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Date:	June 20, 2017
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Topic 2.2: Changes in PA Data

Recommendation 17: Maintain this data package as the official PA-CA baseline. Qualify new radionuclide, element and dose information through the UDQ screening process before incorporating into the radionuclide baseline.

Recommended Henry's Law Constants for Non-Groundwater Pathways Models in GoldSim

Scope Abstract

This memorandum documents the source and numerical value of Henry's law constants for volatile radionuclides of interest used in the non-groundwater (air and radon) pathways models for the 2018 E-Area Performance Assessment.

Results / Conclusions

Table 1 summarizes recommended values of dimensionless[1] Henry's law constants for the following potentially volatile radionuclides: Ar-37, Ar-39, and Ar-42 (Ar^0); C-14 (CO_2); Cl-36 (HCl); H-3 (H_2O); Hg-194 and Hg-203 (Hg^0); I-125 and I-129 (HI or I_2); Kr-81 and Kr-85 (Kr^0); Rn-222 (Rn); Ra-226 ($RaCl_2$); S-35 (SO_2); Sb-124 and Sb-125 ($SbCl_3$); Se-75 and Se-79 (H_2Se and $SeCl_4$); Sn-113, Sn-119m, Sn-121m, Sn-123, and Sn-126 ($SnCl_4$); Xe-127 (Xe^0). Henry's law constants were added or updated for the volatile radionuclides of interest to be consistent with the dimensionless units required by the GoldSim code and the geochemistry of the disposal unit of interest. Most importantly, for aqueous electrolytes such as carbon dioxide, sulfur dioxide, hydrogen chloride, etc., the reported Henry's law constants properly account for the effect of pH on volatility.

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[1] $C_{i\,Vapor}$ (mol L^{-1}) / $C_{i\,Liquid}$ (mol L^{-1}) where C_i is the concentration of species i

Table 1. Recommended Dimensionless[1] Henry's Law Constants for Air and Radon Pathways Models

Elemental Isotope	**Potential Volatile Species of Interest**	**Dimensionless H_i Soil at pH 5.4 (molar vapor/molar liq.)**	**Dimensionless H_i Oxidized Region III, pH 8.23 (molar vapor/molar liq.)**
Ar-37 Ar-39 Ar-42	Ar^0	29	29
C-14	CO_2	1.1	0.015
Cl-36	HCl	7.9E-14	1.1E-16
H-3	H_2O	1.9E-05	1.9E-05
Hg-194 Hg-203	Hg^0 (Soil pH 5.4) $HgCl_2$ (Soil pH 5.4) $HgCl_2$ (Oxid'd, pH 8.23)	0.32 (Hg^0) 1.1E-07 ($HgCl_2$)	8.6E-11 ($HgCl_2$)
I-125 I-129	HI (Soil pH 5.4) I_2 (Oxid'd, pH 8.23)	6.5E-17	3.1E-31
Kr-81 Kr-85	Kr^0	17	17
Ra-226	$RaCl_2$	1.0E-30	1.0E-30
Rn-222	Rn^0	4.5	4.5
S-35	SO_2	9.4E-06	1.03E-09
Sb-124 Sb-125	$SbCl_3$	5.9E-35	8.3E-41
Se-75 Se-79	H_2Se (Soil pH 5.4) SeCl4 (Oxid'd, pH 8.23)	1.5E-27	1.1E-89
Sn-113 Sn-119m Sn-121m Sn-123 Sn-126	$SnCl_4$	4.3E-56	6.7E-64
Xe-127	Xe^0	9.4	9.4

Discussion

Dimensionless Henry's law constants reported by Gorensek (2015) via Denham (2010) for

C-14 (CO_2)
Cl-36 (HCl)

H-3 (H_2O)
I-125 and I-129 (HI or I_2 depending on pH/redox conditions)
Sb-124 and Sb-125 ($SbCl_3$)
Se-75 and Se-79 (H_2Se or $SeCl_4$ depending on pH/redox conditions)
Sn-113, Sn-119m, Sn-121m, Sn-123, and Sn-126 ($SnCl_4$)

are reproduced “as is” in Table 1. The reported values correctly account for the impact of pH on volatility and are in the desired dimensionless form[1] (molar vapor/molar liquid).

Henry’s law constants not reported by Gorensek (2015) and Denham (2010) were calculated as described in detail below.

Recommended Dimensionless Henry's Law Constant for Ar-37, Ar-39, and Ar-42 as Ar^0 (g)

H_{Ar} (dimensionless, mol L^{-1} vapor/mol L^{-1} liquid) = 29

Inverse (liquid/vapor) Henry’s law constants for Ar^0 with units mol m^{-3} Pa^{-1} are given by Sander (2015)—a literature compilation of 17,350 values of inverse Henry’s law constants for 4632 species, including the noble gases. The noble gases will not ionize in water; therefore, Henry’s law constants reported by Sander (2015) do not require adjustment for pH. The values reported by Sander (2015) were transformed to the desired molar vapor/molar liquid dimensionless form using a units conversion factor equal to 2479.038 Pa m^3 mol^{-1}.

Dimensionless <u>Inverse</u> H_{Ar} = (1.4E-05 mol m^{-3} Pa^{-1}) (2479.038 Pa m^3 mol^{-1}) = 0.0347

The reciprocal gives the desired dimensionless Henry's law constant (molar vapor/molar liquid)

H_{Ar} = (Dimensionless Inverse H_{Ar})$^{-1}$ = 1/0.0347 = 29

Recommended Dimensionless Henry's Law Constant for Kr-81 and Kr-85 as Kr^0 (g)

H_{Kr} (dimensionless, mol L^{-1} vapor/mol L^{-1} liquid) = 17

Inverse (liquid/vapor) Henry’s law constants for Kr^0 with units mol m^{-3} Pa^{-1} are also provided by Sander (2015). The reported value was transformed to the desired molar vapor/molar liquid dimensionless form using a units conversion factor equal to 2479.038 Pa m^3 mol^{-1}.

Dimensionless <u>Inverse</u> H_{Kr} = (2.4E-05 mol m^{-3} Pa^{-1}) (2479.038 Pa m^3 mol^{-1}) = 0.0595

The reciprocal gives the desired dimensionless Henry's law constant (molar vapor/molar liquid)

H_{Kr} = (Dimensionless Inverse H_{Kr})$^{-1}$ = 1/0.0595 = 17

Recommended Dimensionless Henry's Law Constant for Xe-127 as Xe^0 (g)

H_{Xe} (dimensionless, mol L^{-1} vapor/mol L^{-1} liquid) = 9.4

Inverse (liquid/vapor) Henry's law constants for Xe^0 (g) with units mol m^{-3} Pa^{-1} are summarized by Sander (2015). The reported value was transformed to the desired molar vapor/molar liquid dimensionless form using a units conversion factor equal to 2479.038 Pa m^3 mol^{-1}.

Dimensionless <u>Inverse</u> H_{Xe} = (4.3E-05 mol m^{-3} Pa^{-1}) (2479.038 Pa m^3 mol^{-1}) = 0.1066

The reciprocal gives the desired dimensionless Henry's law constant (molar vapor/molar liquid)

H_{Xe} = (Dimensionless Inverse H_{Xe})$^{-1}$ = 1/0.1066 = 9.4

Recommended Dimensionless Henry's Law Constants for S-35 as SO_2 (g)

Soil at pH 5.4 (Condition A; Denham, 2010):	9.4E-06
Oxidized Region III at pH 8.23 (Denham, 2010):	1.03E-09

SO_2 (g) will hydrolyze in water to form H_2SO_3 (aq) and subsequently dissociate to form bisulfite and sulfite ions depending on pH. Because ions do not exert a vapor pressure, an aqueous environment will suppress SO_2 volatility, especially when pH exceeds the first pK_a for H_2SO_3 (H_2SO_3/HSO_3^-, pK_a = 1.89 from Dean, 1992). H_2SO_3 (aq) is a much stronger acid than H_2CO_3 (aq); therefore, its volatility will be lower. The Henry's law constant for S-35 used in the 2010 atmospheric release model (ARM) was 1.0E+38. The revised Henry's law constants above will dramatically reduce the volatility of S-35.

The OLI Stream Analyzer software was used to estimate Henry's law values for S-35 using the same pore water compositions and temperature, pressure, pH, and E_h conditions summarized in Table 2 in SRNL-TR-2010-00096 (Denham, 2010).

T = 298.15 K
P = 1 atm total pressure
Case 1: Condition A (soil at pH 5.4, E_h 0.37 V, background groundwater)
Case 2: Oxidized Region III (pH 8.23, E_h 0.73 V, calcite saturation)

For Cases 1 and 2 (pH 5.4 to 8.23 and E_h 0.37 to 0.73 V), the thermodynamically favored speciation of sulfur in water at 25 °C and 1 atm will most probably be SO_2 in the gas phase and $H_2SO_3/HSO_3^-/SO_3^{-2}$ in the aqueous phase. E_h-pH diagrams in the literature confirm this assumption.

The aqueous reactions of interest for SO_2 are:

SO_2 (g) = SO_2 (aq)
SO_2 (aq) + H_2O = H_2SO_3 (aq)
H_2SO_3 (aq) = HSO_3^- + H^+
HSO_3^- = SO_3^{-2} + H^+

The pore water cation and anion concentrations given by Denham (2010) in Table 2 for each case were first reconciled for pH and electroneutrality (charge balanced) using the Water Analyzer module within the OLI Stream Analyzer software. The resulting background electrolyte solution was then mixed with 0.01 millimolal SO_2 and 1.0 millimolal N_2 in a single equilibrium stage using OLI Stream Analyzer. In both steps, HCl and NaOH were used to adjust pH to the desired set point. The "Aqueous Electrolyte" thermodynamic framework and database within the OLI software served as the source of the relevant gas- and liquid-phase chemical equilibrium reactions as well as the associated equilibrium constants and activity coefficients (see Appendix A). Real (non-ideal) solution conditions were assumed.

Henry's law constants were calculated using the resulting equilibrium vapor-phase concentration of SO_2 (g) and the total aqueous-phase concentration of S(IV) species (H_2SO_3 (aq), HSO_3^-, SO_3^{-2}, $S_2O_5^{-2}$) in mol L^{-1}.

