

Appendix A: Reactions and equations

The aim of Appendix A is to give a summary of reactions and reactants that are at present solved in ACCRETE, and provide a list of the main equations and parameters used to solve the reactions. The equations are numbered consecutively as they appear in the ACCRETE fortran code. To ease future reading and modifications of the codes, equations are described with units of variables and constants. The equations are separated into those who are common for both the stand-alone batch code (ACCRETEbatch v. 2.0) and for the reactions module (ACCRETE v. 2.0), and those who are special for and only present in the reaction module. The appendix first lists the reactions and reaction parameters before the equations are listed.

Table A1.

Reactions at present included in ACCRETE with standard state properties of the reactions listed at 298.15 K and 1 bar.

Reac. #	Reaction	ΔG	ΔH	ΔC_p	$\log_{10}(K)$
1	$H_2O + CO_{2,aq} \leftrightarrow HCO_3^- + H^+$	36216.70	9702.70	-353.13	-6.345
2	$HCO_3^- \leftrightarrow CO_3^{2-} + H^+$	58956.74	14698.39	-254.39	-10.329
3	$H_2O \leftrightarrow H^+ + OH^-$	55906.61	51370.41	-190.00	-13.995
4	$Na^+ + HCO_3^- \leftrightarrow NaHCO_{3,aq}$	-924.66	-11702.65	77.82	0.162
5	$Calcite + CO_{2,aq} + H_2O \leftrightarrow Ca^{2+} + 2HCO_3^-$	25564.66	-16012.17	-500.82	-4.496
6	$Magnesite + CO_{2,aq} + H_2O \leftrightarrow Mg^{2+} + 2HCO_3^-$	23124.87	-34794.14	-485.76	-4.051
7	$Siderite + CO_{2,aq} + H_2O \leftrightarrow Fe^{2+} + 2HCO_3^-$	37312.91	-22827.90	-502.50	-6.537
8	$Dawsonite + 3H^+ \leftrightarrow$ $Na^+ + Al^{3+} + HCO_3^- + 2H_2O$	-20893.87	-68583.02	-9.42	3.660
9	$Albite + 4H^+ \leftrightarrow$ $Na^+ + Al^{3+} + 3SiO_{2,aq} + 2H_2O$	-11870.01	-44124.46	-1099.97	2.080
10	$K - feldspar + 4H^+ \leftrightarrow$ $K^+ + Al^{3+} + 3SiO_{2,aq} + 2H_2O$	5481.04	-16213.00	-1110.02	-0.960
11	$Quartz \leftrightarrow SiO_{2,aq}$	22827.90	32949	-362.75	-3.999
12	$Chalcedony \leftrightarrow SiO_{2,aq}$	21279.82	31409.29	-362.75	-3.728
13	$Kaolinite + 6H^+ \leftrightarrow$ $2Al^{3+} + 2SiO_{2,aq} + 5H_2O$	-31057.83	-136318.90	-757.30	5.441
14	$Clinocllore - 14A + 16H^+ \leftrightarrow$ $5Mg^{2+} + 2Al^{3+} + 3SiO_{2,aq} + 12H_2O$	-375986.79	-596910.36	-989.52	65.87
15	$Daphnite - 14A + 16H^+ \leftrightarrow$ $5Fe^{2+} + 2Al^{3+} + 3SiO_{2,aq} + 12H_2O$	-284197.19	-492110.00	-1103.32	49.78
16	$Muscovite + 10H^+ \leftrightarrow$ $K^+ + 3Al^{3+} + 3SiO_{2,aq} + 6H_2O$	-65822.69	-220036.56	-1202.48	11.53
17	$Phlogopite + 10H^+ \leftrightarrow$ $K^+ + Al^{3+} + 3Mg^{2+} + 3SiO_{2,aq} + 6H_2O$	-209798.31	-302770.98	-1044.33	36.76
18	$Annite + 10H^+ \leftrightarrow$ $K^+ + Al^{3+} + 3Fe^{2+} + 3SiO_{2,aq} + 6H_2O$	-164301.50	-252232.44	-1112.53	28.79
19	$Labradorite + 6.4H^+ \leftrightarrow$ $0.4Na^+ + 0.6Ca^{2+} + 1.6Al^{3+} + 2.4SiO_{2,aq} + 3.2H_2O$	-120689.61	-219920.00	-1100.00	21.14
20	$Gibbsite + 3H^+ \leftrightarrow Al^{3+} + 3H_2O$	-39764.74	-95056.30	4.184	6.97

Table A2.

