

## USER'S MANUAL FOR MULTIFLO: PART II—

### MULTIFLO 1.0 AND GEM 1.0 MULTICOMPONENT-MULTIPHASE REACTIVE TRANSPORT MODEL

*Prepared for*

**Nuclear Regulatory Commission  
Contract NRC-02-93-005**

*Prepared by*

**Center for Nuclear Waste Regulatory Analyses  
San Antonio, Texas**

**September 1996**



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Part II: MULTIFLO 1.0 and  
GEM 1.0

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**September 1996**

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# 1 INTRODUCTION

This User's Manual describes the input data for the code General Electrochemical Migration (GEM). In addition, the manual describes how to compile and run MULTIFLO, the driver which sequentially couples GEM and Mass and Energy TRAnsport (METRA). For details on using METRA, the reader is referred to Part I of this manual describing the code METRA and preparation of the input file (Seth and Lichtner, 1996). This manual applies to both the enhanced memory version of the code in which memory is allocated at runtime and a prototype version which does not implement enhanced memory management. The same input data file may be used with both versions of the code. The memory-enhanced version of the code GEM has been optimized to run with METRA, whereas the prototype version is not coupled to METRA.

## 1.1 OVERVIEW OF GEM

The code GEM solves multicomponent-multiphase, nonisothermal, reactive mass transport equations for one-dimensional (1D), two-dimensional (2D), or three-dimensional (3D) problems. Simultaneous transport in both liquid and gas phases is possible. However, transport in a pure gas phase is not currently implemented. Both advective and diffusive transport are incorporated in the code. Chemical reactions consist of homogeneous aqueous reactions in local chemical equilibrium, redox reactions, mineral precipitation and dissolution reactions treated kinetically, and ion-exchange reactions. In stand-alone mode, GEM uses a steady-state flow field provided by the user. In addition, a prescribed saturation field may be read in. One-way coupling to METRA allows the transient flow field computed from METRA to be sequentially fed into GEM. Two-way coupling is also possible in which changes in porosity and permeability resulting from mineral precipitation and dissolution may be fed back to METRA from GEM. The code applies generally to heterogeneous porous media.

A number of solution algorithms are available in GEM including implicit, explicit, and operator-splitting finite difference methods. Solvers available include a tridiagonal solver and the conjugate gradient solver WATSOLV (VanderKwaak et al., 1995). The implicit finite difference algorithm for solving the reactive transport equations is generally only suitable for 1D problems or small 2D problems because of the prohibitive memory requirements for large 2D problems. The operator splitting algorithm, in which the solution algorithm is broken down into a nonreactive followed by a reactive time step, is recommended for large 2D and 3D problems. The explicit finite difference scheme is also applicable to large problems. This scheme may be faster than the operator splitting algorithm if the Courant condition is the limiting factor in the time step size, rather than stability requirements. The explicit finite difference scheme may also be used with the Leonard-Total Variation Diminishing (TVD) algorithm for high peclet number flows.

Two thermodynamic databases are provided with GEM: (i) ms25.r16 and (ii) mstemp.r16. Both databases are derived from the EQ3/6 database version R16 (Wolery, 1983). The first file (ms25.r16) contains equilibrium constants at 25 °C only, whereas the second file (mstemp.r16) contains equilibrium constants over the temperature range from 0–300 °C. These are stored at temperatures of 0, 25, 60, 100, 150, 200, 250, and 300 °C along the saturation curve of water and interpolated at intermediate values using a Mayer-Kelly function.

One major limitation of the current version of GEM is that it cannot handle a pure gas phase system or a spatial region in which only a single gas phase is present. Some amount of liquid must always

be present. This is because the chemistry in GEM is defined through a set of primary species that belong to the aqueous phase. In the presence of a pure gas phase region, it would be necessary to use primary species from the gas phase only. At the interface between a pure liquid or two-phase region and a pure gas phase region, different sets of primary species are necessary to describe the chemical reactions in the system. At present, employing different sets of primary species in different regions of space is not possible. This limitation will be removed in the next major release of the code.

## 1.2 THE MULTIFLO DRIVER

The MULTIFLO code is designed so that the submodules METRA and GEM may be run individually in stand-alone mode without coupling to one another. They may also be run from the MULTIFLO driver program in stand-alone or coupled mode by appropriately setting the parameter 'icode'. The possible choices for 'icode' are:

- icode = 1, METRA stand-alone
- = 2, GEM stand-alone
- = 3, Coupled METRA and GEM in transient mode
- = 4, Coupled METRA and GEM in steady-state mode

The parameter icode is entered following a prompt from MULTIFLO:

---> read icode: (1-metra, 2-gem, 3-coupled, 4-coupled: steady-state)

With icode = 1 and 2, METRA and GEM are run in stand-alone mode. For icode = 3 and 4, METRA and GEM are coupled through the MULTIFLO driver. For icode = 3, GEM is called after each successfully completed METRA time step. For icode = 4, first METRA is run until a steady-state solution is obtained, and then GEM is called using the steady-state METRA solution. In coupled mode (icode = 3 and 4), the target time is taken from the GEM input file 'masin', whereas the grid spacing, porosity, temperature, pressure, and saturation are taken from the METRA input file 'multi.dat'.

## **2 INPUT DATA STRUCTURE**

The input data are associated with keywords in free-format form. The only limitations are a maximum of 120 characters per line, floating point (real) numbers must not exceed 10 entries per line, and integers must not exceed 20 entries per line.

### **2.1 KEYWORDS**

Data are entered through blocks of one or more lines of input identified by keywords. A keyword can be up to 20 characters long. However, only the first four characters are used internally in the code for identification. Keywords may appear in any order in the data set with the exception of the GRID keyword which must be the first keyword following the TITLE lines. Lower or upper case letters, or any combination of them, may be used to type in a keyword in the input file.

### **2.2 COMMENT LINES**

Comment lines may be included in the input file by putting a colon (:) in the first column. These lines are ignored during processing of the data. A colon or an exclamation mark (!) can also appear elsewhere on a line, in which case, the data following the colon or exclamation mark is ignored.

### **2.3 SKIP/NOSKIP KEYWORDS**

Entire blocks of data may be skipped over using the keywords SKIP and NOSKIP. All input lines between the SKIP and NOSKIP keywords are ignored. These keywords may appear anywhere following the title lines.

### **3 INPUT DATA**

#### **3.1 TITLE LINES**

Two title lines are required, and must appear as the first two lines in the data file. Any alphanumeric characters may appear in the title with up to 80 characters per line. Blank lines may also be used for title lines. Comment lines [lines beginning with a colon (:)] can precede the title lines.

#### **3.2 INPUT DATA KEYWORDS**

There are currently 25 keywords used in the GEM input file. Appearing in alphabetical order, they are:

AQCX	Optional
BCON	Required
BRKP	Optional
COMPonents	Required
COUPle	Optional
DEBUG	Optional
DIFF	Required
DTSTep	Required
DXYZ	Required
ENDS	Required (Must be last keyword.)
FLOW	Required
GASEs	Optional
GRID	Required (Must be first keyword.)
IONX	Optional
ISYSstem	Required
MASTER	Optional
MNIR	Optional
MNRL	Optional
OPTS	Required
PLTFfiles	Optional
PTINit	Optional
SOLVE	Required
STOL	Optional
TIME	Required
TOLR	Optional

Each keyword is described in detail in alphabetical order in the following sections with the exception of the GRID keyword which comes first. The order of appearance of the keywords in the input file is arbitrary with the exception of the GRID keyword which must be the first keyword.

### 3.3 GRID GEOMETRY [GRID]

---

Keyword: **GRID**  
Required

---

The GRID keyword defines the grid geometry and solution method.

Read: GRID GEOMETRY NX NY NZ MODE IPRINT

GRID = Keyword defining the grid geometry and solution method.

GEOMETRY = Parameter for selecting geometry of simulation.

= CARtesian, Cartesian geometry.

= RADial, Cylindrical geometry.

= SPHerical, Spherical geometry. (Only implemented for MODE = 1.)

NX = Number of grid blocks in x or r (I) direction.

NY = Number of grid blocks in y (J) direction. (For a radial system, NY = 1.)

NZ = Number of grid blocks in z (K) direction.

MODE = Option for selecting mode of operation of code.

= -1, Read database and stop.

= 0, Batch reaction system. (Not implemented.)

= 1, 1D electrochemical migration model (NX > 1, NY = NZ = 1) using a tridiagonal solver and implicit finite difference time-stepping algorithm. This model is applicable to a single-phase liquid in a fully saturated porous medium. This mode of operation is not coupled to METRA.

= 2, Multidimensional—multiphase transport model with implicit, explicit, and operator-splitting algorithms. This mode allows coupling to METRA through the MULTIFLO driver program.

IPRINT = Parameter for printout control.

= -1, Minimum printout.

= 0, Small printout.

= 1, Intermediate printout.

= 2, Maximum printout.

= 3, Database printout.

Comment(s):

This keyword must appear as the first keyword in the input file.

Problems for 1, 2, and 3D are defined by appropriate assignment of NX, NY, and NZ. Maximum number of grid blocks in any direction and the total number of blocks permissible can be altered by the user in the paramtrs.h file.

For MODE = 2, only cartesian coordinates are possible in this version of the code.

Example:

:	geometry	nx	ny	nz	mode	iprint
GRID	1	100	1	100	2	-1

### 3.4 AQUEOUS SECONDARY SPECIES [AQCX]

---

Keyword: **AQCX**  
Optional

---

This keyword reads in the names of aqueous secondary species. In the absence of secondary species, this keyword is not required.

Read: **AQCX**

Read: **SPECIES DIFFUSION**

**AQCX** = Keyword for reading in a list of aqueous secondary species and their diffusion coefficients. For the case MODE = 1, their corresponding diffusion coefficients are also read in.

**SPECIES** = Name of species.

**DIFFUSION** = Aqueous diffusion coefficient for corresponding species [cm<sup>2</sup>/s]. For MODE = 2, these values are ignored.

Comment(s):

Species-dependent diffusion coefficients are only possible with MODE = 1, which is not implemented in the memory-enhanced version.

The name of the species must agree with the name entered in the databases ms25.r16 or mstemp.r16, or any other database the user provides.

The list of species is terminated with a blank line or a line with one or more zeros.

