Instituto de Ciências Matemáticas e de Computação

ISSN - 0103-2569

Calculation of Ionic Radii at High Pressure in Different Crystals

Maria Carolina Monard/ILTC
Alicia Batana
Jorge Bruno

Nº 112

RELATÓRIOS TÉCNICOS DO ICMC

São Carlos
Abril/2000

Calculation of Ionic Radii at High Pressure in Different Crystals

Maria Carolina Monard*
Universidade de São Paulo/ILTC
Instituto de Ciências Matemáticas de São Carlos
Departamento de Ciências de Computação e Estatística
Caixa Postal 668, 13560-970 - São Carlos, SP, Brasil
e-mail: mcmonard@icmsc.sc.usp.br

Alicia Batana†
Jorge Bruno†
Universidad de Buenos Aires
Facultad de Ciencias Exactas y Naturales
Departamento de Química Inorgánica Analítica y Química Física
Ciudad Universitaria - Pabellón 2
Buenos Aires - Argentina
e-mail: {batana,jbruno}@q1.fcen.uba.ar

Abstract

The evaluation of the pressure dependence of ionic radii is important in itself and due to its relation to the pressure dependence of ionic polarizabilities and dielectric constants.

A new way of obtaining these quantities is given and a computational system developed and applied to several crystals of interest. Results are compared to those obtained with a different method and discussed.

*Work partially supported by National and State Research Council — CAPES/FINEP and FAPESP, Brasil
†Work partially supported by CONICET and ANPCyT, Argentina

Contents

List of Tables

1 Introduction

In a previous work [9] we have mentioned the importance of introducing the concept of ionic properties transferable among families of crystals. In particular we discussed ionic polarizabilities [3, 4, 5, 6, 7, 8, 9] proposing a new empirical method [1] for their evaluation. This method requires values of the pressure dependence of ionic radii; we have given an alternative way of evaluating these quantities starting from the values of $\frac{\partial R}{\partial p}$ obtained from experimental data of the compressibilities of salts.

The methods is applied to different salts and their evaluation is described in detail. Finally the results of $\frac{\partial r_i}{\partial p}$ obtained are compared to those obtained previously via a different method [1].

This work is organized as follows: in Section 2 the theory and method used are described as well as the Maple V module PRad that implements this method. In Section 3 several case study are presented aiming to show the correspondence among the salts being studied and the $\frac{\partial R}{\partial p}$ notation used by the PRad module. For each case study several results obtained using different constraints to run the module are also shown. Conclusions are presented in Section 4.

2 Module PRad Description

In this section the algorithm, implemented in Maple V [2], responsible for the calculation of the maximum values of the absolute value of the quantities $\frac{\partial r_+}{\partial p}$, $\frac{\partial r_-}{\partial p}$ and $\frac{\partial R}{\partial p}$ such that they verify

$$\frac{\partial r_+}{\partial p} + \frac{\partial r_-}{\partial p} \leq \frac{\partial R}{\partial p} \tag{1}$$

is described in detail. To do that, and in order to clearly undestand the notation used as well as the corresponding data structure used by this module, several cases will be ilustrated.

2.1 Evaluation of $\frac{\partial r_+}{\partial p}$ and $\frac{\partial r_-}{\partial p}$

The general notation used by this module is similar to the one used by the PDac module from the Polariz System which is described in detail in [8, 9], but considering only the derivatives, i.e. the input to the system are the derivatives. The notation used by the system is shown in Table 1, assuming we have n_c different cations $\mathbf{c}$ and n_a different anions $\mathbf{a}$ with $md = n_c + n_a$

Cations	$\mathbf{c}_1$	$\mathbf{c}_2$	$\mathbf{c}_3$	$\ldots$	$\mathbf{c}_{n_c}$
	$\frac{\partial r_1}{\partial p}$	$\frac{\partial r_2}{\partial p}$	$\frac{\partial r_3}{\partial p}$	$\ldots$	$\frac{\partial r_{n_c}}{\partial p}$
Anions	$\mathbf{a}_{n_c+1}$	$\mathbf{a}_{n_c+2}$	$\mathbf{a}_{n_c+3}$	$\ldots$	$\mathbf{a}_{n_c+n_a}$
	$\frac{\partial r_{n_c+1}}{\partial p}$	$\frac{\partial r_{n_c+2}}{\partial p}$	$\frac{\partial r_{n_c+3}}{\partial p}$	$\ldots$	$\frac{\partial r_{n_c+n_a}}{\partial p}$

Table 1: General Notation

the system implements the linear programming problem of the form

$$maximize\ Z = \sum_{k=1}^{md} \frac{\partial r_k}{\partial p} \tag{2}$$

subject to the restrictions

$$\frac{\partial r_i}{\partial p} + \frac{\partial r_j}{\partial p} \leq \frac{\partial R_{ij}}{\partial p}\ for \begin{cases} i\ is\ any\ value\ in\ \{1..n_c\} \\ j\ is\ any\ value\ in\ \{n_c+1..n_c+n_a\} \end{cases} \tag{3}$$

all nonnegative. All instances of i and j values are user defined through the corresponding companion matrix, such that they verify the restrictions defined by the system of inequalities (3) as ilustrated later on. To solve this problem the user is also allowed to fix one or more $\frac{\partial r_k}{\partial p}$.

Also, for each one of the equations of the system the linear error e_{ij} is calculated for user's defined i and j as

$$e_{ij} = \frac{\partial r_i}{\partial p} + \frac{\partial r_j}{\partial p} - \frac{\partial R_{ij}}{\partial p} \tag{4}$$

as well as

$$e = \sqrt{\sum_{i,j} (e_{ij})^2} \tag{5}$$

2.2 Implementation

In this section the data structure as well as the Maple commands in the worksheet window that implements the module PRad is explained in detail. There is one region group consisting of input regions where all input should be specified. First of all, the file containing the data related to $\frac{\partial R}{\partial p}$ at Low Temperatures —Table 25 pg. 27 — is read in and afterwards the user can define the specific case being executed.

2.2.1 Data Structure for $\frac{\partial R}{\partial p}$

We use the Maple table data structure to store Table 25. Unlike arrays, where indices must be integers, the indices (or keys) of a table can be any value. In what follows, this table has been stored in the Maple file named `al_derp.m` where the contents of the correspondent file `al_derp.ms` is shown fellow.

```
> der_LT :=table([LiF=0.9514, LiCl=2.7083,LiBr=3.7982,LiI=5.6859,NaF=1.5224,
>  NaCl=3.7000,NaBr=4.6279,NaI=6.8671,KF=2.7363,KCl=5.4634,KBr=6.7088,KI=9.0133,
> RbF=3.5420, RbCl=6.9525, RbBr=8.7410, RbI=11.4645, CsF=4.2308, CsCl=5.3178,
>  CsBr=6.6542,CsI=9.0256,CaF=0.8915,SrF=1.1981,SrCl=3.3128,BaF=1.5703,
> MgO=0.4255,CaO=0.7206,SrO=0.9592,BaO=1.2436,NaClO3=4.2676,NaBrO3=3.6196]):
```

It can be observed that indexes are related to salt's chemical symbols. We have found that this rich data structure is simple to undestand. Furthermore, it is very easy for the user to alter it and/or include more and new salts.

2.2.2 Worksheet Description

In order to exemplify the user's definition needed to correctly execute the Maple V worksheet, case study 1 described in Section 3.1 pg. 7 will be used.

Initially the module is restarted and the necessary Maple packages are loaded through the `with` command. Optionally the user can define the number of digits carried in floats (default is 10) through the `Digits` environment variable.

```
> restart:with(linalg):with(simplex):with(stats): with(student):
> Digits:=6:
```

Next the table stored in the Maple file named `al_derp.m`, or any other file specified by the user, is read and the defined table `der_LT` is stored as table `fcc_TA`. The user needs to set the value of `MD`, which holds the number of cations and anions considered, as well as the value of and `MDEQ` which holds the number of inequality for this run. For case study 1 those values are 8 and 16 respectively. The user also needs to define matrix `A` and vector `R` for this particular problem — see equation (8) pg. 8.

```
> read `al_derp.m`: fcc_TA:=der_LT:
>  MD:=8: MDEQ:=16:
> A:=array([[1,0,0,0,1,0,0,0],[1,0,0,0,0,1,0,0],[1,0,0,0,0,0,1,0],[1,0,0,0,0,0,0,1],
> [0,1,0,0,1,0,0,0],[0,1,0,0,0,1,0,0],[0,1,0,0,0,0,1,0],[0,1,0,0,0,0,0,1],
> [0,0,1,0,1,0,0,0],[0,0,1,0,0,1,0,0],[0,0,1,0,0,0,1,0],[0,0,1,0,0,0,0,1],
> [0,0,0,1,1,0,0,0],[0,0,0,1,0,1,0,0],[0,0,0,1,0,0,1,0],[0,0,0,1,0,0,0,1]]):
> R:=vector([fcc_TA[LiF],fcc_TA[LiCl],fcc_TA[LiBr],fcc_TA[LiI],fcc_TA[NaF],
> fcc_TA[NaCl],fcc_TA[NaBr],fcc_TA[NaI],fcc_TA[KF],fcc_TA[KCl],fcc_TA[KBr],
> fcc_TA[KI],fcc_TA[RbF],fcc_TA[RbCl],fcc_TA[RbBr],fcc_TA[RbI]]):
```

It should be noted that the definition of vector `R` is easily achieved with the Maple table data structure keeping in mind the mapping defined in Table 3 pg. 7, which shows the correspondence among the salts being studied and the $\frac{\partial R_{ij}}{\partial p}$ notation. At any moment the user can display any of those values using for example the Maple function `print` as shown bellow for table `fcc_TA`.

```
> print(fcc_TA):
```

table([

$SrO = .9592$
$BaF = 1.5703$
$LiCl = 2.7083$

$BaO = 1.2436$
$RbI = 11.4645$
$MgO = .4255$
$CsF = 4.2308$
$RbF = 3.5420$
$NaBrO3 = 3.6196$
$SrCl = 3.3128$
$CsBr = 6.6542$
$CsCl = 5.3178$
$CaF = .8915$
$CaO = .7206$
$NaClO3 = 4.2676$
$SrF = 1.1981$
$LiF = .9514$
$NaCl = 3.7000$
$NaBr = 4.6279$
$RbCl = 6.9525$
$RbBr = 8.7410$
$CsI = 9.0256$
$LiI = 5.6859$
$NaF = 1.5224$
$NaI = 6.8671$
$KF = 2.7363$
$KCl = 5.4634$
$KBr = 6.7088$
$KI = 9.0133$
$LiBr = 3.7982$
])

Up to this point, except for the value of variable `more_constr` which should be defined by the user, the necessary input has been defined. Next, knowing the input value of `MD` and `MDEQ` the system prepares the correspondent system of inequalities defined by equation (6) pg. 7, as well as some auxiliar output variables explained latter on.

```
> r:=vector(MD):val_r:=vector(MD):
> c:=vector(MD,1):Z:=[multiply(transpose(c),r)]:
> prod:=multiply(A,r):
> constraints:={seq(prod[i] <=R[i], i=1..MDEQ)}:
```

At this point the user should define other constraints to be considered. In this example we shall use the constraints of test T-7 in Table 4 pg. 9 from case study 1, defined as follows

---

```
> more_constr:={r[1]=0.2780, r[5]=0.6709,r[8]=4.0229}:
```

Observe that if no additional constrains are to be used then `more_constr` should be set as emply, i.e. `more_constr:={}`. After setting the tolal constraints of the system `feasible` returns true if the system has a feasible solution, false otherwise. In this latter case the user can stop execution.

```
> tot_constr:=`union`(constraints,more_constr):
>  print(feasible(tot_constr,NONNEGATIVE)):
```

$$true$$

Afterwards the solution to the system is found and stored in `sols`.

```
> sols:=maximize(Z[1],tot_constr,NONNEGATIVE):
> result:=subs(sols,Z[1]):
```

At this point, all calculations have been done and the user can either investigate on his/her own the calculated values or can use the output facilities provided in this module. For example, the user can see the function that has been maximize by simply displaying the objective function `Z[1]`

```
> Z[1];
```

$$r_1 + r_2 + r_3 + r_4 + r_5 + r_6 + r_7 + r_8$$

The user can print the system of inequalities

```
>  print(`tot_constr=`,tot_constr):
```

$$\begin{aligned}
&tot_constr =, \Big\{r_8 = 4.0229, r_5 = .6709, r_4 + r_8 \leq 11.4645, r_4 + r_7 \leq 8.7410,\\
&\quad r_1 = .2780, r_3 + r_7 \leq 6.7088, r_4 + r_5 \leq 3.5420, r_4 + r_6 \leq 6.9525,\\
&\quad r_3 + r_8 \leq 9.0133, r_2 + r_7 \leq 4.6279, r_1 + r_7 \leq 3.7982, r_1 + r_6 \leq 2.7083,\\
&\quad r_1 + r_8 \leq 5.6859, r_2 + r_5 \leq 1.5224, r_2 + r_6 \leq 3.7000, r_2 + r_8 \leq 6.8671,\\
&\quad r_3 + r_5 \leq 2.7363, r_3 + r_6 \leq 5.4634, r_1 + r_5 \leq .9514\Big\}
\end{aligned}$$

as well as the solutions found

```
> print(`sols=`,sols):
```

$$\begin{aligned}
&sols =, \Big\{r_7 = 3.52020, r_2 = .851500, r_4 = 2.87110, r_3 = 2.06540, r_8 = 4.0229,\\
&\quad r_5 = .6709, r_1 = .2780, r_6 = 2.43030\Big\}
\end{aligned}$$

In order to have a common output, several data variables have been defined holding the results of this module, such as

- `result` which holds the value of the objective function defined by equation (2).