Components used in the aqueous phase vector. Two versions in the code: (1) nw() that contains moles; and (2) xw() that contains mole fractions.

#	Specie	#	Specie
1	H ⁺	9	Mg ²⁺
2	Ca ²⁺	10	OH ⁻
3	CO _{2, aq}	11	SiO _{2, aq}
4	HCO ₃ ⁻	12	K ⁺
5	Na ⁺	13	Fe ²⁺
6	Cl ⁻	14	NaHCO ₃
7	Al ³⁺	15	H ₂ O
8	CO ₃ ²⁻		

Table A3

Coefficients a_{11} to a_{66} for equation A2

a_{11}	$-3.3803410340 \times 10^{-21}$	a_{31}	$-1.7796306552 \times 10^{-15}$	a_{51}	$-3.2360510372 \times 10^{-11}$
a_{12}	$5.5639792653 \times 10^{-18}$	a_{32}	$2.9410588041 \times 10^{-12}$	a_{52}	$5.3848036621 \times 10^{-8}$
a_{13}	$-3.6439136441 \times 10^{-15}$	a_{33}	$-1.9344534434 \times 10^{-9}$	a_{53}	$-3.5679891752 \times 10^{-5}$
a_{14}	$1.1862732957 \times 10^{-12}$	a_{34}	$6.3266787924 \times 10^{-7}$	a_{54}	$1.1761627764 \times 10^{-2}$
a_{15}	$-1.9185324583 \times 10^{-10}$	a_{35}	$-1.0282355457 \times 10^{-4}$	a_{55}	-1.9276764612
a_{16}	$1.2322834905 \times 10^{-8}$	a_{36}	$6.6388938521 \times 10^{-3}$	a_{56}	1.2556700906×10^2
a_{21}	$4.0073137678 \times 10^{-18}$	a_{41}	$3.6185059951 \times 10^{-13}$	a_{61}	$9.3398080811 \times 10^{-10}$
a_{22}	$-6.6076811370 \times 10^{-15}$	a_{42}	$-5.9976115054 \times 10^{-10}$	a_{62}	$-1.5620468551 \times 10^{-6}$
a_{23}	$4.3356784554 \times 10^{-12}$	a_{43}	$3.9572927542 \times 10^{-7}$	a_{63}	$1.0407129649 \times 10^{-3}$
a_{24}	$-1.4143495997 \times 10^{-9}$	a_{44}	$-1.2985952833 \times 10^{-4}$	a_{64}	$-3.451211675089 \times 10^{-1}$
a_{25}	$2.2923655509 \times 10^{-7}$	a_{45}	$2.1180695763 \times 10^{-2}$	a_{65}	5.6936914820×10^1
a_{26}	$-1.4758025981 \times 10^{-5}$	a_{46}	-1.3726958393	a_{66}	$-3.7351399850 \times 10^3$

Table A4.

Coefficients h_{11} to h_{34} for the Henrys law polynomial (Equation A8);

h_{11}	-2.464872×10^3	h_{23}	-3.08861
h_{12}	1.120735×10^2	h_{24}	-6.197265×10
h_{13}	0.87234	h_{31}	-2.459655×10^9
h_{14}	0.17302	h_{32}	1.267036×10^7
h_{21}	1.565812×10^6	h_{33}	-6.072381×10^5
h_{22}	-7.633889×10^5	h_{34}	4.730173×10^3

Table A5.
Truesdell-Jones ion-specific parameters a_i and b_i (Equation A20).

