133 _{Ba} 2+
[co-solute] mmol/L	-0	~0	-0
r _{1 μs} -1	1.0	1.6	10.9
r2 μs ⁻¹	20.6	14.9	162
τ ₁ Sx10 ⁵	9.9	6.1	0.92
t2 Sx10 ⁴	4.9	6.7	0.62
note: subscript1	refers to the	slow reaction.	<u>e</u>

¢

G.

c

c

л

109

المراجع المحافظة المحافظ المحافظ المحافظ المراجع

Table 16 Parameter values r_i and residence times τ_i for single crystals of BaSO₄ under equilibrium conditions with respect to the macro-component.

Crystal(face)	BaSO4(001)	BaSO ₄ (001)	BaSO ₄ (001)
Temp ⁰ K	298	298	298
Exchanging or sorbing ion	133 _{Ba} 2+	133 _{Ba} 2+	210 _{Pb} 2+
[co-solute] mmol/L	0.75 Pb ²⁺	0.075 Pb ²⁺	~0
r ₁ μs ⁻¹		5.74	9.69
r2 μs ⁻¹	25.5	234	171
τ ₁ sx10 ⁵		1.74	1.03
τ2 ^{Sx104}	3.9	0.427	0.58

Ċ,

2

note: subscript1 refers to the slow reaction.

Ģ

ſĘ

Table 17 Parameter values r_j and residence times τ_j for a single crystal of PbSO₄ under equilibrium conditions with respect to the macro-component.

Crystal(face) Temp ⁰K

PbSO₄(001) 298

Exchanging or sorbing ion

210_{Pb}2+

~0

0.38

2.60

 \odot

C

₽.

[co-solute] mmol/L

r μs-1

τsx106

う

£

 \approx

O

3

-

Ü

G ;

ñ

Table 18 Calculated jump frequencies and the corresponding activation free energies ΔG^{\dagger} for some elementary transport processes in the systems PbSO₄/aqueous solution and BaSO₄/aqueous solution.

Process	v s ⁻¹	Pb ²⁺ ∆G†kJ mol ⁻¹	v s ⁻¹	Ba ² ΔG† kJmol ^{- 1}
Diffusion in solution	1.2 x10 ¹⁰	0 15.5	1.3x10 ¹⁰	15.3
Adsorption	4.8x10 ⁴	46.2	2.7x10 ³	53.4
Desorption	1.0x10 ³	55.8	43.1	63.7
Integration at kinks	1x10 ⁷	33	1.5x10 ⁶	37.6
Detachment from kinks	3.0x10 ⁵	41.7	5.5x10 ³	51.6

Diffusion- inProbably not available.Likely tothe solidbe $v = 10^{-16} \text{ s}^{-1}$; $\Delta G^{\dagger} = 200 \text{kJ mol}^{-1}$.

Comment and

Table19Experimentaljumpfrequenciesandthecorrespondingactivationfreeenergies ΔG^+_1 forthesystemBaSO₄/aqueoussolution.

Type of experiment	v s ⁻¹	∆G† kJmol ⁻¹
Crystal growth (89)	1.9 x10 ⁵	42.9
Exchange r1	1 x10-6	107
Exchange r2	20.6 x10 ⁻⁶	99.7

0.5

して

G

e

ت

Ũ

¢

0 1. 1 ø

۰.

o

Ľ.

12

Ŧ

ĥ

í,

 \bigcirc

Figure 22 Crystal/solution interface with various possible positions for a growth unit: (1) in the solution; (2) at a flat surface; (3) at a step site and (4) at a kink site.

Ō

.:

ت

e

C

Ś

;P

1

:72

Ģ

0

±-2

C

V.

ے ______را ______

c

-- c

G

e.





Figure 23 Different hypothetical routes for transport from the solution to the crystal, utilizing the concept of compartment models.

> е С

> > 0

ē

= ;

Ø

E

c

Ċ

6

С

*

c

3



•





ρ 0

> ۲ ۲ ۲ ۲ ۲

> > $\hat{\phi}$

Figure 24 Plot of In (1-F) as a function of time for 133-Ba exchanging on the (001) face of a single crystal of barite at 298K. F is the exchange fraction.

Ð

ų,

10

1

c

¢

(F)

÷

2

٢

3 D

0

į.



(3-1) 4

00

()

Figure 25Plot of In (1-F) as a function of time for 133-Ba exchanging on the (110) face of a single crystal of barite at298K. F is the exchange fraction.

2 3

en er i

1

е .

S.

0.000

G

5

\$ 0

~

-"∢ ¢'.



Figure 26 Plot of ln(1-F) as a function of time for 133-Ba exchanging on the (001) face of a single crystal of barite at 333K. F is the exchange fraction.

'n

,^{...}

Ċ

¢

Æ,

2

Ø

ŝ

Ø

; =

 \mathbb{R}^{n}

Ŀ



. 2

9

· .

Figure 27 Plot of ln (1-F) as a function of time for 133-Ba exchanging on the (001) face of a single crystal of barite, in the presence of 0.75mM Pb²⁺ at 298K. F is the exchange fraction.

c

 \bigcirc

Ċ

С

3

ѷ

 \bigcirc



Q

Figure 28 Plot of ln (1-F) as a function of time for 133-Ba exchanging on the (001) face of a single crystal of barite, in the presence of 75μ M Pb²⁺ at 298K. F is the exchange fraction.

 \mathcal{O}

ji,

ŀ

 \approx

9

¢!

e

5

÷

- 1

(i...

ж, ф

С

C

¢



 \bigcirc

Figure 29 Plot of ln (1-F) as a function of time for 210-Pb being sorbed on the (001) face of a single crystal of barite at 298K. F is the exchange fraction.

ß

0

.,

o

Q

O

¢

C

ç

ę

.

æ

ť

 \mathbb{C}

ii .

ċ

1

÷

Ś

đ

c

Ξ

਼

æ

0

`

0

e


ç

Ø

<u>،</u>

je S

9

1

<u>A</u>

к. Э **Figure 30** Plot of ln (1-F) as a function of time for 210-Pb exchanging on the (001) face of a single crystal of anglesite at 298K. The regression equation is $\ln (1-F) = -$ 6.58299t+0.578468. The correlation coefficient=0.943196.

\$

Ç,

Ç e

Ś

~ .

Ę.

0

0

ø



Figure 31 Comparison of experimental values (+) of F and fitted values (solid line), for 133-Ba exchanging on the (001) face of a single crystal of barite at 298K. F is the exchange fraction.

e e

e

Æ

0

 \sim

00

 \sim

ñ

Ø

С

° 5° ''

0

S

Ð

5



0c

e

Figure 32 Comparison of experimental values (+) of F and fitted values (solid line), for 133-Ba exchanging on the (110) face of a single crystal of barite at 298K. F is the exchange fraction.

¢

Ð

÷

Č).

Ó

C

ං 0

5 ²



-

i.

ت

ġ

Figure 33 Comparison of experimental values (+) of F and fitted values (solid line), for 133-Ba exchanging on the (001) face of a single crystal of barite at 333K. F is the exchange fraction.

ं

0 0

c

0

ç,

Ç

¢

U

\$

0

المبن سن



長近

が出する

ŝ

¢

Figure 34 Comparison of experimental values (+) of F and fitted values (solid line), for 210-Pb being sorbed on the (001) face of a single crystal of barite at 298K. F is the exchange fraction.

¢

C

5

ء ڻ

Figure 34 Comparison of experimental values (+) of F and

برييية

.,

3

0 0

÷

C

 \geq

 \mathcal{C}_{c}



- ,

C

 $6 \circ$

Figure 35 Comparison of experimental values (+) of F and fitted values (solid line), for 133-Ba exchanging on the (001) face of a single crystal of barite, in the presence of 75μ M Pb²⁺ at 298K. F is the exchange fraction.

t

¢

3

الم يتمالر

17

0 00

¢

100

0

#

ú

Û

1

0

Ŷ

:: С

e G



ġ

E

ĉ

Ð

Figure 36 Comparison of experimental values (+) of F and fitted values (solid line), for 133-Ba exchanging on the (001) face of a single crystal of barite, in the presence of 0.75mM Pb²⁺ at 298K. F is the exchange fraction.

¢

ð

2

្រា

D

° e



co

E

-

Chapter 5

Kinetics of growth and dissolution of epitaxial deposits on quartz and mica surfaces.

5.1 Objectives of this phase of the research.

The objectives for this phase of the investigation were originally identified in chapter 1. For convenience, they are summarized below.

(i) Data will be obtained for the rate of desorption of anions and cations implicated in the Hileman-Snodgrass model, from model surfaces. If these data suggest that retention of appropriate ions occurs to a significant degree, then objective (ii) will be pursued.

(ii) Attempts will be made to grow potential host solids on model surfaces. If this proves to be possible, the kinetics of the growth of these potential host solids on the model surfaces will be examined as a function of solution concentrations.

(iii) The dissolution kinetics of the surface deposits prepared in (ii) will be determined using radio-tracer techniques. Surface deposits will then be grown which incorporate radium in the host matrix. The dissolution kinetics of the radium micro-component, followed by counting techniques, will subsequently be related to the rate of dissolution of the host matrix.

G

С

1**29**-

0

•

¢

Ċ

5.2 Kinetics of desorption of ions, involved in the Hileman-Snodgrass model, from Quartz and Mica Surfaces.

1.

5.2.i Introduction

 $\leq N$

attainment and subsequent equilibrium Adsorption desorption of cations at the solid-liquid interface are often rapid unless diffusion in porous particles or a porous surface It has been shown (106) using a layer is encountered (105). radio-tracer technique that sodium ion desorption from vitreous silica does not involve rate-limiting diffusion and is very rapid, being essentially complete in a few seconds. Rapid adsorption-desorption reactions have been studied in a most (107) using relaxation elegant manner by Hachiya et al. In contrast, strongly chemisorbing species (e. g. techniques. silicate or phosphate) desorb slowly from mineral surfaces (108). However, at very low coverages it is known that it can be difficult to desorb small quantities of both anions and That slow cation from solid surfaces (109). cations desorption at low coverage is not necessarily due to slow release from a porous surface layer was shown in the study carried out by Thornton (110), which demonstrated that the kinetics of slow desorption of radioactive ions from а polyurethane surface at very low coverage could be not explained by a diffusion controlled mechanism. This study further demonstrated that changing from one electrolyte to another resulted in an immediate change in the radioactive ion the trace that demonstrating rate, again desorption radioactive cations were adsorbed on the surface rather than permeated into the depth of the adsorbent.

