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User's Guide to PROTOCOL, a Numerical Simulator
for the Dissolution Reactions of Inorganic Solids
in Aqueous Solutions

Gary Pickrell
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October 1984

Lawrence
Livermore
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Laboratory

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User's Guide to PROTOCOL, a Numerical Simulator for the
Dissolution Reactions of Inorganic Solids in Aqueous Solutions

Gary Pickrell[†] and Donald D. Jackson

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2 Abstract

This report provides a user's manual for PROTOCOL, a comprehensive coupled kinetic/equilibrium computer program for analyzing the dissolution reactions of solids with aqueous solutions, specifically applied to the potential corrosion of vitrified nuclear waste by groundwater. The capabilities and available options are summarized as well as instructions for setting up and running problems. Also described in this report and included in the PROTOCOL software package are MASTER, a master file of species thermodynamic data, MANEQL, a preprocessor program and POSTP, a postprocessor. POSTP provides offline plotting using the CRAY-1 DISPLA 9.0 graphics library. PROTOCOL is operational on the CDC-7600 and CRAY-1 computers at the Lawrence Livermore National Laboratory.

3 Introduction

PROTOCOL is a general purpose numerical simulator for the dissolution reactions of solids with aqueous solutions, specifically applied to the potential corrosion of nuclear waste glasses by ground waters. It was developed for the Defense High Level Waste Leaching Mechanisms Program. The work performed in this program was largely experimental, and carried out under laboratory conditions. It was considered essential to also provide a capability for predicting longer term leaching behavior of waste glasses in systems that are not experimentally accessible such as a full scale operating waste repository. The result is a computer code called PROTOCOL (PROgram TO COrrelate Leaching Data). PROTOCOL serves as an interface between the experiment and the chemical performance of the waste form in the repository.

PROTOCOL is implemented as a set of computer files, containing Fortran-coded logic, instructions and data. These files and their use are shown schematically in Figure 1. Supporting software for data file maintenance and graphical output will be discussed in the appendices. It is recommended that the program final report be read for extended discussion of various aspects of PROTOCOL (Jackson 1984, Mendel 1984).

The basic premise of PROTOCOL is that the solid and the bulk aqueous phases of a leaching system can be monitored separately as quasi-independent systems that are coupled at the interface. That is, solid phases act as mass generators and the aqueous phase acts as a mass receiver, in which a redistribution of material takes place at a relatively high rate. In simulation such an evolving system is approximated by evaluating the results of mass transfer and chemical reaction in a sequence of time increments. During each increment, both kinetic and equilibrium computations of reactions leading to mass transfer are made. The results of chemical redistribution provide feedback to the leaching rate functions, where values for such parameters as aqueous activities may be required. Since the primary concern has been to model release of species in a real time repository, PROTOCOL was specifically designed to accept real time as an input parameter.

PROTOCOL makes use of very diverse information about the processes of glass dissolution and about the system in which it occurs. The system is described in terms of a set of parameters, including solid and aqueous chemical compositions, temperature, interfacial area, water flow rate and resident water volume. Solid composition includes phase identity, crystallinity, concentrations of chemical components and thermodynamic stability. Aqueous composition includes activities of chemical species, pH and E_h .

In addition to single phase glasses and their crystalline products, two other types of solid materials can be considered: multiphase waste forms and non-ideal product phases. In multiphase dissolution, components can be leached from different sources at different rates. In the studies of glasses this option has not been exercised.

4 Capabilities

4.1 General Capabilities

4.1.1 Kinetic

PROTOCOL was designed to function as a simulator without exclusive commitment to specific rate expressions or leaching mechanisms. In order to accommodate the variety of rate functions that are expected to result from

intensive investigations of waste glass leaching, they are input to PROTOCOL as submodels. PROTOCOL has the flexibility to accept a variety of models as initial input and provides a means for comparative evaluation of their usefulness as leaching models. The numerical formats have been kept as simple and generic as possible, with a minimal requirement for recoding. The dynamic values for physical parameters and chemical activities that may be required are provided for their evaluation. Their implementation is discussed in section 6.3. Three kinetic submodels are supplied with PROTOCOL as callable internal options.

The first is a general purpose rate expression, providing a menu of terms whose coefficients can be derived by fitting experimental data and which is designed to accommodate most dissolution rate expressions. No mechanistic interpretation of the processes is required or implied. It is by no means implied that empirical rate expressions are necessarily the best description of glass leaching processes. The capability is provided as a test bed for rate models which continue to be developed to interpret experimental data. These functions are composite in that they are likely to be complex summations of the rates of both forward and (unknown) reverse reactions. In this mode, function fitting of aqueous concentration data is done off-line to produce mass fluxes in terms of cumulative mass transferred in unit area and unit time.