Charged ion	$a_i(\text{\AA})$	$b_i(\text{L/mol})$
Na ⁺	4.32	0.06
K ⁺	3.71	0.01
H ⁺	4.78	0.24
Mg ²⁺	5.46	0.22
Fe ²⁺	5.08	0.16
Ca ²⁺	4.86	0.15
Al ³⁺	6.65	0.19
Cl ⁻	3.71	0.01
OH ⁻	10.65	0.21
HCO ₃ ⁻	5.4	0
CO ₃ ²⁻	5.4	0

Table A6
Coefficients k_{ji} to k_{4i} for equation A26: Temperature dependence on equilibrium constants.

Reaction i	k_{1i}	k_{2i}	k_{3i}	k_{4i}
1	$3.16768615 \times 10^{-07}$	$-3.97498327 \times 10^{-04}$	$1.58217283 \times 10^{-01}$	-2.65775173×10
2	$2.60364261 \times 10^{-07}$	$-3.29510443 \times 10^{-04}$	$1.35651070 \times 10^{-01}$	-2.83822562×10
3	$3.82028370 \times 10^{-07}$	$-4.97724891 \times 10^{-04}$	$2.27662669 \times 10^{-01}$	-4.77527372×10
4	$-1.09747887 \times 10^{-07}$	$1.41174272 \times 10^{-04}$	$-6.17676040 \times 10^{-02}$	8.93709772
5	$3.24963076 \times 10^{-07}$	$-3.97011199 \times 10^{-04}$	$1.40664675 \times 10^{-01}$	-1.97556615×10
6	$2.34774701 \times 10^{-07}$	$-2.77193494 \times 10^{-04}$	$8.22639735 \times 10^{-02}$	-1.01593064×10
7	$2.97811559 \times 10^{-07}$	$-3.60460842 \times 10^{-04}$	$1.22116471 \times 10^{-01}$	-1.87960270×10
8	$-2.82953340 \times 10^{-07}$	$3.79039559 \times 10^{-04}$	$-1.90771250 \times 10^{-01}$	3.43423943x10
9	$6.76340042 \times 10^{-07}$	$-8.21813569 \times 10^{-04}$	$2.83761087 \times 10^{-01}$	-2.73939054×10
10	$8.00754080 \times 10^{-07}$	$-9.87924017 \times 10^{-04}$	$3.65988939 \times 10^{-01}$	-4.34812565×10
11	$4.20824498 \times 10^{-07}$	$-5.36505334 \times 10^{-04}$	$2.26976164 \times 10^{-01}$	-3.51329929×10
12	$4.14910445 \times 10^{-07}$	$-5.28408470 \times 10^{-04}$	$2.22825446 \times 10^{-01}$	-3.41873725×10
13	$2.33875219 \times 10^{-08}$	$2.74908240 \times 10^{-05}$	$-1.02553142 \times 10^{-01}$	3.29537646x10
14	$-1.71773000 \times 10^{-06}$	$2.38125517 \times 10^{-03}$	- 1.31168925	2.90796093x10 ²
15	$-1.19118201 \times 10^{-06}$	$1.68374054 \times 10^{-03}$	$-9.74777492 \times 10^{-01}$	2.22305631x10 ²
16	$2.21603287 \times 10^{-08}$	$6.37346161 \times 10^{-05}$	$-1.7292041 \times 10^{-01}$	5.68335207x10
17	$-4.46924267 \times 10^{-07}$	$6.80728379 \times 10^{-04}$	$-4.64209073 \times 10^{-01}$	1.26496325x10 ²
18	$-1.82579625 \times 10^{-07}$	$3.31413724 \times 10^{-04}$	$-2.96797892 \times 10^{-01}$	9.26587423x10
19	$-5.75056515 \times 10^{-08}$	$1.62647821 \times 10^{-04}$	$-2.10582642 \times 10^{-01}$	7.09862302x10
20	$-4.00099342 \times 10^{-07}$	$5.36408334 \times 10^{-04}$	$-2.68861978 \times 10^{-01}$	5.00515567x10

Equations common for both batch- (batchACCRETE v. 2.0) and reaction module ACCRETE v. 2.0):

A1: Compressibility factor for CO₂:

$$Z = \frac{PV}{RT},$$

Values for $Z(T, P)$ calculated using the SRK-EOS, tabulated in ACCRETE and estimated by bilinear interpolation.

