# CALCULATING CATION EXCHANGE WITH PHREEQC (Version 2)

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**ABSTRACT**
**PHREEQC (Version 2) is a computer program for speciation, batch reaction, and one-dimensional transport calculations, distributed free of charge by the U.S. Geological Survey (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/index.html). The thermo-dynamic database accompanying the code includes cation exchange equilibria according to the Gaines-Thomas convention, but the flexible input format enables the application of other exchange equations used in soil science. This note shows that the Gapon, Vanselow, and Rothmund-Kornfeld formulas can be implemented in PHREEQC calculations to obtain the composition of (1) an exchanger in equilibrium with a given solution com-position, (2) a solution in equilibrium with a given exchanger, and (3) a solution and exchanger(s) following the reaction after mixing. With the interface PHREEQC for Win-dows, an isotherm plot can be quickly obtained.**

Bloom and Mansell (2001) reported an algorithm for calculating cation exchange according to the Rothmund-Kornfeld formulation, and noted that to their knowledge no software accom-modates these non-linear exchange equations. However, PHREEQC (Version 2) (Parkhurst and Appelo, 1999) can do these and other cation exchange computations, although the standard option in the databases distributed with the program follows the Gaines-Thomas convention. With the flexibility to specify multiple approaches to cation exchange and the capability to simulate the progress of other equilibrium and kinetically controlled processes, (including the possibility of simulating cation exchange as a *kinetic* reaction), PHREEQC is suitable for a wide range of hydrochemical calculations in the soil sciences. Because it is not immediately clear how to apply PHREEQC for other cation exchange conventions, this note provides examples of the proper specification of PHREEQC input files for a variety of conventions.

## Exchange Composition in Equilibrium with a Solution

As an example, we consider the Gaines-Thomas, Gapon, Vanselow, and Rothmund-Kornfeld formulations for the K-Ca exchange reaction:

$$0.5\,Ca^{2+} + KX \leftrightarrow 0.5 CaX_2 + K^+, \tag{1}$$

where $X^-$ is the exchanger. The law of mass action for eqn (1) yields:

$$(K_{GT})_{Ca\backslash K} = \frac{[CaX_2]^{0.5}}{[KX]} \frac{[K^+]}{[Ca^{2+}]^{0.5}}, \tag{2}$$

where [*i*] denotes an activity (dimensionless). The Gaines-Thomas convention uses equivalent fraction for activity of the exchangeable cations, in contrast to the *Vanselow* convention, which takes mole fractions, but otherwise employs the same reaction equations. In the *Rothmund-Kornfeld* formula, an empirical exponent modifies the solute activity ratio in eqn (2):

$$(K_{GT})_{Ca\backslash K} = \frac{[CaX_2]^{0.5}}{[KX]} \left(\frac{[K^+]}{[Ca^{2+}]^{0.5}}\right)^n. \tag{3}$$

This equation can approximate the sigmoidal shape often observed in binary isotherms (exchangeable cations are relatively preferred when they occupy a small fraction of the exchange sites, cf. Bloom and Mansell, 2001; Bond, 1995).
The *Gapon* convention expresses exchange per mol of exchange sites, rather than per mol of exchanging ion:

$$0.5\,Ca^{2+} + KX \leftrightarrow Ca_{0.5}X + K^+ \tag{4}$$

with the mass action equation:

$$( K_{Gp} )_{Ca \backslash K} = \frac{[Ca_{0.5}X]}{[KX]} \frac{[K^+]}{[Ca^{2+}]^{0.5}} .$$ 

(5)

PHREEQC-2 reads input files that define a hydrochemical problem via KEYWORDS (capitalized in the following examples). These keywords are largely self-explanatory, and are described in the user's manual (Parkhurst and Appelo, 1999).