Example:

```
AQCX
:species      diff. coef.
oh-          5.5e-5
aloh+2       1.0e-5
al(oh)2+     1.0e-5
al(oh)3(aq)  1.0e-5
al(oh)4-
h3siO4-
h2siO4-2
:blank
```

### **3.5 BOUNDARY CONDITIONS [BCON]**

---

**Keyword:** BCON  
**Required**

This keyword reads in the boundary condition data for defining the composition of a multicomponent fluid. In this version of the code, only concentration and zero flux boundary conditions are possible. The boundary condition is applied uniformly over the entire face of the bounding surface which must consist of one of the faces of a rectangular parallelepiped, or the faces of the bounding cylinder in cylindrical coordinates. The origin of coordinates for cartesian coordinates is taken in the upper left corner of the parallelepiped at the front face with the z-axis pointing downward, the y-axis horizontal, and the x-axis perpendicular to the yz-plane forming a left-handed coordinate system. For the case of cylindrical geometry, the origin is at the top, centered on the axis of the cylinder.

Read: BCON

Read: IBND IBNDTYP

Read: SPECIES ITYPE GUESS CTOT CONSPEC

**BCON** = Keyword for specifying boundary conditions.

**IBND** = Boundary at which solution composition is to be determined.

- = 1, Left face or inner radius in cylindrical coordinates ( $I = 1, X = 0$ ).
- = 2, Right face or outer radius in cylindrical coordinates ( $I = NX$ ).
- = 3, Top face ( $K = 1, Z = 0$ ).
- = 4, Bottom face ( $K = NZ$ ).
- = 5, Front face ( $J = 1, Y = 0$ ).
- = 6, Back face ( $J = NY$ ).

**IBNDTYP** = Type of boundary condition.

- = 1, Concentration boundary condition.
- = 2, Flux boundary condition (Not implemented).
- = 3, Zero gradient boundary condition.

**SPECIES** = Name of a primary species.

**ITYPE** = Type of constraint condition imposed on species mass balance equation.

- = -1, Charge balance constraint.
- = 1, Total concentration as specified by CTOT.
- = 3, Mineral constraining species.
- = 4, Gaseous constraining species.
- = 7, Individual species concentration as specified by CTOT.
- = 8, Solution pH as specified by CTOT.

**GUESS** = Initial guess for species concentration [moles/L].

**CTOT** = Total concentration, species concentration, or pH depending on the value of ITYPE. This field is not used for ITYPE = 3, 4, or -1.

**CONSPEC** = Name of mineral or gaseous species with which the solution is to be in equilibrium.

Comment(s):

Names of primary species must be listed in the same order in both keywords BCON and COMPPONENTS, and their spelling must be identical to the names appearing in the thermodynamic database.

The boundary condition block must end with a zero or blank line.

It is not possible to assign the boundary condition to a portion of a face. In the current version of GEM, it can be assigned only to an entire face.

If a constraint mineral or gaseous species is not used, any name may be entered in the CONSPEC field, but it must not be left blank.

Example:

```
BCON
 1 1
:species    itype    guess    ctot    mineral
k+          1        1.e-6   1.e-6   blank
al+3        1        1.e-8   1.e-8   blank
h+          8        1.e-4   4.0     blank
sio2(aq)    1        1.e-6   1.e-6   blank
:
 2 3
:species    itype    guess    ctot    mineral
k+          3        1.e-4   1.e-4   k-feldspar
al+3        3        1.e-15  1.e-4   muscovite
h+          8        1.e-7   7.0     blank
sio2(aq)    3        1.e-4   1.e-3   quartz
:
 5 3
:species    itype    guess    ctot    mineral
k+          3        1.e-4   1.e-4   k-feldspar
al+3        3        1.e-15  1.e-4   muscovite
h+          8        1.e-7   7.0     blank
sio2(aq)    3        1.e-4   1.e-3   quartz
:
 6 3
:species    itype    guess    ctot    mineral
k+          3        1.e-4   1.e-4   k-feldspar
al+3        3        1.e-15  1.e-4   muscovite
h+          8        1.e-7   7.0     blank
sio2(aq)    3        1.e-4   1.e-3   quartz
0 0
```

### **3.6 BREAK-THROUGH NODE POINTS FOR PLOTTING [BRKP]**

---

Keyword: **BRKP**  
Optional

---

This keyword is for reading a list of nodes at which solution composition data is stored at each time step for producing time history plots.

Read: BRKP NDXMAX

Read: (NDX(I), I = 1, NDXMAX)

BRKP = Keyword for reading nodes at which data is stored as a function of time.

NDXMAX = Number of node points to be read in.

NDX = Nodes at which solution composition data is to be stored.

Comment(s):

There is a limit of 20 entries per line.

The node positions are given as a single integer:  $N = I + (J-1)*NX + (K-1)*NX*NY$ , where the indices I, J, and K refer to a particular node point.

Example:

```
BRKP 5
 93    110    130    150    185
```

### **3.7 INITIAL CONDITIONS AND DEFINITION OF COMPONENT SPECIES [COMPonents]**

---

**Keyword: COMPonents  
Required**

---

This is the keyword for defining the initial conditions and specification of primary (component) species that are used to define the chemical system.

Read: COMPonents INLET OUTLET NZONEAQ

Read: SPECIES ITYPE GUESS CTOT CONSPEC DIFFUSION

**COMPonents** = Keyword for assigning system primary species, their initial concentrations, and diffusion coefficients.

**INLET** = Inlet boundary condition (only used if MODE = 1).

- = 1, Concentration boundary condition.
- = 2, Flux boundary condition.
- = 3, Zero gradient boundary condition.

**OUTLET** = Outlet boundary condition (only used if MODE = 1).

- = 1, Concentration boundary condition.
- = 2, Flux boundary condition.
- = 3, Zero gradient boundary condition.

**NZONEAQ** = Number of different reaction zones at which initial conditions are specified (only used if MODE = 1).

**SPECIES** = Name of primary species.

**ITYPE** = Type of constraint condition imposed on species mass balance equation.

- = -1, Charge balance constraint.
- = 1, Total concentration as specified by CTOT.
- = 3, Mineral constraining species.
- = 4, Gaseous constraining species.
- = 7, Individual species concentration as specified by CTOT.
- = 8, Solution pH as specified by CTOT.

**GUESS** = Initial guess for species concentration [moles/L].

**CTOT** = Total concentration, species concentration, or pH depending on ITYPE. This field is not used for ITYPE = 3, 4, or -1.

**CONSPEC** = Name of mineral or gaseous species with which the solution is to be in equilibrium.

**DIFFUSION** = Aqueous diffusion coefficients [cm<sup>2</sup>/s]. This field is used only if MODE = 1 and IDIF ≥ 1 on the DIFF keyword.

Comment(s):

List of initial conditions ends with a blank line.

The order in which primary species are entered in the input file must be the same for the BCON and COMPonents keywords, and their spelling must be identical to the names appearing in the thermodynamic database.

The initial conditions are applied uniformly over the computational domain. Presently, it is not possible to assign different initial conditions for the solution composition to different regions of space.

If a constraint mineral or gaseous species is not used, any name may be entered in the CONSPEC field, but it must not be left blank.

Example:

```
COMPonents
:species    itype    guess    ctot    mineral    diffusion
k+          3        1.e-4    1.e-4    k-feldspar
al+3        3        1.e-15   1.e-4    muscovite
h+          8        1.e-7    7.0      blank
sio2(aq)   3        1.e-4    1.e-3    quartz
:blank
```

### **3.8 KEYWORD FOR COUPLING METRA AND GEM [COUPle]**

---

Keyword: **COUPle**  
Optional

---

This keyword defines parameters to invoke coupling of porosity and permeability and enables synchronization of time steps between METRA and GEM.

Read: COUPle ISYNC IPOR IPERM PERMFAC

**COUPle** = Keyword for coupling changes in porosity and permeability and synchronizing time stepping between METRA and GEM.

**ISYNC** = Parameter for synchronizing time steps with MULTIFLO.

= n, Integer defining fraction of METRA time step attempted by GEM. A value of zero implies no synchronization.

**IPOR** = Parameter for invoking variable porosity.

= 0, Constant porosity.

= 1, Variable porosity.

**IPERM** = Parameter for invoking variable permeability.

= 0, Constant permeability.

= 1, Variable permeability.

**PERMFAC** = Exponent 'n' in permeability/porosity expression [see Eq. (A-27) in the appendix].

Comment(s):

The parameter ISYNC should only be nonzero when running GEM in implicit mode.

Example:

```
:           isync   ipor    iperm  perm. fac.  
COUPle     4       1      1      3.
```

### 3.9 DEBUGGING [DEBUs]

---

Keyword: **DEBUs**  
Optional

---

This keyword turns on the debugging option for specified variables and number of steps.

Read: DEBUs MCYC CC C FLX R SURF QK PK RK COEF

DEBUs = Keyword for printing debug output.

MCYC = Time step at which debugging information is desired [integer].

CC = Concentration of primary species at current time step.

= 0, Do not print.  
= 1, Print.

C = Concentration of primary species at current time step.

= 0, Do not print.  
= 1, Print.

FLX = Flux of primary species.

= 0, Do not print flux at current time step.  
= 1, Print flux at current time step.

R = Residuals of Newton-Raphson solution.

= 0, Do not print.  
= 1, Print.

SURF = Mineral surface area.

= 0, Do not print.  
= 1, Print.

QK = Affinity factor expressed as  $K_m \cdot Q_m$  for the  $m$ th mineral.

= 0, Do not print.  
= 1, Print.

**PK** = Mineral volume fraction.

= 0, Do not print.  
= 1, Print.

**RK** = Mineral reaction rate.

= 0, Do not print.  
= 1, Print.

**COEF** = Jacobian coefficients in I-direction.

= 0, Do not print.  
= 1, Print.

Example:

:	mcyc	cc	c	flx	r	surf	qk	pk	rk	coef
DEBUs	115	1	1	1	1	1	1	1	1	0

### **3.10 AQUEOUS AND GASEOUS DIFFUSION DATA [DIFF]**

---

**Keyword: DIFF**  
**Required**

---

This keyword assigns aqueous and gaseous diffusion coefficients and tortuosities.

Read: DIFF D0 DELHAQ DGAS DGEXP TORTAQ TORTG IDIF

DIFF = Keyword for reading diffusion coefficient data for aqueous and gaseous species.

D0 = Aqueous diffusion coefficient [ $\text{cm}^2/\text{s}$ ].

DELHAQ = Activation enthalpy [kJ/mol].

DGAS = Gaseous diffusion coefficient [ $\text{cm}^2/\text{s}$ ].

DGEXP = Exponent in expression for gaseous diffusion coefficient.