A2: Fugacity coefficient of CO₂ (based on SRK-EOS):

$$\phi = (a_{11}T^5 + a_{12}T^4 + a_{13}T^3 + a_{14}T^2 + a_{15}T + a_{16})P^5, \\ + (a_{21}T^5 + \dots + a_{26})P^4 + \dots + (a_{61}T^5 + \dots + a_{66})$$

where coefficients a_{11} to a_{66} is listed in Table A3, T is temperature (K), and P is pressure (bar).

A3: Moles of minerals present from volume fractions:

$$n_i = 10^6 \cdot \frac{V_{tot} x_i \rho_i}{M_i},$$

where V_{tot} is volume of system (m^3), x is volume fraction of total volume, and ρ and M are respectively density (g/cm^3) and molar weight (g/n) of mineral i .

A4: Porosity ϕ (V_ϕ / V_{tot}):

$$\phi = 1 - \sum_i x_i,$$

where x_i is volume fraction mineral (V_i / V_{tot}).

A5: Calculation of moles of aqueous component i in porespace from mole fractions of aqueous components x_j :

$$n_i = 10^3 \cdot \frac{x_i \rho_{aq} V_{tot} \phi}{\sum_j x_j M_j},$$

where x (n_i / n_{tot}) and M_j (g/n) are mole fraction and moleweight of aqueous component, ρ_{aq} (g/dm^3) is density of aqueous solution, and V_{tot} (m^3) and ϕ (V_ϕ / V_{tot}) are total volume and porosity of the system respectively.

A6: Total dissolved carbon (tdc):

$$tdc = n_{CO_{2,aq}} + n_{HCO_3^-} + n_{CO_3^{2-}} + n_{NaHCO_3},$$

where n is moles.

A7: Fugacity of CO₂ (f_{CO_2}):

$$f_{CO_2} = P \phi \cdot y_{CO_2},$$

where P is pressure (bar), ϕ is the fugacity coefficient (l/bar), and y_{CO_2} is molefraction of CO₂ in gas mixture.

A8: Henrys law coefficient for CO₂:

$$K_H = (h_{11}s^3 + h_{12}s^2 + h_{13}s + h_{14})T^2 \\ + (h_{21}s^3 + \dots + h_{24})T + (h_{31}s^3 + \dots + h_{34}),$$

where h_{11} to h_{34} are tabulated in Table A4, $s = x_{Na^+} + x_{Cl^-}$, and T is temperature (K).

A9: Bubblepoint molefraction CO_2 :

$$x_{CO_2}^b(T, P, S) = \frac{f_{CO_2}}{K_H} \exp\left\{-\frac{\bar{v}^\infty}{RT}(P-1)\right\},$$

where f_{CO_2} and \bar{v}^∞ are fugacity and partial molar volume of CO_2 ($3.4 \text{ cm}^3/0.1n$) respectively, R is the gas constant (8.3145 J/nK), T is temperature (K), and P is pressure (bar).

A10: Activity of charged species:

$$\mathbf{a}_i = \left(\frac{n_i}{V_{aq}}\right) \cdot \gamma_i,$$

where n is moles, V_{aq} is volume of the aqueous phase (dm^3), and γ is the activity coefficient.

A11: Activity of H_2O :

$$\mathbf{a}_{H_2O} = \gamma_{H_2O},$$

where γ_{H_2O} is the activity coefficient for H_2O .

