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subject: Incorporation of Six Solid Phases Including Hydromagnesite (5424) and Hydromagnesite (4323) into EQ3/6 HMW Database and Its Modified Version HMP

(1) Incorporation of Six Solid Phases Including Hydromagnesite (5424) and Hydromagnesite (4323) into EQ3/6 HMW

When Emily Giambalvo left the WIPP Project, she gave me an EQ3/6 database called HMP, generated on October 26, 2001. To create this database, she modified the EQ3/6 HMW database (Wolery, 1992) by incorporating hydromagnesite (5424), $Mg_5(CO_3)_4(OH)_2 \bullet 4H_2O$, abbreviated as Hydromagne5424 in HWP, and hydromagnesite (4323), $Mg_4(CO_3)_3(OH)_2 \bullet 3H_2O$, abbreviated as Hydromagne4323 in HWP, in addition to four other solid phases (see below). However, she did not document this modification. In the following, this modification is described.

The standard free energies of formation ($\Delta_f G^\circ$) for these two hydromagnesite phases were taken from FMT database CHEMDAT, released in 2002 (Giambalvo, 2003), and their dimensionless standard chemical potentials were converted to $\Delta_f G^\circ$ (Table 1).

In HMP, the dissolution constants for hydromagnesite (5424) and hydromagnesite (4323) with regard to the following reactions were also given:

$$Mg_5(CO_3)_4(OH)_2 \bullet 4H_2O(s) + 6H^+ = 5Mg^{2+} + 4HCO_3^- + 6H_2O(l) \quad (1)$$

$$Mg_4(CO_3)_3(OH)_2 \bullet 3H_2O(s) + 5H^+ = 4Mg^{2+} + 3HCO_3^- + 5H_2O(l) \quad (2)$$

The free energy change for reaction (1), $\Delta_{r(1)}G^\circ$, according to the thermodynamic data in Table 2, is calculated to be –44.142 kcal mol^{-1} (Table 3). Based upon $\Delta_r G^\circ$, the equilibrium constant can be obtained according to the following equation:

$$\log K = -\Delta_r G^\circ / (2.303 \times R \times T) \quad (3)$$

in which R is the gas constant (1.98719 cal mol^{-1} K^{-1}), and T is absolute temperature in K (T = 298.15 K at 25 °C).

In addition, Emily Giambalvo directly obtained $MgSO_4$, chloromagnesite ($MgCl_2$), lime (CaO), and periclase (MgO) from the other EQ3/6 database (either ALT, COM, PIT, SUP). However, Emily Giambalvo did not re-calculate their respective dissolution equilibrium constants for these four phases to make sure that they are consistent with the original HMW database, resulting in the slight thermodynamic inconsistency (see Table 3). In this study, the dissolution equilibrium constants are also re-calculated according to the auxiliary thermodynamic data in HMW in order to maintain the internal thermodynamic consistency. The dissolution equilibrium reactions for these phases are as follows:

$$MgSO_4(s) = Mg^{2+} + SO_4^{2-} \quad (4)$$

$$MgCl_2(s) = Mg^{2+} + 2Cl^- \quad (5)$$

$$MgO(s) + 2H^+ = Mg^{2+} + 2H_2O(l) \quad (6)$$

$$CaO(s) + 2H^+ = Ca^{2+} + 2H_2O(l) \quad (7)$$

The equilibrium constants for these reactions are tabulated in Table 3.

(2) HMP Database

Using the standard free energies of formation provided above (Table 1) and the dissolution constants (Table 3) recommended by this memorandum for the six solid phases including hydromagnesite (5424) and hydromagnesite (4323) to modify HMW, the HMP database is formally established. This database has been successfully run by EQPT, an executable with EQ3/6 package (Wolery, 1992), and files of "output.hmp" and "data1f.hmp" (a formatted data file) have been generated. File comparisons between "output.hmp" and "output.hmw", and between "data1f.hmp" and "data1f.hmw" indicate that the only differences between HMP and HMW are those of entries of the above six solid phases (see attached files).

References

Giambalvo, E.R. 2003. "Release of FMT Database FMT_021120.CHEMDAT." Memorandum to L.H. Brush, March 10, 2003. Carlsbad, NM: Sandia National Laboratories. ERMS 526372.