Case 1: Condition A (soil at pH 5.4, E_h 0.37 V)

$C_{SO2(g)}$ (vapor) = 9.3567E-11 mol L^{-1}
$C_{S(IV)\ species}$ (aqueous) = 9.9998E-06 mol L^{-1}

H_{SO2} = 9.3567E-11 mol L^{-1} / 9.9998E-06 mol L^{-1} = 9.4E-06

Case 2: Oxidized Region III (pH 8.23, E_h 0.73 V)

$C_{SO2(g)}$ (vapor) = 1.0336E-14 mol L^{-1}
$C_{S(IV)\ species}$ (aqueous) = 9.9998E-06 mol L^{-1}

H_{SO2} = 1.0336E-14 mol L^{-1} / 9.9998E-06 mol L^{-1} = 1.03E-09

Recommended Dimensionless Henry's Law Constants for C-14 as CO_2 (g)

To build confidence in the recommended values for SO_2, OLI's predictions for CO_2 were compared to the corrected dimensionless Henry's law constants reported by Gorensek (2015). Agreement between OLI and Gorensek (2015) for CO_2 is excellent at both pH 5.4 and 8.23.

Soil at pH 5.4 (Condition A; Denham, 2010): OLI: 1.09 Gorensek: 1.1
Oxidized Region III at pH 8.23 (Denham, 2010): OLI: 0.0143 Gorensek: 0.015

The equivalent equilibrium reactions for CO_2 include:

CO_2 (g) = CO_2 (aq)
CO_2 (aq) + H_2O = H_2CO_3 (aq)
H_2CO_3 (aq) = HCO_3^- + H^+
HCO_3^- = CO_3^{-2} + H^+

Recommended Dimensionless Henry's Law Constants for Hg-194 & Hg-203 as Hg^0 (g) and $HgCl_2$ (g)

$H_{Hg}{}^0$ (Soil at pH 5.4, Condition A per Denham, 2010):	0.32
H_{HgCl2} (Soil at pH 5.4, Condition A per Denham, 2010):	1.1E-07
H_{HgCl2} (Oxidized Region III, pH 8.23 per Denham, 2010):	8.6E-11

The two soil/waste conditions above were chosen to be consistent with assumptions used by Hiergesell and Taylor (2011) in the air pathway modeling special analysis for the E-Area low-level waste facility. Soil Condition A (pH 5.4, E_h 0.37 V, background groundwater) is judged to be representative of a non-cementitious slit or engineered trench, for example, while Oxidized Region III (pH 8.23, E_h 0.73 V, calcite saturation) is thought to approximate conditions in an oxidized cementitious environment (e.g., CIG trench). A conservative assumption from a volatility perspective is that mercury exists as the more volatile elemental mercury (Hg^0) species rather than as less volatile Hg(II) species. For Soil Condition A (pH 5.4), mercury may exist in both oxidation states as Hg^0 and Hg(II) species. For this reason, Henry's law constants will be calculated for both Hg^0 and Hg(II)Cl_2. In an oxidized cementitious environment (pH 8.23), on the other hand, mercury is assumed to originate as $HgCl_2$ and exist only as less volatile Hg(II) species.

Sander (2015) presents a list of measured and calculated inverse (liquid/vapor) Henry's law constants for Hg^0 with units mol m^{-3} Pa^{-1}. Reported values range from 8.7E-04 to 1.4E-03 mol m^{-3} Pa^{-1}. Transformation to the desired molar vapor/molar liquid dimensionless form is accomplished using a units conversion factor equal to 2479.038 Pa m^3 mol^{-1}. For example,

Dimensionless <u>Inverse</u> $H_{Hg}{}^0 = (1.4E\text{-}03 \text{ mol m}^{-3} \text{ Pa}^{-1}) (2479.038 \text{ Pa m}^3 \text{ mol}^{-1}) = 3.4707$

The reciprocal gives the desired dimensionless Henry's law constant (mol L^{-1} vapor/mol L^{-1} liquid)

$H_{Hg}{}^0 = (\text{Dimensionless Inverse } H_{Hg}{}^0)^{-1} = 1/3.4707 = 0.29$

Transformation to molar vapor/molar liquid dimensionless units results in a reported range of 0.29 to 0.46 for $H_{Hg}{}^0$. The most recent value included by Sander (2015) is a measured Henry's law constant from Andersson et al. (2008). The original Andersson et al. (2008) manuscript provides experimentally measured values for $H_{Hg}{}^0$ as a function of temperature and background electrolyte in the desired molar dimensionless form. At 25 °C, the measured values are 0.32, 0.33, and 0.36 in Milli-Q water, artificial seawater, and 1.5 M NaCl, respectively. For purposes of the air pathway model, H_{Hg}^{0} equal to 0.32 will be used.

As was done for SO_2, the OLI Stream Analyzer software was used to estimate Henry's law constants for Hg(II) as $HgCl_2$ using the same pore water compositions and temperature, pressure, pH, and E_h conditions summarized in Table 2 in SRNL-TR-2010-00096 (Denham, 2010). The pore water cation and anion concentrations given by Denham (2010) in Table 2 for each case were first reconciled for pH and electroneutrality (charge balanced) using the Water Analyzer module within the OLI Stream Analyzer software. The resulting background electrolyte solution was then mixed with 0.01 millimolal $HgCl_2$ and 1.0 millimolal N_2 in a single equilibrium stage using OLI Stream Analyzer. In both steps, HCl and NaOH were used to adjust pH to the desired set point. The “Aqueous Electrolyte” thermodynamic framework and database within the OLI software served as the source of the relevant gas- and liquid-phase chemical equilibrium reactions as well as the associated equilibrium constants and activity coefficients (see Appendix C). Real (non-ideal) solution conditions were assumed.

Henry’s law constants were calculated using the resulting equilibrium vapor-phase concentration of $HgCl_2$ (g) and the total aqueous-phase concentration of Hg(II) species ($HgCl_2$ (aq), $Hg(OH)_2$ (aq), $HgCl^+$, etc.) in mol L^{-1}.

Case 1: Condition A (soil at pH 5.4, E_h 0.37 V)

$C_{HgCl2(g)}$ (vapor) = 1.06309E-12 mol L^{-1}
$C_{Hg(II)\ species}$ (aqueous) = 1.0E-05 mol L^{-1}

H_{HgCl2} = 1.06309E-12 mol L^{-1} / 1.0E-05 mol L^{-1} = 1.1E-07

Case 2: Oxidized Region III (pH 8.23, E_h 0.73 V)

$C_{HgCl2(g)}$ (vapor) = 8.56259E-16 mol L^{-1}
$C_{Hg(II)\ species}$ (aqueous) = 1.0E-05 mol L^{-1}

H_{HgCl2} = 8.56259E-16 mol L^{-1} / 1.0E-05 mol L^{-1} = 8.6E-11

Recommended Dimensionless Henry's Law Constant for Rn-222 as Rn (g)

H_{Rn} (dimensionless, mol L^{-1} vapor/mol L^{-1} liquid) = 4.5

The relevant vapor-liquid equilibrium reaction for radon at P = 1atm and T = 25 °C is

Rn (aq) = Rn (g)

This reaction applies for all pH conditions of interest in the E-Area Performance Assessment.

Three methods were used to calculate the dimensionless Henry's law constant for radon.

- OLI Stream Analyzer software
- Published Gibbs Free Energy of Formation data from the *Journal of Physical and Chemical Reference Data* (Oelkers et al., 1995)
- NIST Chemistry WebBook (National Institute of Standards and Technology, 2015)

OLI Stream Analyzer: 1 mM radon was added to pure water and equilibrated with 0.001 moles nitrogen gas at 25 °C and 1 atm total pressure. The "Aqueous Electrolyte" thermodynamic framework and database within the OLI software served as the source of the relevant gas- and liquid-phase chemical equilibrium reactions as well as the associated equilibrium constants and activity coefficients (see Appendix B). Real (non-ideal) solution conditions were assumed.

The vapor- and aqueous-phase concentrations of radon in mol L^{-1} at equilibrium are

C_{Rn} (vapor) = 0.0043291 mol L^{-1}
C_{Rn} (aqueous) = 9.4307E-04 mol L^{-1}

H_{Rn} = 0.0043291 / 9.4307E-04 = 4.59

Calculated from Gibbs Free Energy Data: The standard-state Gibbs Free Energy of Formation for Rn (g) is 0.0 kJ/mol (Wagman et al., 1982) and for Rn (aq) is 11.67315 kJ/mol (Oelkers et al., 1995). For the equilibrium reaction Rn (aq) = Rn (g),

$$\Delta G_{rxn} = 0 - 11.67315 \text{ kJ/mol} = -11.67315 \text{ kJ/mol}$$

$$K = e^{(-\Delta G_{rxn}/RT)} = e^{(-(-11.67315 \text{ kJ/mol}) / (8.314E\text{-}03 \text{ kJ/mol/K})(298.15 \text{ K}))} = 110.96$$

Because the standard and reference states for ΔG^o_f are based on units of atm and mol/kg H_2O, the dimensionless equilibrium constant (K) above must be converted to the desired dimensionless Henry's law units of (mol L^{-1})/(mol L^{-1}). The conversion factor is 24.4662 L atm mol^{-1}.

H_{Rn} = 110.96 / 24.4662 = 4.54 (excellent agreement with OLI software)

NIST Chemistry WebBook: (NIST, 2016) report a value for the inverse (liquid/vapor) Henry's law constant equal to 0.0093 mol kg^{-1} bar^{-1}. The units conversion factor is 24.78819 bar kg mol^{-1}.

Dimensionless Inverse H_{Rn} = (0.0093 mol kg^{-1} bar^{-1}) (24.78819 bar kg mol^{-1}) = 0.23053

The reciprocal gives the desired dimensionless Henry's law constant (molar vapor/molar liquid)

H_{Rn} = (Dimensionless Inverse H_{Rn})$^{-1}$ = 1/0.23053 = 4.34

The NIST Chemistry WebBook value is within 5% of the OLI and ΔG_{rxn} estimates.