Submodels that contain variables other than time are implemented individually by adding coding to the subroutine in which mass increments are calculated. The second submodel to be created, primarily for development purposes, was of this type. It considers the dissolution of silica, where the reactions are relatively simple and where rate constants for both the forward and reverse reactions have been determined. Few systems are likely to be encountered where enough information exists to use this submodel.

The third submodel is that proposed by Kuhn for soluble elements in a specific nuclear waste glass composition, and is based on a surface coverage mechanism (Kuhn and Peters 1982). The terms in the rate functions are associated with specific chemical and physical processes. They also contain constants which are obtained by the investigator by fitting experimental data.

This mechanistic option has been exercised with estimated constants and appears to be working as designed. Further development and analysis have not been attempted at this time, because of the primary experimental emphasis on steady state conditions in waste glass leaching.

4.1.2 Equilibrium

The thermodynamic capability of PROTOCOL is used to monitor reactions in the aqueous phase, which are assumed to be sufficiently fast that local equilibrium is maintained. The activities performed are to redistribute dissolving components, compute solubility constraints on dissolution and identify precipitated or converted solid phases. This equilibrium function has been implemented by the attachment of a geochemical code, MINEQL (Wesla., Zachary and Morel 1976), as sets of subroutines and data files. It will be noted that while many of the original MINEQL subroutines are unmodified except for annotation, others have been reorganized and extended to allow repetitive calculations. This report will not redocument MINEQL routines that have been incorporated into PROTOCOL. An extensive thermodynamic data base in a format resembling that of MINEQL has been provided; this will be discussed in section 6.2.3.

An alternate thermodynamic analysis has been provided for the surface product phases that develop during leaching. The solid materials for which published stability data are available in the data bases of PROTOCOL and other general purpose chemical codes are mostly crystalline phases with well defined stoichiometries and Gibbs free energies of formation. In the leaching of minerals and glasses at low temperatures, however, both crystalline and amorphous solid phases may be formed at the interface, and both may be variable in composition. Although the amorphous materials are thought to be metastable solid solutions, they can persist for long periods of time and appear to act reversibly with dissolved species.

One approach to the chemical modeling of such disordered phases is to treat them numerically as mixtures of discrete component phases with individual stabilities. The advantage of this procedure is that each such component phase can be treated in simulation as a dissolved solid with a stability that can be related to an equilibrium aqueous composition.

The method of Tardy and Garrels (1974) for the estimation of the stabilities for layer silicates has been extended to the alteration products of leached glass. As the experimentally determined concentrations of dissolved species approach steady state, the free energies of reaction

computed from the activity products also become constant and the stabilities of "silicated components" are readily computed. The implementation of this approach in PROTOCOL is described in section 6.2.3.

4.1.3 System monitoring

In its role as a system monitor, PROTOCOL couples experimentally derived rate functions with thermodynamic equilibrium calculations where these are appropriate, and with water flow rates. Each equilibrium calculation provides data for feedback to stored rate functions that may involve water composition, and PROTOCOL computes from them mass fluxes of component species. It also records the redistribution of elements leaving the aqueous phase, whether by precipitation or outflow, and writes a tabular summary of the status of the system with time. This output is a detailed numerical description of the composition of the remaining solid waste form, the composition of the resident water, the identities and masses of the precipitates predicted to form, and a summary of the masses of component elements released to the outflowing groundwater as a function of time.

4.2 Simulation Modes

In addition to the specific set of system parameters, a variety of options can be selected through the instruction files. The following outline summarizes the modes in which the program can presently be run. Sections 6.2.1, 6.2.2, and 6.2.4 will describe the instructions that are used to set up such problems. In all the options a resident water volume is specified. Note that in mode 1, to be described below, the MINEQL input file (PRODTIE) specifies the entire chemistry of the system. This is in contrast to static sequential and flowing systems, where it specifies only the water composition, and leached moles are calculated from rate functions. In modes 1, 3A and 3B the calculation times are generated as terms in the function

$$t_n = t_0 f^{n-1}$$

where t_n is the elapsed time in days, t_0 is an arbitrary time of first calculation, f is the time increment factor, and n is the increment number which starts at 1 and increases to a specified limit. There is also a direct control of the maximum simulation time.

Mode 1: Static Continuous

This is a simulation of an experiment where sampling and analysis are carried out only upon completion. The reaction time, flow rate and leach rate constants may remain in the file but are ignored. This is a "step zero" calculation: it is not in a time sequence and is an equilibration of material specified in the MINEQL input file.