Since the surface coverage of a readily detectable quantity of adsorbed radioactive ions may be fewer than 1 in 10⁵ or 10⁶ of the sites potentially available for adsorption/ion exchange, the nature of the adsorption sites and the trace ion adsorption states must be a matter of conjecture. However, at low coverages surface heterogeneity is likely to be important and ion desorption rates should also be sensitive to average electrical double layer properties characteristic of the whole surface. This section of the thesis gives experimental results for the desorption of cations implicated in the Hileman-Snodgrass model from model surfaces into water, and attempts to provide a formal model for the experimental trace cation desorption kinetics in terms of desorption from random, weakly heterogeneous surfaces.

 \mathbb{C}^{+}

 ~ 2

5.2.ii Design and construction of the desorption/dissolution cell.

Đ.

? c

3

 \hat{U}

The principal features of the desorption and dissolution cell designed, constructed and commissioned for this phase of the investigation are presented in Figures 37 and 38. All the components are of Perspex, Teflon, Mylar, neoprene or stainless steel. The stainless steel washers and machine bolts do not come into contact with the test solutions. Tests performed using the injection of fluorescein dye confirmed that the cell, when operating with flow rates of between 4mL/minute and 28mL/minute, could be characterised as "well-mixed". Further tests, in which a radioactive tracer in the form of a solution of $H_2^{35}SO_4$ in water was injected into the cell, showed that all the detectable activity was removed from the cell after the passage of approximately 18 cell volumes of distilled water. The materials showed no evidence of retaining any detectable amount of radioactivity. The distilled, demineralized water used for all the studies in this

research was deaerated by bubbling nitrogen gas from a cylinder through the water for 15 minutes.

The specimens examined were: (i) muscovite mica, in the form of discs cut from a large slice using a #11 cork borer and (ii) slices of quartz sawn from a very large hand specimen of clear quartz. These slices of quartz were ground to a thickness of less than 1mm using a wheel and carborundum grits.

One flat, unworked surface of each specimen was contacted for 12 hours with a solution of 45Ca as CaCi2 in water, or 133Ba as BaCl2 in water for the cation desorption For the anion desorption experiments the test experiments. solution was H235SO4 in water. The specimens were then rinsed in distilled water, dried, then each mounted onto a separate 8cm diameter sheet of 16µm thick Mylar film using a thin smear of silicone sealant. After setting for 48hours, the edges of the specimens were sealed with molten wax in order to avoid any possibility of the silicone contacting the solution The desorption cell was in the cell during the experiments. then assembed with the radioactive specimen in place with the active face down into the cell in order to contact the solvent. The procedure followed was to pump deaerated, distilled water through the cell at a rate of 10mL/min for some measured period of time, seal the cell using the Teflon stop-cocks, then count the radiation from the surface passing through the specimen with a thin end window Geiger-Mueller tube and

counter. The tube and cell were mounted inside a lead shield during the entire experiment in order to ensure a low background. The background count-rate was 6 counts/minute. The blank specimens gave a count rate of 8 counts/minute. The initial counting was carried out with the cell filled with water, in order to maintain a constant geometry during the entire procedure. Experiments conducted with flow rates ranging up to 28mL/minute (more than 10 cell volumes) demonstrated that the rate of desorption appeared to be independent of flow-rate.

~

G

 $\sum_{i=1}^{n}$

5.2.iii Results and discussion.

1

?

ي.

 \mathcal{D}

The numerical data for this phase of the research are presented in **Appendix 11**. These data are summarized in the form of the graphs shown as **Figures 39**, **41**, **43** and **45**. We define the desorption factor (DF) at a time t to be the reciprocal of the residual coverage, relative to the initial coverage, for the radioacive ion. This factor, DF, is a convenient dimensionless parameter, and is the ratio of the initial coverage Q_0 to the residual coverage Q_0 .

The results of plotting log DF against log time for desorption times greater than 2 hours for SO_4^{2-} , Ba^{2+} and Ca^{2+} desorbing from mica and quartz surfaces into distilled water are shown in **Figures 40**, **42**, **44** and **46**. The log DF against log t plots are linear at t \ge 2 hours, with a range of

slopes, but not with a time dependence characteristic of a diffusion controlled desorption reaction. The lines shown in the **Figures 40, 42, 44** and **46** are best-fit lines produced by linear regression.

It has been found that the kinetics of desorption of cations on a number of adsorbents are explained by rate weakly heterogeneous desorption from random, limitina surface sites. A model proposed in order to explain how such provided by Cerofolini (111).arises was heterogeneity Suppose that a surface reaches adsorption equilibrium and is then removed from the contaminant solution and placed in a solution of such composition that trace ions desorb from the surface. Provided that desorption from surface sites is ratelimiting and that there is no appreciable re-adsorption, then after desorption has proceeded for a time t D, the desorption factor is given by equation (60).

C

$$\frac{\Theta_{o}}{\Theta} = DF = \frac{\int_{q_{m}}^{q_{M}} f \phi \, dq}{\int_{q_{m}}^{q_{M}} f \phi \exp(-k_{2}t_{D}\exp(q/RT)) \, dq}$$
(60)

The symbols are defined in the symbol table. This expression has been evaluated numerically for various trial

 \mathbf{c}

sets of parameters (110) and it has been found that at long desorption times and for Θ in the Freundlich region of the adsorption isotherm the behaviour is described by equation (61).

d(logDF)/d(logt_)=constant

оe

Ċ,

(61)

This agrees with the kinetics observed in the present study (Figures, 40, 42, 44 and 46) and in the study carried out in (110). Thus the data in the present work are consistent with Cerofolini's theory. They do not, however, support Cerofolini's theory in particular; they should be accountable for by any of the models found in the literature relating Freundlich equilibrium to surface heterogeneity. Indeed by making the approximation that there is an exponential distribution of site energies at all coverages, the Freundlich adsorption isotherm results but incorrect asymptotic behaviour is predicted. However, an approximate analytical solution can be readily found for the time dependence of the desorption factor for such a surface during desorption. This has a form which satisfies equation (49) and the experimental The approximate solution has been given (110) and will data. not be discussed further here.

From a purely qualitative point of view it is evident from an inspection of **Figures 41** and **45** that mica surfaces retain

Ba²⁺ for a much longer time than does quartz. This information allowed the work from this point to be focussed on the behaviour of mica as a model surface. The retention of the ions studied, by quartz and mica surfaces, suggests that attempts to grow surface deposits of metal sulfates implicated in the Hileman-Snodgrass model may prove fruitful. These attempts form the subject of the next phase of this study.

5.3 Growth of potential host solids on quartz and mica surfaces.

As one component of this phase of the project the chemical solution growth of hetero-epitaxial deposits of PbSO₄, CaSO₄, SrSO₄, BaSO₄ and mixed (Ba/Pb)SO₄ on quartz and mica surfaces has been investigated. This procedure has previously been used for the production of thin solid films from solution (112).

5.3.i Experimental procedure

)

1

. . . Ŋ

1

The technique used to grow the deposits was alternate immersion of the chosen substrate in a solution containing a soluble salt of the cation (e.g. Pb(NO₃)₂, Ca (NO₃)₂, Ba(NO₃)₂, Sr(NO₃)₂ or a mixture) of the compound to be grown and then in a solution containing a soluble salt of the anion (or an acid containing the anion). The substrate on which the film was growing was rinsed in high-purity distilled deionized water

~---

after immersion in each solution. The substrate was prepared from a large piece of muscovite mica using a #11 cork borer or sawn from a large hand-specimen of quartz using a diamond saw. The resulting specimen was held in nylon forceps for immersion in the solutions.

After formation of deposits the substrates were washed with a vigorous stream of distilled water, followed by rinsing with HPLC grade methanol. The surface deposits were then examined using scanning electron microscopy (SEM). Qualitative identification of the metal ions present was carried out by X-ray emission spectroscopy (XES) in the SEM.

5.3.ii Results

(t

The results of the experiments using mica and quartz as the substrates with the solution dipping technique are the presented in the form of scanning electron microphotographs (Figures 47-49). The mixture of barium, lead and calcium nitrates produced a mixed (Ba/Pb) sulfate crystal deposit rather than individual crvstals cf each compound. No evidence was found for any CaSO₄ deposit. Deposits of CaSO₄ could be made to form on quartz and mica surfaces only in the absence of other ions and at very high supersaturation.

In this approach it would seem reasonable to postulate a heterogeneous growth mechanism proceeding by chemical

combination of adsorbed ions at the solid/solution interface ("ion-by-ion" mechanism, 113) with sites on the surface acting as the initial nuclei for crystal growth.

When the surface nucleation is so slow that each layer originates in a single surface nucleus, it is not difficult to understand the formation of plane faces. The shape of the crystal is entirely given by the nucleation rate on the different faces, those with the lowest nucleation rate becoming the At high present. perhaps the only ones or largest, concentrations, or on large crystals where several surface nuclei contribute to each layer, this mechanism may lead to plane faces, because the rapid spreading of the surface makes them cooperate in they meet crystals until straightening the surface. However, since the rate of surface nucleation depends strongly on concentration, above a certain concentration range, diffusion in the bulk liquid will not be rapid enough to keep the concentration at the same level all over the crystal surface, and when the variations in rate of surface nucleation over the crystal surface are too large to be of the layers by twocompensated by the spreading dimensional growth, the faces will no longer be plane and the corners and edges will grow faster, perhaps resulting in a In apparent contradiction to this, some dendrites dendrite. grow in the direction of the crystal axes. An example is the orthorhombic barium sulfate crystals (114) which at high

2.2

concentrations develop into dendrites through enhanced growth in the direction of the two-fold axes, and not at the corners. This phenomenon has not been explained so far, but the observation of several transition shapes between typical orthorhombic forms and fully developed dendrites indicates a complex mechanism.

Experiments were subsequently performed to investigate the growth kinetics of these deposits on mica and the role of solution parameters in their formation. These experiments form the subject matter of the next section of this thesis.

5.4 Kinetics of the growth of potential host solids on model surfaces as a function of solution concentration.

Electrolytes crystallizing from aqueous solution grow by of the following elementary determined by one a rate (convection and diffusion), transport processes (89): adsorption, integration in surface spiral steps centred at dislocations, or integration in surface steps generated by polynuclear surface nucleation. The corresponding rate laws are linear for transport and for adsorption control, parabolic for spiral steps, and so-called exponential for polynuclear surface control. The frequency by which an ion enters a kink from a nearby leaving position is correlated with the dehydration frequency, and as cations in general have the smaller dehydration frequencies, only the cations determine

ð

e

the rate. The integration frequency for a cation is typically about one thousandth of the dehydration frequency.

If two or more of the four mechanisms have a combined influence on the rate they will be consecutive, and the mechanism that would be slowest at equal driving force will be rate determining. Consequently if the kinetics change with the supersaturation, a transition from parabolic at low to linear at high supersaturation will be found. Distinction between transport controlled growth and surface controlled growth is not always clear.