A12: Estimation of initial values of $CO_{2, aq}$ and HCO_3^- activities for the aqueous speciation solver:

$$\mathbf{a}_i = 10^{\left\{c_{i1} \ln\left(\frac{tdc}{V_{aq}}\right) + c_{i2}\right\}},$$

where indices $i=1$ and $i=2$ are $CO_{2, aq}$ and HCO_3^- respectively, tdc is total dissolved carbon (n), and V_{aq} is volume aqueous phase (dm^3). $c_{11} = 0.4337614$, $c_{12} = 0.0958638$, $c_{21} = 0.220575$, and $c_{22} = -3.25463$.

A13: Calculation of volume fraction minerals:

$$x_i = \frac{1}{10^6} \cdot \frac{n_i M_i}{V_{tot} \rho_i},$$

where M_i is molar weight (g/n), V_{tot} is total volume of system (m^3), and ρ is density (g/cm^3)

A14: Roots from equilibrium reaction (4).

$$\lambda_{1,2} = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a},$$

where

$$a = \gamma_{HCO_3^-} \gamma_{Na^+},$$

$$b = -\left(\gamma_{Na^+} \mathbf{a}_{HCO_3^-} + \gamma_{HCO_3^-} \mathbf{a}_{Na^+} + \frac{1}{K_4}\right)$$

$$c = \mathbf{a}_{HCO_3^-} \mathbf{a}_{Na^+} - \frac{\mathbf{a}_{NaHCO_3}}{K_4}$$

, where $\lambda_{1,2}$ are reaction progress to achieve equilibrium.

A15: Activity of H^+ I:

$$\mathbf{a}_{H^+}^I = \frac{K_1 \mathbf{a}_{CO_{2, aq}} \mathbf{a}_{H_2O}}{\mathbf{a}_{HCO_3^-}},$$

A16: Activity of H^+ II:

$$\mathbf{a}_{H^+}^{\prime\prime} = -\gamma_{H^+} \sum_{i=1}^N m_i z_i,$$

where m_i is the molar concentrations of charged species i , and z is charge. This is the central equations to be solved in the speciation solver. System is solved when $\sqrt{(\mathbf{a}_{H^+}^I - \mathbf{a}_{H^+}^{\prime\prime})^2} \leq 10^{-8}$. Equations **A15** and **A16** are also constrained by the remaining equilibrium reactions (2) to (4) and the total dissolved carbon tdc .

A17: Temperature dependence on Debye-Hückel parameter A for the Truesdell-Jones activity model:

$$A_T = A_1 T^2 + A_2 T + A_3,$$

where $A_1 = 2.74 \cdot 10^{-6}$, $A_2 = -7.60 \cdot 10^{-4}$, $A_3 = 0.4916$, and T is temperature (K).

A18: Temperature dependence on Debye-Hückel parameter B for the Truesdell-Jones activity model:

$$B_T = B_1 T + B_2,$$

where $B_1 = 1.62 \cdot 10^{-4}$, $B_2 = 0.2799$, and T is temperature (K).

A19: Ionic strength:

$$I = 0.5 \sum_i m_i z_i^2,$$

where m is molar concentration and z is ionic charge.

A20: Activity coefficient of charged species according to the Truesdell-Jones model (Truesdell and Jones, 1974):

$$\gamma_i = 10^{\left\{ \frac{A(T)z^2\sqrt{I}}{1+a_i B(T)\sqrt{I}} + b_i I \right\}},$$

where I is ionic strength, A and B are Debye-Hückel parameters, and ion-specific parameters a_i and b_i are listed in Table 5.

A21: Activity coefficient of CO_2 according to Drummond et al. (1981):

$$\gamma_{CO_2,aq} = \exp \left\{ \left(g_1 + g_2 T + \frac{g_3}{T} \right) \cdot I - \frac{I \cdot (g_4 + g_5 T)}{I+1} \right\},$$

where $g_1 = -1.0312$, $g_2 = 0.0012806$, $g_3 = 255.9$, $g_4 = 0.4445$, $g_5 = -0.001606$, T is temperature (K), and I is ionic strength.