The recommendation is to use a rounded value of 4.5 for radon.

Recommended Dimensionless Henry's Law Constant for Ra-226 as $RaCl_2$ (g)

Unlike radon, radium (Ra-226) will have negligible volatility under the damp/wet, oxidizing conditions encountered in the E-Area disposal units. Ra-226 will exist in the +2 oxidation state and ionize to Ra^{++} (aq) in aqueous solution. Possible solid precipitates that may limit radium solubility include $RaSO_4$ and, to a lesser extent, $RaCl_2.2H_2O$ and $Ra(NO_3)_2$. $RaSO_4$ solubility in water is very low and will likely limit radium concentration in aqueous solution if sulfate is present. A review of the literature uncovered no references to gas-phase radium species other than elemental radium (Ra). For purposes of the air and radon pathway models, the recommendation is to assume a very small dimensionless Henry's law constant equal to 1.0E-30.

References

Andersson, M. E., Gårdfeldt, K., Wängberg, I., and Strömberg, D. (2008) Determination of Henry's Law Constant for Elemental Mercury. *Chemosphere* **73**, 587-592.

Dean, J. A. (1992) *Lange's Handbook of Chemistry*. 14th Ed., McGraw-Hill, Inc., New York, NY.

Denham, M. E. (2010) Vapor-Aqueous Solution Partition Coefficients for Radionuclides Pertinent to High Level Waste Tank Closure. SRNL-TR-2010-00096. Savannah River National Laboratory, Aiken, SC, 29808.

Gorensek, M. B. (2015) Review of E-Area Low-Level Waste Facility Air Pathway Model (SRNL-STI-2011-00327). Interoffice Memorandum. Savannah River National Laboratory, Aiken, SC, 29808.

Hiergesell, R. A., and Taylor, G. A. (2011) Special Analysis: Air Pathway Modeling of E-Area Low-Level Waste Facility. SRNL-STI-2011-00327. Savannah River National Laboratory, Aiken, SC, 29808.

Oelkers, E. H., Helgeson, H. C., Shock, E. L., Sverjensky, D. A., Johnson, J. W., and Pokrovskii, V. A. (1995) Summary of the Apparent Standard Partial Molal Gibbs Free Energies of Formation of Aqueous Species, Minerals, and Gases at Pressures 1 to 5000 Bars and Temperatures 25 to 1000 °C. *J. Phys. Chem. Ref. Data* **24**, 1401-1560.

National Institute of Standards and Technology (2015) NIST Standard Reference Database Number 69. *NIST Chemistry WebBook*. http://webbook.nist.gov/chemistry/.

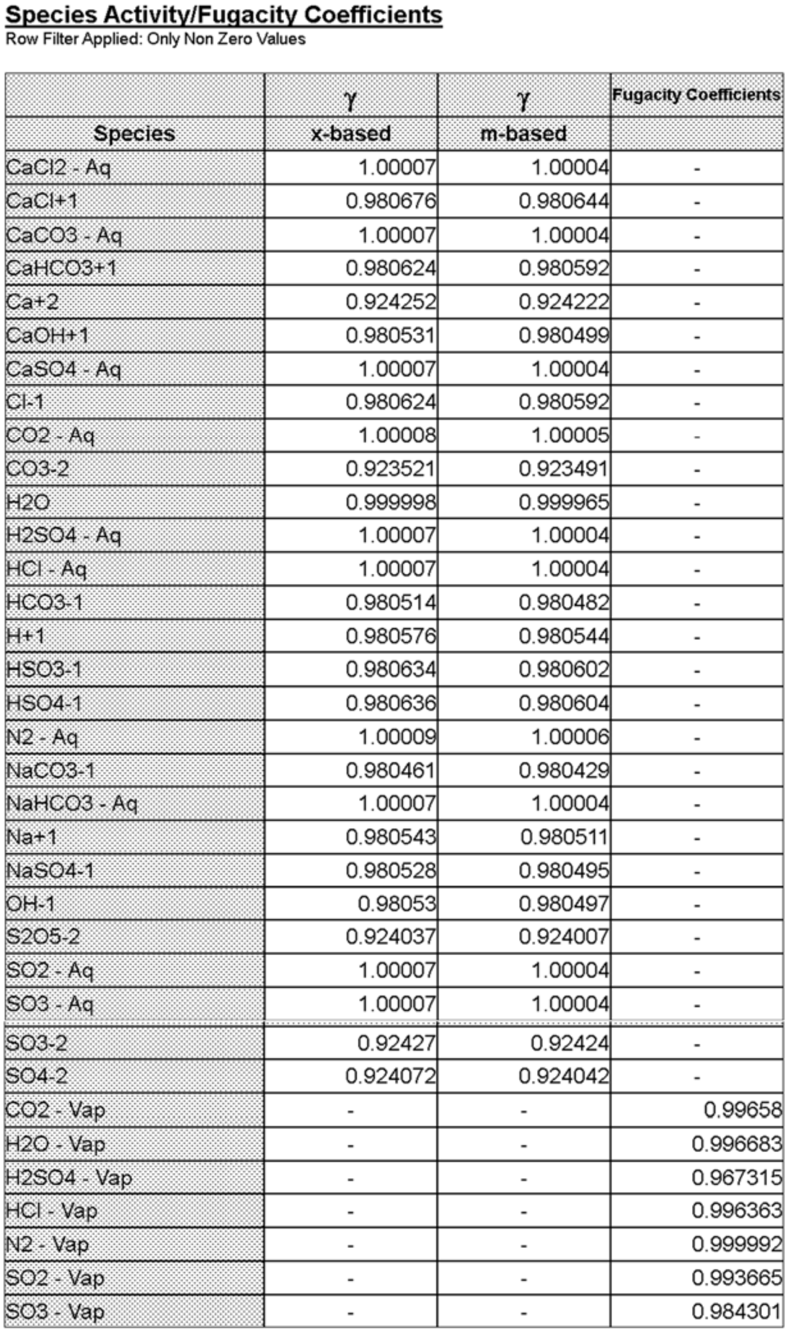
Sander, R. (2015) Compilation of Henry's Law Constants (version 4.0) for Water as Solvent. *Atmos. Chem. Phys.* **15**, 4399–4981.

Wagman, D. D., Evans, W. H., Parker, V. B., Schumm, R. H., Halow, I., Bailey, S. M., Churney, K. L., and Nuttall, R. I. (1982) The NBS Tables of Chemical Thermodynamic Properties: Selected Values for Inorganics and C1 and C2 Organic Substances in SI Units. Suppl. No. 2. *J. Phys. Chem. Ref. Data* **11**, 1-392.

Appendix A – SO_2

Species activity/fugacity coefficients, chemical equilibrium reactions, and equilibrium constants used by the OLI Stream Analyzer software for SO_2 Cases 1 and 2 are summarized below.

Case 1: Condition A (soil at pH 5.4, E_h 0.37 V)