TORTAQ = Tortuosity factor for aqueous diffusion.

TORTG = Tortuosity factor for gaseous diffusion.

IDIF = Parameter to specify species-dependent or -independent aqueous diffusion coefficients and corrosion model. This option is only applicable if MODE=1. If IDIF  $\geq 1$ , data for diffusion coefficients are read from the COMPonent and AQCX keywords. (Default=0.)

= 0, Species-independent aqueous diffusion coefficients.

= 1, Species-dependent aqueous diffusion coefficients.

= 2, Corrosion model (not implemented in this version of the code).

= 3, Corrosion model (not implemented in this version of the code).

Example:

```
: d0[cm2/s] delhaq[kJ/mol] dgas[cm2/s] dgexp tortaq tortg idif
DIFF 1.d-5      12.6       2.13d-1     1.8      1.d0    1.d0    0
```

### 3.11 INITIAL AND MAXIMUM TIME STEP [DTSTep]

---

Keyword: **DTSTep**  
Required

This keyword assigns the initial time step for the run and the maximum allowed time step within a specified time interval.

Read: DTSTep[u] NSTPMax (TSTEP(I), I=1,NSTPMax)

Read: (DT (I), I=1, NSTPMax+1)

**DTSTep[u]** = Keyword for specifying the initial and maximum time steps within a prescribed time interval. The variable [u] in brackets allows different units to be chosen for the target time and time step, defined as follows:

units of time	variable [u]
years	[y], [Y]
days	[d], [D]
minutes	[m], [M]
hours	[h], [H]
seconds	[s], [S]

The keyword DTSTep[u] is treated as a single keyword without any blank spaces.

**NSTPMax** = Number of time intervals for which the maximum time step is specified.

**TSTEP** = Times at which maximum time step is changed [u]. The first line may contain a maximum of 9 values and succeeding lines up to 10 values per line.

**DT** = Maximum time step size [u] for time interval [TSTEP(I-1), TSTEP (I)] for I=1, ..., NSTPMax, with TSTEP(0)=0.

Comment(s):

In implicit mode, DT[NSTPMax+1] represents the largest possible time step. In operator-splitting and explicit modes, DT[NSTPMax+1] represents the time step once the system has reached a stationary state. DT[1] in all case represents the initial time step.

Example:

DTST[y]	1 3.e-8
1.e-8	1.e2

### **3.12 GRID-BLOCK SIZES [DXYZ]**

---

**Keyword: DXYZ**  
**Required**

This keyword reads in grid spacing for GEM in stand-alone mode. In coupled mode, the grid size specified in the METRA input file is used. Different read statements are used depending on the value of the parameter MODE in the GRID keyword.

Read: DXYZ RW RE

If MODE = 1:

Read: XUNIT, XIN, ND, (NVG(I), XSEG(I), I=1, ND)

If MODE = 2:

RW = Inner boundary radius for cylindrical coordinates [m].

RE = Outer boundary radius for cylindrical coordinates [m].

Read: (DX(I), I = 1, NX)

Read: (DY(J), J = 1, NY)

Read: (DZ(K), K = 1, NZ)

DXYZ = Keyword for reading grid-block sizes.

XUNIT = Unit for distance ('m', 'dm', 'cm', 'mm').

XIN = Initial position [XUNIT].

ND = Number of subintervals.

NVG = Number of nodes in each subinterval.

XSEG = Length of subinterval [XUNIT].

DX = Block sizes in x-direction or radial direction [m].

DY = Block sizes in y-direction [m].

DZ = Block sizes in z-direction [m].

Comment(s):

For Cartesian geometry, RW and RE are not required.

**Example:**

**MODE = 1:**

DXYZ  
grid 'm' 0. 1 200 200.

**MODE = 2:**

DXYZ  
100\*1.  
50\*1.  
1.

### **3.13 END OF RUN KEYWORD [ENDS]**

---

**Keyword: ENDS**  
**Required**

---

This keyword terminates the run and must be the last keyword in the input file.

Read: ENDS

ENDS = Keyword terminating run.

Any data appearing after this keyword is not processed and remains intact in the input file.

Example:

```
: run completion keyword  
Ends
```

### 3.14 FLOW VELOCITY AND DISPERSIVITY [FLOW]

---

Keyword: **FLOW**  
Required

---

This keyword defines flow parameters for stand-alone mode of GEM. For icode = 3 and 4, the values for the velocities are taken from METRA.

Read: FLOW VX0 VY0 VZ0 ALPHAX ALPHAY ALPHAZ COURNR

**FLOW** = Keyword for defining flow field.

**VX0** = Flow velocity in the I-direction [m/y].

**VY0** = Flow velocity in the J-direction [m/y].

**VZ0** = Flow velocity in the K-direction [m/y].

**ALPHAX** = Dispersion length in the I-direction [m].

**ALPHAY** = Dispersion length in the J-direction [m].

**ALPHAZ** = Dispersion length in the K-direction [m].

**COURNR** = Courant number. Not used for the implicit method.

Comment(s):

The courant number is only used to control the time step size for the operator-splitting and explicit algorithms.

Example:

```
: vx0 vy0 vz0[m/yr] alphax alphay alphaz cournr
FLOW 0. 0. 10. 0. 0. 0. .15
```

### **3.15 GASEOUS SPECIES [GASEs]**

---

**Keyword: GASEs**  
Optional

---

This keyword reads in the names of gases. This keyword is not needed if there are no gaseous species.

Read: GASEs

Read: NAME

GASEs = Keyword for reading in the names of gaseous species.

NAME = Name of gaseous species.

Comment(s):

The names of gaseous species must be identical to the corresponding names read from the thermodynamic database file.

Example:

```
GASEs  
co2(g)  
:blank
```

### **3.16 ION-EXCHANGE REACTIONS [IONX]**

---

**Keyword: IONX**  
Optional

---

Keyword for reading input data for ion-exchange reactions.

Read: IONX NEX CEC

Read: (ALOGEX(I)=1,NEX-1)

IONX = Keyword for reading ion-exchange data.

NEX = Number of cations participating in ion-exchange reactions.

CEC = Cation exchange capacity [moles/L].

ALOGEX = Logarithm of selectivity coefficient. NEX-1 values are to be read in with up to 10 entries per line.

Comment(s):

Cations involved in ion-exchange reactions must appear first in the list of primary species in the BCON and COMPonents keywords.

Example:

```
:ion-exchange reactions
IONX 4      1.1
      5.0    1.0    0.30103
```

### 3.17 SYSTEM PARAMETERS [ISYSstem]

---

Keyword: **ISYSstem**  
Required

This keyword defines whether the system is isothermal or nonisothermal and reads in values for the porosity and saturation as well as other parameters. This keyword is only applicable for MODE = 2.

Read: ISYSstem ISAT ISOTHRM IREAD PORO PHIR SAT W LAMBDA TOLDELT TOLPOR

ISYSstem = Keyword for assigning system parameters.

ISAT = -1, Pure liquid system.  
= 0, Two-phase liquid-gas system.  
= 1, Pure gas system (not implemented).

ISOTHRM = 0, Isothermal system.  
= 1, Nonisothermal system.

IREAD = Index for reading the velocity field or saturation from external files, or computing internally a random permeability field.  
= 0, Do not read input data or compute permeability field.  
= 1, Read x-y-stochastic velocity fields from files xvelocity and yvelocity with the binary format:  
    open(3, file='xvelocity', form='unformatted', status='old')  
    open(4, file='yvelocity', form='unformatted', status='old')  
    read(3) ((vlx(ix+(iy-1)\*nxp1),ix=1,nxp1),iy=1,ny)  
    read(4) ((vly(ix+(iy-1)\*nx),ix=1,nx),iy=1,nyp1)  
= 2, Read from binary files with the same name as in 1 with the format:  
    open(3, file='xvelocity', status='old')  
    open(4, file='yvelocity', status='old')  
    read(3,\*) ((vlx(ix+(iy-1)\*nxp1),ix=1,nxp1),iy=1,ny)  
    read(4,\*) ((vly(ix+(iy-1)\*nx), ix=1,nx), iy=1,nyp1)  
= 3, Compute random permeability field.  
= 4, Read saturation profile from file sat.dat with the format:  
    read(3,\*,err=333) ltitle  
    do n = 1, nmax  
        read(3,\*) xx,sat0(n)   for 1D problems  
        read(3,\*) xx,yy,sat0(n)   for 2D problems  
    enddo  
= 5, Read density, temperature, and velocity fields computed from METRA (not implemented).  
PORO = Initial porosity if constant.

**PHIR** = Initial reacting volume.

**SAT** = Initial saturation of liquid phase.

**W** = Spatial averaging factor. Not implemented.

**LAMBDA** = Time-weighting factor in the implicit finite difference algorithm.

**TOLDELT** = Zone boundary tolerance. Not implemented.

**TOLPOR** = Minimum allowed porosity. If the porosity becomes lower than this value due to mineral precipitation, it is set equal to this value.

Example:

:	isat	isotherm	iread	por0	phir	sat	w	lambda	toldelt	tolpor
ISYSstem	0	1	0	0.1	1.	0.5	.5	1.	1.e-3	1.e-3

### **3.18 SETTING MASTER SPECIES FOR TIME STEP CONTROL [MASTER]**

---

Keyword: **MASTER**  
Optional

---

This keyword defines the master species for controlling the time step size.

Read: **MASTER MASPEC**

**MASTER** = Keyword for specifying master species.

**MASPEC** = Name of primary species for controlling time step size. Specifying ALL implies all primary species are used. (Default = ALL.)

Example:

```
:master species for controlling time stepping
MASTER h+
```

### **3.19 KINETIC (IRREVERSIBLE) MINERAL REACTIONS [MNIR]**

---

**Keyword:** **MNIR**  
**Optional**

---

This keyword reads in the names of irreversibly reacting minerals and associated data. This includes the type of reaction, kinetic rate constant, initial volume fraction, surface area and others.

Read: MNIR

Read: MINERAL ITYPKIN BETA FKin DELH RKPH RK TAU

Read: I1 I2 J1 J2 K1 K2 PHI AREA

**MNIR** = Keyword for reading in mineral names.

**MINERAL** = Name of mineral.

**ITYPKIN** = Type of reaction.

= 0, Transition state based rate law.

= 1, pH-dependent rate law.

