

EQBRM — a FORTRAN Speciation Program

EQBRM is a program written in FORTRAN77 which calculates the concentrations of all aqueous species in a system at equilibrium. The program calculates activity coefficients of ionic species by calling a subroutine called ACTCF, which calculates activity coefficients using the Davies revision of the Debye-Hückel equation:

$$\log \gamma_i = \frac{-Z_i^2 A \sqrt{\bar{I}}}{1 + \sqrt{\bar{I}}} + 0.2 A Z_i^2 \bar{I}$$

where \bar{I} is the true ionic strength, representing concentrations of all species as corrected for ion-pair and complex formation:

$$\bar{I} = \frac{1}{2} \sum_{i=1}^N m_i Z_i^2$$

This is a fairly crude approximation of the activity coefficients, especially if you are modeling a system at high T and P . Subroutine ACTCF should be rewritten with a more suitable algorithm if more accuracy is needed.

How to set up data for the program EQBRM

EQBRM was designed to be completely general, letting you define the species, reactions and component concentrations of interest to you. To do this systematically, go through the following steps:

1. Write all N species of interest and assign each a number from 1 to N . The concentrations of these species are the N unknowns.
2. Write out M mass balance or equilibrium constant equations ($j = 1, 2, \dots, M$). These should be written so the lowest activities are in the denominator to reduce the chances of matrix singularity. Equilibrium constants might be obtained from SUPCRT92 for the T and P of interest.
3. Assign the reaction coefficients ν_{ij} based on the number of times the i th species appears in the j th reaction; these coefficients are negative for reactants and positive for products for each reaction as written.
4. Write $N - M - 1$ mass balances, giving the total concentration of each element or component B_e , (such as total Na, total Cl, or total NH_3 in the system).

5. Assign the parameters $b_{e,i}$ which refer to the number of atoms of each element or component in the formula of each species. For example, from the formula for the species H_2SO_4 we can set $b_{\text{H}} = 1$, $b_{\text{S}} = 1$, $b_{\text{O}} = 4$, and $b_{e,i} = 0$ for all other elements.
6. Write valences, Z_i , of all species.
7. Make reasonable first guesses at concentrations of all species.
8. Choose a value for the A term in the activity coefficient expression.

Example worksheet for data input to EQBRM

Here we will solve for the equilibrium concentrations of all species in the 4-component, 10-species system $0.25m \text{ NH}_4\text{Cl} - 0.25m \text{ NaCl} - 0.25m \text{ KCl} - \text{H}_2\text{O}$ at 300°C and vapor-saturated pressure. Set up a data worksheet following the six steps outlined above.

Step 1: There are 10 species of interest in this system (knowing that it is acidic and that m_{OH^-} is negligible). We assign these species numbers, as follows:

Species	NH_4^+	$\text{NH}_4\text{OH}^\circ$	H^+	HCl°	$\text{NH}_4\text{Cl}^\circ$	Cl^-	Na^+	NaCl°	K^+	KCl°
Assigned Number	1	2	3	4	5	6	7	8	9	10

Step 2: There are 5 known mass action equations and equilibrium constants relating these species:

$$\frac{a_{\text{NH}_4^+}}{a_{\text{NH}_4\text{OH}^\circ} a_{\text{H}^+}} = K_1; \quad \log K_1 = 4.677$$

$$\frac{a_{\text{NH}_4^+} a_{\text{Cl}^-}}{a_{\text{NH}_4\text{Cl}^\circ}} = K_2; \quad \log K_2 = -0.82$$

$$\frac{a_{\text{Na}^+} a_{\text{Cl}^-}}{a_{\text{NaCl}^\circ}} = K_3; \quad \log K_3 = -1.013$$

$$\frac{a_{\text{HCl}^\circ}}{a_{\text{H}^+} a_{\text{Cl}^-}} = K_4; \quad \log K_4 = 1.24$$

$$\frac{a_{\text{K}^+} a_{\text{Cl}^-}}{a_{\text{KCl}^\circ}} = K_5; \quad \log K_5 = -0.735$$

Step 3: Assign reaction coefficients to each species in each of the above five reactions:

Species	Reaction Coefficients									
	NH_4^+	$\text{NH}_4\text{OH}^\circ$	H^+	HCl°	$\text{NH}_4\text{Cl}^\circ$	Cl^-	Na^+	NaCl°	K^+	KCl°
Rxn 1	1	-1	-1	0	0	0	0	0	0	0
Rxn 2	1	0	0	0	-1	1	0	0	0	0
Rxn 3	0	0	0	0	0	1	1	-1	0	0
Rxn 4	0	0	-1	1	0	-1	0	0	0	0
Rxn 5	0	0	0	0	0	1	0	0	1	-1

Steps 4 and 5: Write the 4 available mass balances and assign the parameters $b_{e,i}$, the number of times each component or element (e) occurs in the formula of each species (i) in each mass balance:

$$B_1 = \sum \text{NH}_3 = 0.25m = m_{\text{NH}_4^+} + m_{\text{NH}_4\text{OH}^\circ} + m_{\text{NH}_4\text{Cl}^\circ}$$

$$B_2 = \sum \text{Cl} = 0.75m = m_{\text{HCl}^\circ} + m_{\text{NH}_4\text{Cl}^\circ} + m_{\text{Cl}^-} + m_{\text{NaCl}^\circ} + m_{\text{KCl}^\circ}$$

$$B_3 = \sum \text{Na} = 0.25m = m_{\text{Na}^+} + m_{\text{NaCl}^\circ}$$

$$B_4 = \sum \text{K} = 0.25m = m_{\text{K}^+} + m_{\text{KCl}^\circ}$$

Species (i)	NH_4^+	$\text{NH}_4\text{OH}^\circ$	H^+	HCl°	$\text{NH}_4\text{Cl}^\circ$	Cl^-	Na^+	NaCl°	K^+	KCl°
$b_{\text{NH}_3,i}$	1	1	0	0	1	0	0	0	0	0
$b_{\text{Cl},i}$	0	0	0	1	1	1	0	1	0	1
$b_{\text{Na},i}$	0	0	0	0	0	0	1	1	0	0
$b_{\text{K},i}$	0	0	0	0	0	0	0	0	1	1

Step 6: Write the charge balance for ionic species, and assign valences, Z_i :

$$m_{\text{NH}_4^+} + m_{\text{H}^+} + m_{\text{Na}^+} + m_{\text{K}^+} = m_{\text{Cl}^-}$$

Species	NH_4^+	$\text{NH}_4\text{OH}^\circ$	H^+	HCl°	$\text{NH}_4\text{Cl}^\circ$	Cl^-	Na^+	NaCl°	K^+	KCl°
Z_i	1	0	1	0	0	-1	1	0	1	0

Step 7: First guesses at concentrations of all species:

Species	NH_4^+	$\text{NH}_4\text{OH}^\circ$	H^+	HCl°	$\text{NH}_4\text{Cl}^\circ$	Cl^-	Na^+	NaCl°	K^+	KCl°
$\sim m$	0.1	0.002	0.002	0.005	0.15	0.2	0.1	0.15	0.1	0.15

Step 8: Choose the A parameter (0.51, 0.53, 0.60, 0.69, 0.81, 0.98, 1.256 at 25, 50, 100, 150, 200, 250, and 300°C respectively). See Helgeson et al. (1981) for a more complete list.

Creating the input file

This completes the definition of our system. The above information is then written in a data file named EQBRM.DAT for use by the program. You must

create this file yourself, using a text editor such as program EDIT on most DOS systems, or even WordPerfect or Microsoft Word. If you do use a word processor, be sure to save the file in ASCII format. The name of the file must be EQBRM.DAT.

Enter N and M , the number of species and equilibrium constants, on the first line. Enter the reaction coefficients for each species from 1 to 10, taking one line for each of the 5 reactions. Enter the total molality of NH_3 on the next line, and the $b_{\text{NH}_3,i}$ parameters for species 1 to 10 on the next line. Repeat this sequence of two data lines for each of the mass balances on Cl, Na and K. Write the log of the equilibrium constants in order on the next line or lines, with no more than 8 entries per line. Enter the valences of each species on the following line. Write the initial guesses at species concentrations on the following lines, again with no more than 8 entries per line. Finally, on the last line, enter a value for the Debye-Hückel A parameter. Here is what the listing looks like, with comments:

Contents of the file EQBRM.DAT

10,5	N, M (No. species; no. K 's)
1,-1,-1,0,0,0,0,0,0,0	signed reaction coefficients for species 1,2,...,10
1,0,0,0,-1,1,0,0,0,0	
0,0,0,0,0,1,1,-1,0,0	
0,0,-1,1,0,-1,0,0,0,0	
0,0,0,0,0,1,0,0,1,-1	
0.25	total NH_3 (B_1)
1,1,0,0,1,0,0,0,0,0	NH_3 mass balance parameters ($b_{\text{NH}_3,i}$)
0.75	total Cl (B_2)
0,0,0,1,1,1,0,1,0,1	Cl mass balance parameters ($b_{\text{Cl},i}$)
0.25	total Na (B_3)
0,0,0,0,0,0,1,1,0,0	Na mass balance parameters ($b_{\text{Na},i}$)
0.25	total K (B_4)
0,0,0,0,0,0,0,0,1,1	K mass balance parameters ($b_{\text{K},i}$)
4.677,-0.82,-1.013,1.24,-0.735	$\log(K_1, K_2, K_3, K_4, K_5)$
1,0,1,0,0,-1,1,0,1,0	valences (Z_i)
0.1,0.002,0.002,0.005,0.15,0.2,0.1,0.15	
0.1,0.15	two lines of first guesses at m_i .
1.256	Debye-Hückel A parameter.

Program Output

The results of each iteration leading to the final result are sent to the screen, but scroll by too fast to read. They are usually of no great interest. The final results are written to a file named EQBRM.OUT. Remember to rename this file if you wish to save it, as it will be overwritten next time the program is run. The final results in this case are:

GAMMA ITERATION NUMBER = 5

GAMMA(1)= 4.04D-01	that is, $\gamma_{\text{NH}_4^+} = 0.404$
GAMMA(2)= 1.00D+00	$\gamma_{\text{NH}_4\text{OH}} = 1.0$
GAMMA(3)= 4.04D-01	$\gamma_{\text{H}^+} = 0.404$
GAMMA(4)= 1.00D+00	$\gamma_{\text{HCl}^\circ} = 1.0$
GAMMA(5)= 1.00D+00	$\gamma_{\text{NH}_4\text{Cl}^\circ} = 1.0$
GAMMA(6)= 4.04D-01	$\gamma_{\text{Cl}^-} = 0.404$
GAMMA(7)= 4.04D-01	$\gamma_{\text{Na}^+} = 0.404$
GAMMA(8)= 1.00D+00	$\gamma_{\text{NaCl}^\circ} = 1.0$
GAMMA(9)= 4.04D-01	$\gamma_{\text{K}^+} = 0.404$
GAMMA(10)= 1.00D+00	$\gamma_{\text{KCl}^\circ} = 1.0$

In this simple scheme, all singly charged ions have the same γ , and all doubly charged ions would have another γ .

FINAL CONCENTRATIONS

A(1)= 1.630D-01	that is, $m_{\text{NH}_4^+} = 0.1630$
A(2)= 2.844D-03	$m_{\text{NH}_4\text{OH}} = 0.002844$
A(3)= 1.206D-03	$m_{\text{H}^+} = 0.001206$
A(4)= 1.638D-03	$m_{\text{HCl}^\circ} = 0.001638$
A(5)= 8.416D-02	$m_{\text{NH}_4\text{Cl}^\circ} = 0.08416$
A(6)= 4.782D-01	$m_{\text{Cl}^-} = 0.4782$
A(7)= 1.385D-01	$m_{\text{Na}^+} = 0.1385$
A(8)= 1.115D-01	$m_{\text{NaCl}^\circ} = 0.1115$
A(9)= 1.755D-01	$m_{\text{K}^+} = 0.1755$
A(10)= 7.450D-02	$m_{\text{KCl}} = .07450$

As a check, you might calculate one or two K values, and compare with the input. For example

$$\begin{aligned}
 K_6 &= \frac{a_{\text{HCl}^\circ}}{a_{\text{H}^+} a_{\text{Cl}^-}} \\
 &= \frac{0.001638 \times 1.0}{(0.001206 \times 0.404)(0.4782 \times 0.404)} \\
 &= 17.40 \\
 \log K_6 &= 1.24 \quad \text{which is the input value.}
 \end{aligned}$$