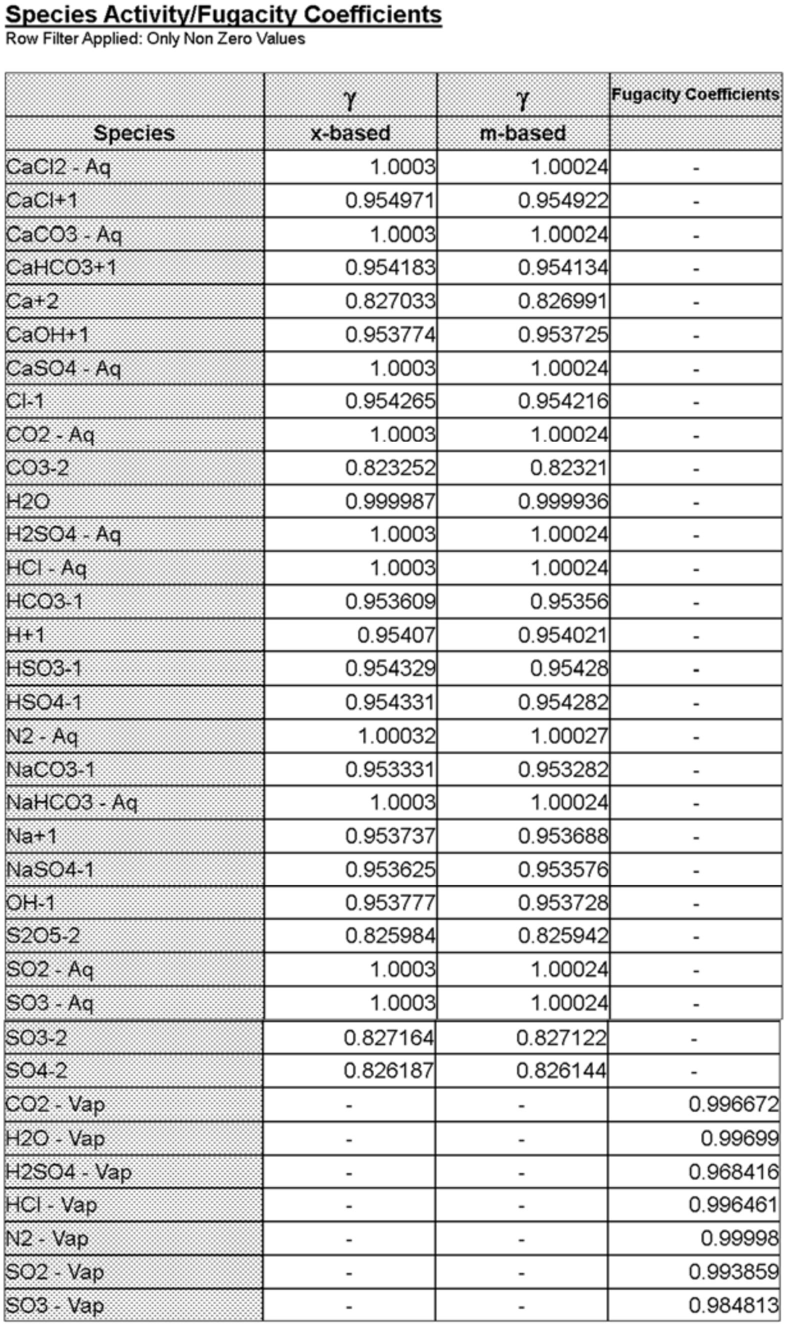


Species Activity/Fugacity Coefficients

Row Filter Applied: Only Non Zero Values

	γ	γ	Fugacity Coefficients
Species	x-based	m-based	
CaCl2 - Aq	1.00007	1.00004	-
CaCl+1	0.980676	0.980644	-
CaCO3 - Aq	1.00007	1.00004	-
CaHCO3+1	0.980624	0.980592	-
Ca+2	0.924252	0.924222	-
CaOH+1	0.980531	0.980499	-
CaSO4 - Aq	1.00007	1.00004	-
Cl-1	0.980624	0.980592	-
CO2 - Aq	1.00008	1.00005	-
CO3-2	0.923521	0.923491	-
H2O	0.999998	0.999965	-
H2SO4 - Aq	1.00007	1.00004	-
HCl - Aq	1.00007	1.00004	-
HCO3-1	0.980514	0.980482	-
H+1	0.980576	0.980544	-
HSO3-1	0.980634	0.980602	-
HSO4-1	0.980636	0.980604	-
N2 - Aq	1.00009	1.00006	-
NaCO3-1	0.980461	0.980429	-
NaHCO3 - Aq	1.00007	1.00004	-
Na+1	0.980543	0.980511	-
NaSO4-1	0.980528	0.980495	-
OH-1	0.98053	0.980497	-
S2O5-2	0.924037	0.924007	-
SO2 - Aq	1.00007	1.00004	-
SO3 - Aq	1.00007	1.00004	-
SO3-2	0.92427	0.92424	-
SO4-2	0.924072	0.924042	-
CO2 - Vap	-	-	0.99658
H2O - Vap	-	-	0.996683
H2SO4 - Vap	-	-	0.967315
HCl - Vap	-	-	0.996363
N2 - Vap	-	-	0.999992
SO2 - Vap	-	-	0.993665
SO3 - Vap	-	-	0.984301

Case 2: Oxidized Region III (pH 8.23, E_h 0.73 V)

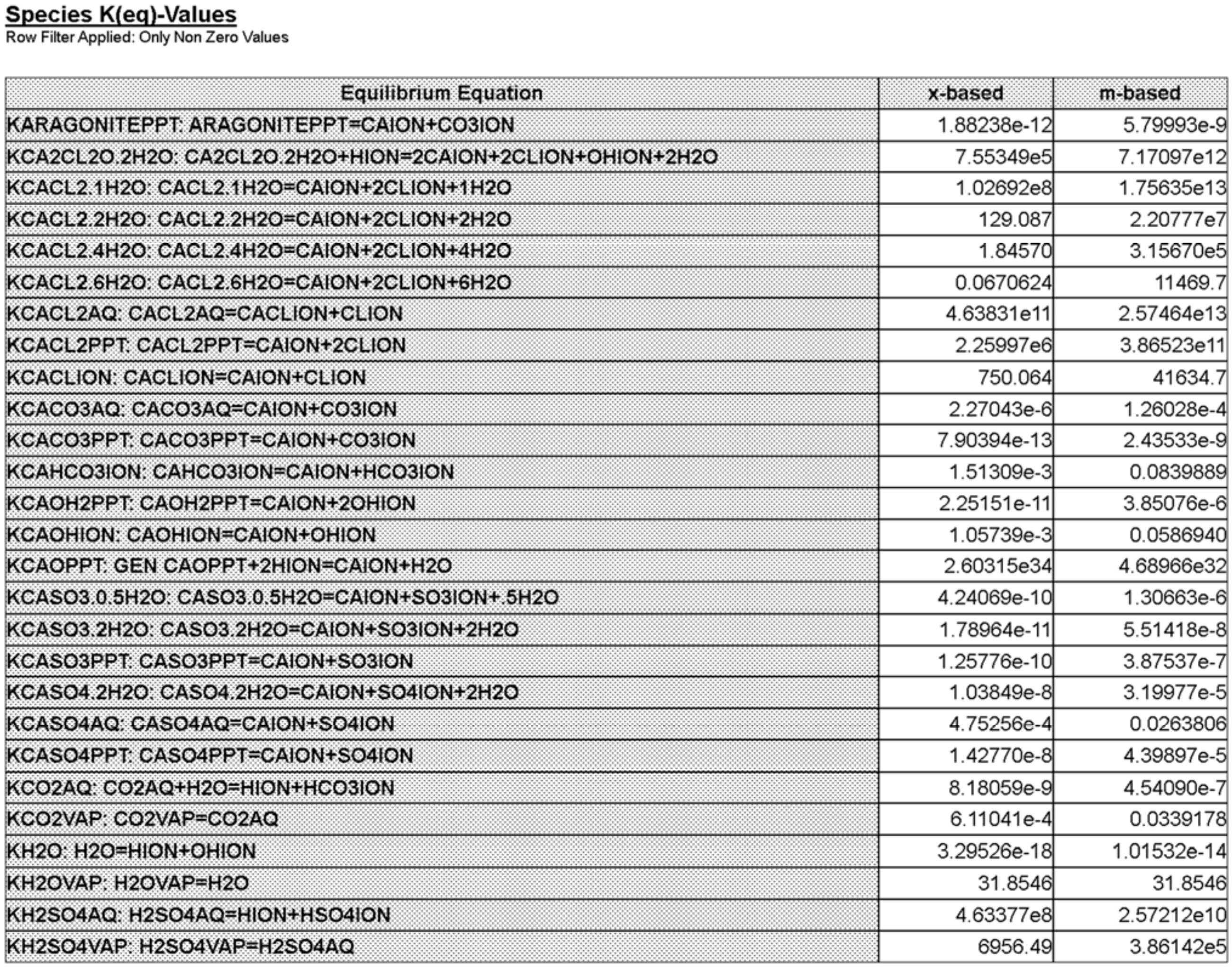


Species Activity/Fugacity Coefficients

Row Filter Applied: Only Non Zero Values

	γ	γ	Fugacity Coefficients
Species	x-based	m-based	
CaCl2 - Aq	1.0003	1.00024	-
CaCl+1	0.954971	0.954922	-
CaCO3 - Aq	1.0003	1.00024	-
CaHCO3+1	0.954183	0.954134	-
Ca+2	0.827033	0.826991	-
CaOH+1	0.953774	0.953725	-
CaSO4 - Aq	1.0003	1.00024	-
Cl-1	0.954265	0.954216	-
CO2 - Aq	1.0003	1.00024	-
CO3-2	0.823252	0.82321	-
H2O	0.999987	0.999936	-
H2SO4 - Aq	1.0003	1.00024	-
HCl - Aq	1.0003	1.00024	-
HCO3-1	0.953609	0.95356	-
H+1	0.95407	0.954021	-
HSO3-1	0.954329	0.95428	-
HSO4-1	0.954331	0.954282	-
N2 - Aq	1.00032	1.00027	-
NaCO3-1	0.953331	0.953282	-
NaHCO3 - Aq	1.0003	1.00024	-
Na+1	0.953737	0.953688	-
NaSO4-1	0.953625	0.953576	-
OH-1	0.953777	0.953728	-
S2O5-2	0.825984	0.825942	-
SO2 - Aq	1.0003	1.00024	-
SO3 - Aq	1.0003	1.00024	-
SO3-2	0.827164	0.827122	-
SO4-2	0.826187	0.826144	-
CO2 - Vap	-	-	0.996672
H2O - Vap	-	-	0.99699
H2SO4 - Vap	-	-	0.968416
HCl - Vap	-	-	0.996461
N2 - Vap	-	-	0.99998
SO2 - Vap	-	-	0.993859
SO3 - Vap	-	-	0.984813