- `val_r` is a vector `{1..MD}` which holds the values of $\frac{\partial r_k}{\partial p}$ that maximizes the objective function defined by equation (2).
- `error_linear` is a vector `{1..MDEQ}` which holds the values of e_{ij} defined by equation (4) using the same mapping than vector **R**.
- `error_quadrado` is a real variable which holds the value of e defined by equation (5)

`val_r` is calculated by the following region

```
> k:='k':
> for k from 1 to MD do val_r[k]:=subs(sols,r[k]) od:
```

`error_linear` and `error_quadrado` are calculated by the following region

```
> error_linear:=add(multiply(A,val_r),scalarmul(b,-1)):
>
> error_quadrado:=map(x->x^2,error_linear):
> sum_error_quadrado:=sum(error_quadrado[m],m=1..MDEQ):
> error_total:=sqrt(sum_error_quadrado):
```

The last region of this module simply prints this results. It is up to the user to keep them in a file or otherwise for futher use.

```
> print(`Z=`, result): print(`val_r=`,val_r):
> print(`error_linear=`,error_linear):  print(`error_total=`,error_total):
```

$$Z =, 16.7103$$

$$val\_r =, [.2780\ .851500\ 2.06540\ 2.87110\ .6709\ 2.43030\ 3.520204.0229]$$

$$error\_linear =, [-.0025\ 0\ 0\ -1.3850\ 0\ -.41820\ -.25620\ -1.99270\ 0$$
$$-.96770\ -1.12320\ -2.92500\ 0\ -1.65110\ -2.34970\ -4.57050]$$

$$error\_total =, 6.78380$$

3 Examples and Results

In this section several case study are presented aiming to show the correspondence among the salts being studied and the $\frac{\partial R_{ij}}{\partial p}$ notation used by this module. Furthermore, we show the results of using different constraints to run the module. It should be observed that the system has too many degree of liberty and some times a solution $\frac{\partial r_{ij}}{\partial p} = 0$ is factible. Adding constraints allows the user to study the behavior of the system as well as testing specific $\frac{\partial r_{ij}}{\partial p}$ values.

In what follows the symbol $\oplus$ in front of a value means that this value has been fixed by the user for that run, while a $\bullet$ indicates that a zero value is a solution to the system.

3.1 Case Study 1

This case study corresponds to the cations and anions in Table 2.

Cations	Li^+	Na^+	K^+	Rb^+
	$\frac{\partial r_1}{\partial p}$	$\frac{\partial r_2}{\partial p}$	$\frac{\partial r_3}{\partial p}$	$\frac{\partial r_4}{\partial p}$
Anions	F^-	Cl^-	Br^-	I^-
	$\frac{\partial r_5}{\partial p}$	$\frac{\partial r_6}{\partial p}$	$\frac{\partial r_7}{\partial p}$	$\frac{\partial r_8}{\partial p}$

Table 2: Case 1 – Cations and Anions Considered

Thus $n_c = 4$, $n_a = 4$ and $md = 8$ with

$$maximize\ Z = \sum_{k=1}^{8} \frac{\partial r_k}{\partial p} \tag{6}$$

subject to the restrictions

$$\frac{\partial r_i}{\partial p} + \frac{\partial r_j}{\partial p} \leq \frac{\partial R_{ij}}{\partial p}\ for \begin{cases} i = 1..4 \\ j = 5..8 \end{cases}$$

all nonnegative making 16 inequalities. It is very important to understand the correspondence among the salts being studied and the $\frac{\partial R_{ij}}{\partial p}$ notation. In this case the correspondence shown in Table 3 is used.

LiF	LiCl	LiBr	LiI	NaF	NaCl	NaBr	NaI
$\frac{\partial R_{1,5}}{\partial p}$	$\frac{\partial R_{1,6}}{\partial p}$	$\frac{\partial R_{1,7}}{\partial p}$	$\frac{\partial R_{1,8}}{\partial p}$	$\frac{\partial R_{2,5}}{\partial p}$	$\frac{\partial R_{2,6}}{\partial p}$	$\frac{\partial R_{2,7}}{\partial p}$	$\frac{\partial R_{2,8}}{\partial p}$
KF	KCl	KBr	KI	RbF	RbCl	RbBr	RbI
$\frac{\partial R_{3,5}}{\partial p}$	$\frac{\partial R_{3,6}}{\partial p}$	$\frac{\partial R_{3,7}}{\partial p}$	$\frac{\partial R_{3,8}}{\partial p}$	$\frac{\partial R_{4,5}}{\partial p}$	$\frac{\partial R_{4,6}}{\partial p}$	$\frac{\partial R_{4,7}}{\partial p}$	$\frac{\partial R_{4,8}}{\partial p}$

Table 3: Case 1 – Correspondence Among Salts

In matrix form this can be written as

$$\mathbf{Ar} \leq \mathbf{R} \tag{7}$$

where

$$\mathbf{A} = \begin{pmatrix} 1&0&0&0&1&0&0&0\\ 1&0&0&0&0&1&0&0\\ 1&0&0&0&0&0&1&0\\ 1&0&0&0&0&0&0&1\\ 0&1&0&0&1&0&0&0\\ 0&1&0&0&0&1&0&0\\ 0&1&0&0&0&0&1&0\\ 0&1&0&0&0&0&0&1\\ 0&0&1&0&1&0&0&0\\ 0&0&1&0&0&1&0&0\\ 0&0&1&0&0&0&1&0\\ 0&0&1&0&0&0&0&1\\ 0&0&0&1&1&0&0&0\\ 0&0&0&1&0&1&0&0\\ 0&0&0&1&0&0&1&0\\ 0&0&0&1&0&0&0&1 \end{pmatrix} \quad \mathbf{r} = \begin{pmatrix} \frac{\partial r_1}{\partial p}\\ \frac{\partial r_2}{\partial p}\\ \frac{\partial r_3}{\partial p}\\ \frac{\partial r_4}{\partial p}\\ \frac{\partial r_5}{\partial p}\\ \frac{\partial r_6}{\partial p}\\ \frac{\partial r_7}{\partial p}\\ \frac{\partial r_8}{\partial p} \end{pmatrix} \quad \mathbf{R} = \begin{pmatrix} \frac{\partial R_{1,5}}{\partial p}\\ \frac{\partial R_{1,6}}{\partial p}\\ \frac{\partial R_{1,7}}{\partial p}\\ \frac{\partial R_{1,8}}{\partial p}\\ \frac{\partial R_{2,5}}{\partial p}\\ \frac{\partial R_{2,6}}{\partial p}\\ \frac{\partial R_{2,7}}{\partial p}\\ \frac{\partial R_{2,8}}{\partial p}\\ \frac{\partial R_{3,5}}{\partial p}\\ \frac{\partial R_{3,6}}{\partial p}\\ \frac{\partial R_{3,7}}{\partial p}\\ \frac{\partial R_{3,8}}{\partial p}\\ \frac{\partial R_{4,5}}{\partial p}\\ \frac{\partial R_{4,6}}{\partial p}\\ \frac{\partial R_{4,7}}{\partial p}\\ \frac{\partial R_{4,8}}{\partial p} \end{pmatrix} \tag{8}$$

Table 4 shows the results obtained by different tests T under the restrictions given by equations (7) and (8) where

$$\mathbf{R}^t = (.9514 \quad 2.7083 \quad 3.7982 \quad 5.6859 \quad 1.5224 \quad 3.7000 \quad 4.6279 \quad 6.8671 \quad 2.7363 \quad 5.4634 \quad 6.7088 \quad 9.0133 \quad 3.5420 \quad 6.9525 \quad 8.7410 \quad 11.4645)$$

The Z column correspond to the Z value defined by equation (6) and the e column is defined by equation (9).

$$e = \sqrt{\sum_{i,j} (e_{ij})^2} \; for \begin{cases} i = 1..4 \\ j = 5..8 \end{cases} \tag{9}$$

Table 5 shows, for each one of the equations, the linear error as defined by equation (10).

$$e_{ij} = \frac{\partial r_i}{\partial p} + \frac{\partial r_j}{\partial p} - \frac{\partial R_{ij}}{\partial p} \; for \begin{cases} i = 1..4 \\ j = 5..8 \end{cases} \tag{10}$$

3.2 Case Study 2

This case study corresponds to the cations and anions in Table 6.

$\frac{\partial r_i}{\partial p}$	T-1	T-2	T-3	T-4	T-5	T-6	T-6b	T-7
$\frac{\partial r_1}{\partial p}$	$\oplus$.2780	$\bullet$	$\oplus$.2780	$\bullet$	$\oplus$.2780	$\oplus$.2780	$\oplus$.2780	$\oplus$.2780
$\frac{\partial r_2}{\partial p}$	$\oplus$.8466	.9917	1.2697	.82970	.8515	1.2697	1.1077	.8515
$\frac{\partial r_3}{\partial p}$	$\oplus$2.0636	2.7363	2.7363	$\oplus$2.0636	2.0654	2.7363	2.7363	2.0654
$\frac{\partial r_4}{\partial p}$	$\oplus$2.8707	3.5420	3.5420	2.8693	2.8711	3.5420	3.5420	2.8711
$\frac{\partial r_5}{\partial p}$	$\oplus$.6709	$\bullet$	$\bullet$	.6727	$\oplus$.6709	$\bullet$	$\bullet$	$\oplus$.6709
$\frac{\partial r_6}{\partial p}$	$\oplus$1.9148	2.7083	2.4303	2.7083	2.4303	2.4303	2.4303	2.4303
$\frac{\partial r_7}{\partial p}$	$\oplus$2.6866	3.6362	3.3582	3.7982	3.5202	3.3582	3.5202	3.5202
$\frac{\partial r_8}{\partial p}$	$\oplus$4.0229	5.6859	5.4079	5.6859	5.4079	$\oplus$4.0229	$\oplus$4.0229	$\oplus$4.0229
Z	15.3541	19.3004	19.0224	18.6277	18.0953	17.6374	17.6374	16.7103
e	7.6994	3.1064	3.5317	4.2041	4.8553	5.4812	5.4722	6.7838

Table 4: Case Study 1: Tests using Absolute Values of $\frac{\partial r_i}{\partial p}$