5.4.i Experimental

12

The technique used for the growth of the BaSO₄ and PbSO₄ deposits on mica discs has already been described in section 5.3.i of this work. The growth of these deposits was followed quantitatively as a function of the number of "immersion cycles" by determining the mass of the discs after some number of cycles, using a Mettler M55A Micro-gramatic balance with a tolerance of $\pm 1\mu g$. An "immersion cycle" is defined as 2 minutes of immersion in the cation solution, 2 minutes in the distilled water rinse, then 2 minutes immersion in the sulfuric, acid solution. The rinse water was changed after every 5 cycles. Final washing was with a vigorous stream of HPLC grade methanol. Drying was carried out in the open air. The effect of different concentrations of sulfuric

С

Ð

e 9

acid or cations on the rate of deposition was investigated by changing the concentration of each species in turn.

5.4.ii Results and Discussion

The raw numerical data obtained are presented in **Appendix II**. They are summarized in the form of the graphs shown as **Figures 51-59**. The data demonstrate the repeatability of the growth experiments for both BaSO₄ and PbSO₄. Further, they demonstrate a difference in behaviour for the two solutes in that the rate of growth of PbSO₄ appears to be linear as a function of both concentration of H₂SO₄ and concentration of Pb(NO₃)₂ while the growth of BaSO₄ is curvilinear in concentration of H₂SO₄.

Nucleation on substrates, according to Kitaev et al. (115) takes place by adsorption of primary species (moities). Growth takes place as a result of surface coagulation of these (moities), resulting in thin, adherent deposits. species However, the surface of mica and of quartz is fairly smooth and it is an experimentally observed fact that "cluster-bycluster" growth of films occurs more readily on rough surfaces (115). A cluster-by-cluster growth mechanism for growth of deposits would be supported by a structure for the deposits similar to that of the precipitate (orthorhombic). This is in fact observed (Figures 47-49) for PbSO₄. For BaSO₄ the crystals formed on the surface are not similar to those commonly encountered for this substance. Formation of MSO4 (M=Pb²⁺ or Ba²⁺) nuclei by the combination of ions on the substrate, on the other hand, requires preferential adsorption of at least one type of the reacting ions on the substrate. Ba^{2+} and SO_4^{2+} both are From this work it is known that strongly adsorbed on mica. Lead is well-known to be strongly adsorbed on many surfaces. It is possible that one of the two mechanisms may apply for the case of the PbSO4 growth (the alternative while the cluster-by-cluster mechanism) mechanism (the ion-by-ion mechanism) may apply for the Alternatively, the two mechanisms may both BaSO₄ case. compete. Further research will be required in order to clarify this situation.

Inspection of **Figure 60** shows that the concentration of SO_4^2 - increases with increasing concentration of H_2SO_4 . The value of the supersaturation in each case could probably be estimated, using Ficks Law and ionic diffusion coefficients in order to calculate the concentration of the ions involved in the adsorption layer. One may assume, for example, that lead ions are adsorbed onto the mica surface, reaching some equilibrium concentration; then, during the rinse cycle they diffuse out of the adsorption layer until some limiting concentration is reached. When the disk is immersed in the sulfuric acid solution, sulfate ions diffuse out). Reaction then occurs on the surface resulting in the formation of a PbSO₄ deposit. These

¢

11

calculations were not done. Such detailed calculations seem pointless in the context of this work; it is sufficient to conclude that the rate of growth is proportional to the concentration of H_2SO_4 and the concentration of the Pb in the case of the lead deposits. In the case of the growth of the BaSO₄, there appears to be a difference in the kinetics in terms of the effect of the sulfuric acid. The rate appears to be proportional to the concentration of $H_2SO_4^{1/2}$.

5.5 Kinetics of the dissolution of potential host solids, including 228-Ra as a micro-component, from model surfaces.

The objective of this phase of the research is to investigate the kinetics of dissolution of the potential host solids using radio-tracer methods. Once the behaviour of the host matrix is understood, a radium micro-component will be incorporated in the host solid and the dissolution followed radio-metrically. In order to achieve the second objective of this phase of the research a radium tracer is required. Consideration of the properties of the isotopes of radium led to the belief that the most convenient form of radium to use for our purposes was 228-Ra. This isotope, a very weak β -emitter with a half-life of 5.75a (68), may be determined radio-metrically by allowing it to reach secular equilibrium with its daughter, 228-Ac; this latter is a powerful β -emitter and is readily counted. Equilibrium is attained in a time of approximately 24h, based on a half-life of 6.4h for 228-Ac

(68). The preparation of 228-Ra, an isotope not available commercially, forms the material of the next section of this work.

5.5.i The preparation of carrier-free 228-Radium from thorium, using cation exchange columns.

During the entire procedure the 1977 Recommendations of the International Commission on Radiological Protection were followed with respect to working conditions and radiation exposure. All reagents and water used were of the best available quality.

The procedure that was used was similar to that described in (116). A mass of 100g of thorium nitrate was taken from a sample known not to have been separated from This was dissolved in its' daughter products for 20 years. 200mL of 8M nitric acid and the resulting solution was extracted six times over a period of 20 minutes with 100mL aliquots of a 40% (v/v) solution of tri-butyl phosphate (TBP) in the aqueous phase was After the sixth extraction, benzene. washed twice with 200mL portions of dry benzene (taking the usual precautions when working with this carcinogenic compound) in order to remove residual TBP and it was then evaporated to dryness in a round-bottom flask. The residue was treated with a small volume of equal amounts of 71% perchloric acid and concentrated nitric acid and this was

evaporated to dryness. The dry residue was dissolved in 70mL of 0.5M ammonium lactate. This solution was then passed through a 50-100 mesh column (2cm in diameter and 20 cm in length) of Dowex[™] 50W-X8. This was carried out at reduced pressure using the apparatus shown in Figure 50. The column was then washed with 50mL of an 0.7M solution of ammonium lactate, using a flow rate of 10 mL min⁻¹, to remove any rare earth cations originally present in the thorium. The column was then washed with 450 mL (approximately 30 column volumes) of distilled, demineralized water. Toward the end of this washing procedure small volumes of the eluate were evaporated to dryness on a hot plate in order to test for the presence of excess lactate.

The 228-radium was washed from the column with 200mL of 3M nitric acid, using a flow rate of 10 mL min⁻¹. The solution was then evaporated to dryness in a 100mL Pyrex beaker. A small amount of white residue was destroyed by boiling with freshly prepared agua regia. Upon evaporating no obvious material remained in the beaker. but intense radioactivity was found to be present when a survey radiation detector was placed at the mouth of the beaker. The trace of material in the beaker was taken up in 1.0mL of 0.5M HCl (two 0.5mL portions) and stored in glass vials.

en

ര

ς.

Gamma-ray spectroscopic analysis of a sample prepared using this procedure was carried out using an intrinsic

~

germanium detector and a multi-channel analyser (Canberra System 90). The resulting data are shown in Table 20.

A 3cm column of Dowex 50W-X12 was then used to separate out 212Bi and 212Pb followed by 228Ac, daughters of 232Th. Ammonium lactate (0.65M) was the eluant.

Samples of equal volume (10 drops) were deposited onto aluminium planchets at intervals of one minute, evaporated to dryness and counted. All counting was performed using a Mullard MX168 thin end window G.M. tube operating at a plateau voltage of 420V, and a Griffin Timer/Scaler unit. The column was then washed with 150 mL (approximately 50 column volumes) of distilled, demineralized water to remove lactate from the column. The ²²⁸Ra was then stripped from the column using 3M nitric acid, the solution evaporated to dryness in a small Teflon beaker and the trace of ²²⁸Ra taken up in 1mL of 0.5M HCl and stored in a snap-top glass vial.

5.5.ii Discussion

The performance of the final separation was verified by the radiometric identification of the separated components using their half-life. In the case of 228-Ra, an extremely soft β - emitter, the method used to verify the identity of the nuclide was the observation of the rate of ingrowth of the 228-Ac daughter. The results of these investigations are presented in the form of the regression equations presented in **Table 22.** The slopes of the straight lines represent the radioactive decay constants λ for the appropriate isotope and enable the half-life of the isotope to be calculated from the equation:

 $T_{1/2} = \ln 2/\lambda = 0.6931/slope of the line$ (62)

с С

ι÷.

As 16 hours had elapsed between the initial preparation and the gamma ray spectroscopic examination, it was expected that extensive ingrowth of 228Ac (T_{1/2} = 6.13h) and traces of other 232Th progeny would have occurred. A version of the decay scheme of 232Th (117) is shown in Table 21. From a perusal of this Table, the accompanying listing of gamma ray energies obtained from the spectroscopic examination (Table 20), and tabulated gamma energies of the nuclides (118), it is possible to assign all the peaks. The results of this assignment are summarized in Table 20, column 3. Α comparison of the experimental and literature values for the half-life of each of the resolved components of the decay Table series is presented in 23. The results of the assignment of the identity of each peak and the values for the half-life of each resolved component confirm both the identity of the ²²⁸Ra and the success of the separation.

3

 \odot

5.5.iii Dissolution of the host matrix, as followed by radiotracer techniques.

The procedure followed was to grow BaSO4 and PbSO4 hetero-epitaxial deposits on the surface of mica disks using the "solution dipping" technique previously described. In this case, however, a 500µL aliquot of a stock solution of either 133Ba2+ or 35SO42- was added to each of the 0.1M Ba(NO3)2 or Pb(NO3)2 solutions used in the deposition experiment. This resulted in the production of a specific activity for the deposited BaSO₄ of approximately 2x10⁵cpm/g of BaSO₄. The specific activity for the deposited PbSO4 was approximately 8x104 cpm/g of PbSO4. The counting of the specimens was Development & Machine Atomic using an out carried gas-filled counter operating at 2.6kV with a P4 Corporation potential ensured that the counter was filler gas. This operating in the linear range of its characteristic. In each case a constant geometry was maintained by counting the specimens as they lay on the surface of the Mylar film of the dissolution cell. This was filled with the sulfuric acid used for the dissolution experiments. The concentration of the sulfuric acid used for the dissolution experiments was 1.0x10-3 M. In each case, at least 10,000 total counts was collected for each datum shown on a graph.

5.5.iv Results and discussion.

6

0

Ŋ)

The numerical data are found in Appendix II. They are summarized here for BaSO4 in the form of the graphs shown as

Figures 62-64. Inspection of Figures 62-64 shows that the rate of dissolution of $BaSO_4$ appears to depend on the flow-rate of the solvent. This fact is demonstrated by Figure 65, a plot of rate of dissolution against flow rate. A plausible explanation of this phenomenon would be that some of the $BaSO_4$ re-precipitates onto the surface of the solid at low flow rates, but is swept away by the solvent at the higher flow-rate before re-precipitation can occur. In each case the dissolution appears to be congruent dissolution; that is a layer by layer dissolution occurs.