Applicable to SO_2 Cases 1 and 2

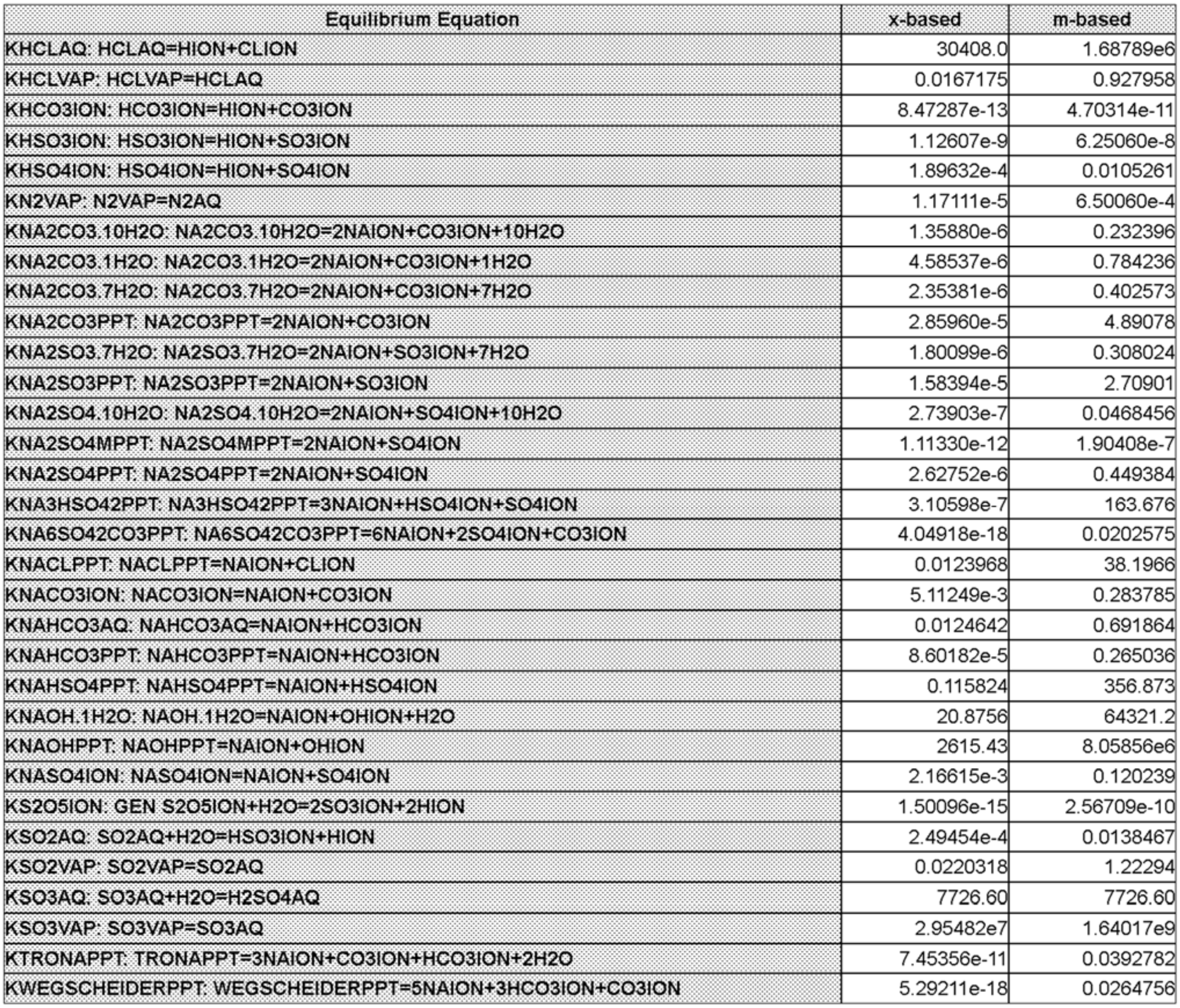


Species K(eq)-Values

Row Filter Applied: Only Non Zero Values

Equilibrium Equation	x-based	m-based
KARAGONITEPPT: ARAGONITEPPT=CAION+CO3ION	1.88238e-12	5.79993e-9
KCA2CL2O.2H2O: CA2CL2O.2H2O+HION=2CAION+2CLION+OHION+2H2O	7.55349e5	7.17097e12
KCACL2.1H2O: CACL2.1H2O=CAION+2CLION+1H2O	1.02692e8	1.75635e13
KCACL2.2H2O: CACL2.2H2O=CAION+2CLION+2H2O	129.087	2.20777e7
KCACL2.4H2O: CACL2.4H2O=CAION+2CLION+4H2O	1.84570	3.15670e5
KCACL2.6H2O: CACL2.6H2O=CAION+2CLION+6H2O	0.0670624	11469.7
KCACL2AQ: CACL2AQ=CACLION+CLION	4.63831e11	2.57464e13
KCACL2PPT: CACL2PPT=CAION+2CLION	2.25997e6	3.86523e11
KCACLION: CACLION=CAION+CLION	750.064	41634.7
KCACO3AQ: CACO3AQ=CAION+CO3ION	2.27043e-6	1.26028e-4
KCACO3PPT: CACO3PPT=CAION+CO3ION	7.90394e-13	2.43533e-9
KCAHCO3ION: CAHCO3ION=CAION+HCO3ION	1.51309e-3	0.0839889
KCAOH2PPT: CAOH2PPT=CAION+2OHION	2.25151e-11	3.85076e-6
KCAOHION: CAOHION=CAION+OHION	1.05739e-3	0.0586940
KCAOPPT: GEN CAOPPT+2HION=CAION+H2O	2.60315e34	4.68966e32
KCASO3.0.5H2O: CASO3.0.5H2O=CAION+SO3ION+.5H2O	4.24069e-10	1.30663e-6
KCASO3.2H2O: CASO3.2H2O=CAION+SO3ION+2H2O	1.78964e-11	5.51418e-8
KCASO3PPT: CASO3PPT=CAION+SO3ION	1.25776e-10	3.87537e-7
KCASO4.2H2O: CASO4.2H2O=CAION+SO4ION+2H2O	1.03849e-8	3.19977e-5
KCASO4AQ: CASO4AQ=CAION+SO4ION	4.75256e-4	0.0263806
KCASO4PPT: CASO4PPT=CAION+SO4ION	1.42770e-8	4.39897e-5
KCO2AQ: CO2AQ+H2O=HION+HCO3ION	8.18059e-9	4.54090e-7
KCO2VAP: CO2VAP=CO2AQ	6.11041e-4	0.0339178
KH2O: H2O=HION+OHION	3.29526e-18	1.01532e-14
KH2OVAP: H2OVAP=H2O	31.8546	31.8546
KH2SO4AQ: H2SO4AQ=HION+HSO4ION	4.63377e8	2.57212e10
KH2SO4VAP: H2SO4VAP=H2SO4AQ	6956.49	3.86142e5

Note: m-based refers to molality-based equilibrium constants. The m-based equilibrium constants are compatible with the "Aqueous Electrolyte" thermodynamic framework used in this study. The x-based K(eq) values are mole-fraction-based equilibrium constants, and are used with OLI's "Mixed Solvent Electrolyte" thermodynamic framework.

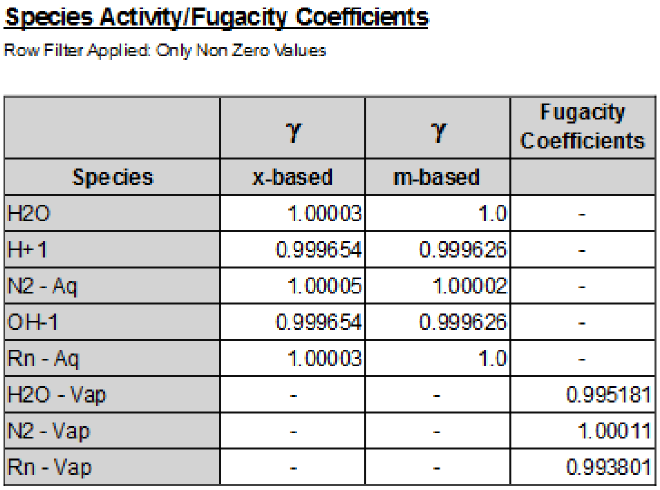


Equilibrium Equation	x-based	m-based
KHCLAQ: HCLAQ=HION+CLION	30408.0	1.68789e6
KHCLVAP: HCLVAP=HCLAQ	0.0167175	0.927958
KHCO3ION: HCO3ION=HION+CO3ION	8.47287e-13	4.70314e-11
KHSO3ION: HSO3ION=HION+SO3ION	1.12607e-9	6.25060e-8
KHSO4ION: HSO4ION=HION+SO4ION	1.89632e-4	0.0105261
KN2VAP: N2VAP=N2AQ	1.17111e-5	6.50060e-4
KNA2CO3.10H2O: NA2CO3.10H2O=2NAION+CO3ION+10H2O	1.35880e-6	0.232396
KNA2CO3.1H2O: NA2CO3.1H2O=2NAION+CO3ION+1H2O	4.58537e-6	0.784236
KNA2CO3.7H2O: NA2CO3.7H2O=2NAION+CO3ION+7H2O	2.35381e-6	0.402573
KNA2CO3PPT: NA2CO3PPT=2NAION+CO3ION	2.85960e-5	4.89078
KNA2SO3.7H2O: NA2SO3.7H2O=2NAION+SO3ION+7H2O	1.80099e-6	0.308024
KNA2SO3PPT: NA2SO3PPT=2NAION+SO3ION	1.58394e-5	2.70901
KNA2SO4.10H2O: NA2SO4.10H2O=2NAION+SO4ION+10H2O	2.73903e-7	0.0468456
KNA2SO4MPPT: NA2SO4MPPT=2NAION+SO4ION	1.11330e-12	1.90408e-7
KNA2SO4PPT: NA2SO4PPT=2NAION+SO4ION	2.62752e-6	0.449384
KNA3HSO42PPT: NA3HSO42PPT=3NAION+HSO4ION+SO4ION	3.10598e-7	163.676
KNA6SO42CO3PPT: NA6SO42CO3PPT=6NAION+2SO4ION+CO3ION	4.04918e-18	0.0202575
KNACLPPT: NACLPPT=NAION+CLION	0.0123968	38.1966
KNACO3ION: NACO3ION=NAION+CO3ION	5.11249e-3	0.283785
KNAHCO3AQ: NAHCO3AQ=NAION+HCO3ION	0.0124642	0.691864
KNAHCO3PPT: NAHCO3PPT=NAION+HCO3ION	8.60182e-5	0.265036
KNAHSO4PPT: NAHSO4PPT=NAION+HSO4ION	0.115824	356.873
KNAOH.1H2O: NAOH.1H2O=NAION+OHION+H2O	20.8756	64321.2
KNAOHPPT: NAOHPPT=NAION+OHION	2615.43	8.05856e6
KNASO4ION: NASO4ION=NAION+SO4ION	2.16615e-3	0.120239
KS2O5ION: GEN S2O5ION+H2O=2SO3ION+2HION	1.50096e-15	2.56709e-10
KSO2AQ: SO2AQ+H2O=HSO3ION+HION	2.49454e-4	0.0138467
KSO2VAP: SO2VAP=SO2AQ	0.0220318	1.22294
KSO3AQ: SO3AQ+H2O=H2SO4AQ	7726.60	7726.60
KSO3VAP: SO3VAP=SO3AQ	2.95482e7	1.64017e9
KTRONAPPT: TRONAPPT=3NAION+CO3ION+HCO3ION+2H2O	7.45356e-11	0.0392782
KWEGSCHEIDERPPT: WEGSCHEIDERPPT=5NAION+3HCO3ION+CO3ION	5.29211e-18	0.0264756

Note: m-based refers to molality-based equilibrium constants. The m-based equilibrium constants are compatible with the "Aqueous Electrolyte" thermodynamic framework used in this study. The x-based K(eq) values are mole-fraction-based equilibrium constants, and are used with OLI's "Mixed Solvent Electrolyte" thermodynamic framework.