Wolery, T.J. 1992. *EQ3/6, A Software Package for Geochemical Modeling of Aqueous Systems: Package Overview and Installation Guide (Version 7.0).* UCRL-MA-110662 PT I. Livermore, CA: Lawrence Livermore National Laboratory.

Table 1. Standard Free Energies of Formation for Hydromagnesite (5424) and Hydromagnesite (4323) in HMP at Reference State (298.15 K and 1 bar)

Phase	μ^o/RT in FMT_021120.CHEMDAT	Δ_fG^o, kcal mol^{-1}, in HMP
Hydromagnesite (5424)	–2364.06	–1400.53* (–1400.526)
Hydromagnesite (4323)	–1856.104	–1099.6* (–1099.601)

Note: * entered by E. Giambalvo (generated on 10/26/2001); numbers in parentheses are re-calculated values in this study.

Table 2. Standard Free Energy of Formation (Δ_fG^o) for Relevant Species at 298.15 K and 1 bar for Calculation of Dissolution Constants of Six Solid Phases Including Hydromagnesite (5424) and Hydromagnesite (4323) Incorporated in HMP

Species	Δ_fG^o (kcal mol^{-1})	References
Hydromagne5424(s)	–1400.526	This memo, EQ3/6 data0.hmp (abbreviated as HMP)
Hydromagne4323(s)	–1099.601	This memo, EQ3/6 data0.hmp (abbreviated as HMP)
$MgSO_4$(s)	–279.780	EQ3/6 data0.pit (abbreviated as PIT)
$MgCl_2$ (s)	–141.440	EQ3/6 data0.pit (abbreviated as PIT)
MgO(s)	–136.086	EQ3/6 data0.pit (abbreviated as PIT)
CaO(s)	–144.366	EQ3/6 data0.pit (abbreviated as PIT)
H_2O(l)	–56.679	EQ3/6 data0.hmw (abbreviated as HMW)
H^+(aq)	0	EQ3/6 data0.hmw (abbreviated as HMW)
Mg^{2+}(aq)	–108.702	EQ3/6 data0.hmw (abbreviated as HMW)
Ca^{2+}(aq)	–132.302	EQ3/6 data0.hmw (abbreviated as HMW)
HCO_3^-(aq)	–140.271	EQ3/6 data0.hmw (abbreviated as HMW)
SO_4^{2-}(aq)	–177.947	EQ3/6 data0.hmw (abbreviated as HMW)
Cl^-(aq)	–31.375	EQ3/6 data0.hmw (abbreviated as HMW)

Table 3. Dissolution Constants for Reactions Investigated in This Memo at 298.15 K and 1 bar.