$e_{i,j}$	T-1	T-2	T-3	T-4	T-5	T-6a	T-6b	T-7
$e_{1,5}$	-.0025	-.9514	-.6734	-.2787	-.0025	-.6734	-.6734	-.0025
$e_{1,6}$	-.5155	0	0	0	0	0	0	0
$e_{1,7}$	-.8336	-.1620	-.1620	0	0	-.1620	0	0
$e_{1,8}$	-1.3850	0	0	0	0	-1.3850	-1.3850	-1.3850
$e_{2,5}$	-.0049	-.5307	-.2527	-.0200	0	-.2527	-.4147	0
$e_{2,6}$	-.9386	0	0	-.16200	-.4182	0	-.1620	-.4182
$e_{2,7}$	-1.0947	0	0	0	-.2562	0	0	-.2562
$e_{2,8}$	-1.9976	-.1895	-.1895	-.3515	-.6077	-1.5745	-1.7365	-1.9927
$e_{3,5}$	-.0018	0	0	0	0	0	0	0
$e_{3,6}$	-1.4850	-.0188	-.2968	-.6915	-.9677	-.2968	-.2968	-.9677
$e_{3,7}$	-1.9586	-.3363	-.6143	-.8470	-1.1232	-.6143	-.4523	-1.1232
$e_{3,8}$	-2.9268	-.5911	-.8691	-1.2638	-1.5400	-2.2541	-2.2541	-2.9250
$e_{4,5}$	-.0004	0	0	0	0	0	0	0
$e_{4,6}$	-2.1670	-.7022	-.9802	-1.3749	-1.6511	-.9802	-.9802	-1.6511
$e_{4,7}$	-3.1837	-1.5628	-1.8408	-2.0735	-2.3497	-1.8408	-1.6788	-2.3497
$e_{4,8}$	-4.5709	-2.2366	-2.5146	-2.9093	-3.1855	-3.8996	-3.8996	-4.5705

Table 5: Case Study 1: Linear Error using Absolute Values

Thus $n_c = 5$, $n_a = 4$ and $md = 9$ with

$$maximize\ Z = \sum_{k=1}^{9} \frac{\partial r_k}{\partial p} \tag{11}$$

subject to the restrictions

$$\frac{\partial r_i}{\partial p} + \frac{\partial r_j}{\partial p} \leq \frac{\partial R_{ij}}{\partial p}\ for \begin{cases} i = 1..5 \\ j = 6..9 \end{cases}$$

Cations	Li^+	Na^+	K^+	Rb^+	Cs+
	$\frac{\partial r_1}{\partial p}$	$\frac{\partial r_2}{\partial p}$	$\frac{\partial r_3}{\partial p}$	$\frac{\partial r_4}{\partial p}$	$\frac{\partial r_5}{\partial p}$
Anions	F^-	Cl^-	Br^-	I^-	
	$\frac{\partial r_6}{\partial p}$	$\frac{\partial r_7}{\partial p}$	$\frac{\partial r_8}{\partial p}$	$\frac{\partial r_9}{\partial p}$	

Table 6: Case 2 – Cations and Anions Considered

all nonnegative making 20 inequalities. The correspondence among the salts being studied and the $\frac{\partial R_{ij}}{\partial p}$ notation is shown in Table 7.

LiF	LiCl	LiBr	LiI	NaF	NaCl	NaBr	NaI	KF	KCl
$\frac{\partial R_{1,6}}{\partial p}$	$\frac{\partial R_{1,7}}{\partial p}$	$\frac{\partial R_{1,8}}{\partial p}$	$\frac{\partial R_{1,9}}{\partial p}$	$\frac{\partial R_{2,6}}{\partial p}$	$\frac{\partial R_{2,7}}{\partial p}$	$\frac{\partial R_{2,8}}{\partial p}$	$\frac{\partial R_{2,9}}{\partial p}$	$\frac{\partial R_{3,6}}{\partial p}$	$\frac{\partial R_{3,7}}{\partial p}$
KBr	KI	RbF	RbCl	RbBr	RbI	CsF	CsCl	CsBr	CsI
$\frac{\partial R_{3,8}}{\partial p}$	$\frac{\partial R_{3,9}}{\partial p}$	$\frac{\partial R_{4,6}}{\partial p}$	$\frac{\partial R_{4,7}}{\partial p}$	$\frac{\partial R_{4,8}}{\partial p}$	$\frac{\partial R_{4,9}}{\partial p}$	$\frac{\partial R_{5,6}}{\partial p}$	$\frac{\partial R_{5,7}}{\partial p}$	$\frac{\partial R_{5,8}}{\partial p}$	$\frac{\partial R_{5,9}}{\partial p}$

Table 7: Case 2 – Correspondence Among Salts

In matrix form $\mathbf{Ar} \leq \mathbf{R}$ where $\mathbf{A}$, $\mathbf{r}$, and $\mathbf{R}$ are defined as shown in (12).

$$\mathbf{A} = \begin{pmatrix} 1&0&0&0&0&1&0&0&0\\ 1&0&0&0&0&0&1&0&0\\ 1&0&0&0&0&0&0&1&0\\ 1&0&0&0&0&0&0&0&1\\ 0&1&0&0&0&1&0&0&0\\ 0&1&0&0&0&0&1&0&0\\ 0&1&0&0&0&0&0&1&0\\ 0&1&0&0&0&0&0&0&1\\ 0&0&1&0&0&1&0&0&0\\ 0&0&1&0&0&0&1&0&0\\ 0&0&1&0&0&0&0&1&0\\ 0&0&1&0&0&0&0&0&1\\ 0&0&0&1&0&1&0&0&0\\ 0&0&0&1&0&0&1&0&0\\ 0&0&0&1&0&0&0&1&0\\ 0&0&0&1&0&0&0&0&1\\ 0&0&0&0&1&1&0&0&0\\ 0&0&0&0&1&0&1&0&0\\ 0&0&0&0&1&0&0&1&0\\ 0&0&0&0&0&0&0&0&1 \end{pmatrix} \quad \mathbf{r} = \begin{pmatrix} \frac{\partial r_1}{\partial p}\\ \frac{\partial r_2}{\partial p}\\ \frac{\partial r_3}{\partial p}\\ \frac{\partial r_4}{\partial p}\\ \frac{\partial r_5}{\partial p}\\ \frac{\partial r_6}{\partial p}\\ \frac{\partial r_7}{\partial p}\\ \frac{\partial r_8}{\partial p}\\ \frac{\partial r_9}{\partial p} \end{pmatrix} \quad \mathbf{R} = \begin{pmatrix} \frac{\partial R_{1,6}}{\partial p}\\ \frac{\partial R_{1,7}}{\partial p}\\ \frac{\partial R_{1,8}}{\partial p}\\ \frac{\partial R_{1,9}}{\partial p}\\ \frac{\partial R_{2,6}}{\partial p}\\ \frac{\partial R_{2,7}}{\partial p}\\ \frac{\partial R_{2,8}}{\partial p}\\ \frac{\partial R_{2,9}}{\partial p}\\ \frac{\partial R_{3,6}}{\partial p}\\ \frac{\partial R_{3,7}}{\partial p}\\ \frac{\partial R_{3,8}}{\partial p}\\ \frac{\partial R_{3,9}}{\partial p}\\ \frac{\partial R_{4,6}}{\partial p}\\ \frac{\partial R_{4,7}}{\partial p}\\ \frac{\partial R_{4,8}}{\partial p}\\ \frac{\partial R_{4,9}}{\partial p}\\ \frac{\partial R_{5,6}}{\partial p}\\ \frac{\partial R_{5,7}}{\partial p}\\ \frac{\partial R_{5,8}}{\partial p}\\ \frac{\partial R_{5,9}}{\partial p} \end{pmatrix} \tag{12}$$

Table 8 shows the results obtained by different tests T under the restrictions given by equation (12) where

$$\mathbf{R}^t = (.9514 \;\; 2.7083 \;\; 3.7982 \;\; 5.6859 \;\; 1.5224 \;\; 3.7000 \;\; 4.6279 \;\; 6.8671 \;\; 2.7363 \;\; 5.4634 \;\; 6.7088 \;\; 9.0133 \;\; 3.5420 \;\; 6.9525 \;\; 8.7410 \;\; 11.4645 \;\; 4.2308 \;\; 5.3178 \;\; 6.6542 \;\; 9.0256)$$

The Z column correspond to the Z value defined by equation (11) and the e column is defined by equation (13).

$$e = \sqrt{\sum_{i,j} (e_{ij})^2} \; for \begin{cases} i = 1..5 \\ j = 6..9 \end{cases} \tag{13}$$

$\frac{\partial r_i}{\partial p}$	T-1	T-2	T-3	T-4	T-5	T-6a	T-6b
$\frac{\partial r_1}{\partial p}$	$\oplus$.2780	.6927	•	$\oplus$.2780	$\oplus$.2780	$\oplus$.2780	$\oplus$.2780
$\frac{\partial r_2}{\partial p}$	$\oplus$.8466	1.5224	.8515	.8515	1.5224	.8515	.8515
$\frac{\partial r_3}{\partial p}$	$\oplus$2.0636	2.7363	2.0654	2.0654	2.7363	2.0654	2.0654
$\frac{\partial r_4}{\partial p}$	$\oplus$2.8707	3.5420	2.8711	2.8711	3.5420	2.8711	2.8711
$\frac{\partial r_5}{\partial p}$	3.4030	3.5487	2.8778	3.1340	3.5487	2.8875	3.1340
$\frac{\partial r_6}{\partial p}$	$\oplus$.6709	•	$\oplus$.6709	$\oplus$.6709	•	$\oplus$.6709	$\oplus$.6709
$\frac{\partial r_7}{\partial p}$	$\oplus$1.9148	1.7691	2.4400	2.1838	1.7691	2.4303	2.1838
$\frac{\partial r_8}{\partial p}$	$\oplus$2.6866	3.1055	3.7764	3.5202	3.1055	3.5202	3.5202
$\frac{\partial r_9}{\partial p}$	$\oplus$4.0229	4.9932	5.6859	5.4079	$\oplus$4.0229	$\oplus$4.0229	$\oplus$4.0229
Z	18.7571	21.9099	21.2390	20.9828	20.5249	19.5978	19.5978
e	7.8856	4.4825	4.4607	5.0725	6.0422	7.1419	7.1717

Table 8: Case Study 2: Tests using Absolute Values of $\frac{\partial r_i}{\partial p}$

Table 9 shows, for each one of the equations, the linear error as defined by equation (14).

$$e_{ij} = \frac{\partial r_i}{\partial p} + \frac{\partial r_j}{\partial p} - \frac{\partial R_{ij}}{\partial p} \; for \begin{cases} i = 1..5 \\ j = 6..9 \end{cases} \tag{14}$$

$e_{i,j}$	T-1	T-2	T-3	T-4	T-5	T-6a	T-6b
$e_{1,6}$	-.0025	-.25870	-.2805	-.0025	-.6734	-.0025	-.0025
$e_{1,7}$	-.5155	-.2465	-.2683	-.2465	-.6612	0	-.2465
$e_{1,8}$	-.8336	0	-.0218	0	-.4147	0	0
$e_{1,9}$	-1.3850	0	0	0	-1.3850	-1.3850	-1.3850
$e_{2,6}$	-.0049	0	0	0	0	0	0
$e_{2,7}$	-.9386	-.4085	-.4085	-.6647	-.4085	-.4182	-.6647
$e_{2,8}$	-1.0947	0	0	-.2562	0	-.2562	-.2562
$e_{2,9}$	-1.9976	-.3515	-.3297	-.6077	-1.3218	-1.9927	-1.9927
$e_{3,6}$	-.0018	0	0	0	0	0	0
$e_{3,7}$	-1.4850	-.9580	-.9580	-1.2142	-.9580	-.9677	-1.2142
$e_{3,8}$	-1.9586	-.8670	-.8670	-1.1232	-.8670	-1.1232	-1.1232
$e_{3,9}$	-2.9268	-1.2838	-1.2620	-1.5400	-2.2541	-2.9250	-2.9250
$e_{4,6}$	-.0004	0	0	0	0	0	0
$e_{4,7}$	-2.1670	-1.6414	-1.6414	-1.8976	-1.6414	-1.6511	-1.8976
$e_{4,8}$	-3.1837	-2.0935	-2.0935	-2.3497	-2.0935	-2.3497	-2.3497
$e_{4,9}$	-4.5709	-2.9293	-2.9075	-3.1855	-3.8996	-4.5705	-4.5705
$e_{5,6}$	-.1569	-.6821	-.6821	-.4259	-.6821	-.6724	-.4259
$e_{5,7}$	0	0	0	0	0	0	0
$e_{5,8}$	-.5646	0	0	0	0	-.2465	0
$e_{5,9}$	-1.5997	-.4837	-.4619	-.4837	-1.4540	-2.1152	-1.8687

Table 9: Case Study 2: Linear Error using Absolute Values

3.3 Case Study 3

The third case study corresponds to the cations and anions in Table 10

Cations	Li^+	Na^+	K^+	Rb^+	Cs^+	Ca^{2+}	Sr^{2+}	Ba^{2+}	Mg^{2+}
	$\frac{\partial r_1}{\partial p}$	$\frac{\partial r_2}{\partial p}$	$\frac{\partial r_3}{\partial p}$	$\frac{\partial r_4}{\partial p}$	$\frac{\partial r_5}{\partial p}$	$\frac{\partial r_6}{\partial p}$	$\frac{\partial r_7}{\partial p}$	$\frac{\partial r_8}{\partial p}$	$\frac{\partial r_9}{\partial p}$
Anions	F^-	Cl^-	Br^-	I^-	O^{2-}				
	$\frac{\partial r_{10}}{\partial p}$	$\frac{\partial r_{11}}{\partial p}$	$\frac{\partial r_{12}}{\partial p}$	$\frac{\partial r_{13}}{\partial p}$	$\frac{\partial r_{14}}{\partial p}$				

Table 10: Case 3 – Cations and Anions Considered

Thus $n_c = 9$, $n_a = 5$ and $md = 14$ with

$$maximize\ Z = \sum_{k=1}^{14} \frac{\partial r_k}{\partial p} \tag{15}$$

subject to the restrictions

$$\frac{\partial r_i}{\partial p} + \frac{\partial r_j}{\partial p} \leq \frac{\partial R_{ij}}{\partial p}\ for \begin{cases} i \in \{1..9\} \\ j \in \{10..14\} \end{cases}$$

all nonnegative making 28 inequalities where the correspondence among the salts being studied and the $\frac{\partial R_{ij}}{\partial p}$ notation is shown in Table 11.