A22: \dot{B} parameter for the activity coefficient model for water in accordance with the b -dot activity model (Helgeson, 1969):

$$\dot{B} = \dot{b}_1 T^4 + \dot{b}_2 T^3 + \dot{b}_3 T^2 + \dot{b}_4 T + \dot{b}_5,$$

where

$\dot{b}_1 = -3.2603 \cdot 10^{-11}$, $\dot{b}_2 = 4.87313 \cdot 10^{-8}$, $\dot{b}_3 = -2.73898 \cdot 10^{-5}$, $\dot{b}_4 = 6.9044 \cdot 10^{-3}$, $\dot{b}_5 = -0.616616$, and T is temperature (K).

A23: σ -parameter for the activity coefficient model of water (in accordance with the b-dot equation (Helgeson, 1969)):

$$\sigma = \frac{3.0}{x} \left\{ 1 + x - \frac{1}{1+x} - 2 \ln(1+x) \right\},$$

where $x = 4B\sqrt{I}$, I is ionic strength, and B is the Debye-Hückel B -parameter.

A24: Activity coefficient of H_2O in accordance with the b-dot equation (Helgeson, 1969):

$$\gamma_{H_2O} = 10^{\left\{ \frac{1}{55.5} \left(-\sum_i m_i \frac{1}{\ln 10} + \left(\frac{2}{3} A \cdot I^{\frac{3}{2}} \right) \sigma - B \cdot I^2 \right) \right\}},$$

where m is molar concentration, index i cover all aqueous species except H_2O , A is the Debye-Hückel A -parameter, and I is ionic strength.

A25: Temperature dependence on kinetic constants:

$$k = k^0 \exp \left\{ -\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T^0} \right) \right\},$$

where E_a is the apparent activation energy for the reaction, R is the gas constant (8.3145 J/nK), T is temperature (K), and $T^0 = 298.15$.

A26: Change of equilibrium constants with temperature:

$$\log K_i = k_{1,i} T^3 + k_{2,i} T^2 + k_{3,i} T + k_{4,i},$$

where coefficients k_{ji} is listed in Table 6. Polynomial is interpolated from:

$$\ln \left(\frac{K^T}{K^0} \right) = - \int_{T^0}^T \frac{\Delta H_r^0(T^0, P^0) + \int_{T^0}^T \Delta C_{p,r}(\theta, P^0) d\theta}{R} d \left(\frac{1}{T} \right),$$

where ΔH_r^0 and $\Delta C_{p,r}$ are listed in Table A1.

A27: Density of aqueous solution as a function of T , P , and salinity:

$$\rho_w^s = \rho_w^p + S \{ a + bS + cP - dPS + T(e + fT - gS - hP + iPS) \},$$

where

$$\rho_w^p = 1 + jT - kT^2 + lT^3 + P(m - nT + oT^2 - pT^3 - qP - rTP),$$

where coefficients a to r in expressions are listed in Batzle and Wang (1992), S is salinity (g/g H_2O), T is temperature ($^{\circ}C$) and P is pressure (Mpa).

A28: Density of aqueous solution as a function of T , P , salinity and dissolved CO_2 :

$$\rho_w = \rho_w^s + c_{CO_2} \left\{ M_{CO_2} - (\bar{v}_{CO_2} \rho_w^s) \right\},$$

where ρ_w^s is given in A27 (g/dm³), c_{CO_2} is molar concentration of dissociated CO_2 , M is molar weight CO_2 (44.01 g/n), and \bar{v}_{CO_2} is partial molar volume of CO_2 (0.034 dm³/n)

A29: Volume aqueous phase:

$$V_{aq} = \frac{\sum_i n_i M_i}{\rho_w},$$

where ρ_w is given in **A28** (g/dm^3), n is moles, and M is molar weight (g/n).

A30: Total reactive surface area of sediment/rock (m^2):

$$S_{tot} = 10^{-4} \sum_i \frac{n_i M_i \beta_i \tau}{\rho_i},$$

where n , M , β , and ρ are moles, molar weight (g/n), specific reactive surface area (cm^2/cm^3) and density (g/cm^3) of mineral i respectively. The reactive surface for dissolution equals the individual contribution of a mineral in equation **A30**.