*Gaines-Thomas convention*

An input file for PHREEQC-2 with cation exchange following the Gaines Thomas equations may look like:

```
EXCHANGE_MASTER_SPECIES                                  # text after a # is not read...
 X X-                                                        # ...define exchange site X
EXCHANGE_SPECIES
 X- = X-; log_k 0                                        # semicolon is logical end of line
 X- + K+ = KX; log_k 0.7                           # define the half-reactions of ion exchange
 2X- + Ca+2 = CaX2; log_k 0.8                                # log K's relative to NaX

SOLUTION 1
 K 1                                                     # concentrations in mmol/kg H2O
 Ca 0.1
 Cl 1.2 charge
EXCHANGE
 X 1                                                                              # 1 mol
 -equilibrate 1                                  # ...calculate iX in equilibrium with solution 1
END
```

The exchange reactions are defined in the form of half-reactions entered under keyword EXCHANGE_SPECIES. The ion-exchange reaction is generated by combining two half reactions, for example subtracting the one for KX twice from the one for $CaX_2$ and dividing the result by two, will give reaction (1). Normally, the exchangeable species need not be defined in the input file as they are read from the thermodynamic database. Running this file gives the output:

```
---------------------------Exchange composition-----------------------------

X               1.000e+00 mol

                            Equiv-   Equivalent      Log
     Species        Moles   alents     Fraction    Gamma

     CaX2       4.065e-01  8.129e-01  8.129e-01     0.000
     KX         1.871e-01  1.871e-01  1.871e-01     0.000
```

The constants of exchange reactions according to Gaines-Thomas, Gapon, and Vanselow can be converted from one to another for a given exchangeable fraction (cf. Appelo and Postma, 1993).

*Gapon convention*

To obtain the same exchange composition with the Gapon formula as with Gaines-Thomas, the Gapon constant

$$(K_{Gp})_{Ca \backslash K} = (K_{GT})_{Ca \backslash K} \cdot (1 - [KX])^{0.5},$$

(6)

is defined in the input file:

```
EXCHANGE_MASTER_SPECIES
 G G-                                                        # ...exchange site G
EXCHANGE_SPECIES
 G- = G-; log_k 0
 G- + K+ = KG; log_k 0.7
```

```
                               # Gapon exchange K_Gp = K_GT * (1 - [KX])^0.5.  (K_GT)_Ca\K = 10^-0.3
 G- + 0.5 Ca+2 = Ca0.5G; log_k 0.355019                                       # log(K_Gp) + 0.7

SOLUTION 1; K 1; Ca 0.1; Cl 1.2 charge
EXCHANGE 1; G 1; -equilibrate 1
END
```

This input file gives exactly the same exchangeable fractions ($iG$) for the specified conditions as the previous file for ($iX$).

In case multiple multivalent ions are present in Gapon exchange, the formulation:

```
EXCHANGE_SPECIES
 G- + 0.5 Mg+2 = Mg0.5G; log_k 0.355019                                                  (7)
```

does not give the expected linear isotherm for $Ca^{2+}/Mg^{2+}$ exchange, although the exchange coefficients are the same for the two cations. Instead, a sigmoidal isotherm will be found because the power of 0.5 for the solute species favors the small fractions on the exchanger (Figure 1). The form is characteristic for what is called a thixotropic mixture in thermodynamics. For a linear isotherm, the mass-action equation should be defined as:

```
EXCHANGE_SPECIES
 Ca0.5G + Mg+2 = Mg0.5G + Ca+2; log_k 0; -no_check; -mole_balance Mg0.5G                (8)
```

In PHREEQC, the mass-action equation is derived from the coefficients in the chemical reaction equation. In this case, the coefficients of the solute species are 1 and these will be used as the exponents in the mass-action equation. The 'no_check' option allows the equation to be processed even though it is not balanced, but the mass balance for the species needs to be indicated explicitly with the 'mole_balance' option.

*Vanselow convention*

For the Vanselow convention in PHREEQC, the ion-exchange half-reactions are assigned to solids that can assemble in a solid solution. The Vanselow $K$ for reaction (1) is obtained from:

$$(K_V)_{Ca\backslash K} = (K_{GT})_{Ca\backslash K} \cdot (1 + [KX])^{0.5}/2 .  \hspace{2cm} (9)$$

The solubility products of the exchanger-solids are set relative to an arbitrary reference level, and should yield the correct $K_V$ when two solubility reactions are combined.