LiF	LiCl	LiBr	LiI	NaF	NaCl	NaBr	NaI
$\frac{\partial R_{1,10}}{\partial p}$	$\frac{\partial R_{1,11}}{\partial p}$	$\frac{\partial R_{1,12}}{\partial p}$	$\frac{\partial R_{1,13}}{\partial p}$	$\frac{\partial R_{2,10}}{\partial p}$	$\frac{\partial R_{2,11}}{\partial p}$	$\frac{\partial R_{2,12}}{\partial p}$	$\frac{\partial R_{2,13}}{\partial p}$
KF	KCl	KBr	KI	RbF	RbCl	RbBr	RbI
$\frac{\partial R_{3,10}}{\partial p}$	$\frac{\partial R_{3,11}}{\partial p}$	$\frac{\partial R_{3,12}}{\partial p}$	$\frac{\partial R_{3,13}}{\partial p}$	$\frac{\partial R_{4,10}}{\partial p}$	$\frac{\partial R_{4,11}}{\partial p}$	$\frac{\partial R_{4,12}}{\partial p}$	$\frac{\partial R_{4,13}}{\partial p}$
CsF	CsCl	CsBr	CsI				
$\frac{\partial R_{5,10}}{\partial p}$	$\frac{\partial R_{5,11}}{\partial p}$	$\frac{\partial R_{5,12}}{\partial p}$	$\frac{\partial R_{5,13}}{\partial p}$				
CaF	CaO	SrF	SrCl	SrO	BaF	BaO	MgO
$\frac{\partial R_{6,10}}{\partial p}$	$\frac{\partial R_{6,14}}{\partial p}$	$\frac{\partial R_{7,10}}{\partial p}$	$\frac{\partial R_{7,11}}{\partial p}$	$\frac{\partial R_{7,14}}{\partial p}$	$\frac{\partial R_{8,10}}{\partial p}$	$\frac{\partial R_{8,14}}{\partial p}$	$\frac{\partial R_{9,14}}{\partial p}$

Table 11: Case 3 – Correspondence Among Salts

In matrix form $\mathbf{Ar} \leq \mathbf{R}$ where $\mathbf{A}$, $\mathbf{r}$, and $\mathbf{R}$ are defined as shown in (16).

$$
\mathbf{A} = \begin{pmatrix}
1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\
1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\
1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\
1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\
0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\
0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 1 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 1
\end{pmatrix}
\quad
\mathbf{r} = \begin{pmatrix}
\frac{\partial r_1}{\partial p} \\ \frac{\partial r_2}{\partial p} \\ \frac{\partial r_3}{\partial p} \\ \frac{\partial r_4}{\partial p} \\ \frac{\partial r_5}{\partial p} \\ \frac{\partial r_6}{\partial p} \\ \frac{\partial r_7}{\partial p} \\ \frac{\partial r_8}{\partial p} \\ \frac{\partial r_9}{\partial p} \\ \frac{\partial r_{10}}{\partial p} \\ \frac{\partial r_{11}}{\partial p} \\ \frac{\partial r_{12}}{\partial p} \\ \frac{\partial r_{13}}{\partial p} \\ \frac{\partial r_{14}}{\partial p}
\end{pmatrix}
\quad
\mathbf{R} = \begin{pmatrix}
\frac{\partial R_{1,10}}{\partial p} \\ \frac{\partial R_{1,11}}{\partial p} \\ \frac{\partial R_{1,12}}{\partial p} \\ \frac{\partial R_{1,13}}{\partial p} \\
\frac{\partial R_{2,10}}{\partial p} \\ \frac{\partial R_{2,11}}{\partial p} \\ \frac{\partial R_{2,12}}{\partial p} \\ \frac{\partial R_{2,13}}{\partial p} \\
\frac{\partial R_{3,10}}{\partial p} \\ \frac{\partial R_{3,11}}{\partial p} \\ \frac{\partial R_{3,12}}{\partial p} \\ \frac{\partial R_{3,13}}{\partial p} \\
\frac{\partial R_{4,10}}{\partial p} \\ \frac{\partial R_{4,11}}{\partial p} \\ \frac{\partial R_{4,12}}{\partial p} \\ \frac{\partial R_{4,13}}{\partial p} \\
\frac{\partial R_{6,10}}{\partial p} \\ \frac{\partial R_{6,14}}{\partial p} \\
\frac{\partial R_{7,10}}{\partial p} \\ \frac{\partial R_{7,11}}{\partial p} \\ \frac{\partial R_{7,14}}{\partial p} \\
\frac{\partial R_{8,10}}{\partial p} \\ \frac{\partial R_{8,14}}{\partial p} \\
\frac{\partial R_{9,14}}{\partial p}
\end{pmatrix}
\qquad (16)
$$

Table 12 shows the results obtained by different tests T under the restrictions given by equation (16) where

$$
\mathbf{R}^t = (.9514 \;\; 2.7083 \;\; 3.7982 \;\; 5.6859 \;\; 1.5224 \;\; 3.7000 \;\; 4.6279 \;\; 6.8671 \\
2.7363 \;\; 5.4634 \;\; 6.7088 \;\; 9.0133 \;\; 3.5420 \;\; 6.9525 \;\; 8.7410 \;\; 11.4645 \\
4.2308 \;\; 5.3178 \;\; 6.6542 \;\; 9.0256 \;\; .8915 \;\; .7206 \;\; 1.1981 \;\; 3.3128 \\
.9592 \;\; 1.5703 \;\; 1.2436 \;\; .4255)
$$

The Z column correspond to the Z value defined by equation (15) and the e column is defined by equation (17).

$$
e = \sqrt{\sum_{i,j} (e_{ij})^2} \; for \begin{cases} i \in \{1..9\} \\ j \in \{10..14\} \end{cases} \qquad (17)
$$

$\frac{\partial r_i}{\partial p}$	T-1a	T-1b	T-2a	T-2b	T-3a	T-3b	T-3c
$\frac{\partial r_1}{\partial p}$	$\oplus$.2780	$\oplus$.2780	$\oplus$.2780	$\oplus$.2780	$\oplus$.2780	$\oplus$.2780	$\oplus$.2780
$\frac{\partial r_2}{\partial p}$	$\oplus$.8466	$\oplus$.8466	.8515	.8515	.8515	.8515	.8515
$\frac{\partial r_3}{\partial p}$	$\oplus$2.0636	$\oplus$2.0636	2.0654	2.0654	2.0654	2.0654	2.0654
$\frac{\partial r_4}{\partial p}$	$\oplus$2.8707	$\oplus$2.8707	2.8711	2.8711	2.8711	2.8711	2.8711
$\frac{\partial r_5}{\partial p}$	3.4030	3.4030	3.1340	2.8875	2.8875	2.8875	3.1340
$\frac{\partial r_6}{\partial p}$	.2206	.2206	.2206	.2206	.2206	.2206	.2206
$\frac{\partial r_7}{\partial p}$	.5272	.5272	.5272	.5272	.5272	.5272	.5272
$\frac{\partial r_8}{\partial p}$	.8994	.8994	.8994	.8994	.8994	.8994	.8994
$\frac{\partial r_9}{\partial p}$	.4255	.0813	.0813	.0813	.3455	.0813	.0813
$\frac{\partial r_{10}}{\partial p}$	$\oplus$.6709	$\oplus$.6709	$\oplus$.6709	$\oplus$.6709	$\oplus$.6709	$\oplus$.6709	$\oplus$.6709
$\frac{\partial r_{11}}{\partial p}$	$\oplus$1.9148	$\oplus$1.9148	2.1838	2.4303	2.4303	2.4303	2.1838
$\frac{\partial r_{12}}{\partial p}$	$\oplus$2.6866	$\oplus$2.6866	3.5202	3.5202	3.5202	3.5202	3.5202
$\frac{\partial r_{13}}{\partial p}$	$\oplus$4.0229	$\oplus$4.0229	5.4079	5.4079	5.4079	5.4079	5.4079
$\frac{\partial r_{14}}{\partial p}$	$\bullet$	.3442	.3442	.3442	Δ.0800	Δ.3442	Δ.3442
Z	20.8298	20.8298	23.0555	23.0555	23.0555	23.0555	23.0555
e	7.9685	7.9356	5.1112	4.9778	5.01164	4.9778	5.1112

Table 12: Case Study 3: Tests using Absolute Values of $\frac{\partial r_i}{\partial p}$

Cases marked with Δ, such as testes T-3a, T-3b and T-3c in Table 12, correspond to the additional constraint $\frac{\partial r_{14}}{\partial p} \geq 0.08$.

It is interesting to observe that results from tests T-2b and T-3b as well as T-2a and T-3c in Table 12 are identical. The only difference between T-3 and T2 cases is that in the former the additional constraint $\frac{\partial r_{14}}{\partial p} \geq 0.08$ has been added. As the result of test T-3b has the smallest error e, it seems that $\frac{\partial r_{14}}{\partial p} = 0.3442$ has reached a stable value.

Table 13 shows, for each one of the equations, the linear error as defined by equation (18).

$$e_{ij} = \frac{\partial r_i}{\partial p} + \frac{\partial r_j}{\partial p} - \frac{\partial R_{ij}}{\partial p} \; for \begin{cases} i \in \{1..9\} \\ j \in \{10..14\} \end{cases} \tag{18}$$

Several other thests have been carried out such as

- With no constraint, i.e. not fixing any value of $\frac{\partial r_i}{\partial p}$, then $\frac{\partial r_{10}}{\partial p}$ and $\frac{\partial r_{14}}{\partial p}$, related to F^- and O^{2-} respectively are zero.
- With $\frac{\partial r_1}{\partial p} = 0.2780$, related to Li^+, as constraint then $\frac{\partial r_{10}}{\partial p}$ and $\frac{\partial r_{14}}{\partial p}$, related to F^- and O^{2-} respectively, are zero.
- With $\frac{\partial r_2}{\partial p} = 0.8466$, related to Na^+, as constraint then $\frac{\partial r_{10}}{\partial p}$ and $\frac{\partial r_{14}}{\partial p}$, related to F^- and O^{2-} respectively, are zero. Sometimes also $\frac{\partial r_1}{\partial p}$, related to Li^+ is also zero.
- With $\frac{\partial r_3}{\partial p} = 2.0636$, related to K^+, as constraint then $\frac{\partial r_1}{\partial p}$, $\frac{\partial r_{10}}{\partial p}$ and $\frac{\partial r_{14}}{\partial p}$, related to Li^+, F^- and O^{2-} respectively, are zero.
- With $\frac{\partial r_4}{\partial p} = 2.8707$, related to Rb^+, as constraint then $\frac{\partial r_{10}}{\partial p}$ and/or $\frac{\partial r_{14}}{\partial p}$, related to F^- and O^{2-} respectively, are zero.

