

Electronic Supplementary Material

A projected Newton algorithm based on chemically allowed interval for chemical equilibrium computations

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Appendix A

The following tables provide the stoichiometric coefficients, chemical equilibrium constants, and total concentrations for each test case presented in the work.

Table A1 Valocchi Test Case

	Na ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	≡S	log (K)
Na ⁺	1	0	0	0	0	0.000
Ca ²⁺	0	1	0	0	0	0.000
Mg ²⁺	0	0	1	0	0	0.000
Cl ⁻	0	0	0	1	0	0.000
≡S-Na	1	0	0	0	1	4.000
≡S ₂ -Ca	0	1	0	0	2	8.602
≡S ₂ -Mg	0	0	1	0	2	8.355
Total (M)	2.48E-01	1.65E-01	1.58E-01	1.61E-01	7.50E-01	
X value	variable	variable	1.58E-01	1.61E-01	variable	
Min value	1.00E-15	1.00E-15			1.00E-15	
Max value	1.00E-02	1.00E-02			1.00E-02	

Table A2 Phosphoric Acid Test Case

	H ⁺	H ₃ PO ₄	Na ⁺	Cl ⁻	log (K)
H ⁺	1	0	0	0	0.000
OH ⁻	-1	0	0	0	-14.000
H ₃ PO ₄	0	1	0	0	0.000
H ₂ PO ₄ ⁻	-1	1	0	0	-2.000
HPO ₄ ²⁻	-2	1	0	0	-9.000
PO ₄ ³⁻	-3	1	0	0	-21.000
Na ⁺	0	0	1	0	0.000

Cl ⁻	0	0	0	1	0.000
Total (M)	-2.10E-02	1.00E-02	2.20E-02	1.00E-03	
X value	variable	variable	2.20E-02	1.00E-03	
Min value	1.00E-09	1.00E-09			
Max value	1.00E-01	1.00E-01			

Table A3 Gallic Acid Test Case

	H ⁺	Al ³⁺	H ₃ L	log (K)
H ⁺	1	0	0	0.000
Al ³⁺	0	1	0	0.000
H ₃ L	0	0	1	0.000
OH ⁻	-1	0	0	-14.000
H ₂ L ⁻	-1	0	1	-4.150
HL ²⁻	-2	0	1	-12.590
L ³⁻	-3	0	1	-23.670
AlHL ⁺	-2	1	1	-4.930
AlL	-3	1	1	-9.430
AlL ₂ ³⁻	-6	1	2	-21.980
AlL ₃ ⁶⁻	-9	1	3	-37.690
Al ₂ (OH) ₂ (HL) ₃ ²⁻	-8	2	3	-22.650
Al ₂ (OH) ₂ (HL) ₂ L ³⁻	-9	2	3	-27.810
Al ₂ (OH) ₂ (HL)L ₂ ⁴⁻	-10	2	3	-32.870
Al ₂ (OH) ₂ L ₃ ⁵⁻	-11	2	3	-39.560
Al ₄ L ₃ ³⁺	-9	4	3	-20.250
Al ₃ (OH) ₄ (H ₂ L) ⁴⁺	-5	3	1	-12.520
Total (M)	1.58E-06	1.00E-03	1.00E-03	
X value	1.58E-06	variable	variable	
Min value		1.00E-12	1.00E-12	
Max value		1.00E-03	1.00E-03	

Table A4 Calcium Carbonate Test Case

	Ca ²⁺	CO ₃ ²⁻	H ⁺	K
CaCO ₃	1	1	0	1000
HCO ₃ ⁻	0	1	1	1.580E+10
H ₂ CO ₃	0	1	2	3.160E+16
CaHCO	1	1	1	3.980E+11
CaOH ⁻	1	0	-1	6.310E-13
OH ⁻	0	0	-1	1.000E-14
Ca ²⁺	1	0	0	1.000
CO ₃ ²⁻	0	1	0	1.000
H ⁺	0	0	1	1.000
Total (M)	1.00E-03	1.00E-04	1.00E-10	

X value	variable	variable	variable
Min value	1.00E-12	1.00E-12	1.00E-12
Max value	1.00E-03	1.00E-03	1.00E-03

Table A5 MoMaS Easy Test Case

	X1	X2	X3	X4	S	log (K)
X1	1	0	0	0	0	0.000
X2	0	1	0	0	0	0.000
X3	0	0	1	0	0	0.000
X4	0	0	0	1	0	0.000
C1	0	-1	0	0	0	-12.000
C2	0	1	1	0	0	0.000
C3	0	-1	0	1	0	0.000
C4	0	-4	1	3	0	-1.000
C5	0	4	3	1	0	35.000
S	0	0	0	0	1	0.000
CS1	0	3	1	0	1	6.000
CS2	0	-3	0	1	2	-1.000
Total (M)	0.3	0.3	0.3	2	10	
X value	0.3	variable	variable	variable	variable	
Min value		1.00E-10	1.00E-10	0.1	0.1	
Max value		1	1	10	10	