Mode 2: Static Sequential

This approach can model either a series of sacrificial duplicates or repeated sampling of the composition of a single experiment, assuming negligible perturbation. Although the procedures are similar to the simple leach experiment of mode 1, periodic measurements of the changes in concentrations can be used to derive rate functions.

Mode 3: Flowing Water

A time sequence of analyses of a single sample at constant residence time is assumed. The following suboptions are available:

- A. The flow rate is specified as a fixed value.
- B. The flow rate is calculated from a specified linear velocity, a repository configuration and a simple model of water flow.
- C. The flow rate and a set of additional calculation times are specified by a water change schedule. The times and fractions of leachate replaced are listed as input parameters.

Mode 4: Steady State

A metastable equilibrium may be reached in which the activities of the components remain constant within analytical precision. This assumption requires only a volume flow rate of water to estimate release as a function of time. PROTOCOL can examine speciation and the stabilities of elements as silicated components of the saturated phase.

4.3 Options

4.3.1 Congruency

An option has been provided to calculate congruent rates automatically, based on the input rate for any component that is selected: all other input rate functions are ignored. This option makes it possible to study the effects of assuming that a constant fraction of the waste form reacts at a specified rate.

4.3.2 Aqueous Complex Selection

The number of iterations can be substantially reduced by the deletion of trivial aqueous complexes during a run. Many such species in the data base are of such low relative stability that they cannot possibly be significant (in a specified system). An option is available by which the user can specify some conservative threshold activity: species not meeting this criterion are tagged and not considered further.

4.3.3 Water Flow and Change

Two types of simulations for water movement have been provided. In the flow mode, which may be on either an experimental or a repository scale, the mass of water in each time increment is computed from an input volume flow rate. The moles of dissolved components and complexes in this volume increment are added to the arrays for released species and subtracted from the total mass of the system that is available for the next distribution.

Similarly, the moles of components in the inflowing test water or groundwater are added to the inventory of available material.

In some experimental designs sampling is done at scheduled intervals. An option is therefore provided for the exchange of specified fractions of the resident water volume on a schedule listed in the input instruction file. The exchange intervals are independent of the step timer, so that the progress of reactions may be studied between exchanges.

5 Detailed Program Description

5.1 Subroutine Calls

A complex relationship exists between the main program and subprograms, and between the subprograms themselves. In order to present the actual pattern of flow, we use the following notation: The subroutines have been numbered and assigned symbols to indicate calls and returns.

/ = Return to caller

> = The routine listed in boldface type calls the one to the right of the arrow or when followed by a slash (/) the command is returned to the routine which called it.

The principal functions of MAIN are to assign input and output devices, dimension and define variables, initialize some arrays, and call input subroutines. Control of the problem is then passed to subroutine RELEASE.

The macroscopic flow of the main program is shown below. The subroutines listed are those that are called directly by the main program. In all there are 239 subroutine calls performed in the execution of the program.

MAIN > 8 > 9 > 8 > 8 > 30 > 32 > 8 > 33 > 28 > 31 > 2
> 1 > 5 > end

The seven subroutines 1 - 7 listed below do not make calls to other routines. Their statements are executed and command is returned from them to the program which called them.

```
1 TIMEUSED > /  
2 TIMEDATE > /  
3 EMPTY > /  
4 REWIND > /  
5 EXIT > /  
6 RECYCLE > /  
7 SCPHAS > /
```

Subroutines 8-21 execute their statements, call TIMEUSED, and then return command to the caller. Subroutine OUTPUT is an exception to this pattern in that it also calls TIMEDATE, and SCPHAS, before returning command to the caller. For example, in this notation, the flow for subroutine OUTPUT would be: OUTPUT calls TIMEUSED, which returns command to OUTPUT, OUTPUT calls TIMEDATE, which returns command to OUTPUT. OUTPUT calls SCPHAS, which returns command to OUTPUT, and finally command is returned to the caller from OUTPUT. It should not be interpreted as OUTPUT calls TIMEUSED, and then TIMEUSED calls TIMEDATE, etc.

```
8 KINOUT > 1 > /  
9 RESET > 1 > /  
10 INBAL > 1 > /  
11 OUTPUT > 1 > 2 > 7 > /  
12 INITEX > 1 > /  
13 EXROW > 1 > /  
14 INION > 1 > /  
15 IONCOR > 1 > /  
16 EXCOL > 1 > /  
17 JACOB > 1 > /  
18 TIMER > 1 > /  
19 GQUAD > 1 > /  
20 WATER > 1 > /  
21 REFERENS > 1 > /
```