÷

Attempts to perform the same experiments for PbSO₄ failed. The rate of dissolution into the sulfuric acid at even the lowest flow rate was too rapid to permit the flow-rate dependence to be investigated using this technique. Further comment on this case will be deferred until the final chapter of this thesis, when it will be briefly discussed under the topic of "suggestions for further research". No further investigations of the dissolution of lead-based solid solutions were performed.

5.5.v Dissolution of BaSO₄ labelled with 228-Ra.

The procedure followed was to grow BaSO₄ deposits on the surface of mica disks, using the "solution dipping" technique previously described. In this case, however, 500μ L of a solution of 228Ra²⁺, prepared using the technique described in section 5.5.i, was added to the 0.1M Ba(NO₃)₂

з
solution used in the deposition experiment. This resulted in the production of a specific activity for the deposited BaSO4 of approximately 1.8x10⁵cpm/g of BaSO₄. The dissolution cell previous procedure for the in the used as then was with dissolution of BaSO₄ labelled investigation of the The solvent, as before, was 1.0x10⁻³ M sulfuric 133_{Ba}2+ acid. The flow rate was set at 19.5mL/minute, in order to be in the flow-rate independent region for the dissolution of BaSO4. As before, the counting was carried out using a gas-For each measurement a total of at least filled counter. 10,000 counts was collected.

5.5.vi Results of the dissolution of BaSO₄ labelled with 228-Ra.

The raw numerical data are presented in Appendix II. They are summarized in the form of the graph shown as Figure 68. It would appear that the dissolution of the BaSO₄ host matrix, followed in this case by counting of the 228-Ra, follows the same pattern as before-namely congruent dissolution-with the surface area remaining constant.

Absolute dissolution rates are not available, due to the lack of information concerning the actual surface area of the deposits. Nevertheless it would appear from the relative rate of loss of BaSO₄ as measured by these two different methods-133Ba labelling and 228Ra labelling-that the radium is lost at the same rate as the barium sulfate. This is demonstrated by comparing the slope of the graph from each experiment. Within the experimental error due to counting, these values-0.0828 for the ²²⁸Ra label and 0.0815 for the ¹³³Ba label-are the same. It may be concluded that the radium appears to follow the barium in the dissolution process.

Experiments on dissolution kinetics are usually carried out with variable driving force by changing the undersaturation (119, 120), in order to relate the kinetics to the microscopic processes operating at the crystal/solution interface. The relationships obtained in this research must, at present, be left as empirical relationships. Replication of the dissolution experiments in order to provide appropriate ⁽⁾ confidence intervals for these data was not performed.

in.

0

ۍ:

0

 \bigcirc

Table 20Selected peaks from the gamma ray spectrum of the
eluent (Canberra Series 90 system with an intrinsic Ge
detector)

Peak/FWHM

e

Identity

238.4	212 _{Pb}
1.14	208-11
277.3 1.31	20011
327.9	228 _{Ac}
.1.22	[%] 208тı
1.55	
911.2	228 _{Ac}
1.55	· · · ·

228Ra gamma peaks are < 31keV and consequently were not observable.

÷.,

С

ວ

Radionuclide	Half life	Alpha & beta en	ergies(Mev)
	· <u>-</u>	α	β
232-	4.44.4010-		
	1.41X10 ⁻⁹ a	3.95	-
228 _{Ra}	5.75a	4.01	0.039
28 _{Ac}	6.13h	-	0.49
			0.61
			0.98
			1.01
			1.17
			1.74
		L.	2.08
²⁸ Th	1.91a	^{//} 5.341	_
-		5.423	_
²⁴ Ra	3.62d	5.449	_
20 _{Rn}	55.6s	6.288	-
216 _{Po}	0.15s	6.779	-
212 _{Pb}	10.6h	~	0.158
			0.334
			0.573
²¹² Bi	1.01h	6.051	2.246
		6.090	1.519
212 _{P0}	298ns	8.875	
208Ti	3.05m		1.031
	1	-	1.283
,			1.517
		9.00 - 10 - 10 - 10 - 10 - 10 - 10 - 10 -	1.794
208pb	stable	- -	_
		9.0 <u>1</u>	· · ·
		2	c
		· .	·
	С		
a a		e,	8 °
	- 2		х ^а н Г
1			0
, ,			. · · · .
18 C			-
5	•		
	o		~ <u>~</u> ~
	,		19 - S
		e .	5 4

ů ç

с

20

2.2

=

ę

а

Table 21 Decay scheme for 232-Thorium

Table 22 Regression equations for the radioactive decay constants of the daughter products of radium-228.

- Ú		
Isotope	Regression equation	Correlation
		<u>coefficient</u>
228 _{AC}	In Net Counts = 7.1236 - 0.0018 Time	1.00
212 _{Pb}	In Net Counts = 7.0186 - 0.001 Time	0.99
212 _{Bi}	In Net Counts = 6.5959 - 0.0108 Time	1,00

 \mathbb{C}^{n}

ł

، ،

2

5

Ċ

c

9 ^C

e

£

0

2

G -

0

;

 ϕ

¢

.

С

e.

\$

æ

0

Ŀ,

t;

ø

155

Table 23 Comparison of experimental and literature values for half-life.

1.0111	6
10.6h	6.7
6.13h	4.7
	10.6h 6.13h ⁽⁾

 σ

c

C

ç

c

C

ु ु

Q

;

С

с

0

୍ କ

73

5

e

c,

٢

 ρ

0

-

0

ć

¢

Ċ

¢,

Q

Figure 37 Drawing of desorption/dissolution cell used in order to study (i) desorption of various ions and (ii) dissolution of BaSO₄ and (Ba/Ra)SO₄ hetero-epitaxial deposits, from mica surfaces.

ñ

ş

C

 $\langle \cdot \rangle$

, ċ



Figure 38 Showing the arrangement of the dissolution cell and the solution reservoir and receiver. The flow rate is controlled by (i) the pump speed and (ii) the internal diameter of the pump tubing.

 \mathcal{D}

÷,

. بې ا





. T

o

Fraction of Ba remaining

:-

a

Ø

Ĺ

¢

- ----

Figure 39 Plot of fraction of ${}^{35}SO_4$ retained on a specimen of muscovite mica. The ${}^{35}SO_4$ is desorbing into distilled, demineralized water which has been deaerated using nitrogen.

e

Э

 ζ_{i}

с

Ø

 \vec{b}

o

o

e e

Æ

٤,

 ${\mathcal O}$

ċ

5

-

4

 ∂_{2}

X

ţ



Figure 40 Plot of log (desorption factor) as a function of log (time of desorption) for ${}^{35}SO_4$ desorbing from mica into distilled water. The line fitted by regression analysis has an equation: log(DF)=0.213570*log(time)-0.00782. The correlation coefficient was 0.9942.

0

¢

0

c



Log desorption factor.

Ĵ

20

¢

Figure 41 Plot of fraction of ¹³³Ba retained on a specimen of muscovite mica. The ¹³³Ba is desorbing into distilled, demineralized water which has been deaerated by means of nitrogen.

 $\dot{\alpha}$

0

С

0



Figure 42 Plot of log (desorption factor) as a function of log (time of desorption) for 133Ba desorbing from mica into distilled water. The line fitted by regression analysis has an equation: log(DF)=0.38146*log(time)-0.49777. The correlation coefficient was 0.9676.

С

(9) 4

0

с с Ù

୍ତି ୧ ٠ł ا

ĩ,



Figure 43 Plot of fraction of 45 Ca retained on a specimen of muscovite mica. The 45 Ca is desorbing into distilled, demineralized water which has been deaerated by means of nitrogen.

()

ē

\$

λĮ.

c

.

ú

0

್ರಾರಿ



Proction remaining.

Ģ

5

0

ø

Figure 44 Plot of log (desorption factor) as a function of log (time of desorption) for 45 Ca desorbing from mica into distilied water. The line fitted by regression analysis has an equation: $\log(DF)=0.36451*\log(time)-0.04032$. The correlation coefficient was 0.9697.

ŋ

c

0

С

Ð

 \mathfrak{L}



ථ

Ĩ.

Figure 45 Plot of fraction of ^{133}Ba retained on a specimen of quartz. The ^{133}Ba is desorbing into distilled, demineralized water which has been deaerated by means of nitrogen.

С

Ċ

5

Û

Q

e, c

æ

c



Fraction romaining.

.

ø

Figure 46 Plot of log (desorption factor) as a function of log (time of desorption) for 133Ba desorbing from quartz into distilled water. The line fitted by regression analysis has an equation: log(DF)=1.26407*log(time)+0.59768 The correlation coefficient was 0.9894.

С

Ģ

ø

Ο

С

ÿ

ŋ



ົງ) (L_{ີ 1)}

يتبيته ترز

C

Figure 47 Scanning electron micro-photographs of heteroepitaxial deposits on mica, grown from aqueous solution: (a) BaSO₄ (b) PbSO₄ (c) mixed (Ba/Pb)SO₄.

ı,

5

١.

Ō

0.0

¢

6

ß

 $\mathbb{C}^{(n)}$



75

e

З



О 10 и m 200 kW 570ЕЗ 0096-005 МІСА

•

•

Figure 48 Scanning electron micro-photographs of heteroepitaxial deposits on quartz, grown from aqueous solution: (a) BaSO₄ (b) PbSO₄ (c) mixed (Ba/Pb)SO₄.

c

0

. 3







. .

.

•

 \mathcal{C}

Figure 49 Scanning electron micro-photographs of heteroepitaxial deposits on muscovite mica, grown from aqueous solution: (a) SrSO₄ at 6500x (b) SrSO₄ at 3540x.

ς.

 \lesssim

Ċ.

З._т

Ű

Û

168

Q





'n

¢

Figure 50 Apparatus used to pass solution through ion exchange columns at reduced pressure. Column shown is 3-cm long of Dowex 50W-X12.

Ϋ́,

]į

σ

O

:20

¢

 \circ

Ċ

é

Ũ



ý.

Figure 51 Plot of rate of growth of $BaSO_4$ on mica. The concentration of the $Ba(NO_3)_2$ solution used as a source of Ba^{2+}_{eq} ions was 0.1M; the sulfuric acid concentration was 6m. The regression line drawn for the mean behaviour has an equation: Mean mass/cm²=2.09652e-5*Number of cycles+1.27753e-4. The correlation coefficient was 0.9874

Q

-

 \mathcal{Z}

C

ų,


b

ť

Figure 52 Rate of growth of BaSO₄ on mica from 0.1M barium nitrate solution and various concentrations of sulfuric acid. The four sets of points correspond to:

#1 $[H_2SO_4]=9.9\times10^{-3}$ M; the regression equation for these data is: g/cm².cycle=9.1258e-6*Number of cycles-7.53100e-6. The correlation coefficient=0.983.