Table A6 Iron-Chromium Test Case

	H ⁺	e ⁻	H ₂ CO ₃	Fe ²⁺	CrO ₄ ²⁻	K ⁺	SO ₄ ²⁻	log K
H ⁺	1	0	0	0	0	0	0	0.000
OH ⁻	-1	0	0	0	0	0	0	-14.000
O ₂	-4	-4	0	0	0	0	0	-83.170
H ₂	2	2	0	0	0	0	0	0.000
H ₂ O ₂	-2	-2	0	0	0	0	0	-59.000
K ⁺	0	0	0	0	0	1	0	0.000
SO ₄ ²⁻	0	0	0	0	0	0	1	0.000
KSO ₄ ⁻	0	0	0	0	0	1	1	0.500
H ₂ CO ₃	0	0	1	0	0	0	0	0.000
HCO ₃ ⁻	-1	0	1	0	0	0	0	-6.300
CO ₃ ²⁻	-2	0	1	0	0	0	0	-16.600
Fe ²⁺	0	0	0	1	0	0	0	0.000
FeOH ⁺	-1	0	0	1	0	0	0	-8.980
FeOOH ⁻	-3	0	0	1	0	0	0	-33.210
Fe(OH) ₂	-2	0	0	1	0	0	0	-20.600
Fe(OH) ₃ ⁻	-3	0	0	1	0	0	0	-31.000
Fe(OH) ₄ ⁻	-4	0	0	1	0	0	0	-46.000

FeHCO ₃ ⁺	-1	0	1	1	0	0	0	-3.580
FeSO ₄	0	0	0	1	0	0	1	1.200
Fe ³⁺	0	-1	0	1	0	0	0	-13.070
FeOH ²⁺	-1	-1	0	1	0	0	0	-15.200
Fe(OH) ₂ ⁺	-2	-1	0	1	0	0	0	-19.970
Fe(OH) ₄ ⁻	-4	-1	0	1	0	0	0	-34.620
Fe ₂ (OH) ₂ ⁴⁺	-2	-2	0	2	0	0	0	-29.000
FeSO ₄ ⁺	0	-1	0	1	0	0	1	-9.020
Fe(SO ₄) ₂ ⁻	0	-1	0	1	0	0	2	-7.620
Cr ²⁺	8	4	0	0	1	0	0	68.090
CrOH ⁺	7	4	0	0	0	0	0	62.560
Cr ³⁺	8	3	0	0	1	0	0	74.980
CrOH ²⁺	7	3	0	0	1	0	0	71.170
Cr(OH) ₂ ⁺	6	3	0	0	1	0	0	64.950
Cr(OH) ₃	5	3	0	0	1	0	0	80.900
Cr(OH) ₄ ⁻	4	3	0	0	1	0	0	47.500
CrO ₄ ²⁻	0	0	0	0	1	0	0	0.000
HCrO ₄ ⁻	1	0	0	0	1	0	0	-6.450
H ₂ CrO ₄	2	0	0	0	1	0	0	-6.30
FeCrO ₄ ⁺	0	-1	0	1	1	0	0	-19.310
CrSO ₄ ⁺	8	3	0	0	1	0	1	76.300
KCrO ₄ ⁻	0	0	0	0	1	1	0	0.570
Total (M)	0	0	1.00E-06	9.00E-03	3.00E-03	6.00E-03	9.00E-03	
X value	variable	variable	1.00E-06	9.00E-03	variable	6.00E-03	9.00E-03	
Min value	1.00E-12	1.00E-12			1.00E-15			
Max value	1.00E-02	1.00E+21			1.00E-02			

Appendix B

The BVLS algorithm and backtracking line search technique mentioned in Section 2.2 are given below. The boundary least-squares problem (eq 20) for the BVLS algorithm is modified as follows:

$$\min_{l \leq X \leq u} \frac{1}{2} \|A \cdot X - b\|_2^2 \quad (B.1)$$

Algorithm B1: Bounded-variable Least Squares (BVLS) Algorithm

Input: A, b, l, u, X_0

Output: X^*

$L = \{j | X_j \leq l_j\}, U = \{j | X_j \geq u_j\}, F = \{j | l_j < X_j < u_j\}$, execute Steps 2-5, then go to Step 11