**BETA** = Exponent in kinetic rate law. Not implemented.

**FKIN** = Degree of supersaturation required before mineral can precipitate.

**DELH** = Activation enthalpy of reaction.

**RKPH** = pH-dependent rate constant [moles/cm<sup>2</sup>/s].

**RK** = pH-independent rate constant [moles/cm<sup>2</sup>/s].

**TAU** = Tolerance for allowed maximum change in mineral volume fraction over a time step.

**I1 I2** = Indices bounding region in the I-direction.

**J1 J2** = Indices bounding region in the J-direction.

**K1 K2** = Indices bounding region in the K-direction.

**PHI** = Initial volume fraction in specified region.

**AREA** = Initial specific area in specified region [1/cm].

Comment(s):

Each mineral name must also appear in the MNRL keyword and must agree with the name appearing in the thermodynamic database.

Any number of region specifications are allowed for a given mineral, but the entire computational domain must be covered. A blank line or zero ends the region specification. If two regions overlap, the last data read in applies.

The entire block ends with a blank line.

Example:

```
MNIR
:irr mineral    itypkin   beta    fkin      delh      rkph     rk       tau
k-feldspar      0          1.0     1.0       0.        2.24e-13  3.02e-16  1.e-2
:i1              i2          j1      j2        k1        k2        vol      area
1                100         1       1         1          1         0.2      12.
0
gibbsite         0          1.0     1.0       0.        0.        1.00e-14  1.e-2
1                100         1       1         1          1         0.        1.
0
kaolinite        0          1.0     1.0       0.        0.        1.00e-14  1.e-2
1                100         1       1         1          1         0.        1.
0
muscovite        0          1.0     1.0       0.        0.        1.00e-14  1.e-2
1                100         1       1         1          1         0.        1.
0
quartz           0          1.0     1.0       1.        0.        3.16e-18  1.e-2
1                100         1       1         1          1         0.7      40.
0
:blank
```

### **3.20 MINERAL SPECIES [MNRL]**

---

**Keyword: MNRL**  
Optional

This is the keyword to read in the names of minerals.

Read: MNRL  
Read: NAME

MNRL = Keyword to read in the names of minerals.

NAME = Name of mineral. The mineral name must agree with the entry in the thermodynamic database.

Comment(s):

The list of minerals ends with a blank line.

Example:

```
MNRL
quartz
kaolinite
k-feldspar
muscovite
gibbsite
:blank
```

## 3.21 KEYWORD FOR VARIOUS PARAMETERS AND OPTIONS [OPTS]

---

Keyword: **OPTS**  
Required

---

This keyword defines various parameters and options.

Read: OPTS

Read: IDATA ISTART IMOD IEXACT

Read: ITMAX IHALMAX IVMAX NDAMP

Read: METHOD IOPS IFOR ISURF IACT LOGLIN ICON

OPTS = Keyword for defining various parameters and options.

IDATA = Parameter to select how the thermodynamic database is read.

= 0, Read in selected species only.

= 1, Read all species consistent with primary species.

ISTART = Parameter for selecting startup state.

= 0, Normal run.

= 1, Restart run. (Not implemented.)

IMOD = Frequency of screen printout.

IEXACT = Compute analytical solution. Not implemented.

ITMAX = Maximum number of Newton-Raphson iterations.

IHALMAX = Maximum number of time step cuts.

IVMAX = Maximum number of phase changes. Not implemented.

NDAMP = Damping factor used in calculating initial and boundary condition solution compositions.

METHOD = Parameter for selecting implicit, operator-splitting, or explicit time-stepping algorithm.

= 1, Implicit time-stepping algorithm.

= 2, Operator splitting.

= 3, Explicit time-stepping algorithm.

IOPS = Parameter for selecting operator-splitting algorithm.

= 0, Operator-splitting algorithm with explicit time-stepping.

= 1, Operator-splitting algorithm with implicit time-stepping.

- IFOR** = Parameter for selecting spatial finite differencing.
- = 1, Central finite difference.
  - = 2, Hybrid.
  - = 3, First order upwinding.
  - = 4, Explicit Leonard-TVD algorithm.
- ISURF** = Parameter for computing changes in mineral surface area.
- = 0, Constant surface area.
  - = 1, Variable surface area.
- IACT** = Parameter for selecting activity coefficient algorithm.
- = 0, Do not compute activity coefficients.
  - = 1, Compute activity coefficients.
- LOGLIN** = Parameter for selecting concentration variable.
- = 0, Use logarithm of concentrations.
  - = 1, Do not use logarithms.
- ICON** = Parameter for choosing between arithmetic averaging or harmonic averaging of interface properties. Used only if MODE = 1.
- = 0, Use arithmetic averaging at interface.
  - = 1, Use harmonic averaging at interface.

#### Comment(s):

For the operator splitting mode (IOPS = 0 and 1), the implicit and explicit algorithms apply to the nonreactive step in the operator-splitting algorithm. The second step involving chemical reactions is always done implicitly.

The higher-order Leonard-TVD algorithm (IFOR = 4) can only be run in explicit mode.

#### Example:

```

OPTS
:    idata      istart      imod      iexact
:    0          0           10         0
:
:    itmax      ihalmax     ivmax     ndamp
:    16          8           3          5
:
:    method     iops        ifor       isurf      iact      loglin      icon      id
:    1          1           3          1          0          0           1           1

```

### **3.22 KEYWORD FOR WRITING PLOT FILES [PLTFiles]**

---

Keyword: **PLTFiles**  
Optional

---

This keyword determines which plot files are to be produced during the run.

Read: **PLTFiles**

Read: **I PLOT A S T M SI SF V Z B IN E EX TI G ITEX**

**I PLOT** = Parameter to determine if plot files should be created.

- = 0, No plot file written. (Default = 0.)
- = 1, Plot file written.

**A** = Aqueous primary species.

**S** = Secondary species.

**T** = Total concentrations.

**M** = Mineral reaction rates.

**SI** = Saturation indices.

**SF** = Surface area.

**V** = Mineral volume fractions.

**Z** = Mineral zone boundary positions.

**B** = Breakthrough curve.

**IN** = Time-dependent inlet fluid composition.

**E** = Electrical potential.

**EX** = Ion exchange solid concentration.

**TI** = Not used.

**G** = Gaseous species concentrations.

**ITEX** = Generate LaTeX (Goosens et al., 1994) table of inlet fluid composition for use in word processing.

**Example:**

```
PLTFiles
:iplot:    iplot a   s   t   m   si   sf   v   z   b   in   e   ex   ti   g   itex
           1     1   1   1   1     0     0   1   0   0     0   0     0   0   1     1
```

### 3.23 KEYWORD FOR READING INITIAL TEMPERATURE AND PRESSURE [PTINit]

---

Keyword: **PTINit**  
Optional

This keyword defines initial temperature and pressure for stand-alone mode. In coupled mode (icode = 3 or 4), the temperature and pressure are provided by METRA.

Read: PTINit P(BARS) TEMP FLAG A B C D X0 XLEN

PTINit = Keyword for reading in initial temperature and pressure.

P = Initial pressure [bars]. (Default = 1 bar.)

TEMP = Initial temperature [ $^{\circ}$ C]. (Default = 25  $^{\circ}$ C.)

FLAG = Flag for specifying temperature profile.

= 0, Constant temperature.

= 1,  $T(X) = D X^3 + A X^2 + B X + C$  (METERS)

= 2,  $T(X) = A + (B-A) \exp[-((X-X0)/C)^2] + (D - A) * X / XLEN$

= 3,  $T(X,T) = A + 1/2(B-A) (\text{ERF}[(X+C-X0)/(2\sqrt{DT})] - \text{ERF}[(X-C-X0)/(2\sqrt{DT})])$

A = Parameter used in temperature profile.

B = Parameter used in temperature profile.

C = Parameter used in temperature profile.

D = Parameter used in temperature profile.

X0 = Parameter used in temperature profile.

XLEN = Parameter used in temperature profile.

Example:

:	p (bars)	temp	flag	a	b	c	d	x0	xlen
PINIt	1.0	25.	0	25	300	250	125	1000.	2.d3

### 3.24 METHOD OF SOLUTION [SOLVe]

---

Keyword: SOLVe  
Required

This keyword specifies the method of solution as the WATSOLV conjugate gradient solver, or a tridiagonal solver for 1D problems.

Read: SOLVe ISOLV LEVEL NORTH NITMAX IDETAIL RMAXTOL RTWOTOL SMAXTOL

SOLVe = Keyword for specifying the matrix solver.

ISOLVE = 1, Tridiagonal solver.

= 2, Not used.

= 3, WATSOLV (ILU factorization) with GMRES accelerator.

= 4, WATSOLV (ILU factorization) with CGSTAB accelerator.

LEVEL = Degree of fill in incomplete LU factorization for WATSOLV. (Default = 1.)

NORTH = Maximum number of vectors used for orthogonalization in WATSOLV. Used only if ISOLVE = 3 (GMRES). (Default = 4.)

NITMAX = Maximum number of inner iterations for WATSOLV. (Default = 100.)

IDETAIL = Debugging option. (Default = 0.)

RMAXTOL = Absolute value of residual. (Default = 1.e-12.)

RTWOTOL = WATSOLV tolerance parameter.

SMAXTOL = Maximum of  $|dx, dx/x|$ , where x = solution vector. (Default = 1.e-12.)

Comment(s):

For further details on use of the WATSOLV conjugate gradient solver, see the WATSOLV User's Manual (VanderKwaak et al., 1995).

Example:

:	isolv	level	north	nitmax	ideital	rmaxtol	rtwotol	smaxtol
SOLV	3	1	1	100	0	1.e-20	1.e-20	1.e-12

### **3.25 RELATIVE TOLERANCES [STOL]**

---

**Keyword:** STOL  
**Optional**

---

This keyword reads in relative tolerances for primary species.

Read: STOL (ATOL(I), I=1,NCOMP)

STOL = Keyword for reading relative tolerances.

ATOL = Relative primary species tolerances (maximum 10 per line).

Example:

STOL 1. 1. 1. 1. 1. 1. 1.

### **3.26 TARGET TIME [TIME]**

---

**Keyword: TIME**  
Required

---

This keyword reads the target times at which plot files and output of the run are produced.

Read: TIME NPRIN (TPLOT(I),I=1,NPRIN)

TIME = Keyword for specifying the target time.

NPRIN = Number of target times specified.

TPLOT = Target times [y]. Up to 9 entries are allowed on the first line and a maximum of 10 on succeeding lines.

Example:

TIME 4 2.5e4 5.e4 1.e5 2.e5

### 3.27 CONVERGENCE TOLERANCES [TOLR]

---

Keyword: **TOLR**  
Required

This keyword reads various parameters to control tolerances determining convergence of the solution.