Reactions	$\Delta_r G^o$ (kcal mol^{-1})	log K, E. Giambalvo (10/26/2001)	log K, This memo
Reaction 1	–44.142	32.2529	32.3507
Reaction 2	–39.415	28.8104	28.8864
Reaction 4	–6.8959	4.8781	5.0538
Reaction 5	–30.012	21.8604	21.9951
Reaction 6	–29.295	21.3354	21.4697
Reaction 7	–44.615	32.5761	32.6974

```
Comparing files data1f.hmw and DATA1F.HMP
***** data1f.hmw
    9   10
data0.hmw.V8.R6
CII: GEMBOCHS.V2-EQ8-data0.hmw.V8.R6
THERMODYNAMIC DATABASE
***** DATA1F.HMP
    9   10
data0.hmp.V8.R6
CII: GEMBOCHS.V2-EQ8-data0.hmp.V8.R6
THERMODYNAMIC DATABASE
*****

***** data1f.hmw
Output package:  eq3
Data set:        hmw
+------------------------------------------------------------------------
***** DATA1F.HMP
Output package:  eq3
Data set:        hmp
+------------------------------------------------------------------------
*****

***** data1f.hmw
 9.999999000E+06 0.000000000E+00 0.000000000E+00 0.000000000E+00 0.000000000E+00
Bloedite                        5    5
***** DATA1F.HMP
 9.999999000E+06 0.000000000E+00 0.000000000E+00 0.000000000E+00 0.000000000E+00
MgSO4                           3    3
        120.369   0.    45.250
     1.0000  Mg           4.0000  O
     1.0000  S
    -1.0000  MgSO4                          1.0000  Mg++
     1.0000  SO4--
 6.239598262E+00-3.982247938E-02-3.732890481E-04 2.756440157E-06 0.000000000E+00
 1.280900000E+00 0.000000000E+00 0.000000000E+00 0.000000000E+00 0.000000000E+00
Bloedite                        5    5
*****

***** data1f.hmw
 9.999999000E+06 0.000000000E+00 0.000000000E+00 0.000000000E+00 0.000000000E+00
Dolomite                        4    5
***** DATA1F.HMP
 9.999999000E+06 0.000000000E+00 0.000000000E+00 0.000000000E+00 0.000000000E+00
Chloromagnesite                 2    3
         95.210   0.  500.000
     2.0000  Cl           1.0000  Mg
    -1.0000  Chloromagnesite              1.0000  Mg++
     2.0000  Cl-
 2.432742099E+01-9.209804215E-02-8.975863689E-05 1.678669595E-06 0.000000000E+00
 2.392090000E+01-9.425283333E-02 1.512150000E-04-8.766666667E-08-2.140000000E-10
Dolomite                        4    5
*****

***** data1f.hmw
 9.999999000E+06 0.000000000E+00 0.000000000E+00 0.000000000E+00 0.000000000E+00
K2CO3:1.5H2O                    4    5
***** DATA1F.HMP
 9.999999000E+06 0.000000000E+00 0.000000000E+00 0.000000000E+00 0.000000000E+00
Hydromagne5424                  4    5
        467.638   0.     0.000
    10.0000  H            5.0000  Mg
    18.0000  O            4.0000  C
    -1.0000  Hydromagne5424              -6.0000  H+
     5.0000  Mg++                         4.0000  HCO3-
     6.0000  H2O
 3.235070000E+01 0.000000000E+00 0.000000000E+00 0.000000000E+00 0.000000000E+00
 9.999999000E+06 0.000000000E+00 0.000000000E+00 0.000000000E+00 0.000000000E+00
Hydromagne4323                  4    5
        365.308   0.     0.000
```

```
   8.0000  H             4.0000  Mg
  14.0000  O             3.0000  C
  -1.0000  Hydromagne4323               -5.0000  H+
   4.0000  Mg++                          3.0000  HCO3-
   5.0000  H2O
 2.888640000E+01 0.000000000E+00 0.000000000E+00 0.000000000E+00 0.000000000E+00
 9.999999000E+06 0.000000000E+00 0.000000000E+00 0.000000000E+00 0.000000000E+00
K2CO3:1.5H2O                    4    5
*****

***** data1f.hmw
 9.999999000E+06 0.000000000E+00 0.000000000E+00 0.000000000E+00 0.000000000E+00
Magnesite                       3    4
***** DATA1F.HMP
 9.999999000E+06 0.000000000E+00 0.000000000E+00 0.000000000E+00 0.000000000E+00
Lime                            2    4
        56.077   0.   16.764
   1.0000  Ca            1.0000  O
  -1.0000  Lime                        -2.0000  H+
   1.0000  Ca++                         1.0000  H2O