#2 $[H_2SO_4]=0.504M$; the regression equation for these data is: g/cm².cycle=3.257200e-5*Number of cycles-1.7900e-6. The correlation coefficient=0.978.

#3 $[H_2SO_4]=0.99M$; the regression equation for these data is: g/cm².cycle=5.22620e-5*Number of cycles+3.82600e-5. The correlation coefficient=0.992.

#4 $[H_2SO_4]=5.994M$; the regression equation for these data is: g/cm².cycle=8.4156e-5*Number of cycles+1.23380e-4. The correlation coefficient=0.970.

i, N

c

1

iŁ.

С



9 r

Figure 53 Rate of growth of $BaSO_4$ on mica as a function of concentration of sulfuric acid. Concentration of Ba^{2+} is constant at 0.1M.

5

ć

:

Ç

С

.



÷

Rate of growth g/cm2.cycle. (Times 10E-5)

Figure 54 Rate of growth of BaSO₄ on mica as a function of $\sqrt{concentration}$ of sulfuric acid. Concentration of Ba²⁺ is constant at 0.1M. The regression equation is: Rate of growth=3.11436e-05*[H₂SO₄]^{0.5}+1.14178e-05. The correlation coefficient is 0.977.

1

 \mathbb{C}^{+}

٨

 \mathcal{O}_{ii}

 \mathcal{O}



Rate of growth of BaSO4 (g/cm2.cyale). (Times 10E-5)

c

.

Figure 55 Rate of growth of $BaSO_4$ on mica as a function of concentration of barium nitrate. Concentration of sulfuric acid is constant at 6m. The regression equation for the line is: Rate of growth=4.510442e-04*[Ba]+2.093576e-05. The correlation coefficient is 0.995.

0

ć

Ċ

6

¢

 \bigcirc

순

 $\simeq \odot$

G



ĥ

0

Figure 56 Plot of rate of growth of PbSO₄ on mica. The concentration of the Pb(NO₃)₂ solution used as a source of Pb²⁺_{aq} ions was 0.1M; the sulfuric acid concentration was 6m. The regression line drawn for the mean behaviour has an equation: Mean change in mass/cm²=8.65688e-5*Number of cycles+1.7976e-4. The correlation coefficient was 0.9769.

Ü

17

G

Ğ

12

C

 $\mathcal{O}_{i_{1}}^{i_{1}} \rightarrow$



(È)

ù

Figure 57 Rate of growth of PbSO₄ on mica from 0.1M lead nitrate solution and various concentrations of sulfuric acid. The four sets of points correspond to:

#1 $[H_2SO_4]=9.9x10^{-3}M$; the regression equation for these data is: g/cm².cycle=9.924e-6*Number of cycles-6.972e-6. The correlation coefficient=0.98.

#2 $[H_2SO_4]=0.504M$; the regression equation for these data is: g/cm².cycle=2.017e-5*Number of cycles+8.886e-6. The correlation coefficient=0.976.

#3 $[H_2SO_4]=0.99M$; the regression equation for these data is: $g/c_{\underbrace{m}^2}.cycle=3.441e-5*Number$ of cycles-6.920e-6. The correlation coefficient=1.00.

#4 $[H_2SO_4]=5.994M$; the regression equation for these data is: g/cm².cycle=1.663e-4*Number of cycles+9.662e-6 The correlation coefficient=1.00.

5

5

 i^{\simeq}

 \mathcal{O}

ıtı

176



Æ

Ð

Figure 58 Rate of growth of PbSO₄ on mica as a function of concentration of sulfuric acid. Concentration of Pb²⁺ is constant at 0.1M. The regression equation is: Rate=2.63331e- $05*[H_2SO_4]+8.3402e-06$. The correlation coefficient=0.999.

ũ

¢

Ą.

0

Ø

(j

Ŋ.

Q

С



Ċ

Figure 59 Rate of growth of PbSO₄ on mica as a function of concentration of lead. Concentration of H₂SO₄ is constant at 6M. Equation of the regression line: Rate=7.79522e-04*[Pb]+2.38414e-05. Correlation coefficient=0.9982.

(C)

Ŀ

Q

Q

0

F

2

2

c

 $\langle \cdot \rangle$

0

 \odot

. میر بر ا



Figure 60 Plot of concentration of SO_4^2 and HSO_4^- species in H_2SO_4 as a function of [H_2SO_4].

5

c e

c

e

o

σ

0

с

()

0

С

12 12

æ









Figure 61 Plot of net counts per minute against mass change per cm² for $(133-Ba/Ba)SO_4$ growing on mica. Three replicates are shown. The deposits were grown from 0.1M Ba(NO₃)₂ solution and 6M H₂SO₄ solution.

Ū,

~

 \mathbb{C}^{2}

 \overline{C}



 \bigcirc

ċ

ŝ

ing nimi vetnuoo teV

Ę.

Figure 62 Plot of mean net counts per minute against mean mass change per cm² for $(133-Ba/Ba)SO_4$ growing on mica. The deposits were grown from 0.1M Ba(NO₃)₂ solution and 6M H₂SO₄ solution. The regression equation is:

Mean net counts/minute=1.01462e06*Mean change in mass/cm²+2.07473e01. The correlation coefficient is 0.987.

C

Ø

0 0

\$

Q

0

177.

٢

e

G

Ο

 $^{\circ}$

2

C

¢



.etunim\etnuco ten noeM

Figure 63 Dissolution of 133-Ba labelled $BaSO_4$ into $1.0 \times 10^{-3} M H_2SO_4$ at 2.8mL/minute flow rate. The equation of the line is: $(A_0 - A_1)/A_0 = 0.055516*Time$ of flow+0.001050.

0

V,

٢

The correlation coefficient is 0.999.

ķС

n°

ŝ,



n Ti

0

ĉ

Figure 64 Dissolution of 133-Ba labelled $BaSO_4$ into 1.0x10⁻³MH₂SO₄ at 10mL/minute flow rate. The equation of the line is: $(A_0-A_t)/A_0=0.072684*$ Time of flow+0.007543. The correlation coefficient is 0.990.

C

<

J

c

1

4)

 $^{\circ}\rho$

ĨĿ

5

 $\mathbf{\hat{c}}$

<u>।</u>

Ċ,

¢

 \mathcal{G} :

ہ ن

 ${\mathfrak{S}}$

ç

ſ

c

ę.

c

P

ø

Ċ

0



2

ຸດ

Figure 65 Dissolution of 133-Ba labelled BaSO₄ into 1.0×10^{-3} MH₂SO₄ at 19.5mL/minute flow rate. The equation of the line is: (A₀-A_t)/A₀=0.081485*Time of flow-0.0015.

Ģ

e

 \mathfrak{O}

C

The correlation coefficient is 0.999.

 $\leq \langle \cdot \rangle$

ζ1

 σ



5

04\(14--04)

Figure 66 Rate of dissolution of 133-Ba labelled $BaSO_4$ into $1.0x10^{-3}MH_2SO_4$ as a function of flow rate. Each datum represents the slope of the graph in the previous three Figures.

0

n.

0

ے

đ

Ċ

Ø

()

ė



Ú

ø

ŧ

Ŀ

Ö

Normalized rate of dissolution.

; 2

Figure 67 Growth of (228-Ra/Ba)So₄ on mica. The count rate was determined using a gas-flow proportional counter, with the mica specimen resting on the desorption/dissolution cell window. The equation of the line is: Counts/minute=1.772128e05*Mass+7.167618.

11

Ũ

The correlation coefficient is 0.9946.

 ϕ



i E

Figure 68 Rate of dissolution of $(228-Ra/Ba)SO_4$ solid solution into $1.0x10^{-3}MH_2SO_4$ at 298K. Flow rate =19.5mL/minute. The equation of the line is: Normalized rate of dissolution=8.28e-02*Time+2.4e-03.

The correlation coefficient is 0.988.

0

С

.

ĺŕ:



t

J

Summary and conclusion to the Thesis.

6.i Contributions to knowledge.

Consideration of the gaps in the data required to evaluate the Hileman-Snodgrass model led to the definition of the goals for this research. These goals were:

(i) To determine the solubility of potential host solids such as $BaSO_4$ and $PbSO_4$ in H_2SO_4 - H_2O solutions from 0 to 6M in concentration and at 25^0C and 60^0C .

(ii) To model such data for solubility in sulfuric acid using the Pitzer activity coefficient model. Where parameters required for the model were not available in the literature, these parameters were to be estimated using appropriate numerical techniques.

(iii) Data were to be obtained for the rate of desorption of anions and cations implicated in the model, from appropriate surfaces.

(iv) Attempts would then be made to grow potential host solids on model surfaces, if the desorption experiments suggested that these growth experiments held hope of being successful.

188

d'
(v) The kinetics of the exchange and adsorption of cations implicated in the model were to be investigated and modelled.

(vi) The kinetics of the growth of the potential host solids on the model surfaces would be examined as a function of solution concentrations.

(vii) The dissolution kinetics of these surface deposits would be determined using radio-tracer techniques. Surface deposits would then be grown which incorporated radium as a micro-component in the host matrix. The dissolution kinetics of the radium micro-component, followed by counting, would subsequently be related to the rate of disolution of the host matrix.

Consideration of the content of the previous chapters shows that, with the exception of the investigation of the dissolution kinetics of lead-based solid solutions involving 228Ra, these objectives have all been successfully achieved.

(i) The solubility of potential host solids such as BaSO₄ and PbSO₄ in H₂SO₄-H₂O solutions from 0 to 6M in concentration and at 25° C and 60° C have been determined experimentally by (a) the radiotracer method in the case of BaSO₄ in H₂SO₄ at 25°C and 60° C; (b) a method using ICP/MS in the case of PbSO₄ in H₂SO₄ at 60° C.

(ii) The data obtained for the solubility of PbSO₄ and BaSO₄ in sulfuric acid were then modelled using the Pitzer

8 ¹ °

189

<u>یم د</u>:

Į.

÷,

e

 \mathcal{X}_{i}

activity coefficient model. Parameters required for the model were estimated using computer programs developed for the purpose. These programs are available for both IBM and MacIntosh computers and, in themselves, form a useful contribution from this research.