Read: TOLR TOL TTOL TOLNEG TOLPOS TOLEXP DTHALF QKMAX TOLSTDST

**TOLR** = Keyword defining various tolerances.

**TOL** = Convergence tolerance. (Default = 1.e-10.)

**TTOL** = Time step accelerator. (Default = 1.e-3.)

**TOLNEG** = Maximum negative mineral volume fraction allowed. (Default = 1.e-3.)

**TOLPOS** = Maximum positive change in volume fraction allowed. Not implemented.

**TOLEXP** = Maximum concentration change in log formulation. (Default = 5.0.)

**DTHALF** = Time step reduction factor. (Default = 0.5.)

**QKMAX** = Maximum activity product change in log formulation. (Default = 500.)

**TOLSTDST** = Steady-state test for convergence. (Default = 1.e-6.)

Comment(s):

For operator splitting and explicit solution algorithms, TTOL should be set to a value greater than one. For the implicit solution algorithm, TTOL should generally be less than one. The optimal value must be determined by experimentation to obtain the smallest run time.

Example:

:	tol	ttol	tolneg	tolpos	tolexp	dthalf	qkmax	tolstdst
TOLR	1.d-10	2.e0	1.e0	1.e-2	5.d0	.5	590.	1.e-6

## 4 SAMPLE INPUT DATA: ONE-DIMENSIONAL REPOSITORY PROBLEM

The repository problem presented in Part I (Seth and Lichtner, 1996) is run here, as an example, in coupled mode using the implicit finite difference algorithm of GEM (method = 1). In order to avoid complete dryout in the vicinity of the repository, the heat loading is reduced to 80 MTU/acre. No other modifications need be made to the METRA input file to run in coupled mode.

The GEM input file 'masin' takes into account seven primary species:  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{H}^+$ ,  $\text{HCO}_3^-$ ,  $\text{SiO}_2$ , and  $\text{Cl}^-$ ; three minerals: quartz, calcite and halite; one gaseous species:  $\text{CO}_{2(g)}$ ; and a number of aqueous complexes. The initial fluid composition is derived from J-13 groundwater, and the initial host rock is assumed to consist of pure quartz with 90 percent by volume and 10 percent porosity. The simulation is run to 2,000 years. The 'masin' input file for this problem is presented below. Zero gradient boundary conditions are imposed at the top and bottom of the computational domain.

Test Data for Multiflo Simulator (Yucca Mt., 1D, 80 MTU/acre)  
July 22, 1996

```

:
:      geometry  nx  ny  nz    mode  iprint
GRID  XYZ      1    1   238    2     -1
:
OPTS
:      idata      istart    imod   iexact
:      0          0         10      0
:
:      itmax      ihalmax  ivmax  ndamp
:      16         8         3       5
:
:      method     iops     ifor    isurf   iact    loglin icon
:      1          1         3       1       0       0       1
:
:      isync      ipor     iperm   perm.  fac.
COUPle  0          0         0       3.
:
PLTFiles
:      iplot     a   s   t   m   si   sf   v   z   b   in   e   ex   ti   g   itex
:      1       1   1   1   1   0    0   1   0   0   0   0   0   0   1   1
:
:      tol       ttol    tolneg    tolpos   tolexp dthalf   qkmax   tolstdste
:      TOLR    1.d-10  2.e-3   1.e01.e-2  5.d0   .5      590.    1.e-6
:
:      mcyc     cc      c   flx   r   sp   qk   pk   rk   a1   a2   a3
:      DEBUG   0       1   1   0   1   1   1   1   1
:
:      isat      isotherm  iread   por0   phir   sat    w      lambda   toldelt   tolpor
ISYSstem 0        1       0     .10162  1.     0.5    .5      1.      1.e-3   1.e-3
:
```

```

:      vx0    vy0    vz0[m/yr]    alphax    alphay    alphaz    cournr
FLOW 0.      0.      1.          0.          0.          0.          1.
:
:      d0[cm2/s]    delhaq[kJ/mol]    dgas[cm2/s]    dgexp    tortaq    tortg
DIFF 1.d-5      12.6      2.13d-1      1.8        1.d0      1.d0
:
:flag   1: T(x) = d x^3 + a x^2 + b x + c (meters)
:      2: T(x) = a + (b-a) exp[-((x-x0)/c)^2] + (d - a) * x / xlen
:      3: T(x,t) = a+1/2(b-a)(erf[(x+c-x0)/2sqr(dt)]-erf[(x-c-x0)/2sqr(dt)])
:      p (bars) temp   flag   a     b     c     d     x0     xlen
PTINInit 1.0      25.      0      25     300    250    125   1000.    2.d3
:
:master species for controlling time stepping
MASTER h+
:
:grid m 0. 1 200 200.
:
DXYZ
1.
1.
238*1.
:
:      isolv  level  north  nitmax  idetail  rmaxtol  rtwotol  smaxtol
SOLV 3      1      1      100      0      1.e-20    1.e-20    1.e-12
:
:initial and boundary conditions: 1-conc., 2-flux, 3-zero gradient
:      inlet  outlet  nzoneaq
COMP 1      3      3
:
:species      itype  guess  ctot      mineral  diffusion
ca+2         1      2.9e-4 2.9e-4  blank    0.8e-5
na+          1      2.e-3  2.e-3   blank    0.8e-5
k+           1      1.4e-4 1.e-4   blank    0.8e-5
h+           8      1.e-7  6.9     blank    9.6e-5
hco3-        7      2.7e-3 2.7e-3  blank    2.0e-5
sio2(aq)     1      1.1e-3 1.1e-3  blank    1.4e-5
cl-          1      1.8e-4 1.8e-4  blank    1.4e-5
:blank
:
BCON
3      1
:species      itype  guess  ctot      mineral
ca+2         1      2.9e-4 2.9e-4  blank
na+          1      2.e-3  2.e-3   blank
k+           1      1.4e-4 1.e-4   blank
h+           8      1.e-7  6.9     blank
hco3-        7      2.7e-3 2.7e-3  blank
sio2(aq)     1      1.1e-3 1.1e-3  blank

```

```

cl-      1    1.8e-4 1.8e-4 blank
:
4      3
:species  itype  guess  ctot   mineral
ca+2     1    2.9e-4 2.9e-4 blank
na+      1    2.e-3  2.e-3  blank
k+       1    1.4e-4 1.e-4 blank
h+       8    1.e-7  6.9   blank
hco3-    7    2.7e-3 2.7e-3 blank
sio2(aq) 1    1.1e-3 1.1e-3 blank
cl-      1    1.8e-4 1.8e-4 blank
:
0      0
:
CMIR  0  0
:blank
:
STOL 1. 1. 1. 1. 1. 1.
:
AQCX
oh-
co2(aq)
co3-2
caco3(aq)
cahco3+
caoh+
cacl+
cacl2(aq)
nahco3(aq)
nacl(aq)
naoh(aq)
kcl(aq)
h3sio4-
h2sio4-2
:blank
:
MNRL
quartz
calcite
halite
:blank
:
GASEs
co2(g)
:blank
:
MNIR
:      irr      mineral      itypkin   beta    fkin    delh    rkph    rk     tau

```

```

:      i1      i2          j1      j2      k1      k2      vol      area
quartz           0       1.0     1.0     75.      0.    1.e-17  1.e-3
      1       1          1       1       1      238     0.9      1.

0
calcite    0   1.0   1.0  35.  0.  1.e-10  1.e-3
1 1 1 1 1 238  0.  1.

0
halite     0   1.0   1.0  30.  0.  1.e-12  1.e-3
1 1 1 1 1 238  0.  1.

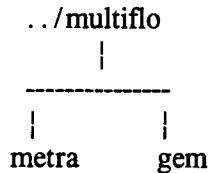
0
      :blank
:
:
:ion-exchange reactions
IONX  0   1.0
:
:BRKP  5
:93  110  130  150  185
:
DTSTep[y]    1 3.e-8
1.e-8        1.e2
:
TIME[y]  9 1. 10. 25. 50. 100. 250. 500. 1000. 2000.
:
ENDS

```

## 5 INSTALLATION AND EXECUTION

### 5.1 INSTALLATION

The source code for MULTIFLO is installed in a hierarchical directory structure. The topmost level directory (e.g., `../multiflo`) contains the main program for MULTIFLO and the source code for sequentially coupling METRA and GEM. In addition, there are two subdirectories containing the source code for METRA and GEM.



The default databases for GEM, `ms25.r16` and `mstemp.r16`, are stored in the directory ‘database’ which is located in the user’s home directory under the `~/bin` subdirectory (`~/bin` must be in the user’s search path in the `.cshrc` file): `~/bin/database`.

The include files, `paramtrs.h`, `impl.h`, `metragem.h`, and `watsolv.h`, must be identical to run the code in coupled mode.

To compile the code, type:

```
make multiflo
```

in the top level directory to create the MULTIFLO executable, type:

```
make metra
```

in the `metra` subdirectory to create the stand-alone METRA executable, and type:

```
make gem
```

in the `gem` subdirectory to create the stand-alone GEM executable.

To make the executables accessible in any subdirectory in the user’s home directory, make soft links to the subdirectory `~/bin` as follows:

```
cd ~/bin
ln -s ../multiflo/multiflo
ln -s ../multiflo/metra/metra
ln -s ../multiflo/gem/gem
```

These commands assume the directory ‘`multiflo`’ is located in the user’s home directory. The file `~/bin` must appear in the user’s search path in the `.cshrc` file.

## **5.2 EXECUTION OF MULTIFLO AND GEM**

To run MULTIFLO, type:

```
multiflo
```

A prompt will appear:

```
--> enter icode: (1-metra, 2-gem, 3-coupled, 4-coupled: steady-state)
```

After the prompt, the user enters a single digit in the range 1–4 to select the mode of operation desired.

Similarly, it is possible to run the stand-alone versions of GEM by typing:

```
gem [options]
```

The options available are:

<b>[ -i ]</b>	< masin >
<b>-o</b>	< masout >
<b>-a</b>	< maspltaq >
<b>-s</b>	< maspltsec >
<b>-t</b>	< maspltpsi >
<b>-d</b>	< data1 >
<b>-m</b>	< maspltmin >
<b>-si</b>	< maspltsat >
<b>-sf</b>	< maspltsrf >
<b>-v</b>	< maspltvol >
<b>-z</b>	< maspltznb >
<b>-b</b>	< maspltbrk >
<b>-l</b>	< maspltini >
<b>-ex</b>	< maspltsor >
<b>-g</b>	< maspltgas >
<b>-r</b>	< restart >

To run METRA, type:

```
metra filename
```

where *filename.dat* refers to the input file. The default name is *multi.dat*. See the METRA User's Manual for more information on running METRA.