$X_F = (l_F + u_F)/2, X_L = l_L, X_U = u_U$

$p = b - A \cdot X$

$w = A^T \cdot p$

$p = p + A_F \cdot X_F$

1	5.56E-10	-2.11E-05	5.56E-10	5.00E-05	1.82E-10	2.44E-04	5.56E-10	2.50E-08
2	1.92E-06	-1.17E-04	3.83E-08	5.00E-06	8.09E-10	1.19E-04	2.88E-04	6.24E-06
3	9.51E-06	2.31E-04	1.11E-06	5.00E-07	2.89E-09	5.81E-05	2.83E-04	4.23E-06
4	9.59E-06	1.53E-04	2.09E-05	5.00E-08	9.48E-09	2.84E-05	2.75E-04	2.92E-06
5	9.70E-06	1.01E-04	2.09E-06	5.34E-07	2.55E-08	1.67E-05	2.59E-04	2.08E-06
6	9.84E-06	6.61E-05	2.32E-05	5.34E-08	5.30E-08	1.13E-05	2.34E-04	1.55E-06
7	1.00E-05	4.34E-05	2.32E-06	4.81E-07	9.19E-08	8.31E-06	2.00E-04	1.20E-06
8	1.01E-05	2.86E-05	2.56E-05	4.81E-08	1.52E-07	6.13E-06	1.63E-04	9.71E-07
9	1.00E-05	1.92E-05	2.56E-06	4.48E-07	2.27E-07	4.84E-06	1.26E-04	8.03E-07
10	9.57E-06	1.34E-05	2.75E-05	4.48E-08	3.32E-07	3.83E-06	9.45E-05	6.74E-07
11	8.41E-06	1.00E-05	2.75E-06	4.25E-07	4.80E-07	3.02E-06	6.90E-05	5.71E-07
12	6.63E-06	8.07E-06	2.88E-05	4.25E-08	6.87E-07	2.39E-06	4.95E-05	4.85E-07
13	4.93E-06	6.75E-06	2.88E-06	4.10E-07	9.76E-07	1.89E-06	3.52E-05	4.14E-07
14	4.17E-06	5.18E-06	2.97E-05	4.10E-08	1.38E-06	1.49E-06	2.57E-05	3.53E-07
15	4.38E-06	3.26E-06	2.97E-06	4.00E-07	1.55E-06	1.38E-06	2.09E-05	3.02E-07
16	5.83E-06	1.45E-06	3.03E-05	4.00E-08	1.74E-06	1.27E-06	2.00E-05	2.66E-07
17	1.10E-05	1.23E-07	3.03E-06	3.94E-07	1.95E-06	1.17E-06	2.02E-05	2.57E-07
18	2.09E-05	5.73E-07	3.07E-05	3.94E-08	2.19E-06	1.08E-06	2.02E-05	2.57E-07
19	1.71E-05	4.58E-07	3.07E-06	3.91E-07	2.45E-06	9.95E-07		
20	1.78E-05	3.24E-07	3.09E-05	3.91E-08	2.74E-06	9.20E-07		
21	1.99E-05	2.59E-07	3.09E-06	3.88E-07	3.13E-06	8.34E-07		
22	2.02E-05	2.57E-07	3.10E-05	3.88E-08	3.57E-06	7.59E-07		
23	2.02E-05	2.57E-07	3.10E-06	3.87E-07	4.04E-06	6.93E-07		
24			3.11E-05	3.87E-08	4.66E-06	6.23E-07		
25			3.11E-06	3.86E-07	5.49E-06	5.51E-07		
26			3.12E-05	3.86E-08	6.57E-06	4.80E-07		
27			3.12E-06	3.86E-07	8.25E-06	4.02E-07		
28			3.12E-05	3.86E-08	1.13E-05	3.12E-07		
29			3.12E-06	3.85E-07	1.68E-05	2.39E-07		
30			3.12E-05	3.85E-08	1.89E-05	2.49E-07		
31			3.12E-06	3.85E-07	1.96E-05	2.53E-07		
32			3.12E-05	3.85E-08	1.99E-05	2.55E-07		
33			3.12E-06	3.85E-07	2.01E-05	2.56E-07		
34			3.12E-05	3.85E-08	2.02E-05	2.56E-07		
35			3.12E-06	3.85E-07	2.02E-05	2.56E-07		
36			3.12E-05	3.85E-08	2.02E-05	2.57E-07		
37			3.12E-06	3.85E-07	2.02E-05	2.57E-07		
38			3.12E-05	3.85E-08	2.02E-05	2.57E-07		
39			3.12E-06	3.85E-07	2.02E-05	2.57E-07		
40			3.12E-05	3.85E-08	2.02E-05	2.57E-07		
41			3.12E-06	3.85E-07	2.02E-05	2.57E-07		
42			3.12E-05	3.85E-08	2.02E-05	2.57E-07		
43			3.12E-06	3.85E-07	2.02E-05	2.57E-07		
44			3.12E-05	3.85E-08	2.02E-05	2.57E-07		

45	3.12E-06	3.85E-07	2.02E-05	2.57E-07
46	3.12E-05	3.85E-08	2.02E-05	2.57E-07
47	3.12E-06	3.85E-07		
48	3.12E-05	3.85E-08		
...				
300	3.13E-06	3.85E-07		