(iii) Data were successfully obtained for the desorption of SO_4^{2-} , Ba^{2+} , Ca^{2+} , ions implicated in the model, from mica and quartz surfaces. These data were subsequently modelled, using a model produced by Cerefolini (111) and found to be useful in situations where a model of desorption at low coverages was needed.

(iv) Potential host solids, including SrSO₄, were successfully grown on quartz and mica surfaces using a "solution dipping" technique. Their identity and morphology was established using scanning electron microscopy.

Ś.

5

The kinetics of the exchange and adsorption of (v) cations implicated in the model, onto the surfaces of large, were investigated and modelled, at room sinale crystals temperature and at 60⁰C. It was found that the parameters of the model could be related to rate constants for transport processes occurring at the surfaces of the crystals. Values derived for the activation free energy for some were processes-such as adsorption, desorption, integration at kinks and detachment from kinks-believed to be involved in the exchange and crystal growth processes.

(vi) The kinetics of the growth of the potential host solids on model surfaces was examined as a function of solution concentrations. It was found that the rate of growth of surface deposits was highly repeatable and was related to the solution concentrations.

(vii) The dissolution of these surface deposits into dilute sulfuric acid was followed using radio-tracer techniques, by labelling the BaSO₄ with ¹³³Ba²⁺ and the PbSO₄ with 35SO₄² - as tracers. The experiment for PbSO₄ dissolution failed-dissolution was too rapid to be followed under the experimental conditions used. Surface deposits were then grown, which incorporated radium as a micro-component in the host matrix. This necessitated the production of 228Ra, а radio-nuclide not available commercially. The radiochemical procedure needed was developed in our laboratories. The dissolution rate of the radium micro-component, followed by counting, was found to be essentially the same as the rate of disolution of the BaSO₄ matrix.

6.ii Contributions to the literature.

One paper based on the data for the solubility of PbSO₄ in H_2SO_4 is currently undergoing revision for re-submission to Geochimica et Cosmochimica Acta; another based on the solubility of BaSO₄ in H_2SO_4 is "in preparation" for publication in the same journal. The available literature data for the

solubility of $RaSO_4$ in H_2SO_4 has been modelled using the Pitzer formalism, which appears to give a reasonable description of the solubility. This will also be submitted for publication as a Letter in Geochimica et Cosmochimica Acta.

Three papers have been produced and published as a result of the investigations into the growth of surface deposits on quartz and mica surfaces (121, 122, 123).

The radio-chemical procedure needed to prepare 228Ra was developed in our laboratories and formed the basis of a publication in International Journal of Environmental Analytical Chemistry (124).

A paper is "in preparation" based on the data and the modelling of the desorption experiments, for submission to the Journal of Radioanalytical and Nuclear Chemistry, Articles.

A paper is "in preparation" based on the data for the exchange and adsorption of cations implicated in the model, for submission to the International Journal of Environmental Analytical Chemistry.

A paper is "in preparation", based upon the investigations of the rate of growth and dissolution of potential host solids, including those involving 228Ra, for submission to International Journal of Environmental Analytical Chemistry.

Ű

Ö

σ

(1

6.iii Suggestions for further research.

During the course of the researches described in this thesis, a number of other activities were attempted, or suggested themselves. A series of solid solutions with various mole fractions of barium and lead, containing 228Ra as a micro-component, were prepared by the solution dipping technique used in this work. The intent was to investigate the dissolution kinetics of the lead/barium/radium solid solution series, following up the work of Kornicker et al. (125). It was apparent from the work of Kornicker that this investigation would represent a major undertaking, probably constituting a of thesis. The surface constitution new unlabelled barium/lead solid solutions prepared using this technique was determined by dissolving the surface deposits from the mica using alkaline E. D. T. A. and an ultrasonic cleaner. The ratio of Ba/Pb was then determined using A. A. S. techniques with barium, and lead standards. The data provided by the A. A. S. analysis, using the available equipment, was not of a quality to permit unequivocal conclusions to be reached with regard to the ratio of barium to lead in the surface deposits. In the authors opinion this work should be repeated using ICP/MS or some other technique of equivalent precision (e. g. graphite furnace A. A. S.); the surface deposits of known constitution could then be used as standards for X-ray emission spectroscopy in the S. E. M. It is not possible to determine the

G

composition of the surface deposits by X-ray emission spectroscopy in the S. E. M. without such standards, due to interference from elements, such as barium, in the substrate.

The parameters for the lead and barium sulfate systems, obtained by modelling using the Pitzer formalism, should be subjected to testing in other regions of the phase diagrams of these substances. Following a suggestion made by Professor Monin in his review of the paper submitted to Geochimica et Cosmochimica Acta, this could be done for PbSO₄ by using existing parameters and data for the PbSO₄-H₂SO₄-HCl system. These data are found in Seidel (57).

The kinetics of dissolution of PbSO₄ into dilute sulfuric acid could not be followed by means of the technique used for BaSO₄. Thus the possible relationship between PbSO₄ and RaSO₄ is still not clear. A different approach would have to be followed-perhaps the use of a column technique (126). In addition, an investigation of the kinetics of dissolution of Ba/RaSO₄ as a function of concentration of H₂SO₄ should be performed. This could readily be accomplished using the dissolution cell used in this research.

(;

 \mathcal{L}

From the point of view of the Hileman-Snodgrass model, these researches tend to support the major hypotheses of this model. The required surface deposits of BaSO₄, PbSO₄ and

2

0

ñ

mixed (Ba/Pb)SO₄ do form readily on both quartz and mica surfaces-materials likely to be present in the mill process streams.

c

ć

с) (З

 $\dot{\mathbb{O}}$

n

0

ŗ,

С

õ

÷

2)

4

¢

0

ē

c

5

ŝ

ે ડિજે

¢

Ċ

q p

Ç

0

 $\|$

-____

Ċ

0

Ą

" р

÷

ŝ

Appendix I (a) Graphical results for the solubility of PbSO₄ in Na₂SO₄ solutions.

The top graph in each case shows the experimental data and identifies the source. The lower graph shows the result of fitting the data using the Pitzer model for the activity In each case the coefficients for all of the ions involved. solubility of the PbSO4 in water, at the temperature of the experiment, was included in the data being regressed. The data were given in (57) as mol/L and mg/L units of concentration. These data were converted to the molal concentration scale using the conversion formulae in the Chemical Rubber Company Handbook of Chemistry and Physics, 55th edition, D-119. Where the density of the solution was required it was assumed equal to that of the Na2SO4 solution. Data for the density of these solutions were taken from the Table in the same Handbook. í., ي ج

c

0 c

Ø

15

C



Ċ



· ·

Ð



(b) Numerical data for the filtration of radio-barium using cellulose acetate and P.T.F.E filter media.

21

e

 $\langle N \rangle$

The nature of the filter materials used for the filtration of radio-active, trace-level solutions is a source of concern. Lind et al. (80) appear to have lost much of the 226Ra activity from solutions in water due to filter losses. The use of cellulose acetate filters appears to be common in connection with recent tracer experiments in the N. U. M. T. project.

However, our experience in this investigation leads to reservations concerning the use of such filters. The following data, obtained for an aqueous solution of $133Ba^{2+}$ in distilled water, lends some support to this concern:

Solution #1: Unfiltered 25279counts/200s

Solution #1: <u>Filtered</u>through 0.22µm cellulose acetate (Sartorius III) 1163/200s

The filter, counted in the well of the scintillation counter, gave 25582/200s; essentially all the activity is on the filter (to within 1.2%).

Background counts: 1036/200s

2.0

Solution #2: Unfiltered 2083/200s

Solution #2; <u>Filtered</u> through 0.45µm P. T. F. E. filter media (Gelman Scientific) 2207/200s

At this point in the program we began to use the 0.2 μ m P. T. F. E. filter media used throughout the project.

¢

Table	11.1	Desorption	of	Ва	from	mica		
		Time(hours	<u>;)</u>		<u>Co</u>	unts/minute	<u>(net)</u>	
		0.00				301.90	30min	counts
		0.36				285.60		
		0.53				278.80		
		1.22				266.70		
		2.12				262.30		
		18.27				224.70		
		21.07				212.20		
		22.89		1.5		209.40		
		67.10	5			190.20		
		67.80				178.50	ŀ	
		91.00				173.50		
		97.00				169.70		
		115.20				160.30	,	
		139.20				146.04		
		162.60				143.52		
.*		185.45				136.08		•
		186.10				126.57		
		210.10				121.36		
		211.90				113.58		

Appendix II Numerical results for the desorption, growth and dissolution experiments

Natural background=5.13c.p.m.

Blank count of mica=7.07c.p.m.

 \mathcal{O}^{+}

С.

Both of the above determinations base on 15m counts.

 $^{\circ}$

Table II.2 Desorption of Ca from n	nica
------------------------------------	------

τ

:

`

ç

a

ć

ວ

<u> Time(hours)</u>	<u>Counts/minute (net)</u>		
0.00	2240.8	5min counts	
0.33	2088.6		
0.53	1988.2		
0.78	1880.4		
1.03	1794.8		
1.37	1709.2		
1.62	1597.8		
9.03	1371.2		
9.28	1228.6		
9.58	1144.4	<i>,</i> ,	
10.31	1123.2 <u>~</u>		
10.58	1100.2 /}		
10.87	1061.2 🖉	¢	
11.45	1048.8		
12.70	927.4		
13.53	886.2		
14.28	885.2		
15.28	884.2		
32.40	768.8		
32.98	725.2		
34.45	700.8		
35.87	692.0	· •	
37.37	638.0		
38.13	620.0		
56.95	560.2		
58.12	546.0		
59.15	543.4		
60.45	519.6		
80.95	488.8		
82.23	456.6	Ę	
83.00	454.8	~	

J

2

ŝ

Ъ

•

ir.

<u>Time(hours)</u>	<u>Counts/minute (net)</u>
0.00	13399.0
0.10	10519.0
0.22	8614.0
0.63	7563.0
0.96	3886.0
1.41	2061.5
2.59	1630.3
2.62	1212.8
3.20	770.7
3.95	609.6
4.43	445.9
5.72	395.9

7

,

2

Ģ

.*

. .

e

Table II.3 Desorption of Ba from quartz.

ι.

-[5

<u>Time(hours)</u>	<u>Counts/minute</u>	<u>(net)</u>
. 0	157.4	
0.016	130.8	
0.033	125.0	
0.05	124.5	
0.066	122.0	
0.317	116.3	
16.317	89.8	ţ
112.3	58.79	
129.7	57.30	
131.4	54.87	
133.04	56.30	
135.71	56.19	
137.71	56.68	
155.18	55.31	

Q

c

Ċ

, **.**

· 2

\$

0

0

\$

c

С

\$

...

с

σ

ŀ

ç

0 9

J

4

e

ľ.