$e_{i,j}$	T-1a	T-1b	T-2a	T-2b	T-3a	T-3b	T-3c
$e_{1,10}$	-.0025	-.0025	-.0025	-.0025	-.0025	-.0025	-.0025
$e_{1,11}$	-.5155	-.5155	-.2465	0	0	0	-.2465
$e_{1,12}$	-.8336	-.8336	0	0	0	0	0
$e_{1,13}$	-1.3850	-1.3850	0	0	0	0	0
$e_{2,10}$	-.0049	-.0049	0	0	0	0	0
$e_{2,11}$	-.9386	-.9386	-.6647	-.4182	-.4182	-.4182	-.6647
$e_{2,12}$	-1.0947	-1.0947	-.2562	-.2562	-.2562	-.2562	-.2562
$e_{2,13}$	-1.9976	-1.9976	-.6077	-.6077	-.6077	-.6077	-.6077
$e_{3,10}$	-.0018	-.0018	0	0	0	0	0
$e_{3,11}$	-1.4850	-1.4850	-1.2142	-.9677	-.9677	-.9677	-1.2142
$e_{3,12}$	-1.9586	-1.9586	-1.1232	-1.1232	-1.1232	-1.1232	-1.1232
$e_{3,13}$	-2.9268	-2.9268	-1.5400	-1.5400	-1.5400	-1.5400	-1.5400
$e_{4,10}$	-.0004	-.0004	0	0	0	0	0
$e_{4,11}$	-2.1670	-2.1670	-1.8976	-1.6511	-1.6511	-1.6511	-1.8976
$e_{4,12}$	-3.1837	-3.1837	-2.3497	-2.3497	-2.3497	-2.3497	-2.3497
$e_{4,13}$	-4.5709	-4.5709	-3.1855	-3.1855	-3.1855	-3.1855	-3.1855
$e_{5,10}$	-.1569	-.1569	-.4259	-.6724	-.6724	-.6724	-.4259
$e_{5,11}$	0	0	0	0	0	0	0
$e_{5,12}$	-.5646	-.5646	0	-.2465	-.2465	-.2465	0
$e_{5,13}$	-1.5997	-1.5997	-.4837	-.7302	-.7302	-.7302	-.4837
$e_{6,10}$	0	0	0	0	0	0	0
$e_{6,14}$	-.5000	-.1558	-.1558	-.1558	-.4200	-.1558	-.1558
$e_{7,10}$	0	0	0	0	0	0	0
$e_{7,11}$	-.8708	-.8708	-.6018	-.3553	-.3553	-.3553	-.6018
$e_{7,14}$	-.4320	-.0878	-.0878	-.0878	-.3520	-.0878	-.0878
$e_{8,10}$	0	0	0	0	0	0	0
$e_{8,14}$	-.3442	0	0	0	-.2642	0	0
$e_{9,14}$	0	0	0	0	0	0	0

Table 13: Case Study 3: Linear Error using Absolute Values

- With $\frac{\partial r_{10}}{\partial p} = 0.6709$, related to F^-, as constraint then $\frac{\partial r_1}{\partial p}$ and/or $\frac{\partial r_{14}}{\partial p}$, related to Li^+ and O^{2-} respectively, are zero.
- With $\frac{\partial r_1}{\partial p} = 0.2780$ and $\frac{\partial r_{10}}{\partial p} = 0.6709$, related to Li^+ and F^-, two tests T-2a and T-2b with non zero solution are shown in Table 12. Still, it should be mentioned that the system also have a solution with $\frac{\partial r_{14}}{\partial p}$, related to O^{2-}, as zero.

These results are sumarized in Table 14

3.4 Case Study 4

The forth case study considers the same anions and cations than in case 3, incremented by the two new anions ClO_3^- and BrO_3^-, as shown in Table 15.

Thus $n_c = 9$, $n_a = 7$ and $md = 16$ with

$$maximize\ Z = \sum_{k=1}^{16} \frac{\partial r_k}{\partial p} \tag{19}$$

subject to the restrictions

$\frac{\partial r_i}{\partial p}$	T_0-1	T_0-2	T_0-3a	T_0-3b	T_0-4	T_0-5a	T_0-5b	T_0-5c	T_0-6a	T_0-6b	T_0-6c	T_0-7
$\frac{\partial r_1}{\partial p}$		$\oplus$		•	•				•		•	$\oplus$
$\frac{\partial r_2}{\partial p}$			$\oplus$									
$\frac{\partial r_3}{\partial p}$					$\oplus$							
$\frac{\partial r_4}{\partial p}$						$\oplus$	$\oplus$	$\oplus$				
$\frac{\partial r_5}{\partial p}$												
$\frac{\partial r_6}{\partial p}$												
$\frac{\partial r_7}{\partial p}$												
$\frac{\partial r_8}{\partial p}$												
$\frac{\partial r_9}{\partial p}$												
$\frac{\partial r_{10}}{\partial p}$	•	•	•	•	•	•		•	$\oplus$	$\oplus$	$\oplus$	$\oplus$
$\frac{\partial r_{11}}{\partial p}$												
$\frac{\partial r_{12}}{\partial p}$												
$\frac{\partial r_{13}}{\partial p}$												
$\frac{\partial r_{14}}{\partial p}$	•	•	•	•	•		•	•		•	•	•

Table 14: Case Study 3: Tests with Zero Solutions

Cations	Li^+	Na^+	K^+	Rb^+	Cs^+	Ca^{2+}	Sr^{2+}	Ba^{2+}	Mg^{2+}
	$\frac{\partial r_1}{\partial p}$	$\frac{\partial r_2}{\partial p}$	$\frac{\partial r_3}{\partial p}$	$\frac{\partial r_4}{\partial p}$	$\frac{\partial r_5}{\partial p}$	$\frac{\partial r_6}{\partial p}$	$\frac{\partial r_7}{\partial p}$	$\frac{\partial r_8}{\partial p}$	$\frac{\partial r_9}{\partial p}$
Anions	F^-	Cl^-	Br^-	I^-	O^{2-}	ClO_3^-	BrO_3^-		
	$\frac{\partial r_{10}}{\partial p}$	$\frac{\partial r_{11}}{\partial p}$	$\frac{\partial r_{12}}{\partial p}$	$\frac{\partial r_{13}}{\partial p}$	$\frac{\partial r_{14}}{\partial p}$	$\frac{\partial r_{15}}{\partial p}$	$\frac{\partial r_{16}}{\partial p}$		

Table 15: Case 4 – Cations and Anions Considered

$$\frac{\partial r_i}{\partial p} + \frac{\partial r_j}{\partial p} \le \frac{\partial R_{ij}}{\partial p} \; for \begin{cases} i \in \{1..9\} \\ j \in \{10..16\} \end{cases}$$

all nonnegative making 30 inequalities where the correspondence among the salts being studied and the $\frac{\partial R_{ij}}{\partial p}$ notation is shown in Table 16.

In matrix form $\mathbf{Ar} \le \mathbf{R}$ where $\mathbf{A}$, $\mathbf{r}$, and $\mathbf{R}$ are defined as shown in (20).

LiF $\frac{\partial R_{1,10}}{\partial p}$	LiCl $\frac{\partial R_{1,11}}{\partial p}$	LiBr $\frac{\partial R_{1,12}}{\partial p}$	LiI $\frac{\partial R_{1,13}}{\partial p}$	NaF $\frac{\partial R_{2,10}}{\partial p}$	NaCl $\frac{\partial R_{2,11}}{\partial p}$	NaBr $\frac{\partial R_{2,12}}{\partial p}$	NaI $\frac{\partial R_{2,13}}{\partial p}$	$NaClO_3$ $\frac{\partial R_{2,15}}{\partial p}$	$NaBrO_3$ $\frac{\partial R_{2,16}}{\partial p}$
KF $\frac{\partial R_{3,10}}{\partial p}$	KCl $\frac{\partial R_{3,11}}{\partial p}$	KBr $\frac{\partial R_{3,12}}{\partial p}$	KI $\frac{\partial R_{3,13}}{\partial p}$	RbF $\frac{\partial R_{4,10}}{\partial p}$	RbCl $\frac{\partial R_{4,11}}{\partial p}$	RbBr $\frac{\partial R_{4,12}}{\partial p}$	RbI $\frac{\partial R_{4,13}}{\partial p}$		
CsF $\frac{\partial R_{5,10}}{\partial p}$	CsCl $\frac{\partial R_{5,11}}{\partial p}$	CsBr $\frac{\partial R_{5,12}}{\partial p}$	CsI $\frac{\partial R_{5,13}}{\partial p}$						
CaF $\frac{\partial R_{6,10}}{\partial p}$	CaO $\frac{\partial R_{6,14}}{\partial p}$	SrF $\frac{\partial R_{7,10}}{\partial p}$	SrCl $\frac{\partial R_{7,11}}{\partial p}$	SrO $\frac{\partial R_{7,14}}{\partial p}$	BaF $\frac{\partial R_{8,10}}{\partial p}$	BaO $\frac{\partial R_{8,14}}{\partial p}$	MgO $\frac{\partial R_{9,14}}{\partial p}$		

Table 16: Case 4 – Correspondence Among Salts

$$\mathbf{A} = \begin{pmatrix}
1&0&0&0&0&0&0&0&0&1&0&0&0&0&0&0\\
1&0&0&0&0&0&0&0&0&0&1&0&0&0&0&0\\
1&0&0&0&0&0&0&0&0&0&0&1&0&0&0&0\\
1&0&0&0&0&0&0&0&0&0&0&0&1&0&0&0\\
0&1&0&0&0&0&0&0&0&1&0&0&0&0&0&0\\
0&1&0&0&0&0&0&0&0&0&1&0&0&0&0&0\\
0&1&0&0&0&0&0&0&0&0&0&1&0&0&0&0\\
0&1&0&0&0&0&0&0&0&0&0&0&1&0&0&0\\
0&1&0&0&0&0&0&0&0&0&0&0&0&0&1&0\\
0&1&0&0&0&0&0&0&0&0&0&0&0&0&0&1\\
0&0&1&0&0&0&0&0&0&1&0&0&0&0&0&0\\
0&0&1&0&0&0&0&0&0&0&1&0&0&0&0&0\\
0&0&1&0&0&0&0&0&0&0&0&1&0&0&0&0\\
0&0&1&0&0&0&0&0&0&0&0&0&1&0&0&0\\
0&0&0&1&0&0&0&0&0&1&0&0&0&0&0&0\\
0&0&0&1&0&0&0&0&0&0&1&0&0&0&0&0\\
0&0&0&1&0&0&0&0&0&0&0&1&0&0&0&0\\
0&0&0&1&0&0&0&0&0&0&0&0&1&0&0&0\\
0&0&0&0&1&0&0&0&0&1&0&0&0&0&0&0\\
0&0&0&0&1&0&0&0&0&0&1&0&0&0&0&0\\
0&0&0&0&1&0&0&0&0&0&0&1&0&0&0&0\\
0&0&0&0&1&0&0&0&0&0&0&0&1&0&0&0\\
0&0&0&0&0&1&0&0&0&1&0&0&0&0&0&0\\
0&0&0&0&0&1&0&0&0&0&0&0&0&1&0&0\\
0&0&0&0&0&0&1&0&0&1&0&0&0&0&0&0\\
0&0&0&0&0&0&1&0&0&0&1&0&0&0&0&0\\
0&0&0&0&0&0&1&0&0&0&0&0&0&1&0&0\\
0&0&0&0&0&0&0&1&0&1&0&0&0&0&0&0\\
0&0&0&0&0&0&0&1&0&0&0&0&0&1&0&0\\
0&0&0&0&0&0&0&0&1&0&0&0&0&1&0&0
\end{pmatrix}
\quad
\mathbf{r} = \begin{pmatrix}
\frac{\partial r_1}{\partial p}\\ \frac{\partial r_2}{\partial p}\\ \frac{\partial r_3}{\partial p}\\ \frac{\partial r_4}{\partial p}\\ \frac{\partial r_5}{\partial p}\\ \frac{\partial r_6}{\partial p}\\ \frac{\partial r_7}{\partial p}\\ \frac{\partial r_8}{\partial p}\\ \frac{\partial r_9}{\partial p}\\ \frac{\partial r_{10}}{\partial p}\\ \frac{\partial r_{11}}{\partial p}\\ \frac{\partial r_{12}}{\partial p}\\ \frac{\partial r_{13}}{\partial p}\\ \frac{\partial r_{14}}{\partial p}\\ \frac{\partial r_{15}}{\partial p}\\ \frac{\partial r_{16}}{\partial p}
\end{pmatrix}
\quad
\mathbf{R} = \begin{pmatrix}
\frac{\partial R_{1,10}}{\partial p}\\ \frac{\partial R_{1,11}}{\partial p}\\ \frac{\partial R_{1,12}}{\partial p}\\ \frac{\partial R_{1,13}}{\partial p}\\ \frac{\partial R_{2,10}}{\partial p}\\ \frac{\partial R_{2,11}}{\partial p}\\ \frac{\partial R_{2,12}}{\partial p}\\ \frac{\partial R_{2,13}}{\partial p}\\ \frac{\partial R_{2,15}}{\partial p}\\ \frac{\partial R_{2,16}}{\partial p}\\ \frac{\partial R_{3,10}}{\partial p}\\ \frac{\partial R_{3,11}}{\partial p}\\ \frac{\partial R_{3,12}}{\partial p}\\ \frac{\partial R_{3,13}}{\partial p}\\ \frac{\partial R_{4,10}}{\partial p}\\ \frac{\partial R_{4,11}}{\partial p}\\ \frac{\partial R_{4,12}}{\partial p}\\ \frac{\partial R_{4,13}}{\partial p}\\ \frac{\partial R_{5,10}}{\partial p}\\ \frac{\partial R_{5,11}}{\partial p}\\ \frac{\partial R_{5,12}}{\partial p}\\ \frac{\partial R_{5,13}}{\partial p}\\ \frac{\partial R_{6,10}}{\partial p}\\ \frac{\partial R_{6,14}}{\partial p}\\ \frac{\partial R_{7,10}}{\partial p}\\ \frac{\partial R_{7,11}}{\partial p}\\ \frac{\partial R_{7,14}}{\partial p}\\ \frac{\partial R_{8,10}}{\partial p}\\ \frac{\partial R_{8,14}}{\partial p}\\ \frac{\partial R_{9,14}}{\partial p}
\end{pmatrix} \tag{20}$$