In the following input file, first the anion $Xv^-$ for the solid solution is defined, followed by the solids under keyword PHASES.

```
SOLUTION_MASTER_SPECIES
 Xv Xv- 0 1 1                                                        # define new anion
SOLUTION_SPECIES;  Xv- = Xv-; log_k 0.0
PHASES
                                                                    # Endmembers for ss
 KXv;  KXv = K+ + Xv-
  log_k  -20.7                                    # ...Xv- is small when log_k is small
                        # Vanselow exchange K_V = (K_GT)_Ca\K * (1 + {KX})^.5 / 2 = 0.273
 CaXv2;  CaXv2 = Ca+2 + 2Xv-
  log_k  -40.2724                                        # = 2*( -20.7 - log10(K_V) )

                                                       # Fix the K/Ca concentrations...
  Fix_K;  K+ = K+;  log_k  0.0
  Fix_Ca;  Ca+2 = Ca+2;  log_k  0.0
EQUILIBRIUM_PHASES
 Fix_K -3.0175 KCl                                     # [K+] = 10^-3.0175. K_tot = 1 mM
 Fix_Ca -4.069 CaCl2

SOLID_SOLUTION 1
 KCaXv_Vans
  -comp KXv  0.5
  -comp CaXv2  0.25                                          # Total Xv = 1 mol
SOLUTION 1
```

```
 K 1; Ca 0.1; Cl 1.2 charge
END
```

The $K^+$ and $Ca^{2+}$ activities would change when the solid solution reacts with the solution, but they are buffered by equilibrium with the phases 'Fix_K' and 'Fix_Ca', which were also defined under PHASES. The activities are fixed by adding the chloride salts indicated under keyword EQUILIBRIUM_PHASES. After reaction, the composition of the solid solution is:

```
------------------------------Solid solutions------------------------------


      Solid solution          Component       Moles  Delta moles   Mole fract
      KCaXv_Vans                            5.94e-01
                                CaXv2       4.06e-01     1.56e-01     6.85e-01
                                KXv         1.87e-01    -3.13e-01     3.15e-01
```

Thus, the moles of K and Ca in the solid solution are the same as previously found exchangeable on X with the Gaines-Thomas formulation (the default printout for solid solutions is rounded to 3 digits). Note that due to the low solubility of the components of the solid solution, and because the concentration of cations is higher than of the anion, the concentration of anion $Xv^-$ will be negligible and does not affect the solution calculations.

*Rothmund-Kornfeld convention*

To apply the Rothmund-Kornfeld formula with PHREEQC requires the option to uncouple the mass-action and the mass-balance equations. The following example is from Bloom and Mansell (2001), and calculates the composition of solution and exchanger after the two have mixed and reacted. To be commensurate with Bloom and Mansell (who did not apply activity corrections), the activity coefficients of the exchangeable cations were set equal to the activity coefficients for the solute cations by using '-gamma' in the following example. The exchange constants were taken from Table 1 in Bloom and Mansell, recalculated to activities. Running this file will provide the equilibrium distribution of a K, Ca solution reacting with a Na-soil.

```
PRINT; -reset false; -user_print true
EXCHANGE_SPECIES
 Na+ + X- = NaX; log_k 0
 -gamma 4.0 0.075
 0.789K+ + NaX = KX + 0.789Na+; -log_k 0.705; -no_check; mole_balance KX
 -gamma 3.5 0.015
 0.618Ca+2 + 2KX = CaX2 + 1.236K+; -log_k -0.281; -no_check; mole_balance CaX2
 -gamma 5.0 0.165
                                              # should give the same result...
 0.931Ca+2 + 2NaX = CaX2 + 1.862Na+; -log_k 1.135; -no_check; mole_balance CaX2
 -gamma 5.0 0.165

SOLUTION 1
 K 100; Ca 50
EXCHANGE 1
 NaX 0.417
                                              # For customized printout...
USER_PRINT
 -start
 10 print '             K           Na            Ca'
 20 print 'C_final', 1e3*tot("K"), 1e3*tot("Na"), 2e3*tot("Ca"), 'mol_charge/m3 water'
 30 print 'X_final', 546.39*mol("KX"), 546.39*mol("NaX"), 2*546.39*mol("CaX2"),\
         'mol_charge/Mg soil'           # backslash,\, is line continuation char...
 -end
END
```