A31: Reactive surface area of precipitating phases:

$$S_{prec} = \varpi \cdot S_{tot},$$

where ϖ is a fraction of the total surface area. This is currently set to 0.01.

A32: Solubility indices for the mineral reactions:

$$\Omega_k = \frac{q_k}{K_k},$$

where

$$q_k = \frac{\prod_i a_{i,k}^{v_i}}{\prod_j a_{j,k}^{v_j}},$$

where indices i and j covers products and reactants respectively in mineral reactions k , and K is the equilibrium constant for the reaction.

A33: Change of mineral i with time:

$$\Delta n_i = k_i S_i \{\Omega - 1\} \cdot \Delta t,$$

where k is the kinetic constant of the reaction (n/m^2s), S is the reactive surface area (m^2), Ω is the solubility index, and t is time (s).

Equations specific for the reaction module (ACCRETE v. 2.0):

A34: Volume CO_2 :

$$V_{CO_2} = \frac{n_{CO_2} \cdot Z \cdot RT}{P_{atm}},$$

where n is moles, Z is the compressibility factor of CO_2 , R is the gas constant ($0.0821 L \cdot atm / n \cdot K$), T is temperature (K), and P is pressure (atm).

A35: Test to see if input volume of CO_2 is larger or equal porespace of sediment:

$$x_{CO_2}^{TEST} = \frac{1}{10^3} \frac{V_{CO_2}}{V_{tot} \cdot \varphi},$$

where V_{CO_2} is volume of CO_2 (dm^3), V_{tot} is total volume of system (m^3), and φ is

porosity. If $x_{CO_2}^{TEST} \geq 1$ then no water is present as a reactive agent in the sediment and the code returns without further calculations.

A36: Calculation of moles of aqueous component i in porespace from mole fractions of aqueous components x_j :

$$n_i = 10^3 \cdot \frac{x_i \rho_{aq} V_{tot} \phi}{\sum_j x_j M_j} \cdot (1 - x_{CO_2}).$$

This equation is identical to **A5**, except for the last part which scales the aqueous solution volume fraction at the presence of a free CO₂ phase.

A37: Density of CO₂:

$$\rho_{CO_2} = \frac{P_{atm} M_{CO_2}}{Z \cdot RT},$$

where P_{atm} (atm) is pressure, M_{CO_2} is molar weight of CO₂ (44.01 g/n), Z is compressibility factor, R is the gas constant (0.0821 L · atm / n · K), and T is temperature in Kelvin.

A38: Partial derivative of CO₂ density with pressure at constant temperature:

$$\left(\frac{\partial \rho_{CO_2}}{\partial P} \right)_T = \frac{1}{Z \cdot RT} \cdot \left\{ 1 - P_{atm} \left(\frac{\partial Z}{\partial P} \right)_T \right\},$$

where Z is the compressibility factor of CO₂, R is the gas constant (0.0821 L · atm / n · K), T is temperature (K), and P is pressure (atm). The last part is found by:

$$\left(\frac{\partial Z}{\partial P} \right)_T = \frac{Z(T_x, P_2) - Z(T_x, P_1)}{P_2 - P_1},$$

where

$$Z(T_x, P_i) = Z(T_1, P_i) + \Delta T \cdot \left\{ \frac{Z(T_2, P_i) - Z(T_1, P_i)}{T_2 - T_1} \right\}$$

,

where

$$\Delta T = T_x - T_1,$$

where i is 1 or 2, and the subscripts address the table position in the $Z(T, P)$ table.

A39: Change of moles of mineral i with time:

$$\Delta n_i = k_i S_i \{ \Omega - 1 \} \cdot (1 - x_{CO_2}) \cdot \Delta t.$$

This is identical to equation **A33**, except for the term reducing the rate proportional with the reduced volume of reactive aqueous phase at the presence of a free CO₂ phase.