Table 17 shows the results obtained by different tests T under the restrictions given by equation (20) where

$$\mathbf{R}^t = (.9514 \;\; 2.7083 \;\; 3.7982 \;\; 5.6859 \;\; 1.5224 \;\; 3.7000 \;\; 4.6279 \;\; 6.8671 \;\; 4.2676 \;\; 3.6196 \;\; 2.7363 \;\; 5.4634 \;\; 6.7088 \;\; 9.0133 \;\; 3.5420 \;\; 6.9525 \;\; 8.7410 \;\; 11.4645 \;\; 4.2308 \;\; 5.3178 \;\; 6.6542 \;\; 9.0256 \;\; .8915 \;\; .7206 \;\; 1.1981 \;\; 3.3128 \;\; .9592 \;\; 1.5703 \;\; 1.2436 \;\; .4255))$$

The Z column correspond to the Z value defined by equation (19) and the e column is defined by equation (21).

$$e = \sqrt{\sum_{i,j}(e_{ij})^2} \; for \begin{cases} i \in \{1..9\} \\ j \in \{10..16\} \end{cases} \tag{21}$$

$\frac{\partial r_i}{\partial p}$	T-1a	T-1b	T-2
$\frac{\partial r_1}{\partial p}$	⊕.2780	⊕.2780	.⊕2780
$\frac{\partial r_2}{\partial p}$	⊕.8466	⊕.8466	⊕.8466
$\frac{\partial r_3}{\partial p}$	⊕2.0636	⊕2.0636	2.0654
$\frac{\partial r_4}{\partial p}$	⊕2.8707	⊕2.8707	2.8711
$\frac{\partial r_5}{\partial p}$	3.4030	3.4030	2.8875
$\frac{\partial r_6}{\partial p}$	.2206	.2206	.2206
$\frac{\partial r_7}{\partial p}$	.5272	.5272	.5272
$\frac{\partial r_8}{\partial p}$	.8994	.8994	.8994
$\frac{\partial r_9}{\partial p}$	.4255	.0813	.0813
$\frac{\partial r_{10}}{\partial p}$	⊕.6709	⊕.6709	⊕.6709
$\frac{\partial r_{11}}{\partial p}$	⊕1.9148	⊕1.9148	2.4303
$\frac{\partial r_{12}}{\partial p}$	⊕2.6866	⊕2.6866	3.5202
$\frac{\partial r_{13}}{\partial p}$	⊕4.0229	⊕4.0229	5.4079
$\frac{\partial r_{14}}{\partial p}$	•	.3442	.3442
$\frac{\partial r_{15}}{\partial p}$	3.4210	3.4210	3.4210
$\frac{\partial r_{16}}{\partial p}$	2.7730	2.7730	2.7730
Z	27.0238	27.0238	29.2446
e	7.9685	7.9356	4.9791

Table 17: Case Study 4 Tests using Absolute Values of $\frac{\partial r_i}{\partial p}$

Table 18 shows, for each one of the equations, the linear error as defined by equation (22).

$$e_{ij} = \frac{\partial r_i}{\partial p} + \frac{\partial r_j}{\partial p} - \frac{\partial R_{ij}}{\partial p} \; for \begin{cases} i \in \{1..9\} \\ j \in \{10..16\} \end{cases} \tag{22}$$

Several other thests have been carried out such as

- With no constraint, i.e. not fixing any value of $\frac{\partial r_i}{\partial p}$, then $\frac{\partial r_1}{\partial p}$, $\frac{\partial r_2}{\partial p}$, $\frac{\partial r_{10}}{\partial p}$ and $\frac{\partial r_{14}}{\partial p}$ related to Li^+, Na^+, F^- and O^{2-} respectively are zero.

$e_{i,j}$	T-1a	T-1b	T-2
$e_{1,10}$	-.0025	-.0025	-.0025
$e_{1,11}$	-.5155	-.5155	0
$e_{1,12}$	-.8336	-.8336	0
$e_{1,13}$	-1.3850	-1.3850	0
$e_{2,10}$	-.0049	-.0049	-.0049
$e_{2,11}$	-.9386	-.9386	-.4231
$e_{2,12}$	-1.0947	-1.0947	-.2611
$e_{2,13}$	-1.9976	-1.9976	-.6126
$e_{2,15}$	0	0	0
$e_{2,16}$	0	0	0
$e_{3,10}$	-.0018	-.0018	0
$e_{3,11}$	-1.4850	-1.4850	-.9677
$e_{3,12}$	-1.9586	-1.9586	-1.1232
$e_{3,13}$	-2.9268	-2.9268	-1.5400
$e_{4,10}$	-.0004	-.0004	0
$e_{4,11}$	-2.1670	-2.1670	-1.6511
$e_{4,12}$	-3.1837	-3.1837	-2.3497
$e_{4,13}$	-4.5709	-4.5709	-3.1855
$e_{5,10}$	-.1569	-.1569	-.6724
$e_{5,11}$	0	0	0
$e_{5,12}$	-.5646	-.5646	-.2465
$e_{5,13}$	-1.5997	-1.5997	-.7302
$e_{6,10}$	0	0	0
$e_{6,14}$	-.5000	-.1558	-.1558
$e_{7,10}$	0	0	0
$e_{7,11}$	-.8708	-.8708	-.3553
$e_{7,14}$	-.4320	-.0878	-.0878
$e_{8,10}$	0	0	0
$e_{8,14}$	-.3442	0	0
$e_{9,14}$	0	0	0

Table 18: Case Study 4: Linear Error using Absolute Values

- With $\frac{\partial r_1}{\partial p} = 0.2780$, related to Li^+, as constraint then $\frac{\partial r_2}{\partial p}$, $\frac{\partial r_{10}}{\partial p}$ and $\frac{\partial r_{14}}{\partial p}$, related to Na^+, F^- and O^{2-} respectively, are zero.
- With $\frac{\partial r_2}{\partial p} = 0.8466$, related to Na^+, as constraint then $\frac{\partial r_{10}}{\partial p}$ and $\frac{\partial r_{14}}{\partial p}$, related to F^- and O^{2-} respectively, are zero. Sometimes also $\frac{\partial r_1}{\partial p}$, related to Li^+ is also zero.
- With $\frac{\partial r_3}{\partial p} = 2.0636$, related to K^+, as constraint then $\frac{\partial r_1}{\partial p}$, $\frac{\partial r_2}{\partial p}$, $\frac{\partial r_{10}}{\partial p}$ and $\frac{\partial r_{14}}{\partial p}$, related to Li^+, Na^+, F^- and O^{2-} respectively, are zero, or $\frac{\partial r_1}{\partial p}$, $\frac{\partial r_2}{\partial p}$ and $\frac{\partial r_{14}}{\partial p}$, or $\frac{\partial r_2}{\partial p}$, $\frac{\partial r_{10}}{\partial p}$ and $\frac{\partial r_{14}}{\partial p}$,
- With $\frac{\partial r_4}{\partial p} = 2.8707$, related to Rb^+, as constraint then $\frac{\partial r_2}{\partial p}$, $\frac{\partial r_{10}}{\partial p}$ and $\frac{\partial r_{14}}{\partial p}$, related to Na^+, F^- and O^{2-} respectively, are zero, or $\frac{\partial r_1}{\partial p}$, $\frac{\partial r_{10}}{\partial p}$ and $\frac{\partial r_{14}}{\partial p}$, or $\frac{\partial r_2}{\partial p}$ and $\frac{\partial r_{14}}{\partial p}$.
- With $\frac{\partial r_1}{\partial p} = 0.2780$ and $\frac{\partial r_2}{\partial p} = 0.8466$, related to Li^+ and Na^+, as constraints then $\frac{\partial r_{10}}{\partial p}$ and $\frac{\partial r_{14}}{\partial p}$, related to F^- and O^{2-} respectively, are zero
- With $\frac{\partial r_1}{\partial p} = 0.2780$ and $\frac{\partial r_{10}}{\partial p} = 0.6709$, related to Li^+ and F^-, as constraints then $\frac{\partial r_2}{\partial p}$ and/or $\frac{\partial r_{14}}{\partial p}$, related to Na^+ and O^{2-} respectively, are zero
- With $\frac{\partial r_1}{\partial p} = 0.2780$, $\frac{\partial r_2}{\partial p} = 0.8455$ and $\frac{\partial r_{10}}{\partial p} = 0.6709$, related to Li^+, Na^+ and F^-, as constraints then although the system has a solution — T-2 in Table 17 —, it also has

a solution with $\frac{\partial r_{14}}{\partial p}$, related to O^{2-}, as zero.

These results are sumarized in Table 19

$\frac{\partial r_i}{\partial p}$	T_0-1	T_0-2	T_0-3a	T_0-3b	T_0-4a	T_0-4b	T_0-4c	T_0-5a	T_0-5b	T_0-5c	T_0-6
$\frac{\partial r_1}{\partial p}$	•	⊕		•	•	•			•		⊕
$\frac{\partial r_2}{\partial p}$	•	•	⊕	⊕	•	•	•	•		•	⊕
$\frac{\partial r_3}{\partial p}$					⊕	⊕	⊕				
$\frac{\partial r_4}{\partial p}$								⊕	⊕	⊕	
$\frac{\partial r_5}{\partial p}$											
$\frac{\partial r_6}{\partial p}$											
$\frac{\partial r_7}{\partial p}$											
$\frac{\partial r_8}{\partial p}$											
$\frac{\partial r_9}{\partial p}$											
$\frac{\partial r_{10}}{\partial p}$	•	•	•	•	•		•	•	•		•
$\frac{\partial r_{11}}{\partial p}$											
$\frac{\partial r_{12}}{\partial p}$											
$\frac{\partial r_{13}}{\partial p}$											
$\frac{\partial r_{14}}{\partial p}$	•	•	•	•	•	•	•	•	•	•	•
$\frac{\partial r_{15}}{\partial p}$											
$\frac{\partial r_{16}}{\partial p}$											

	T_0-7a	T_0-7b	T_0-7c	T_0-8							
$\frac{\partial r_1}{\partial p}$	⊕	⊕	⊕	⊕							
$\frac{\partial r_2}{\partial p}$	⊕	•	•	⊕							
$\frac{\partial r_3}{\partial p}$											
$\frac{\partial r_4}{\partial p}$											
$\frac{\partial r_5}{\partial p}$											
$\frac{\partial r_6}{\partial p}$											
$\frac{\partial r_7}{\partial p}$											
$\frac{\partial r_8}{\partial p}$											
$\frac{\partial r_9}{\partial p}$											
$\frac{\partial r_10}{\partial p}$	⊕	⊕	⊕	⊕							
$\frac{\partial r_11}{\partial p}$											
$\frac{\partial r_12}{\partial p}$											
$\frac{\partial r_13}{\partial p}$											
$\frac{\partial r_14}{\partial p}$	•		•	•							
$\frac{\partial r_15}{\partial p}$											
$\frac{\partial r_16}{\partial p}$											

Table 19: Case Study 4: Tests with Zero Solutions

3.5 Case Study 5

The fifth case study considers the same anions and cations than in case 4, incremented by just one cation NH_4^+ as shown in Table 20.