Appendix B – Radon

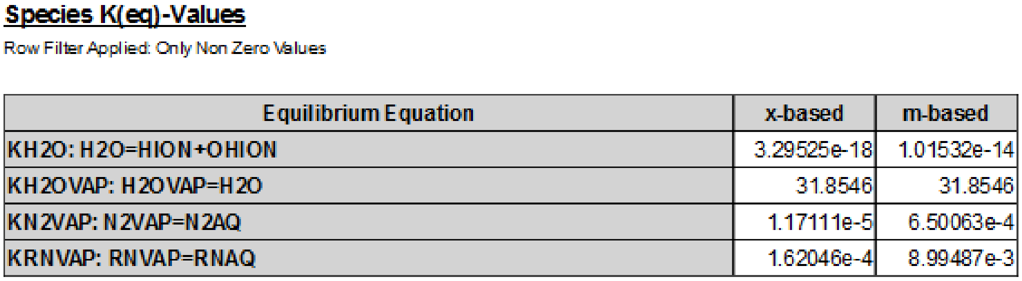
Species activity/fugacity coefficients, chemical equilibrium reactions, and equilibrium constants used by the OLI Stream Analyzer software for calculating the Henry's law constant for radon are summarized below.



Species Activity/Fugacity Coefficients

Row Filter Applied: Only Non Zero Values

	γ	γ	Fugacity Coefficients
Species	x-based	m-based	
H2O	1.00003	1.0	-
H+1	0.999654	0.999626	-
N2 - Aq	1.00005	1.00002	-
OH-1	0.999654	0.999626	-
Rn - Aq	1.00003	1.0	-
H2O - Vap	-	-	0.995181
N2 - Vap	-	-	1.00011
Rn - Vap	-	-	0.993801



Species K(eq)-Values

Row Filter Applied: Only Non Zero Values

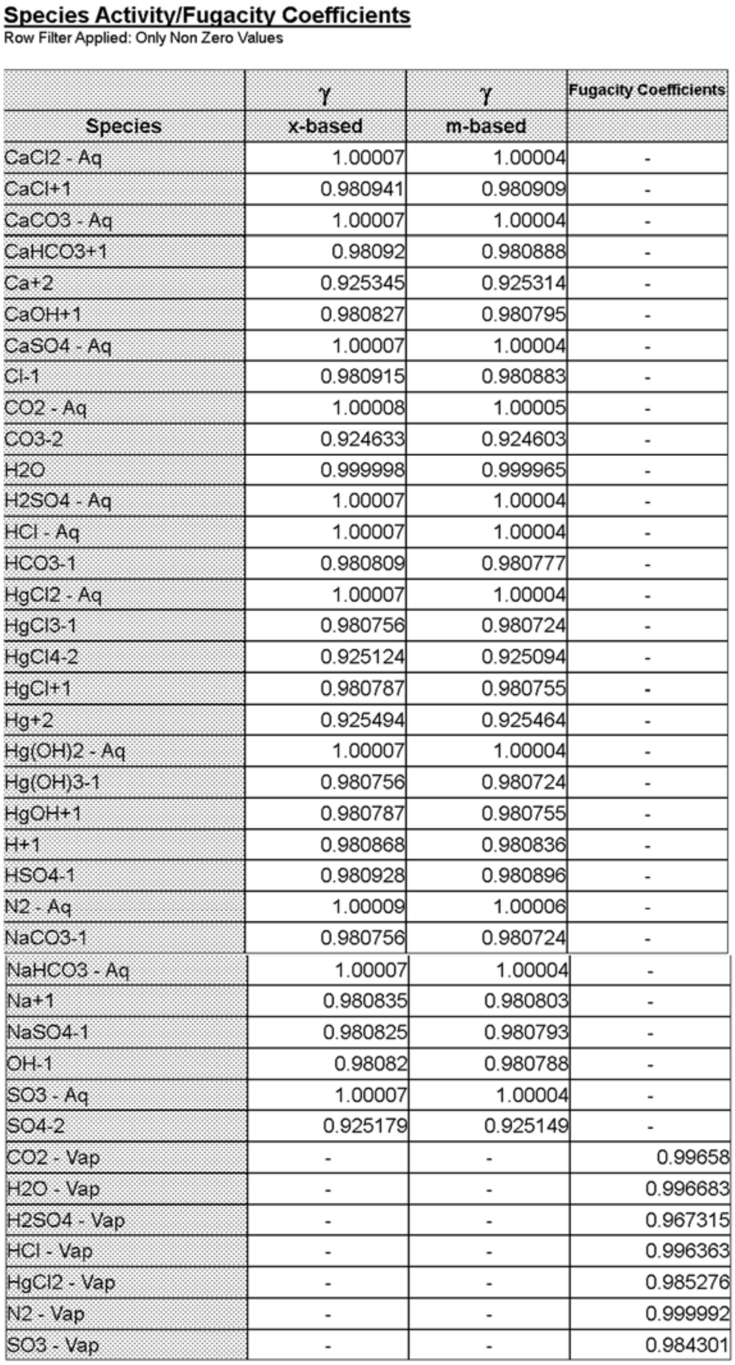
Equilibrium Equation	x-based	m-based
KH2O: H2O=HION+OHION	3.29525e-18	1.01532e-14
KH2OVAP: H2OVAP=H2O	31.8546	31.8546
KN2VAP: N2VAP=N2AQ	1.17111e-5	6.50063e-4
KRNVAP: RNVAP=RNAQ	1.62046e-4	8.99487e-3

Note: m-based refers to molality-based equilibrium constants. The m-based equilibrium constants are compatible with the "Aqueous Electrolyte" thermodynamic framework used in this study. The x-based K(eq) values are mole-fraction-based equilibrium constants, and are used with OLI's "Mixed Solvent Electrolyte" thermodynamic framework.

Appendix C – $HgCl_2$

Species activity/fugacity coefficients, chemical equilibrium reactions, and equilibrium constants used by the OLI Stream Analyzer software for $HgCl_2$ Cases 1 and 2 are summarized below.

Case 1: Condition A (soil at pH 5.4, E_h 0.37 V)

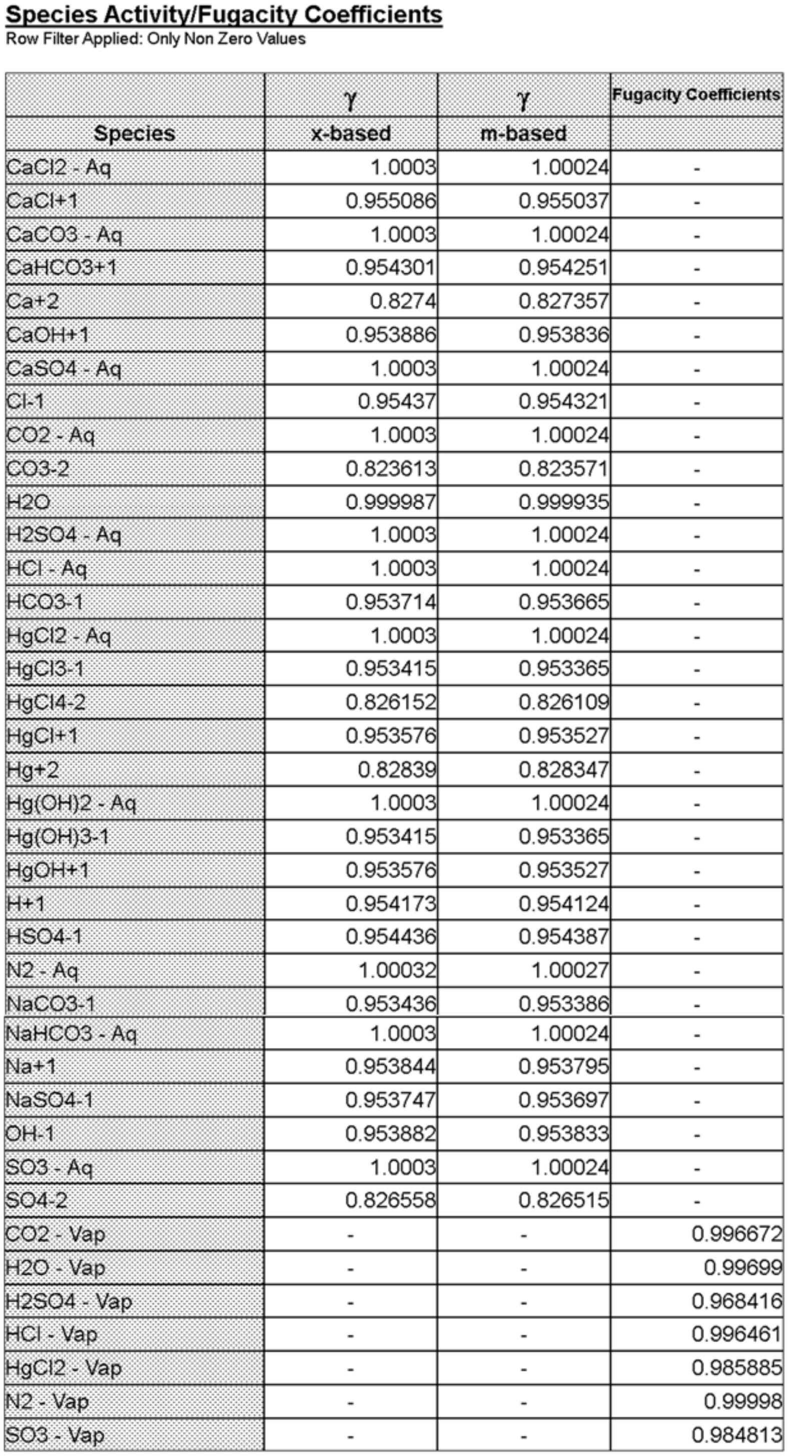


Species Activity/Fugacity Coefficients

Row Filter Applied: Only Non Zero Values

	γ	γ	Fugacity Coefficients
Species	x-based	m-based	
CaCl2 - Aq	1.00007	1.00004	-
CaCl+1	0.980941	0.980909	-
CaCO3 - Aq	1.00007	1.00004	-
CaHCO3+1	0.98092	0.980888	-
Ca+2	0.925345	0.925314	-
CaOH+1	0.980827	0.980795	-
CaSO4 - Aq	1.00007	1.00004	-
Cl-1	0.980915	0.980883	-
CO2 - Aq	1.00008	1.00005	-
CO3-2	0.924633	0.924603	-
H2O	0.999998	0.999965	-
H2SO4 - Aq	1.00007	1.00004	-
HCl - Aq	1.00007	1.00004	-
HCO3-1	0.980809	0.980777	-
HgCl2 - Aq	1.00007	1.00004	-
HgCl3-1	0.980756	0.980724	-
HgCl4-2	0.925124	0.925094	-
HgCl+1	0.980787	0.980755	-
Hg+2	0.925494	0.925464	-
Hg(OH)2 - Aq	1.00007	1.00004	-
Hg(OH)3-1	0.980756	0.980724	-
HgOH+1	0.980787	0.980755	-
H+1	0.980868	0.980836	-
HSO4-1	0.980928	0.980896	-
N2 - Aq	1.00009	1.00006	-
NaCO3-1	0.980756	0.980724	-
NaHCO3 - Aq	1.00007	1.00004	-
Na+1	0.980835	0.980803	-
NaSO4-1	0.980825	0.980793	-
OH-1	0.98082	0.980788	-
SO3 - Aq	1.00007	1.00004	-
SO4-2	0.925179	0.925149	-
CO2 - Vap	-	-	0.99658
H2O - Vap	-	-	0.996683
H2SO4 - Vap	-	-	0.967315
HCl - Vap	-	-	0.996363
HgCl2 - Vap	-	-	0.985276
N2 - Vap	-	-	0.999992
SO3 - Vap	-	-	0.984301