The keyword USER_PRINT provides access to the BASIC interpreter programmed into PHREEQC and can be used to obtain a specific printout. In this case the print is tailored to the units used by Bloom and Mansell.

```
--------------------------------User print----------------------------------
                    K           Na          Ca
C_final   7.6463e+00  1.8916e+02   3.1900e+00 mol_charge/m3 water
X_final   5.0461e+01  1.2449e+02   5.2896e+01 mol_charge/Mg soil
```

These results are very nearly the same as those given by Bloom and Mansell (2001). Note that for the Rothmund-Kornfeld equations, and this holds for any other set of exchange formulas, it suffices to give one definition of the $CaX_2$ species only (PHREEQC uses the last definition). Indeed, the two equations for $CaX_2$ in the input file above, yield very nearly the same results.

**Solution Composition in Equilibrium with an Exchanger**

The PHREEQC option '-equilibrate' was used to define an exchanger in equilibrium with a known solution composition. It is also possible to define the solution composition in equilibrium with a given exchanger composition, by mixing the exchanger with a small fraction of solution. The number of moles in the exchanger is not (much) affected if we mix it with a NaCl solution that contains 1 µg of water, but after equilibration, the water composition will change to the $(K, Ca_{0.1})Cl_{1.2}$ composition that we have used in the previous examples.

```
EXCHANGE_SPECIES
 X- + K+ = KX; log_k 0.7
 2X- + Ca+2 = CaX2; log_k 0.8
EXCHANGE 1
CaX2 0.4065                                 # exchangeable Ca and K in mol
 KX 0.1871
SOLUTION 1
 Na 1.2; Cl 1.2 charge                     # Na in solution, exchanges for K and Ca
MIX 1; 1 1e-9                              # ...Take 1e-9 of solution 1 = 1 µg water
END
```

The resulting solution can be 'saved' in temporary memory and 'used' in subsequent simulations, and it can be restored to contain 1 kg water if needed.

**Reactions and Isotherm plots**

Lastly, it is easy to obtain an isotherm and plot it with PHREEQC for Windows (written by Vincent Post). For example the K-Ca isotherm given as illustration by Bloom and Mansell (2001) will be calculated in less than a second on any Pentium III computer.

```
EXCHANGE_SPECIES
 K+ + X- = KX; -log_k 0.705; -gamma 3.5 0.015
 0.618Ca+2 + 2KX = CaX2 + 1.236K+; -log_k -0.281; -no_check; mole_balance CaX2
 -gamma 5.0 0.165
SOLUTION 1
 K 100                                         # 100 mmol K+ / kg H2O
EXCHANGE 1
 KX 0.417                                    # 417 mmol KX, total K = 517 mmol
                              # Remove 517 mmol K+ , replace with 258.5 mmol Ca2+...
REACTION; K -1 Ca 0.5; 0.517 in 20 steps

USER_GRAPH
 -head alpha_K beta_K
 -axis_titles "Solute K /(K + 2Ca)" "Exchangeable K /(K + 2Ca)"
 -axis_scale x_axis 0 1 0.2 0.1
 -axis_scale y_axis 0 1 0.2 0.1
  -start
10 graph_x tot("K")/0.1
20 graph_y mol("KX")/0.417
 -end
END
```

In this calculation, we start with a solution and exchanger with $K^+$ only, and change the composition stepwise by removing K and adding Ca with the REACTION keyword. The plot is

obtained with the USER_GRAPH keyword data block, and is shown in Figure 2.