Thus $n_c = 10$, $n_a = 7$ and $md = 17$ with

Cations	Li^+	Na^+	K^+	Rb^+	Cs^+	Ca^{2+}	Sr^{2+}	Ba^{2+}	Mg^{2+}	NH_4^+
	$\frac{\partial r_1}{\partial p}$	$\frac{\partial r_2}{\partial p}$	$\frac{\partial r_3}{\partial p}$	$\frac{\partial r_4}{\partial p}$	$\frac{\partial r_5}{\partial p}$	$\frac{\partial r_6}{\partial p}$	$\frac{\partial r_7}{\partial p}$	$\frac{\partial r_8}{\partial p}$	$\frac{\partial r_9}{\partial p}$	$\frac{\partial r_{10}}{\partial p}$
Anions	F^-	Cl^-	Br^-	I^-	O^{2-}	ClO_3^-	BrO_3^-			
	$\frac{\partial r_{11}}{\partial p}$	$\frac{\partial r_{12}}{\partial p}$	$\frac{\partial r_{13}}{\partial p}$	$\frac{\partial r_{14}}{\partial p}$	$\frac{\partial r_{15}}{\partial p}$	$\frac{\partial r_{16}}{\partial p}$	$\frac{\partial r_{17}}{\partial p}$			

Table 20: Case 5 – Cations and Anions Considered

$$maximize\ Z = \sum_{k=1}^{17} \frac{\partial r_k}{\partial p} \tag{23}$$

subject to the restrictions

$$\frac{\partial r_i}{\partial p} + \frac{\partial r_j}{\partial p} \leq \frac{\partial R_{ij}}{\partial p}\ for \begin{cases} i \in \{1..0\} \\ j \in \{11..17\} \end{cases}$$

all nonnegative making 34 inequalities where the correspondence among the salts being studied and the $\frac{\partial R_{ij}}{\partial p}$ notation is shown in Table 21.

LiF	LiCl	LiBr	LiI	NaF	NaCl	NaBr	NaI	$NaClO_3$	$NaBrO_3$
$\frac{\partial R_{1,11}}{\partial p}$	$\frac{\partial R_{1,12}}{\partial p}$	$\frac{\partial R_{1,13}}{\partial p}$	$\frac{\partial R_{1,14}}{\partial p}$	$\frac{\partial R_{2,11}}{\partial p}$	$\frac{\partial R_{2,12}}{\partial p}$	$\frac{\partial R_{2,13}}{\partial p}$	$\frac{\partial R_{2,14}}{\partial p}$	$\frac{\partial R_{2,16}}{\partial p}$	$\frac{\partial R_{2,17}}{\partial p}$
KF	KCl	KBr	KI	RbF	RbCl	RbBr	RbI		
$\frac{\partial R_{3,11}}{\partial p}$	$\frac{\partial R_{3,12}}{\partial p}$	$\frac{\partial R_{3,13}}{\partial p}$	$\frac{\partial R_{3,14}}{\partial p}$	$\frac{\partial R_{4,11}}{\partial p}$	$\frac{\partial R_{4,12}}{\partial p}$	$\frac{\partial R_{4,13}}{\partial p}$	$\frac{\partial R_{4,14}}{\partial p}$		
CsF	CsCl	CsBr	CsI						
$\frac{\partial R_{5,11}}{\partial p}$	$\frac{\partial R_{5,12}}{\partial p}$	$\frac{\partial R_{5,13}}{\partial p}$	$\frac{\partial R_{5,14}}{\partial p}$						
CaF	CaO	SrF	SrCl	SrO	BaF	BaO	MgO		
$\frac{\partial R_{6,11}}{\partial p}$	$\frac{\partial R_{6,15}}{\partial p}$	$\frac{\partial R_{7,11}}{\partial p}$	$\frac{\partial R_{7,12}}{\partial p}$	$\frac{\partial R_{7,15}}{\partial p}$	$\frac{\partial R_{8,11}}{\partial p}$	$\frac{\partial R_{8,15}}{\partial p}$	$\frac{\partial R_{9,15}}{\partial p}$		
$NaBrO_3F$	$NaBrO_3Cl$	$NaBrO_3Br$	$NaBrO_3I$						
$\frac{\partial R_{10,11}}{\partial p}$	$\frac{\partial R_{10,12}}{\partial p}$	$\frac{\partial R_{10,13}}{\partial p}$	$\frac{\partial R_{10,14}}{\partial p}$						

Table 21: Case 5 – Correspondence Among Salts

In matrix form $\mathbf{Ar} \leq \mathbf{R}$ where $\mathbf{A}$, $\mathbf{r}$, and $\mathbf{R}$ are defined as shown in (24).

$$
\mathbf{A} = \begin{pmatrix}
1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\
1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\
1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\
0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\
0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0
\end{pmatrix}
\quad
\mathbf{r} = \begin{pmatrix}
\frac{\partial r_1}{\partial p} \\ \frac{\partial r_2}{\partial p} \\ \frac{\partial r_3}{\partial p} \\ \frac{\partial r_4}{\partial p} \\ \frac{\partial r_5}{\partial p} \\ \frac{\partial r_6}{\partial p} \\ \frac{\partial r_7}{\partial p} \\ \frac{\partial r_8}{\partial p} \\ \frac{\partial r_9}{\partial p} \\ \frac{\partial r_{10}}{\partial p} \\ \frac{\partial r_{11}}{\partial p} \\ \frac{\partial r_{12}}{\partial p} \\ \frac{\partial r_{13}}{\partial p} \\ \frac{\partial r_{14}}{\partial p} \\ \frac{\partial r_{15}}{\partial p} \\ \frac{\partial r_{16}}{\partial p} \\ \frac{\partial r_{17}}{\partial p}
\end{pmatrix}
\quad
\mathbf{R} = \begin{pmatrix}
\frac{\partial R_{1,11}}{\partial p} \\ \frac{\partial R_{1,12}}{\partial p} \\ \frac{\partial R_{1,13}}{\partial p} \\ \frac{\partial R_{1,14}}{\partial p} \\ \frac{\partial R_{2,11}}{\partial p} \\ \frac{\partial R_{2,12}}{\partial p} \\ \frac{\partial R_{2,13}}{\partial p} \\ \frac{\partial R_{2,14}}{\partial p} \\ \frac{\partial R_{2,16}}{\partial p} \\ \frac{\partial R_{2,17}}{\partial p} \\ \frac{\partial R_{3,11}}{\partial p} \\ \frac{\partial R_{3,12}}{\partial p} \\ \frac{\partial R_{3,13}}{\partial p} \\ \frac{\partial R_{3,14}}{\partial p} \\ \frac{\partial R_{4,11}}{\partial p} \\ \frac{\partial R_{4,12}}{\partial p} \\ \frac{\partial R_{4,13}}{\partial p} \\ \frac{\partial R_{4,14}}{\partial p} \\ \frac{\partial R_{5,11}}{\partial p} \\ \frac{\partial R_{5,12}}{\partial p} \\ \frac{\partial R_{5,13}}{\partial p} \\ \frac{\partial R_{5,14}}{\partial p} \\ \frac{\partial R_{6,11}}{\partial p} \\ \frac{\partial R_{6,15}}{\partial p} \\ \frac{\partial R_{7,11}}{\partial p} \\ \frac{\partial R_{7,12}}{\partial p} \\ \frac{\partial R_{7,15}}{\partial p} \\ \frac{\partial R_{8,11}}{\partial p} \\ \frac{\partial R_{8,15}}{\partial p} \\ \frac{\partial R_{9,15}}{\partial p} \\ \frac{\partial R_{10,11}}{\partial p} \\ \frac{\partial R_{10,12}}{\partial p} \\ \frac{\partial R_{10,13}}{\partial p} \\ \frac{\partial R_{10,14}}{\partial p}
\end{pmatrix}
\tag{24}
$$

Table 22 shows the results obtained by different tests T under the restrictions given by equation (24) where

$$\mathbf{R}^t = (.9514\ \ 2.7083\ \ 3.7982\ \ 5.6859\ \ 1.5224\ \ 3.7000\ \ 4.6279\ \ 6.8671\\ 4.2676\ \ 3.6196\ \ 2.7363\ \ 5.4634\ \ 6.7088\ \ 9.0133\ \ 3.5420\ \ 6.9525\\ 8.7410\ \ 11.4645\ \ 4.2308\ \ 5.3178\ \ 6.6542\ \ 9.0256\ \ .8915\ \ .7206\\ 1.1981\ \ 3.3128\ \ .9592\ \ 1.5703\ \ 1.2436\ \ .4255\ \ 6.79417\ \ 6.24216\\ 7.54768\ \ 8.35223))$$

The Z column correspond to the Z value defined by equation (23) and the e column is defined by equation (25).

$$e = \sqrt{\sum_{i,j} (e_{ij})^2}\ for \begin{cases} i \in \{1..10\} \\ j \in \{11..17\} \end{cases} \tag{25}$$

$\frac{\partial r_i}{\partial p}$	T-1a	T-1b	T-2a	T-2b	T-3
$\frac{\partial r_1}{\partial p}$	$\oplus$.2780	$\oplus$.2780	$\oplus$.2780	$\oplus$.2780	$\oplus$.2780
$\frac{\partial r_2}{\partial p}$	$\oplus$.8466	$\oplus$.8466	$\oplus$.8466	$\oplus$.8466	$\oplus$.8466
$\frac{\partial r_3}{\partial p}$	$\oplus$2.0636	$\oplus$2.0636	2.0654	2.0654	2.0654
$\frac{\partial r_4}{\partial p}$	$\oplus$2.8707	$\oplus$2.8707	2.8711	2.8711	2.8711
$\frac{\partial r_5}{\partial p}$	3.4030	3.4030	2.8875	3.1340	3.1340
$\frac{\partial r_6}{\partial p}$	.2206	.2206	.2206	.2206	.2206
$\frac{\partial r_7}{\partial p}$	.5272	.5272	.5272	.5272	.5272
$\frac{\partial r_8}{\partial p}$	.8994	.8994	.8994	.8994	.8994
$\frac{\partial r_9}{\partial p}$	.0813	.4255	.0813	.0813	.0813
$\frac{\partial r_{10}}{\partial p}$	4.3274	4.3274	3.8119	2.9443	2.9443
$\frac{\partial r_{11}}{\partial p}$	$\oplus$.6709	$\oplus$.6709	$\oplus$.6709	$\oplus$.6709	$\oplus$.6709
$\frac{\partial r_{12}}{\partial p}$	$\oplus$1.9148	$\oplus$1.9148	2.4303	2.1838	$\oplus$1.9148
$\frac{\partial r_{13}}{\partial p}$	$\oplus$2.6866	$\oplus$2.6866	3.5202	3.5202	3.5202
$\frac{\partial r_{14}}{\partial p}$	$\oplus$4.0229	$\oplus$4.0229	4.5404	5.4079	5.4079
$\frac{\partial r_{15}}{\partial p}$	.3442	$\bullet$	.3442	.3442	.3442
$\frac{\partial r_{16}}{\partial p}$	3.4210	3.4210	3.4210	3.4210	3.4210
$\frac{\partial r_{17}}{\partial p}$	2.7730	2.7730	2.7730	2.7730	2.7730
Z	31.3512	31.3512	32.1890	32.1890	31.9199
e	8.1538	8.1858	6.6687	6.2176	6.5004

Table 22: Case Study 5 Tests using Absolute Values of $\frac{\partial r_i}{\partial p}$

Related with the results shown in Table 22 it should be observed that

- Test T-2, where $\frac{\partial r_1}{\partial p}$, $\frac{\partial r_2}{\partial p}$ and $\frac{\partial r_{11}}{\partial p}$ have been fixed, also have a solution with $\frac{\partial r_{15}}{\partial p} = 0$ and $e = 7.0219$ which is greater than the error found in T-2a and T-2b.
- Test T-3, where $\frac{\partial r_1}{\partial p}$, $\frac{\partial r_2}{\partial p}$, $\frac{\partial r_{11}}{\partial p}$ and $\frac{\partial r_{12}}{\partial p}$ have been fixed, also have a solution with $\frac{\partial r_{15}}{\partial p} = 0$ and $e = 7.6788$ which is greater than the error found in T-3.