 3.568213960E+01-1.239619497E-01 1.615143203E-04 8.552121682E-07 0.000000000E+00
 2.575630000E+01 0.000000000E+00 0.000000000E+00 0.000000000E+00 0.000000000E+00
Magnesite                       3    4
*****

***** data1f.hmw
 9.999999000E+06 0.000000000E+00 0.000000000E+00 0.000000000E+00 0.000000000E+00
Picromerite                     5    5
***** DATA1F.HMP
 9.999999000E+06 0.000000000E+00 0.000000000E+00 0.000000000E+00 0.000000000E+00
Periclase                       2    4
        40.304   0.   11.248
   1.0000  Mg            1.0000  O
  -1.0000  Periclase                   -2.0000  H+
   1.0000  H2O                         1.0000  Mg++
 2.374252453E+01-9.245318288E-02 2.931096659E-05 1.291884093E-06 0.000000000E+00
 1.608220000E+01 0.000000000E+00 0.000000000E+00 0.000000000E+00 0.000000000E+00
Picromerite                     5    5
*****
```

```
Comparing files output.hmw and OUTPUT.HMP
***** output.hmw

 Run  11:15:55  10Aug1998

***** OUTPUT.HMP

 Run  11:13:32  20Jul2004

*****

***** output.hmw

 data0.hmw.V8.R6
 CII: GEMBOCHS.V2-EQ8-data0.hmw.V8.R6
 THERMODYNAMIC DATABASE
***** OUTPUT.HMP

 data0.hmp.V8.R6
 CII: GEMBOCHS.V2-EQ8-data0.hmp.V8.R6
 THERMODYNAMIC DATABASE
*****

***** output.hmw
 Output package:  eq3
 Data set:        hmw
 +---------------------------------------------------------------------
***** OUTPUT.HMP
 Output package:  eq3
 Data set:        hmp
 +---------------------------------------------------------------------
*****

***** output.hmw
     6 Bischofite
     7 Bloedite
     8 Brucite
     9 Burkeite
    10 Ca2Cl2(OH)2:H2O
    11 Ca4Cl2(OH)6:13H2O
    12 CaCl2:4H2O
    13 Calcite
    14 Carnallite
    15 Dolomite
    16 Epsomite
    17 Gaylussite
    18 Glauberite
    19 Gypsum
    20 Halite
    21 Hexahydrite
    22 K2CO3:1.5H2O
    23 K3H(SO4)2
    24 K8H4(CO3)6:3H2O
    25 KNaCO3:6H2O
    26 Kainite
    27 Kalicinite
    28 Kieserite
    29 Leonite
    30 Magnesite
    31 Mercallite
    32 Mirabilite
    33 Misenite
    34 Na2CO3:7H2O
    35 Na3H(SO4)2
    36 Na4Ca(SO4)3:2H2O
    37 Nahcolite
    38 Natron
    39 Nesquehonite
    40 Oxychloride-Mg
    41 Picromerite
```

```
    42 Pirssonite
    43 Polyhalite
    44 Portlandite
    45 Sylvite
    46 Syngenite
    47 Tachyhydrite
    48 Thenardite
    49 Thermonatrite
    50 Trona
    51 Trona-K

***** OUTPUT.HMP
     6 Bischofite
     7 MgSO4
     8 Bloedite
     9 Brucite
    10 Burkeite
    11 Ca2Cl2(OH)2:H2O
    12 Ca4Cl2(OH)6:13H2O
    13 CaCl2:4H2O
    14 Calcite
    15 Carnallite
    16 Chloromagnesite
    17 Dolomite
    18 Epsomite
    19 Gaylussite
    20 Glauberite
    21 Gypsum
    22 Halite
    23 Hexahydrite
    24 Hydromagne5424
    25 Hydromagne4323
    26 K2CO3:1.5H2O
    27 K3H(SO4)2
    28 K8H4(CO3)6:3H2O
    29 KNaCO3:6H2O
    30 Kainite
    31 Kalicinite
    32 Kieserite
    33 Leonite
    34 Lime
    35 Magnesite
    36 Mercallite
    37 Mirabilite
    38 Misenite
    39 Na2CO3:7H2O
    40 Na3H(SO4)2
    41 Na4Ca(SO4)3:2H2O
    42 Nahcolite
    43 Natron
    44 Nesquehonite
    45 Oxychloride-Mg
    46 Periclase
    47 Picromerite
    48 Pirssonite
    49 Polyhalite
    50 Portlandite
    51 Sylvite
    52 Syngenite
    53 Tachyhydrite
    54 Thenardite
    55 Thermonatrite
    56 Trona
    57 Trona-K

*****

***** output.hmw

 Completed processing the pitzer data file data0.hmw.V8.R6.
```

```
***** OUTPUT.HMP

 Completed processing the pitzer data file data0.hmp.V8.R6.

*****

***** output.hmw

          Start time = 11:15:55  10Aug1998
            End time = 11:15:56  10Aug1998

           run time =  0.330     seconds

***** OUTPUT.HMP

          Start time = 11:13:32  20Jul2004
            End time = 11:13:33  20Jul2004

           run time =  0.390     seconds

*****
```