**Conclusion**

We have shown how various cation-exchange equations can be included in the hydrogeochemical computer program PHREEQC (Version 2). The windows version of the program has an intuitive, user-friendly interface. Numerous options and capabilities make PHREEQC useful for simulations and finding solutions to many practical problems in hydrogeochemistry. The program is available as freeware and was developed for doing 'real world hydrogeochemistry'. It is an excellent tool for the soil sciences as well.

**Acknowledgements**

We thank Pierre Glynn and Alex Blum for commenting a draft version of this note.

**References**

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or
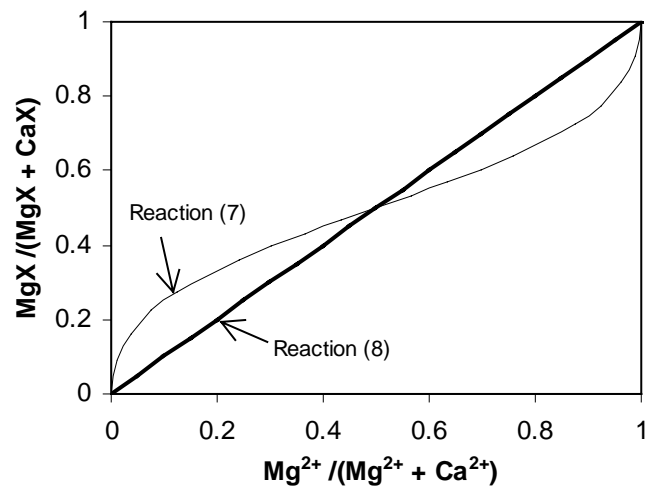http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/index.html}

Figure 1. Binary isotherms for Ca/Mg exchange with the Gapon convention depend on the formulation of the half reaction. Curved isotherm is for reaction (7); linear isotherm (no preference) is for reaction (8) in the text.
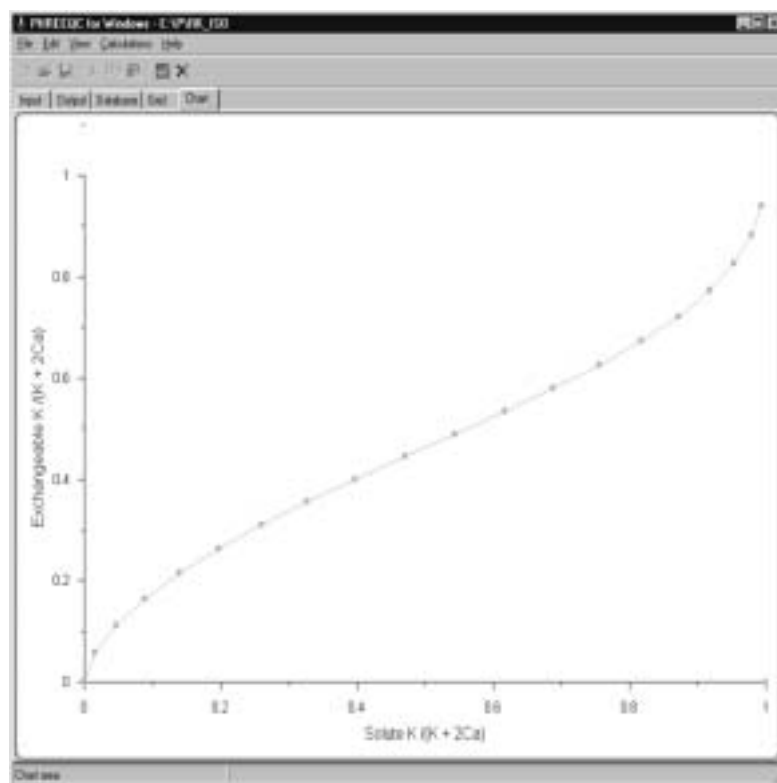


Figure 2. Graphic display by PHREEQC for Windows of the K/Ca isotherm according to a Rothmund-Kornfeld equation.