£

c

 \wp

S

Ŧ,

Ċ.

c

Ъ

Table II.4 Sultate desorption fro	m mica
-----------------------------------	--------

-1

.

201

ð

5

8

۰,

0

μ

Table II.5 Growth of $BaSO_4$ on mica.

:

r,

.

ė

' e

# of cycles	Mass #1	Mass#2	Mass#3	
0	3.44310e-1	2.56216e-1	2.67635e-1	
5	3.44835e-1	2.56739e-1	2.67973e-1	/
10	3.45216e-1	2.57338e-1	2.68405e-1	(1
15	3.45874e-1	2.57486e-1	2.68790e-1	
20	3.46475e-1	2.58064e-1	2.69141e-1	
	Mass#4			
0	 3.60815e-1			
5	3.64205e-1			
10	3.67383e-1			
15	3.68340e-1		÷	
20	3.72035e-1			
	2			
Rate (g/cm ² 2.347e-5 2.816e-5 5.824e-5	.cycle) [Ba 1.006 1.006	erium nitrate]M e-3 e-2 e-1		
1.367e-4	2.506	∋-1	·	

لانېږي. مالې د

¢

ş

~

Table II.6 Growth of PbSO₄ on mica.

Change in mass(g) # of cycle 0.000 0 4.164e-5 2 1.126e-4 5 2.774e-4 10 2.601e-4 15 3.427e-4 18 5.001e-4 23

Rate(g/cm².cycle) [lead nitrate]M 8.002e-4 1.345e-4 2.11e-5 4.913e-6

C

[H2SO4]M	
9.9e-3	
5.04e-1	
9.9e-1	
5.994	
	[H2SO4]M 9.9e-3 5.04e-1 9.9e-1 5.994

203

1.000 1.00e-1

1.00e-2

1.00e-4

£

γ.

 ${\cal C}$

Ğ

lable II.7	Dissolution	or Basu ₄ from mica.
Time (h)	Net Cpm	
0	139.04	
0.1055	137.78	2.8mL/min flow rate
1.472	128	
2.03	122.9	
2.533	119.3	
0	164.12	
0.25	160	
0.38	158.29	10mL/min flow rate
0.883	152.32	
1.883	136.94	
2.95	129.92	- -
		:
0	208.833	ί.
0.25	204.6	19.5mL/min flow rate
1.533	182.95	
2	174.7	
		· · ·

Table II.8 Dissolution of Ba/RaSO4 from mica.

3

Time (h)	Net cpm
0.00	1140.7
0.167	1118.2
0.750	1061.6
1.083 🖕	1035.6

 \hat{i}

Flow rate=19.5mL/minute

\$

متر) ..

¢

υ

÷.

<u>\$</u>.

لاہے

Ē

References

(1) Nirdosh I. and Muthuswami S. V. (1988) Distribution of 230Th and other radionuclides in Canadian uranium mill streams. Hydrometallurgy, 20, 31.

(2) Snodgrass W. J., Lush D. L., McKee P. and Walker R. R. (1982). An approach to the calculation of dose commitment arising from different methods for the long-term management of uranium tailings-technical appendix. Atomic Energy Control Board Report INFO-0097.

(3) Skeaff J. M. (1977) Survey of the occurrence of Ra-226 in the Rio Algom Quirke 1 uranium mill Elliot Lake. CANMET Dept. of Energy Mines and Resources Report No. 77-36(IR).

(4) Constable T. and Snodgrass W. J. (1984) Leachability of radioactive constituents from uranium mill tailings-Final report. Environment Canada.

(5) Snodgrass W. J. and Robertson J. L. (1983). Hydrochemical Studies on WTC Lysimeter Tailings Report for CANMET.

(6) Wiles D. R. (1978) The leaching of radium from Beaverlodge tailings. Proceedings of OECD/NEA seminar on management stabilization and environmental impact of uranium mill tailings, Albuquerque, N. M., 245.

(7) Seeley F. G. (1977) Problems in the separation of radium from uranium ore tailings. Hydrometallurgy, 2, 249.

205

i en f

 \mathbb{D}

(8) Benes P. (1982). Physico-chemical forms and migration in continental waters of radium from uranium mining and milling in Environmental migration of long-lived radionuclides. IAEA Publication No. IAEA-SM-257/84. 3.

(9) Benes P., Odrzalek M. and Cejchanoua M. (1982). The physicochemical forms of traces of radium in aqueous solutions containing chlorides sulfates and carbonates. Radiochem. Radioanal. Letters 50, 4, 227.

(10) Nathwani J. S. and Phillips C. R. (1979). Rate controlling processes in the release of radium-226 from uranium mill tailings I: Leaching study. Wat. Air and Soil Poll. II, 301.

Ċ,

17 [1]

 \odot

25

Ð

(11) Nathwani J. S. and Phillips C. R. (1979). Rate controlling processes in the release of radium-226 from uranium mill tailings II: Kinetic study. Wat. Air and Soil Poll. II, 309.

(12) Nixon A., Keller D., Fritze K., Pidruczay A. and Corsini A. (1982) Radium removal from Elliot Lake uraniummill solids by EDTA leaching. Hydrometallurgy, **8**.

(13) Ryan R. K. and Levins D. M. (1980). Extraction of radium from uranium tailings. CIM Bulletin, **73**, 126.

(14) Nirdosh I. Muthuswami S. V. and Baird M. H. I. (1984) Radium in uranium mill tailings-some observations on retention and removal. Hydrometallurgy, **12**, 151.

e.

 $\langle \cdot \rangle$

ò

Ð,

(15) Shoesmith D. W. (1983). The Behaviour of Radium in Soil and Mine Tailings Environments. AECL (Whiteshell) Pinawa. Final Report.

(16) Benes P. (1984). Migration of radium in the terrestrial hydrosphere in The behaviour of radium in waterways and aquifers. IAEA Report # IAEA-TECDOC-301 119.

(17) Langmuir D. and Reise R. A. (1985) The thermodynamic properties of radium. Geochim. Cosmochim. Acta, **49**, 1593.

(18) Reise R. A. (1983) Adsorption of radium and thorium onto quartz and kaolinite: A comparison of solution/surface equilibrium models. Ph. D. thesis, University of Colorado.

 $\boldsymbol{\lambda}_{j'}$

(19) Steger H. F. and Legeyt M. (1987) Radioanalytical and Nuclear Chemistry, Articles, 111, 1, 95.

Ģ

Ŋ

(20) Radium Monograph (1986). International Atomic Energy Agency Vienna Austria. Prepared by W. J. Snodgrass. Edited by Linsley and Molinari.

(21) Snodgrass W. J. (Principal author) Hileman O. E. (Co-author) (1985). On the geochemical mechanism controlling Ra-226 dissolution in uranium mill wastes (tailings). Report for National Uranium Tailings Program Energy Mines and Flesources Government of Canada Ottawa Ontario. Contract No. 23241-4-1678.

(22) Harvie C. E. and Weare J. H. (1980) The prediction of mineral solubilities in natural waters: the Na-K-Mg-Ca-CI-SO4-H2O system from zero to high concentration at 25⁰C. Geochim. Cosmochim. Acta, **44**, 981.

(23) Harvie C. E. Moller N. and Weare J. H. (1984) The prediction of mineral solubilities in natural waters: the Na-K-Ca-Mg-H-Cl-SO4-OH-CO3-HCO3-H2O system to high ionic strength at 25⁰C. Geochim. Cosmochim. Acta, **48**, 723.

(24) Zemaitis J. F., Clark D. M., Rafal M. and Scrivner N. C. (1986) Handbook of Aqueous Electrolyte Thermodynamics American Institute of Chemical Engineers, Inc., New York.

(25) Pitzer K. S., Roy R. N. and Silvester L. F. (1977) Thermodynamics of Electrolytes 7. Sulfuric Acid. J. Amer. Chem. Soc. **99**, 4930.

(26) Pitzer K. S. (1979) Theory: ion interaction approach. In: Activity Coefficients in Electrolyte Solutions (Editor R. M. Pytckowicz) 1, 157 CRC Press Boca Raton Fla.

(27) Zettlemoyer, A. C. Nucleation (Dekker New York 1969).

(28) Kielland, J. (1937) J. Am. Chem. Soc., 59, 1675.

(29) Smith R. M. and Martell A. E. Critical Stability Constants, 4: Inorganic Complexes (Plenum, New York, 1976).

(30) Abraham, F. F. Homogeneous Nucleation Theory (Academic Press, New York, 1974).

Ð

8

97**-1**7

208

 $\{\cdot\}^{\prime\prime}$

(31) P. Hartman in: Crystal Growth: An Introduction ed. P. Hartman, 367, (North-Holland Amsterdam, 1973).

(32) Hartman P. and Bennema P. (1980) J. Crystal Growth, 49, 145.

(33) Nielsen, A. E. (1984) J. Crystal Growth, 67, 306.

(34) Burton W. K., Cabrera N. and Frank F.C. (1951) Phil. Trans. Roy. Soc. London A243, 299.

(35) Chernov A. A. (1961) Soviet Phys.-Usp. 1, 126.

(36) Bennema P. and Gilmer G. H. in: Crystal Growth: An Introduction ed. P. Hartman, 263 (North-Holland, Amsterdam 1973)

(37) Gilmer G. H., Ghez R. and Cabrera N. (1971) J. Crystal Growth, 8, 79.

(38) Boistelle R. in: Interfacial Aspects of Phase Transformations, Ed. B. Mutaftschiev, 531 (Reidel Dordrecht 1982).

±)

0

ଜ

е 0 (39) O'Hara M. and Reid R. C. Modelling Crystal Growth rates From Solution (Prentice-Hall, Englewood Cliffs, N. J. 1973)

(40) Rosenberger F., Fundamentals of Crystal Growth I (Springer, Berlin, 1979).

(41) Boistelle R. in: Current Topics in Material Science 4, 413, Ed. E. Kaldis (North-Holland Amsterdam 1980).

(42) Davey R. J. (1976) J. Crystal Growth, 34 109.

(43) Boistelle R. in: Interfacial Aspects of Phase Transformations, 621, Ed. B. Mutaftschiev (Reidel Dordrecht 1982).

(44) Ostwald W. Z. (1897) Physik. Chem. 22, 289.

(45) Cardew P. T. and Davey R. J. (1985) Proc. Roy. Soc. (London) A398, 415.

(46) Boistelle R. and Rinaudo C. (1981) J. Crystal Growth 53, 1.

(47) Kahlweit M. (1975) Advan. Colloid Interface Sci. 5, 1.

(48) Greenwood G. W. (1956) Acta Met. 4, 243.

(49) Hohmann H. H. and Kahlweit M. (1972) Ber. Bunsenges. Physik Chem. 76, 933.