  This test has the same solution as test T-2b, exept for the value of $\frac{\partial r_{12}}{\partial p}$, having a smaller value for Z and a greater value for e.

Table 23 shows, for each one of the equations, the linear error as defined by equation (26).

$$e_{ij} = \frac{\partial r_i}{\partial p} + \frac{\partial r_j}{\partial p} - \frac{\partial R_{ij}}{\partial p} \; for \begin{cases} i \in \{1..10\} \\ j \in \{11..17\} \end{cases} \tag{26}$$

$e_{i,j}$	T-1a	T-1b	T-2a	T2-b	T-3
$e_{1,11}$	-.0025	-.0025	-.0025	-.0025	-.0025
$e_{1,12}$	-.5155	-.5155	0	-.2465	-.5155
$e_{1,13}$	-.8336	-.8336	0	0	0
$e_{1,14}$	-1.3850	-1.3850	-.8675	0	0
$e_{2,11}$	-.0049	-.0049	-.0049	-.0049	-.0049
$e_{2,12}$	-.9386	-.9386	-.4231	-.6696	-.9386
$e_{2,13}$	-1.0947	-1.0947	-.2611	-.2611	-.2611
$e_{2,14}$	-1.9976	-1.9976	-1.4801	-.6126	-.6126
$e_{2,16}$	0	0	0	0	0
$e_{2,17}$	0	0	0	0	0
$e_{3,11}$	-.0018	-.0018	0	0	0
$e_{3,12}$	-1.4850	-1.4850	-.9677	-1.2142	-1.4832
$e_{3,13}$	-1.9586	-1.9586	-1.1232	-1.1232	-1.1232
$e_{3,14}$	-2.9268	-2.9268	-2.4075	-1.5400	-1.5400
$e_{4,11}$	-.0004	-.0004	0	0	0
$e_{4,12}$	-2.1670	-2.1670	-1.6511	-1.8976	-2.1666
$e_{4,13}$	-3.1837	-3.1837	-2.3497	-2.3497	-2.3497
$e_{4,14}$	-4.5709	-4.5709	-4.0530	-3.1855	-3.1855
$e_{5,11}$	-.1569	-.1569	-.6724	-.4259	-.4259
$e_{5,12}$	0	0	0	0	-.2690
$e_{5,13}$	-.5646	-.5646	-.2465	0	0
$e_{5,14}$	-1.5997	-1.5997	-1.5977	-.4837	-.4837
$e_{6,11}$	0	0	0	0	0
$e_{6,15}$	-.1558	-.5000	-.1558	-.1558	-.1558
$e_{7,11}$	0	0	0	0	0
$e_{7,12}$	-.8708	-.8708	-.3553	-.6018	-.8708
$e_{7,17}$	-.0878	-.4320	-.0878	-.0878	-.08780
$e_{8,11}$	0	0	0	0	0
$e_{8,15}$	0	-.3442	0	0	0
$e_{9,15}$	0	0	0	0	0
$e_{10,11}$	-1.7959	-1.7959	-2.3114	-3.1789	-3.1789
$e_{10,12}$	0	0	0	-1.1140	-1.3830
$e_{10,13}$	-.5337	-.5337	-.2156	-1.0831	-1.0831
$e_{10,14}$	-.0020	-.0020	0	0	0

Table 23: Case Study 5: Linear Error using Absolute Values

Several other thests have been carried out such as

- With no constraint, i.e. not fixing any value of $\frac{\partial r_i}{\partial p}$, then $\frac{\partial r_1}{\partial p}$, $\frac{\partial r_2}{\partial p}$, $\frac{\partial r_{10}}{\partial p}$ and $\frac{\partial r_{14}}{\partial p}$ related to Li^+, Na^+, F^- and O^{2-} respectively are zero.
- With $\frac{\partial r_1}{\partial p} = 0.2780$, related to Li^+, as constraint then $\frac{\partial r_2}{\partial p}$, $\frac{\partial r_{10}}{\partial p}$ and $\frac{\partial r_{14}}{\partial p}$, related to Na^+, F^- and O^{2-} respectively, are zero.
- With $\frac{\partial r_2}{\partial p} = 0.8466$, related to Na^+, as constraint then $\frac{\partial r_{10}}{\partial p}$ and $\frac{\partial r_{14}}{\partial p}$, related to F^- and O^{2-} respectively, are zero. Sometimes also $\frac{\partial r_1}{\partial p}$, related to Li^+, is zero.
- With $\frac{\partial r_3}{\partial p} = 2.0636$, related to K^+, as constraint then $\frac{\partial r_1}{\partial p}$, $\frac{\partial r_2}{\partial p}$, $\frac{\partial r_{10}}{\partial p}$ and $\frac{\partial r_{14}}{\partial p}$, related to Li^+, Na^+, F^- and O^{2-} respectively, are zero, or $\frac{\partial r_1}{\partial p}$, $\frac{\partial r_2}{\partial p}$ and $\frac{\partial r_{14}}{\partial p}$, or $\frac{\partial r_2}{\partial p}$, $\frac{\partial r_{10}}{\partial p}$ and $\frac{\partial r_{14}}{\partial p}$, are zero.

- With $\frac{\partial r_4}{\partial p} = 2.8707$, related to Rb^+, as constraint then $\frac{\partial r_2}{\partial p}$, $\frac{\partial r_{10}}{\partial p}$ and $\frac{\partial r_{14}}{\partial p}$, related to Na^+, F^- and O^{2-} respectively, are zero, or $\frac{\partial r_1}{\partial p}$, $\frac{\partial r_{10}}{\partial p}$ and $\frac{\partial r_{14}}{\partial p}$, or $\frac{\partial r_2}{\partial p}$ and $\frac{\partial r_{14}}{\partial p}$ are zero.
- With $\frac{\partial r_1}{\partial p} = 0.2780$ and $\frac{\partial r_2}{\partial p} = 0.8466$, related to Li^+ and Na^+, as constraints then $\frac{\partial r_{10}}{\partial p}$ and $\frac{\partial r_{14}}{\partial p}$, related to F^- and O^{2-} respectively, are zero
- With $\frac{\partial r_1}{\partial p} = 0.2780$ and $\frac{\partial r_{10}}{\partial p} = 0.6709$, related to Li^+ and F^-, as constraints then $\frac{\partial r_2}{\partial p}$ and/or $\frac{\partial r_{14}}{\partial p}$, related to Na^+ and O^{2-} respectively, are zero
- With $\frac{\partial r_1}{\partial p} = 0.2780$, $\frac{\partial r_2}{\partial p} = 0.8455$ and $\frac{\partial r_{10}}{\partial p} = 0.6709$, related to Li^+, Na^+ and F^-, as constraints then although the system has a solution — T-2 in Table 17 —, it also has a solution with $\frac{\partial r_{14}}{\partial p}$, related to O^{2-}, as zero.

These results are sumarized in Table 24

$\frac{\partial r_i}{\partial p}$	T_0-1	T_0-2	T_0-3a	T_0-3b	T_04-a	T_04-b	T_04-c	T_0-5a	T_0-5b	T_05-c	T_0-6	T_0-7	T_0-8
$\frac{\partial r_1}{\partial p}$	•	⊕		•	•	•			•		⊕	⊕	⊕
$\frac{\partial r_2}{\partial p}$	•	•	⊕	⊕	•	•	•	•		•	⊕	•	⊕
$\frac{\partial r_3}{\partial p}$					⊕	⊕	⊕						
$\frac{\partial r_4}{\partial p}$								⊕	⊕	⊕			
$\frac{\partial r_5}{\partial p}$													
$\frac{\partial r_6}{\partial p}$													
$\frac{\partial r_7}{\partial p}$													
$\frac{\partial r_8}{\partial p}$													
$\frac{\partial r_9}{\partial p}$													
$\frac{\partial r_{10}}{\partial p}$	•	•	•	•	•		•	•	•		•	⊕	⊕
$\frac{\partial r_{11}}{\partial p}$													
$\frac{\partial r_{12}}{\partial p}$													
$\frac{\partial r_{13}}{\partial p}$													
$\frac{\partial r_{14}}{\partial p}$	•	•	•	•	•	•	•	•	•	•	•	•	•
$\frac{\partial r_{15}}{\partial p}$													
$\frac{\partial r_{16}}{\partial p}$													
$\frac{\partial r_{17}}{\partial p}$													

Table 24: Case Study 5: Tests with Zero Solutions

4 Conclusions

On the basis of the error study and taking into account those tests that reproduce adequately values of some preestablished $\frac{\partial r_i}{\partial p}$ a great number of times, values of $\frac{\partial r_i}{\partial p}$ are now compared with those obtained with a previous method [9]. There is an excellent agreement between the values, the discrepancy never exceeds 10%.

References

[1] Batana, A.; Bruno, J.; Munn, R.W. Anion Polarizability in Alkali Halide Crystals. *Molecular Physics.* **1997**, 92(6), 1029–1033.

[2] Char, B.W.; Geddes, K.O.; Gonnet, G.O.; Leong, B.L.; Monagan, M.B.; Watt, S.M. *Maple V Language Reference Manual.* Springer-Verlag, **1991**

[3] Fowler, P.W.; Madden, P.A. The In-crystal Polarizability of the Fluoride Ion. *Molecular Physics.* **1993**, 49(4), 913-923.

[4] Fowler, P.W.; Madden, P.A. In-crystal Polarizabilities of Alkali and Halide Ions. *Physical Review B.* **1984**, 29(2), 1035–1042.

[5] Fowler, P.W.; Madden, P.A. In-crystal Polarizability of O^{2-}. *J. Phys. Chem.* **1985**, 89, 2581–2585.

[6] Fowler, P.W.; Pyper, N.C. In Crystal Ionic Polarizabilities Derived by Combining Experimental and *ab initio* Results. *Proc. Roy. Soc. A398.* **1985**, 377, 377–391.

[7] Mahan, G.D. Dielectric Parameters of Alkali Halides. *Phys. Rev.* **1986**, 34, 4235–4239.

[8] Monard, M.C.; Batana, A.; Bruno, J. A Computational System for the Calculation of the Pressure Dependence of Ionic Radii in Crystal. Tech. Rep. ICMSC-USP, No. 82, **1999**. `ftp://ftp.icmc.sc.usp.br/pub/BIBLIOTECA/rel_tec/Rt_82.ps.zip`

[9] Monard, M.C.; Batana, A.; Bruno, J. Calculation of the Pressure Dependence of Anionn Polarizabilities in Crystals. *Computers & Chemistry.* **1999**, 23, 493–501.

5 Appendix - Experimental Data

The following values of $\frac{\partial R}{\partial p}$ for different salts at Low Temperature have been obtained from the experimental values of the compressibility of each salt.

Salt	$\frac{\partial R}{\partial p}$	Salt	$\frac{\partial R}{\partial p}$
LiF	0.9514	KF	2.7363
LiCl	2.7083	KCl	5.4634
LiBr	3.7982	KBr	6.7088
LiI	5.6859	KI	9.0133
RbF	3.5420	CsF	4.2308
RbCl	6.9525	CsCl	5.3178
RbBr	8.7410	CsBr	6.6542
RbI	11.4645	CsI	9.0256
NaF	1.5224	NH4F	6.79417
NaCl	3.7000	NH4Cl	6.24216
NaBr	4.6279	NH4Br	7.54768
NaI	6.8671	NH4I	8.35223
NaCLO3	4.2676		
NaBrO3	3.6196		
CaF	0.8915		
CaO	0.7206		
SrF	1.1981		
SrCl	3.3128		
SrO	0.9592		
BaF	1.5703		
BaO	1.2436		
MgO	0.4255		

Table 25: Absolute Values of $\frac{\partial R}{\partial p}$ at Low Temperatures

The following values of $\frac{\partial r_+}{\partial p}$ and $\frac{\partial r_-}{\partial p}$ for different anions and cations at Low Temperature have been used.

Anion	$\frac{\partial r_+}{\partial p}$	Cation	$\frac{\partial r_-}{\partial p}$
Li	0.2780	F	0.6709
K	2.0636	Cl	1.9148
Rb	2.8707	Br	2.6866
Na	0.8466	I	4.0229

Table 26: Absolute Values of $\frac{\partial r_+}{\partial p}$ and $\frac{\partial r_-}{\partial p}$ at Low Temperatures