Case 2: Oxidized Region III (pH 8.23, E_h 0.73 V)

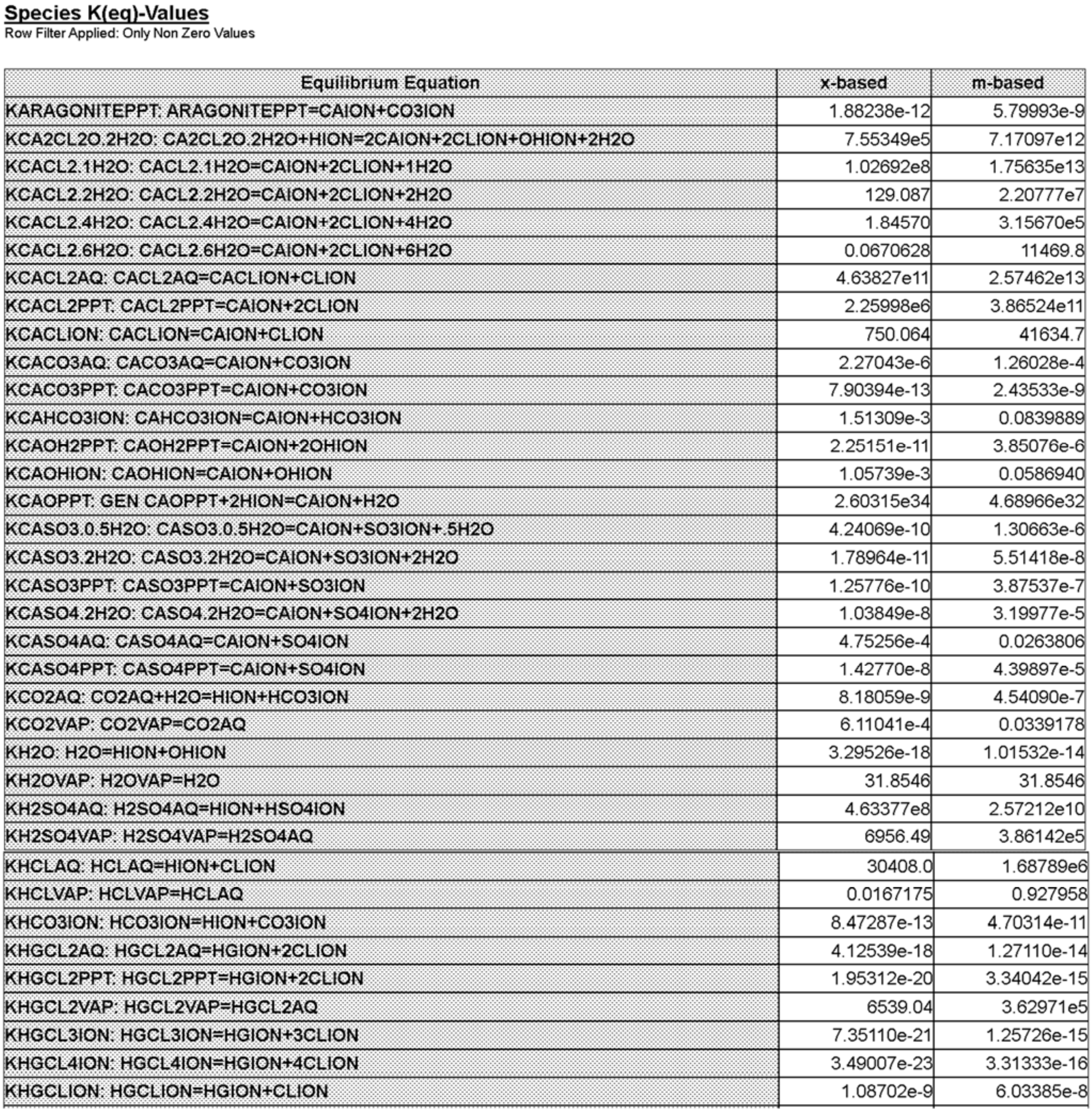


Species Activity/Fugacity Coefficients

Row Filter Applied: Only Non Zero Values

	γ	γ	Fugacity Coefficients
Species	x-based	m-based	
CaCl2 - Aq	1.0003	1.00024	-
CaCl+1	0.955086	0.955037	-
CaCO3 - Aq	1.0003	1.00024	-
CaHCO3+1	0.954301	0.954251	-
Ca+2	0.8274	0.827357	-
CaOH+1	0.953886	0.953836	-
CaSO4 - Aq	1.0003	1.00024	-
Cl-1	0.95437	0.954321	-
CO2 - Aq	1.0003	1.00024	-
CO3-2	0.823613	0.823571	-
H2O	0.999987	0.999935	-
H2SO4 - Aq	1.0003	1.00024	-
HCl - Aq	1.0003	1.00024	-
HCO3-1	0.953714	0.953665	-
HgCl2 - Aq	1.0003	1.00024	-
HgCl3-1	0.953415	0.953365	-
HgCl4-2	0.826152	0.826109	-
HgCl+1	0.953576	0.953527	-
Hg+2	0.82839	0.828347	-
Hg(OH)2 - Aq	1.0003	1.00024	-
Hg(OH)3-1	0.953415	0.953365	-
HgOH+1	0.953576	0.953527	-
H+1	0.954173	0.954124	-
HSO4-1	0.954436	0.954387	-
N2 - Aq	1.00032	1.00027	-
NaCO3-1	0.953436	0.953386	-
NaHCO3 - Aq	1.0003	1.00024	-
Na+1	0.953844	0.953795	-
NaSO4-1	0.953747	0.953697	-
OH-1	0.953882	0.953833	-
SO3 - Aq	1.0003	1.00024	-
SO4-2	0.826558	0.826515	-
CO2 - Vap	-	-	0.996672
H2O - Vap	-	-	0.99699
H2SO4 - Vap	-	-	0.968416
HCl - Vap	-	-	0.996461
HgCl2 - Vap	-	-	0.985885
N2 - Vap	-	-	0.99998
SO3 - Vap	-	-	0.984813