(50) Crockford H. D. and Brawley D. J. (1932) J. Phys. Chem. 36, 1594.

(51) Crockford H. D. and Brawley D. J. (1934) The solubility of lead sulfate in water and aqueous solutions of sulfuric acid. J. Am. Chem. Soc. 56, 2600.

(52) Crockford H. D. and Addlestone J. A. (1936) The solubility of lead sulfate in aqueous solutions of sulfuric acid at high concentrations. J. Phys. Chem. **40**, 303.

(53) Craig D. N. and Vinal G. W. (1939) J. Research Nat. Bureau Stand. 22, 55.

(54) Danel V. and Plichon V. (1982) Study of Pb(II) in various H₂O-H₂SO₄ mixtures by differential pulse

polarography: solubility of lead sulphate diffusion coefficient of Pb(II) and half-wave potential of Pb(Hg)/Pb(II). Electrochimica Acta, 27, 771.

(55) Kolthoff I. M. Perlich R. W. and Weiblen D. (1942) The solubility of lead sulfate and of lead oxalate in various media. J. Phys. Chem. 46, 561.

(56) Huybrechts M. and DeLangeron N. A. (1930). Bull.

(57) Seidel A. (1940) Solubilities of inorganic and metal organic compounds. D. Van Nostrand Company Inc. New York and Supplement to the Third edition (1952).

(58) Monnin C. and Galinier C. (1988) Chemical Geol., 71, 283.

(59) De Lima M. C. P. and Pitzer K. S. (1983) Thermodynamics of saturated electrolyte mixtures of NaCl with Na₂SO₄ and with MgCl₂. J. Solution Chem. **12**, 187.

(60) Rogers P. S. Z. and Pitzer K. S. (1981) High temperature thermodynamic properties of aqueous sodium sulfate solutions. J. Phys. Chem. **85**, 2886.

(61) Reardon E. J. and Beckie R. D. (1987) Modelling chemical equilibria of acid mine-drainage: The FeSO₄-H₂SO₄-H₂O system. Geochim. Cosmochim. Acta, **51** 2355.

(62) GAUSHAUS: Non-linear least squares subroutine produced at the University of Wisconsin Computing Center; Meeter D. A. and Wolfe P. J., 1965.

211

(1

(63) Lieser K. H. (1965) Radiochemische Messung der Loslichkeit von Erdalkalisulfaten in Wasser und in Natriumsulfatlosungen. Z. Anorg. Allgem. Chemie, **335** 225.

(64) Felmy A. R., Rai D. and Amonette J. E. (1990) The solubility of barite and celestite in sodium sulfate: Evaluation of thermodynamic data. J. Solution Chem., **19**, 2.

(65) Mallot M. (1988) private communication of an inhouse developed FORTH routine for the digitizing of data in the form of a curve, using a Hewlett-Packard plotter.

(66) von Weimarn P. P. (1911) Z. Physik. Chem. 76, 218.

(67) Trenner N. R. and Taylor H. A. (1931) The solubility of barium sulphate in sulphuric acid. J. Phys. Chem. **35**, 1336-44.

(68) Brown E. and Firestone R. B., (V. S. Shirley ed.), 133, Table of Radioactive Isotopes (Wiley-Interscience, 1986).

(69) Gordon L ,Salutsky M. L. and Willard H. H. Precipitation from Homogeneous Solution (Wiley, 1959), 73.

(70) Spitsyn V., Torchenkova R. and Glazkova I. (1960) Dokl. Acad. Nauk USSR. 132, 643; 133, 1111.

(71) Ramette R. and Anderson O. (1963) J. Inorg. Nucl. Chem. 25, 763.

(72) Bovington C. H. (1965) J. Inorg. Nucl. Chem. 27, 1975-1979.

?

(73) Berdonosov S. S. (1973) Radiokhimiya, 15, 3, 405

(74) Durup J. and Platzman R. L. (1961) Disc. Faraday Soc. 31, 156.

(75) Nancollas G. H. and Purdie N. (1963) Trans. Faraday Soc., 59, 735.

(76) Reardon E. J. and Armstrong D. K. (1987) Geochimica et Cosmochimica Acta, 51, 63.

(77) Enustun B. V. and Turkevich J. (1960) J. Amer. Chem. Soc., 82, 4502.

(78) Campbell J. R. and Nancollas G. H. (1969) J. Phys. Chem., 73, 1735.

(79) Bagnall K. (1960) Chemistry of the rare radioelements Polonium-Actinium, 223.

(80) Lind S. C., Underwood J. E. and Whittemore C. F. (1918) The solubility of pure radium sulfate. J. Amer. Chem. Soc. 40, 465.

(81) Nikitin B. and Tolmatscheff P. (1933) Ein Beitrag zur Gultigkeit der Massenwirkungsgesetzes. II. Quantitative Bestimmung der Loslichkeit Radiumsulfates in Natriumsulfatlosungen und in Wasser. Z. Physik. Chem., A167, 260.

(82) Myers O. E. and Prestwood R. L. (1951) in Radioactivity Applied to Chemistry (Wahl and Bonner eds.) Wiley, New York, 351.

(83) McKay H. A. C. (1971) Principles of Radiochemistry Butterworths, London.

0

(84) Helfferich F. (1962) Ion exchange. McGraw-Hill, New York.

(85) Kosmulski M. Jaroniec M. and Szczypa J. (1983) Mater. Chem. Phys., 9, 351.

(86) Rodiguin N. M. and Rodiguina E. N. (1964) Consecutive Chemical Reactions. Van Nostrand Princeton.

(87) Campbell I and O'Connon D. (1956) Principles of Use of Radioisotopes (PWN Publications, Warsaw).

(88) Dana's Textbook of Mineralogy (4th ed. 1953) (John Wiley, New York,).

⁶ (89) Nielsen A. E., (1984) J. Crystal Growth, 67, 284.

(90) Bennema P. and Gilmer G. H., in: Crystal Growth: an Introduction ed. P. Hartman, 263 (North-Holland, Amsterdam, 1973).

(91) Tully J. C. and Cardillo M. J., (1984) Science, 223, 445.

(92) Sharpe T. F. in: Encyclopaedia of Electrochemistry of the Elements ed. A. J. Bard, 1, 257 (M. Dekker, New York 1973).

(93) Fortes J. M., Mercier M. and Molenat J. (1974) Chim. Phys., 71, 164.

(94) Pitzer K. S. and Mayorga G., (1974) J. Solution Chem., 3, 543.

(95) Stout G. H. and Jensen L. H. (1968) X-ray Structure Determination , 67, MacMillan, New York.

(96) Gilmer G. H. and Bennema P., (1972) J. Appl. Phys., **43**,,1347.

(97) Lieser K. H., Gutlich P. and Rosenbaum I. (1965) Proc. Symposium Exchange Reactions, 375. IAEA, Wien.

(98) Lieser K. H. and Hild W. (1962) Proc. Symposium Radioisotopes in the Physical Sciences and Industry, 337, IAEA, Wien.

(99) Abdel Salam M. A. and Abu Zahra R. H., (1966) Soil Science, 102, 255.

(100) Huang T. C., Li K. Y. and Hoo S. C. (1972) J. Inorg. Nucl. Chem., **34**, 47.

(101) Huang T. C. and Tsai F. N. (1970) J. Inorg. Nucl. Chem., 32, 17.

(102) Moller P. and Sastri C. S. (1973) Inorg. Nucl. Chem. Letters, 9, 759.

(103) Binsma J. J. M. and Kolar Z. (1984) Faraday Discuss. Chem. Soc., **77**, 257.

(104) Bunzl K. and Schultz W. (1981) J. Inorg. Nucl. Chem., 43, 791.

(105) Adamson, A. W., (1967) Physical Chemistry of Surfaces, 429, (Interscience, New York).

(106) Smith W., Holten C. L. M., Stein H. N., DeGoeij J. J. M. and Theelen H. M. J. (1978) J. Colloid Interface Sci., 63, 120.

Ą

Ċ,

(107) Hachiya K., Ashida M., Sasaki M., Kan H., Inoue T. and Yasunaga T. (1979) J. Phys. Chem., 83, 1866.

(108) Anderson M. A. and Rubin A. J. (1981) Adsorption of Inorganics at Solid-Liquid Interfaces (Ann Arbor Science, Ann Arbor).

(109) Benes P. and Majer V. (1980) Trace Chemistry of Aqueous Solutions, 213, (Elsevier, Amsterdam).

(110) Thornton E. W. (1984) Nuclear Technology, 65, 161.

(111) Cerofolini, G. (1982) J. Colloid Interface Sci., 86, 204.

(112) Nicolau Y. F., (1985) Applications of Surface Science, 22, 1061.

(113) Inderjeet Kaur, Pandya D.K. and Chopra K.L. (1980) J. Electrochem. Soc., 127, 4.

(114) Nielsen A. E., (1964) 130, Kinetics of Precipitation, MacMillan.

(115) Kitaev G. A., Mokrushin S. G. and Uritskaya A. A., (1965) Colloid J. USSR, 27, 38.

(116) A Guide to Practical Radiochemistry, 2, 130, Mir Publishers, Moscow.

(117) Yarwood, J., (1960) Electricity, Magnetism, and Atomic Physics, 2, University Tutorial Press, London.

d,

(118) Table of Isotopes (Seventh edition), Ed. C. Michael Lederer, Wiley, New York.

2

(119) Christoffersen M. R. and Christoffersen J., (1988) J. Cryst. Growth, 87, 51.

(120) Hamza Salem M., Abdul-Rahman A. and Nancollas G. H. (1985) J. Cryst. Growth, **73**, 245.

(121) Paige C. R., Hileman O. E. and Snodgrass W. J. (1988) J. Radioanal. Nucl. Chem., Letters, **127**, 341.

(122) Paige C. R., Hileman O. E., Kornicker W. A. and Snodgrass W. J. (1989) J. Radioanal. Nucl. Chem., Letters, 135, 299.

(123) Paige C. R., Hileman O. E., Kornicker W. A. and Snodgrass W. J. (1989) J. Radioanal. Nucl. Chem., Letters, 137, 319.

(124) Paige C. R., Hileman O. E., Kornicker W. A. and Snodgrass W. J. (1989) Intern. J. Environ. Anal. Chem., **37**, 29.

(125) Kornicker W. A., Presta A., Paige C. R., Johnson D. M., Hileman O. E. and Snodgrass W. J., currently under revision for publication in Geochim. Cosmochim. Acta.

(126) Radiotracer Techniques and Applications, 1 (1977) Eds. Anthony, E. and Muramatsu, M., Marcel Dekker.

217

ĮĮ.

C

~