## 6 INPUT/OUTPUT

The default input file name for GEM is set to masin. The output file is called masout. When running in coupled mode, the output file multiflo.out is produced. A number of plot files are written depending on the specifications in the PLTFiles keyword.

Plot file names are listed in Tables 6-1 and 6-2.

**Table 6-1. Spatial profile data at times specified on the TIME keyword**

File Name	Description
maspltaq[n].xyp	aqueous concentrations
maspltele[n].xyp	electrochemical potential
maspltgas[n].xyp	gaseous species concentrations
maspltrmin[n].xyp	mineral reaction rates
maspltpsi[n].xyp	total aqueous concentrations
maspltsat[n].xyp	mineral saturations
maspltsec[n].xyp	aqueous secondary species concentrations
maspltsor[n].xyp	sorbed species concentrations
maspltsrf[n].xyp	mineral surface area
maspltvol[n].xyp	mineral volume fractions
table.tex	LaTeX formatted table containing the inlet solution composition

The 'n' in square brackets ([n]) labels the plot file with the *n*th target time.

**Table 6-2. Time-history data at spatial nodes specified on the BRKP keyword**

File Name	Description
maspltbrk.xyp	break-through concentrations
maspltini.xyp	inlet concentrations
maspltznb.xyp	positions of reaction zone boundaries

## **7 MODIFYING ARRAY SIZES**

Occasionally, the user may find it necessary to modify the array sizes in order to increase the number of grid blocks, number of primary species, aqueous complexes, minerals, gases, or other properties of the system. This can be done by modifying the entries in the file 'paramtrs.h' as specified.

In addition, it may be necessary to modify the main storage array 'aa' in the main program. The value of 'maxaa' must be changed to the same value as the dimension for the array 'aa'. This is done in 'maingem.f' for stand-alone mode and 'mainmlti.f' in the top level directory of multiflo for running the code in coupled mode.

## 8 REFERENCES

- Goosens, M., F. Mittelbach, and A. Samarin. 1994. *The LaTeX Companion*. Reading, MA: Addison-Wesley.
- Seth, M., and P.C. Lichtner. 1996. *User's Manual for MULTIFLO: Part I—Metra 1.0  $\beta$ , Two-Phase Nonisothermal Flow Simulator*. CNWRA 96-005. San Antonio, TX: Center for Nuclear Waste Regulatory Analyses.
- VanderKwaak, J.E., P.A. Forsyth, and E.A. Sudicky. 1995. *WATSOLV, Sparse Matrix Iterative Solver Package, User's Guide*. Waterloo, Ontario, Canada: Waterloo Centre for Groundwater Research, University of Waterloo.
- Wolery, T.J. 1983. *EQ3NR—A Computer Program for Geochemical Aqueous Speciation Solubility Calculations: User's Guide and Documentation*. UCRL-53414. Livermore, CA: Lawrence Livermore National Laboratory.

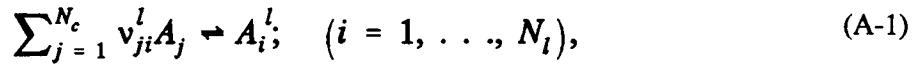
## **APPENDIX**

## APPENDIX A

This appendix provides a brief mathematical description of the underlying equations solved by GEM for MODE = 2. For a description of the equations solved for MODE = 1, see Lichtner (1994).

### A.1 CHEMICAL REACTIONS

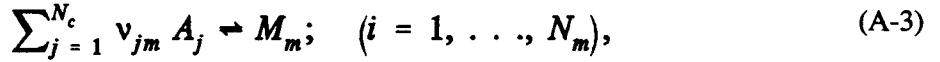
The approach used by GEM is to assume that the various chemical reactions taking place in a geochemical system can be written in terms of a basic set of  $N_c$ -independent species, or components, referred to as primary species and denoted by the set  $\{A_j; j = 1, \dots, N_c\}$  (Lichtner, 1985). Generally,  $N_c = N - N_R$  where  $N$  denotes the total number of chemical constituents or species, and  $N_R$  refers to the number of linearly independent reactions being considered to describe the system. The resulting reactions for aqueous, gaseous, and mineral species can be expressed in the following canonical form (Lichtner, 1985) for aqueous species  $A_i^l$ :



gaseous species  $A_i^g$ :

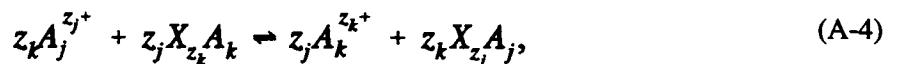


and minerals  $M_m$ :



assumed to occur in numbers  $N_l$ ,  $N_g$ , and  $N_m$ , respectively. The matrices  $v_{ji}^l$ ,  $v_{ji}^g$ , and  $v_{jm}$  denote the stoichiometric reaction coefficients giving the number of moles of the  $j$ th primary species in one mole of the  $i$ th aqueous or gaseous secondary species and  $m$ th mineral, respectively. Each reaction is associated with a single species on the right-hand side which appears with unit stoichiometric coefficient, referred to as a secondary species. A species is distinguished by its chemical formula and the phase to which it belongs. Reactions (A-1) and (A-2) are considered to be reversible, and, hence, the concentrations of the product species appearing on the right hand side are related algebraically to the concentrations of the primary species through mass action equations [see Eqs. (A-15) and (A-17)] representing conditions of local equilibrium. The rates of these reactions are thus determined by the rate of transport within the aqueous and gas phases. Note that all gaseous species are secondary species. Mineral reactions are considered to be irreversible, their rates described by a kinetic rate law [see Eq. (A-24)]. Local equilibrium is achieved by taking the rate constant sufficiently large.

Ion-exchange reactions are assumed to be expressible in the form



for exchange of the  $j$ th and  $k$ th cations, where  $X$  denotes a surface site, and  $X_{z_j} A_j$  an adsorbed species.

The species water in the aqueous phase ( $\text{H}_2\text{O}_{(1)}$ ) is always chosen as a primary species. The remaining primary species may be any independent set of species which conveniently characterize the chemical properties of the system under investigation. In what follows, they are chosen to be a subset of the aqueous species. It is perhaps important to note that considerations with regard to the dominance of certain species over others is not essential in the choice of primary species, and any set of species, only so long as they are independent, may be used. Because of the large spatial (and temporal) variation in concentration that is possible, by many orders of magnitude for some species, it is generally necessary to solve for the logarithm of the concentration, rather than the concentration itself. This also ensures that the concentration is a positive quantity.

### A.1.1 Multiphase–Multicomponent Mass Transport Equations

The transport equations solved by GEM for primary species are in the aqueous and gaseous phases given by

$$\frac{\partial}{\partial t} (\phi \Psi_j + \bar{C}_j) + \nabla \cdot \Omega_j = - \sum_{m=1}^{N_m} v_{jm} I_m, \quad (\text{A-5})$$

where  $\bar{C}_j$  denotes the adsorbed concentration of the  $j$ th primary species, and the generalized concentration  $\Psi_j$  and flux  $\Omega_j$  are defined by

$$\Psi_j = s_l \Psi_j^l + s_g \Psi_j^g, \quad (\text{A-6})$$

and

$$\Omega_j = \Omega_j^l + \Omega_j^g, \quad (\text{A-7})$$

with

$$\Psi_j^\pi = \delta_{\pi l} C_j^\pi + \sum_{i=1}^{N_\pi} v_{ji}^\pi C_i^\pi, \quad (\text{A-8})$$

and

$$\Omega_j^\pi = J_j^\pi + \sum_{i=1}^{N_\pi} v_{ji}^\pi J_i^\pi, \quad (\text{A-9})$$

with  $\pi = l, g$ . The delta function appears in Eq. (A-8) because all gas species are taken as secondary species. The mineral mass transfer equation is given by

$$\frac{\partial \phi_m}{\partial t} = \bar{V}_m I_m. \quad (\text{A-10})$$

The rate of Reaction (A-3) is denoted by  $I_m$  corresponding to mineral precipitation/dissolution. Here  $C_i^\pi$  and  $J_i^\pi$  denote the concentration and flux of the  $i$ th species in the  $\pi$ th phase,  $\phi_m$  and  $\bar{V}_m$  denote the volume fraction and molar volume, respectively, of the  $m$ th mineral. The liquid flux  $J_j^l$  appearing in these equations is defined by

$$J_i^l = -\phi \tau s_l D_l \nabla C_i^l + q_l C_i^l, \quad (\text{A-11})$$

and the gas flux by the equation

$$J_i^g = -\phi \tau s_g D_g \nabla C_i^g + q_g C_i^g, \quad (\text{A-12})$$

where  $D_\pi$  denotes the diffusion coefficient in phase  $\pi$ , and  $q_\pi$  the velocity of phase  $\pi$  defined by Darcy's law as:

$$q_\pi = -\frac{k k_{r\pi}}{\mu_\pi} \nabla(p_\pi - \rho_\pi g z), \quad (\text{A-13})$$

where  $k$  refers to the saturated permeability of the porous medium,  $k_{r\pi}$  represents the relative permeability, and  $\mu_\pi$  the viscosity of phase  $\pi$ ,  $g$  denotes the acceleration of gravity, and  $z$  points in the direction of gravity. The diffusion coefficients for aqueous species are taken to be the same for all species. For species-independent diffusivities, the flux  $\Omega_j^\pi$  simplifies to the expression

$$\Omega_j^\pi = (-\tau \phi s_\pi D_\pi \nabla + q_\pi) \Psi_j^\pi, \quad (\text{A-14})$$

involving directly the generalized concentration  $\Psi_j^\pi$ .

The quantities  $\Psi_j^\pi$  and  $\Omega_j^\pi$  may be interpreted, generally, as the total concentration and flux of the  $j$ th primary species in the liquid and gas phases provided the coefficients  $v_{ji}^\pi$  are positive (Lichtner, 1985). For reactions involving the hydrogen ion or redox reactions,  $\Psi_j^\pi$  may also become negative.

These equations are completely general and include both the solvent and solute species, and gaseous species. Solving the primary species mass conservation equations provides not only the concentrations of both primary and secondary species, but also the mineral reaction rates. Combined with mineral mass transfer equations, an energy balance equation, constitutive relations for rock properties, kinetic rate laws and mass action relations, and finally initial and boundary conditions, they completely describe the system.