Applicable to $HgCl_2$ Cases 1 and 2

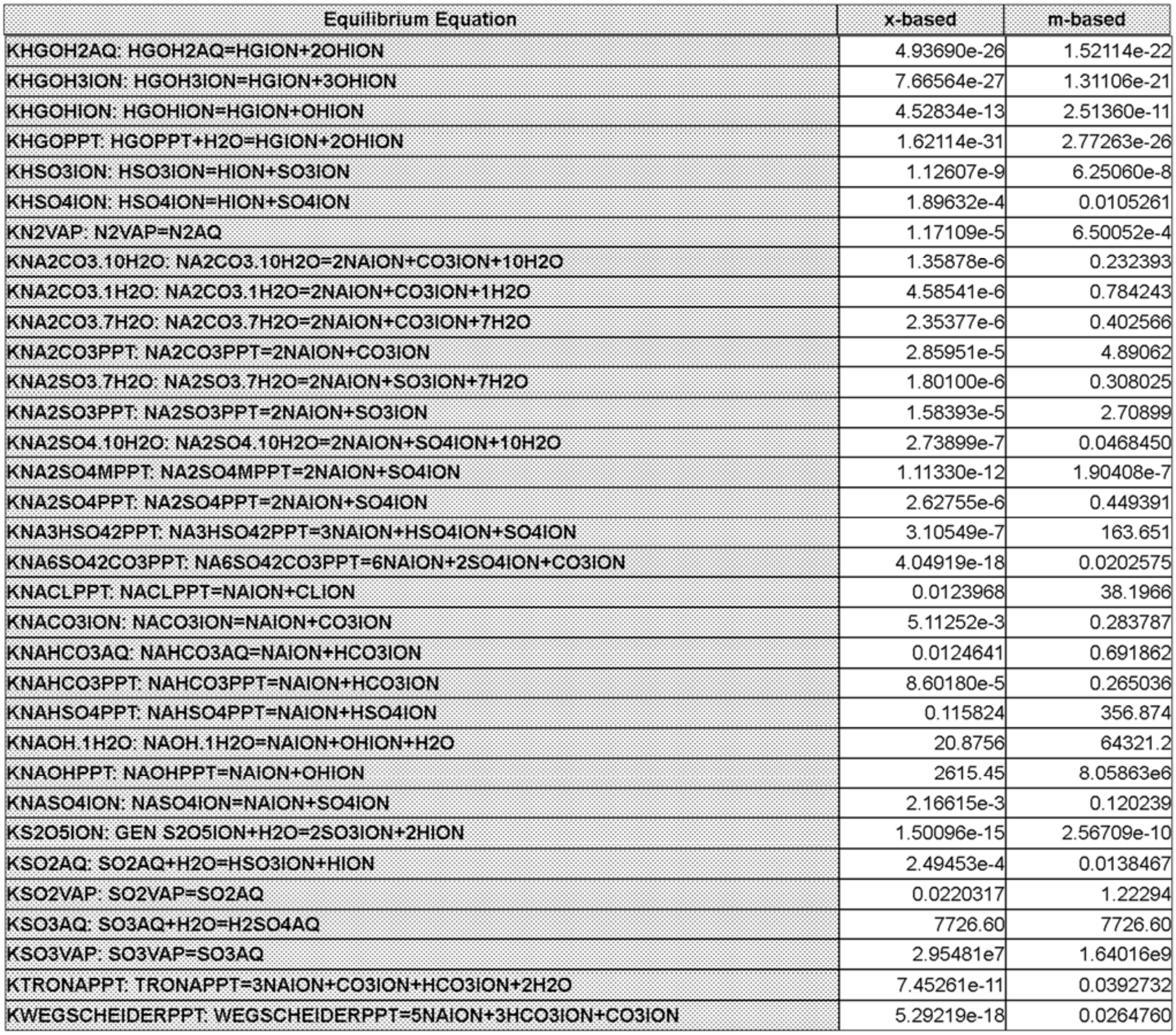


Species K(eq)-Values

Row Filter Applied: Only Non Zero Values

Equilibrium Equation	x-based	m-based
KARAGONITEPPT: ARAGONITEPPT=CAION+CO3ION	1.88238e-12	5.79993e-9
KCA2CL2O.2H2O: CA2CL2O.2H2O+HION=2CAION+2CLION+OHION+2H2O	7.55349e5	7.17097e12
KCACL2.1H2O: CACL2.1H2O=CAION+2CLION+1H2O	1.02692e8	1.75635e13
KCACL2.2H2O: CACL2.2H2O=CAION+2CLION+2H2O	129.087	2.20777e7
KCACL2.4H2O: CACL2.4H2O=CAION+2CLION+4H2O	1.84570	3.15670e5
KCACL2.6H2O: CACL2.6H2O=CAION+2CLION+6H2O	0.0670628	11469.8
KCACL2AQ: CACL2AQ=CACLION+CLION	4.63827e11	2.57462e13
KCACL2PPT: CACL2PPT=CAION+2CLION	2.25998e6	3.86524e11
KCACLION: CACLION=CAION+CLION	750.064	41634.7
KCACO3AQ: CACO3AQ=CAION+CO3ION	2.27043e-6	1.26028e-4
KCACO3PPT: CACO3PPT=CAION+CO3ION	7.90394e-13	2.43533e-9
KCAHCO3ION: CAHCO3ION=CAION+HCO3ION	1.51309e-3	0.0839889
KCAOH2PPT: CAOH2PPT=CAION+2OHION	2.25151e-11	3.85076e-6
KCAOHION: CAOHION=CAION+OHION	1.05739e-3	0.0586940
KCAOPPT: GEN CAOPPT+2HION=CAION+H2O	2.60315e34	4.68966e32
KCASO3.0.5H2O: CASO3.0.5H2O=CAION+SO3ION+.5H2O	4.24069e-10	1.30663e-6
KCASO3.2H2O: CASO3.2H2O=CAION+SO3ION+2H2O	1.78964e-11	5.51418e-8
KCASO3PPT: CASO3PPT=CAION+SO3ION	1.25776e-10	3.87537e-7
KCASO4.2H2O: CASO4.2H2O=CAION+SO4ION+2H2O	1.03849e-8	3.19977e-5
KCASO4AQ: CASO4AQ=CAION+SO4ION	4.75256e-4	0.0263806
KCASO4PPT: CASO4PPT=CAION+SO4ION	1.42770e-8	4.39897e-5
KCO2AQ: CO2AQ+H2O=HION+HCO3ION	8.18059e-9	4.54090e-7
KCO2VAP: CO2VAP=CO2AQ	6.11041e-4	0.0339178
KH2O: H2O=HION+OHION	3.29526e-18	1.01532e-14
KH2OVAP: H2OVAP=H2O	31.8546	31.8546
KH2SO4AQ: H2SO4AQ=HION+HSO4ION	4.63377e8	2.57212e10
KH2SO4VAP: H2SO4VAP=H2SO4AQ	6956.49	3.86142e5
KHCLAQ: HCLAQ=HION+CLION	30408.0	1.68789e6
KHCLVAP: HCLVAP=HCLAQ	0.0167175	0.927958
KHCO3ION: HCO3ION=HION+CO3ION	8.47287e-13	4.70314e-11
KHGCL2AQ: HGCL2AQ=HGION+2CLION	4.12539e-18	1.27110e-14
KHGCL2PPT: HGCL2PPT=HGION+2CLION	1.95312e-20	3.34042e-15
KHGCL2VAP: HGCL2VAP=HGCL2AQ	6539.04	3.62971e5
KHGCL3ION: HGCL3ION=HGION+3CLION	7.35110e-21	1.25726e-15
KHGCL4ION: HGCL4ION=HGION+4CLION	3.49007e-23	3.31333e-16
KHGCLION: HGCLION=HGION+CLION	1.08702e-9	6.03385e-8

Note: m-based refers to molality-based equilibrium constants. The m-based equilibrium constants are compatible with the “Aqueous Electrolyte” thermodynamic framework used in this study. The x-based K(eq) values are mole-fraction-based equilibrium constants, and are used with OLI’s “Mixed Solvent Electrolyte” thermodynamic framework.



Equilibrium Equation	x-based	m-based
KHGOH2AQ: HGOH2AQ=HGION+2OHION	4.93690e-26	1.52114e-22
KHGOH3ION: HGOH3ION=HGION+3OHION	7.66564e-27	1.31106e-21
KHGOHION: HGOHION=HGION+OHION	4.52834e-13	2.51360e-11
KHGOPPT: HGOPPT+H2O=HGION+2OHION	1.62114e-31	2.77263e-26
KHSO3ION: HSO3ION=HION+SO3ION	1.12607e-9	6.25060e-8
KHSO4ION: HSO4ION=HION+SO4ION	1.89632e-4	0.0105261
KN2VAP: N2VAP=N2AQ	1.17109e-5	6.50052e-4
KNA2CO3.10H2O: NA2CO3.10H2O=2NAION+CO3ION+10H2O	1.35878e-6	0.232393
KNA2CO3.1H2O: NA2CO3.1H2O=2NAION+CO3ION+1H2O	4.58541e-6	0.784243
KNA2CO3.7H2O: NA2CO3.7H2O=2NAION+CO3ION+7H2O	2.35377e-6	0.402566
KNA2CO3PPT: NA2CO3PPT=2NAION+CO3ION	2.85951e-5	4.89062
KNA2SO3.7H2O: NA2SO3.7H2O=2NAION+SO3ION+7H2O	1.80100e-6	0.308025
KNA2SO3PPT: NA2SO3PPT=2NAION+SO3ION	1.58393e-5	2.70899
KNA2SO4.10H2O: NA2SO4.10H2O=2NAION+SO4ION+10H2O	2.73899e-7	0.0468450
KNA2SO4MPPT: NA2SO4MPPT=2NAION+SO4ION	1.11330e-12	1.90408e-7
KNA2SO4PPT: NA2SO4PPT=2NAION+SO4ION	2.62755e-6	0.449391
KNA3HSO42PPT: NA3HSO42PPT=3NAION+HSO4ION+SO4ION	3.10549e-7	163.651
KNA6SO42CO3PPT: NA6SO42CO3PPT=6NAION+2SO4ION+CO3ION	4.04919e-18	0.0202575
KNACLPPT: NACLPPT=NAION+CLION	0.0123968	38.1966
KNACO3ION: NACO3ION=NAION+CO3ION	5.11252e-3	0.283787
KNAHCO3AQ: NAHCO3AQ=NAION+HCO3ION	0.0124641	0.691862
KNAHCO3PPT: NAHCO3PPT=NAION+HCO3ION	8.60180e-5	0.265036
KNAHSO4PPT: NAHSO4PPT=NAION+HSO4ION	0.115824	356.874
KNAOH.1H2O: NAOH.1H2O=NAION+OHION+H2O	20.8756	64321.2
KNAOHPPT: NAOHPPT=NAION+OHION	2615.45	8.05863e6
KNASO4ION: NASO4ION=NAION+SO4ION	2.16615e-3	0.120239
KS2O5ION: GEN S2O5ION+H2O=2SO3ION+2HION	1.50096e-15	2.56709e-10
KSO2AQ: SO2AQ+H2O=HSO3ION+HION	2.49453e-4	0.0138467
KSO2VAP: SO2VAP=SO2AQ	0.0220317	1.22294
KSO3AQ: SO3AQ+H2O=H2SO4AQ	7726.60	7726.60
KSO3VAP: SO3VAP=SO3AQ	2.95481e7	1.64016e9
KTRONAPPT: TRONAPPT=3NAION+CO3ION+HCO3ION+2H2O	7.45261e-11	0.0392732
KWEGSCHEIDERPPT: WEGSCHEIDERPPT=5NAION+3HCO3ION+CO3ION	5.29219e-18	0.0264760

Note: m-based refers to molality-based equilibrium constants. The m-based equilibrium constants are compatible with the “Aqueous Electrolyte” thermodynamic framework used in this study. The x-based K(eq) values are mole-fraction-based equilibrium constants, and are used with OLI’s “Mixed Solvent Electrolyte” thermodynamic framework.

Distribution List

S. E. Aleman, 735-A
B. T. Butcher, 773-42A
D. A. Crowley, 773-42A
T. L. Danielson, 703-41A
M. E. Denham, 773-42A
K. L. Dixon, 773-42A
J. A. Dyer, 773-42A
G. P. Flach, 773-42A
L. L. Hamm, 735-A
N. V. Halverson, 773-42A
T. Hang, 773-42A
K. M. Kostelnik, 773-42A
R. L. Nichols, 773-42A
R. R. Seitz, 773-42A
T. Whiteside, 773-42A
J. L. Wohlwend, 703-41A
H. M. Cardona, EM File, 773-42A – Rm. 243