## A.1.2 Constitutive Relations

### A.1.2.1 Mass Action Equations

Constitutive relations are required for the concentrations of secondary aqueous and gaseous species. The concentration of aqueous secondary species are given by

$$C_i^l = \rho_l^{\alpha-1} (\gamma_i^l)^{-1} K_i^l \prod_{j=1}^{N_c} (\gamma_j^l C_j^l)^{v_{ji}^l}, \quad (A-15)$$

where  $\gamma_i^l$  denotes the activity coefficient,  $K_i^l$  the equilibrium constant, and the quantity  $\alpha$ , providing a density correction from molality to molarity units, is defined by

$$\alpha = \rho_l^{\sum_{jl} v_{jl}^l}. \quad (A-16)$$

For gases, it follows, similarly, that the concentrations of gaseous species are given by

$$C_i^g = \rho_l^{\alpha} (\gamma_i^g)^{-1} K_i^g \prod_{j=1}^{N_c} (\gamma_j^l C_j^l)^{v_{ji}^g}. \quad (A-17)$$

The exchange isotherm  $\bar{C}_k$ , with units of moles per bulk volume, is expressed in terms of the concentrations of the primary species using the mass action equations for the exchange reactions which has the form, neglecting activity coefficient corrections,

$$K_{jk} = \left[ \frac{C_k}{\bar{C}_k} \right]^{z_j} \left[ \frac{\bar{C}_j}{C_j} \right]^{z_k}, \quad (A-18)$$

where the quantities  $K_{jk}$  represent selectivity coefficients. Combining this relation with the site conservation equation

$$\omega = (1 - \phi) \rho_{\text{solid}} Q = \sum_j z_j \bar{C}_j, \quad (A-19)$$

yields a single nonlinear equation for the  $j$ th sorption isotherm bar  $\bar{C}_j$ :

$$\omega = z_j \bar{C}_j + \sum_{k \neq j} z_k C_k (K_{jk})^{1/z_k} \left[ \frac{\bar{C}_j}{C_j} \right]^{z_j/z_k}, \quad (A-20)$$

where  $Q$  denotes the cation exchange capacity. This equation implicitly defines the sorption isotherm as a function of the primary species concentrations.

The equilibrium constants  $K_i^x$ , in general, are functions of temperature and pressure. An extensive database is included with the program covering a temperature range of 0–300 °C along the saturation curve of water based on the EQ3/6 database (Wolery, 1983). Log  $K$  values are stored at temperatures of 0, 25, 60, 100, 150, 200, 250, and 300 °C and interpolated according to the expression

$$\log K(T) = \frac{a_{-2}}{T^2} + \frac{a_{-1}}{T} + a_0 \ln T + a_1 + a_2 T, \quad (\text{A-21})$$

where  $T$  denotes the absolute temperature in degrees Kelvin. Pressure lies along the steam saturation curve for temperatures above 100 °C, otherwise it is set at 1 bar. Other databases may be generated for any desired temperature range and pressure using the computer code SUPCRT (Johnson et al., 1992). Because of the small variation in pressure, this is considered an adequate approximation. The density of pure water is determined using the equation of state provided by Haar et al. (1980).

### A.1.2.2 Kinetic Rate Law

Mineral reactions are assumed to be irreversible, with their rates of reaction described through a kinetic rate law. For simplicity and because of lack of knowledge of detailed reaction mechanisms, mineral reactions are represented by an overall reaction between the solid and aqueous solution. The form of the reaction rate is based on transition state theory. Precipitation or dissolution may occur depending on the sign of the affinity  $A_m$  of the reaction, defined by

$$A_m = -RT \ln K_m Q_m, \quad (\text{A-22})$$

where  $K_m$  denotes the corresponding equilibrium constant for the mineral reaction as written in Eq. (A-3), and  $Q_m$  the ion activity product, defined by

$$Q_m = \prod_{j=1}^{N_c} (\gamma_j C_j)^{\nu_j}, \quad (\text{A-23})$$

with  $R$  the gas constant, and  $T$  the temperature. At equilibrium the affinity and the rate vanish. The expression for the reaction rate must take into account the moving boundary nature of the transport-reaction problem. This can be accomplished with the form

$$I_m = \begin{cases} -k_m s_m \left[ \prod_i a_i^{n_i} \right] (1 - e^{-A_m/RT}), & \text{if } \phi_m > 0, \text{ or if } \phi_m = 0 \text{ and } A_m < 0, \\ 0, & \text{otherwise,} \end{cases} \quad (\text{A-24})$$

where  $k_m$  denotes the kinetic rate constant,  $\phi_m$  denotes the mineral volume fraction,  $s_m$  denotes the mineral surface area participating in the reaction,  $a_i$  represents the activity of the  $i$ th species, and  $n_i$  is a constant. The rate has units of moles per unit time per unit volume of bulk porous medium and is taken as positive for precipitation and negative for dissolution. Thus, it represents an average rate taken over a representative elemental volume (REV). This form of the rate also includes overall oxidation/reduction reactions in which electron transfer is not represented explicitly. The rate law given by Eq. (A-24) should really be referred to as a pseudo-kinetic rate law. Because it refers to the overall mineral precipitation/dissolution reaction, it generally does not describe the actual kinetic mechanism by which the mineral reacts. Nevertheless, it provides a useful form to describe departures from equilibrium. Close to equilibrium the rate becomes proportional to the chemical affinity.

The temperature dependence of the kinetic rate constants is calculated through the expression:

$$k_m(T) = \frac{T k_m^0}{T_0} \exp\left[-\left(\frac{1}{T} - \frac{1}{T_0}\right)\frac{\Delta H_m^\ddagger}{R}\right], \quad (\text{A-25})$$

where  $k_m^0$  denotes the rate constant at  $T_0$  and  $\Delta H_m^\ddagger$  denotes the enthalpy of activation.

### A.1.3 Porosity—Permeability Coupling

Porosity and mineral volume fractions are related by the equation

$$\phi = 1 - \sum_{m=1}^{N_m} \phi_m. \quad (\text{A-26})$$

However, this expression is not completely general and may be deceptively simple because no distinction is made between connected and total porosity, which includes deadend porosity. By relating the permeability and tortuosity to porosity through various phenomenological relations, it is possible to couple changes in porosity to the flow field and transport of solutes. One such relation is the power law expression of the form

$$k = k_0 \left( \frac{\phi}{\phi_0} \right)^n, \quad (\text{A-27})$$

where  $k_0$  and  $\phi_0$  denote the initial permeability and porosity where  $n$  is a real number.

## A.2 NUMERICAL SOLUTION

Because of stability considerations, different processes generally require different methods of solution. Effective diffusion coefficients may be defined for the solvent, gaseous species, and aqueous species with the relation:

$$D_w \gg D_g \gg D_l. \quad (\text{A-28})$$

For both the solvent and gaseous species the effective diffusion coefficients are too large to use an explicit method of solution because a prohibitively small time step would be required to ensure stability. Stability requires that

$$\Delta t \leq \frac{\Delta x^2}{2D}, \quad (\text{A-29})$$

for grid spacing  $\Delta x$  and diffusion coefficient  $D$ . Therefore, for these species, an implicit algorithm is used. For aqueous species, several different options are available. The implicit approach is generally superior for one-dimensional (1D) problems. However, for two-dimensional (2D) and three-dimensional (3D) problems, explicit or operator-splitting algorithms may be necessary, especially for large numbers of species and grid points.

An explicit method is used to solve the mineral mass transfer equations (Lichtner, 1988). Thus,

$$\phi_m(r, t + \Delta t) = \phi_m(r, t) + \Delta t \bar{V}_m I_m(r, t), \quad (\text{A-30})$$

where the mineral reaction rate  $I_m(r, t)$  is taken from the previous time step. The time step size  $\Delta t$  depends on how close the solution to the aqueous and gaseous species transport equations is to a stationary state. For the transient case, the same time step  $\Delta t$  is used as in the transient transport equations. When the system has reached a stationary state, however, a much larger time step can be taken without fear of violating the stability conditions. In this case, the time step size is only restricted by the maximum absolute change allowed in the mineral volume fraction. Note that at a reaction front where the mineral volume fraction vanishes, according to Eq. (A-30) in order for the front to move, the volume fraction must become negative at the front. This is, of course, nonphysical and the volume fraction must be set back to zero to eliminate the negative values. The allowable time step size is also controlled by limiting the negative most value of the mineral volume fraction to an acceptable value.

In the transient regime, the change in mineral abundances and, hence, porosity and permeability, is much slower than the change in aqueous and gaseous compositions as well as temperature, pressure, and saturation. The time evolution of the system can be divided into a sequence of transient and stationary state regimes. The term "stationary" is preferred to the term "steady" to distinguish this situation from that of constant velocity. When the fluid compositions become stationary in time, a much larger time step can be taken compared to the transient regime. As minerals dissolve and precipitate and reaction fronts move to new locations, the system reverts again to a transient regime until a new stationary state is established. In this way the time evolution of the system is represented as a sequence of stationary states separated by transient intervals.

### A.2.1 Sequentially Coupled Two-Phase Flow and Transport

A sequentially coupled methodology is used to solve the multidimensional, multiphase, multicomponent fluid and solute flow and transport equations in a partially saturated porous medium. In this approach, heat, air and water vapor, and solvent mass conservation equations are solved separately from solute mass conservation equations. Thus at each new time step, first the heat and mass flow equations are solved simultaneously to obtain the temperature, pressure, saturation and flow field as functions of distance. Second, chemically reacting solutes are transported using the results obtained from solving the heat and solvent mass conservation equations. As a third step, mineral concentrations are calculated enabling changes in porosity, tortuosity and permeability to be computed which can then alter the flow field. This three-step approach can be justified based on the different time scales of the processes involved. Thus alteration of rock properties through chemical reactions proceeds much more slowly compared to changes in the aqueous solution composition and changes in flow and temperature fields caused by decay of the radioactive waste form. Another way to put it, the system adjusts quasi-statically to chemical alteration of the host rock. This is expected to be a good approximation for sufficiently dilute solutions in which density corrections are not important. In the future it may prove necessary to extend the model to fully couple the solvent and solute flow and transport equations.

The time-stepping algorithm used involves different strategies depending on the dimensionality of the problem. For 1D systems a fully implicit time-stepping algorithm with dynamically computed adaptive time steps is used to solve both the heat and solvent transport equations, and the geochemical

reactive transport equations. For 2D problems, an operator-splitting algorithm is employed in which flow and transport time steps are decoupled from the chemical algorithm.

Field variables are linearly interpolated over the METRA time step. Thus

$$F(t') = \frac{t' - t}{\Delta t} F(t + \Delta t) + \left(1 - \frac{t' - t}{\Delta t}\right) F(t), \quad (\text{A-31})$$

where  $F$  represents the flow velocity, saturation, pressure, and temperature, and  $t$  and  $t + \Delta t$  denote METRA time steps, with  $t < t' \leq t + \Delta T$ .

### A.2.2 Implicit Finite Difference

The transport equations are solved using an implicit finite difference scheme. Several different solver options are available for inverting the sparse Jacobian matrix. For 1D problems, a block tridiagonal solver is used. For 2D and 3D problems, an iterative solver WATSOLV is used (VanderKwaak et al., 1995).

### A.2.3 Operator Splitting

An alternative approach, useful for 2D and 3D problems with large numbers of species and grid blocks for which an implicit scheme would require inversion of too large matrices, is the operator-splitting method in which the solute transport equations are solved in a two-step procedure. First, a nonreactive step is taken followed by a reactive step.

- (1) The nonreactive transport equations for gaseous and aqueous species are solved independently of each other over a single time step to provide the total concentrations  $\tilde{\Psi}_j^l(r, t + \Delta t)$  and  $\tilde{\Psi}_j^g(r, t + \Delta t)$  where the tilde ( $\sim$ ) indicates nonreactive transport. The nonreactive transport equations for aqueous and gaseous species read:

$$\frac{\partial}{\partial t} (\phi s_l \tilde{\Psi}_j^l) + \nabla \cdot \tilde{\Omega}_j^l = 0, \quad (\text{A-32})$$

and

$$\frac{\partial}{\partial t} (\phi s_g \tilde{\Psi}_j^g) + \nabla \cdot \tilde{\Omega}_j^g = 0, \quad (\text{A-33})$$

These equations may be solved by an implicit or explicit method over a single time step with initial condition determined by the complete solution at time  $t$ :

$$\tilde{\Psi}_j^\pi(r, t) = \Psi_j^\pi(r, t), (\pi = l, g). \quad (\text{A-34})$$

- (2) Reaction step in which the reaction path equations for dissolution and precipitation of minerals are solved over a single time step using total concentrations obtained from the nonreactive step. At each node, the mass transfer equation

$$\frac{\partial}{\partial t} [\Phi (s_l \Psi_j^l + s_g \Psi_j^g)] = - \sum_m v_{jm} I_m, \quad (\text{A-35})$$

is solved, subject to the initial condition

$$\tilde{\Psi}_j^\pi(r, t) = \tilde{\Psi}_j^\pi(r, t + \Delta t), (\pi = l, g), \quad (\text{A-36})$$

with  $\tilde{\Psi}_j^\pi(r, t + \Delta t)$  obtained from the nonreactive step. Equation (A-35) is solved implicitly. In finite difference form, this equation becomes for the  $n$ th node:

$$s_l \Psi_{jn}^l + s_g \Psi_{jn}^g - (s_l \tilde{\Psi}_{jn}^l + s_g \tilde{\Psi}_{jn}^g) + \frac{\Delta t}{\phi} \sum_m v_{jm} I_{mn} = 0. \quad (\text{A-37})$$

This equation must then be solved for the individual primary species concentrations  $C_{jn}^l$ . This is repeated for each node in the computation domain. The latter equation represents a single reaction path calculation (Lichtner, 1992).

### A.3 FINITE DIFFERENCE EQUATIONS

Finite difference equations based on a block-centered stencil with variable grid spacing are developed for the hybrid scheme. The distance between node points is given as

$$\delta x_n = x_n - x_{n-1} = 2(\Delta x_n + \Delta x_{n-1}), \quad (\text{A-38})$$

where  $\Delta x_n = x_n + 1/2 - x_n - 1/2$ .

At the interface between nodes  $n$  and  $n+1$ ,

$$C_{n+1/2} = \frac{\Delta x_n C_{n+1} + \Delta x_{n+1} C_n}{\Delta x_{n+1} + \Delta x_n}, \quad (\text{A-39})$$

and

$$\left. \frac{\partial C}{\partial x} \right|_{n+1/2} = \frac{C_{n+1} - C_n}{x_{n+1} - x_n}. \quad (\text{A-40})$$

The residual corresponding to the  $j$ th primary species and  $n$ th node point is defined by

$$R_{jn} = \Phi (\Psi_{jn}^{t+\Delta t} - \Psi_{jn}^t) V_n + \Delta t \{ \Omega_{je} A_e - \Omega_{jw} A_w \} + \Delta t V_n \sum_r v_{jr} I_{rn}. \quad (A-41)$$

The fluxes are given by the expressions:

$$A_e \Omega_{je} = -(\phi D A)_e \frac{\Psi_{j,n+1} - \Psi_{jn}}{\delta x_{n+1}} + A_e v_e \Psi_{je}, \quad (A-42a)$$

$$= -T_e (\Psi_{j,n+1} - \Psi_{jn}) + F_e^+ \Psi_{jn} + F_e^- \Psi_{j,n+1}, \quad (A-42b)$$

$$A_w \Omega_{jw} = -(\phi D A)_w \frac{\Psi_{jn} - \Psi_{j,n-1}}{\delta x_n} + A_w v_w \Psi_{je}, \quad (A-42c)$$

$$= -T_w (\Psi_{jn} - \Psi_{j,n-1}) + F_w^+ \Psi_{j,n-1} + F_w^- \Psi_{jn}. \quad (A-42d)$$

The diffusion terms based on central finite difference involve the coefficients  $T_{w,e}$  and are defined by

$$T_e = \frac{(\phi D A)_e}{\delta x_{n+1}}, \quad (A-43a)$$

$$T_w = \frac{(\phi D A)_w}{\delta x_n}. \quad (A-43b)$$

The coefficients  $\Psi_{j,e}$  and  $F_{w,e}^\pm$  are different for central differencing and upwinding. For central differencing, one has:

$$\Psi_j^e = \frac{\Delta x_{n+1} \Psi_{jn} + \Delta x_n \Psi_{j,n+1}}{\Delta x_{n+1} + \Delta x_n}, \quad (A-44a)$$

$$\Psi_j^w = \frac{\Delta x_n \Psi_{j,n-1} + \Delta x_{n-1} \Psi_{jn}}{\Delta x_n + \Delta x_{n-1}}, \quad (A-44b)$$

and

$$F_e^+ = \frac{\Delta x_{n+1}}{\Delta x_{n+1} + \Delta x_n} A_e v_e, \quad (\text{A-45a})$$

$$F_e^- = \frac{\Delta x_n}{\Delta x_{n+1} + \Delta x_n} A_e v_e, \quad (\text{A-45b})$$

$$F_w^+ = \frac{\Delta x_n}{\Delta x_n + \Delta x_{n-1}} A_w v_w, \quad (\text{A-45c})$$

$$F_w^- = \frac{\Delta x_{n-1}}{\Delta x_n + \Delta x_{n-1}} A_w v_w. \quad (\text{A-45d})$$

For the hybrid scheme, one has:

$$F_e^\pm = A_e v_e^\pm, \quad (\text{A-46a})$$

$$F_w^\pm = A_w v_w^\pm, \quad (\text{A-46b})$$

with

$$v_\alpha^\pm = 2(v_\alpha \pm |v_\alpha|). \quad (\text{A-46c})$$

With these results, the finite difference scheme can be expressed in the general form valid for both difference schemes as:

$$\begin{aligned} R_{jn} &= \phi(\Psi_{jn}^{t+\Delta t} - \Psi_{jn}^t) V_n \\ &+ \Delta t \{E_n \Psi_{j,n+1} + P_n \Psi_{jn} + W_n \Psi_{j,n-1}\} + \Delta t V_n \sum_r v_{jr} I_{rn}, \end{aligned} \quad (\text{A-47})$$

where

$$E_n = F_e^- - T_e, \quad (\text{A-48a})$$

$$W_n = - (F_w^+ + T_w), \quad (\text{A-48b})$$

$$\begin{aligned} P_n &= T_e + T_w + F_e^+ - F_w^- \\ &= F_e - F_w - (E_n + W_n). \end{aligned} \quad (\text{A-48c})$$

It follows that

$$(F_w)_{n+1} = (F_e)_n, \quad (T_w)_{n+1} = (T_e)_n \quad (\text{A-49})$$

and

$$W_{n+1} = E_n - (F_e)_n. \quad (\text{A-50})$$

The Jacobian matrix is given by the expression

$$J_{jn, lm} = \frac{\partial R_{jn}}{\partial C_{lm}}, \quad (\text{A-51a})$$

$$= \left( \phi V_n \frac{\partial \Psi_{jn}}{\partial C_{ln}} + \Delta t V_n \sum_r v_{jr} \frac{\partial I_{rn}}{\partial C_{ln}} + \Delta t P_n \frac{\partial \Psi_{jn}}{\partial C_{ln}} \right) \delta_{nm} \quad (\text{A-51b})$$

$$+ \Delta t E_n \frac{\partial \Psi_{j,n+1}}{\partial C_{n+1}} \delta_{n+1,m} + \Delta t W_n \frac{\partial \Psi_{j,n-1}}{\partial C_{l,n-1}} \delta_{n-1,m}.$$

The logarithmic form of the Jacobian is equal to

$$J_{jn, lm} = \frac{\partial R_{jn}}{\partial \ln C_{lm}} \quad (\text{A-52})$$

$$= C_{lm} \frac{\partial R_{jn}}{\partial C_{lm}}. \quad (\text{A-53})$$

Boundary conditions for concentration and zero gradient are given, respectively, by:

$$\Psi_{j0} = 2\Psi_j^\circ - \Psi_{jl}, \quad (\text{A-54})$$

and

$$\Psi_{j,N+1} = \Psi_{jN}. \quad (\text{A-55})$$

### A.3.1 Explicit Finite Difference

Explicit finite difference equations have the form

$$\Psi_{jn}^{t+\Delta t} = \Psi_{jn}^t - \frac{\Delta t}{\phi V_n} \left\{ E_n \Psi_{j,n+1}^t + P_n \Psi_{jn}^t + W_n \Psi_{j,n-1}^t \right\} - \frac{\Delta t}{\phi} \sum_r v_{jr} I_{rn}^t. \quad (\text{A-56})$$

## A.4 REFERENCES

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MULTIFLO 1.0 AND GEM 1.0

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