The following set of subroutines are somewhat more complex than the preceding sets in that they make calls to several subroutines (sometimes many calls to the same routine) before returning command to the caller.

```
15 ERROR   > 1 > 11 > 11 > 1 > /
16 INTYPE  > 1 > 13 > /
17 SOLID   > 1 > 22 > 16 > /
18 SIMQ    > 1 > 22 > /
19 SOLIDX  > 1 > 3 > 13 > 3 > 13 > /
20 MASSES  > 1 > 19 > /
21 GIBTAB  > 1 > 4 > /
22 INPUT   > 1 > 10 > 22 > 12 > /
23 MININ   > 1 > 29 > 25 > 14 > 15 > 11 > 11 > /
24 SOLVE   > 1 > 2 > 1 > 17 > 17 > 30 > 25 > /
25 MINEQL  > 1 > 24 > 31 > 26 > 11 > 11 > 11 > /
26 RELEASE > 1 > 18 > 1 > 9 > 27 > 30 > 32 > 8 > 20 > 8 > 1 > /
```

FUNCTION SUBPROGRAMS

Besides the main program and subroutines, there are also 6 function subprograms that are called at various times during the execution of the program. These function subprograms are listed below along with the flow pattern of each.

```
FQ1 > 1 > /
FQ2 > 1 > /
IADY > 1 > 22 > /
IADX > 1 > 22 > /
FSIN > /
FCOS > /
```

5.2 Program variables

The main variables used in PROTOCOL are listed below with a brief definition. Most floating point variables begin with S, W or C, indicating that they describe properties of the system, waste form, or component, respectively.

DAYS	Total elapsed time, days
YEARS	Total elapsed time, years
SWATV	Water volume flowing in current time increment, mL
SWAVI	Water volume flow rate past waste form, mL/year
SWAVS	SWATV, converted from mL to cubic metres
SWCUM	Cumulative water volume, cubic metres
MWPHS	Number of solid phases
WEXES	Excess waste form mass, that does not appear in sum of component masses (primarily oxygen)
WVOLI	Initial volume
WLENI	Initial length
WRADI	Initial radius
WAREI	Initial surface area
WVOLR	Total waste form volume remaining after leaching, mL
NPIDN	Phase identification number
PPTMOLES	Moles of phase precipitated by MINEQL
NCMOD	Pointer to model in subroutine masses
CMTAB	Tabulated atomic weight for the central atom in a MINEQL component species
CCTAB	Component ionic charge
CDEN2	Component bulk density
CRATI	Component $1/r$, if cylinder
CAREA	Component current surface area
CAOMS	Ratio of component exposed area to contact water mass, square metres/kg
CRTAU	$R*(T-Tzero)/(G*R)$, dimensionless time parameter
CRGPY	Component current mass reaction rate g/year
CRMPS	Component leaching rate mole/sec
CRMPY	Component leaching rate moles/year
CDSUM	Cumulative depth leached (+ for depletion, - for accretion)
CFCUM	Total cumulative fraction of component reacted from beginning of leach to end of time increment
CHCUM	Cumulative reacted mass of component from solid, g
CMASR	Remaining mass of component in original solid phase
CFTOT	Initial sum of component mass fractions

CMTOT	Initial sum of component masses specified
CMOLTOT	Total moles of components in the waste form
CMLYG	Component analytical molality in inflowing groundwater
CMLY1	Component analytical molality before distribution
CMLY1A	Component actual molality after distribution (MINEQL output)
CMLY2A	Molality of complex after distribution
CMLY2A1	Component molality in CMLY2A
CMLY4	Precipitated phase molality (both MINEQL and PROTOCOL)
CMLY41	Component molality in CMLY4
CMLYT	Total moles of component resident at end of time step, before subtracting flow loss
CLOST	Total (cumulative) moles of component lost to outflow
NYDIM	Total number of species, including components, that is allowed by current dimensioning
NXDIM	Maximum number of components
NX	Number of active components
IDYIDX	Identification number of species components
IDYIDXSC	Stoichiometric coefficients for species components
NARAY	Variable descriptor in input file PRODT2K
STORIT	Array for collecting PROSUM data; moles, molalities
IDSTORIT	Identification number for values in STORIT
STORITSMY	Concentrations of solid phases formed, 10 maximum
IDSTORITS	Identification numbers for values in STORITSMY
T	Total moles of component: MINEQL INPUT, PRODT1E
V	Final (output) total moles of components, in all species

6 Instructions on Usage of PROTOCOL

6.1 Usage outline

The input for PROTOCOL is from a set of problem files. The user can run any system desired by changing input parameters in the files listed below. There are seven input files, of which the first two are instruction files and the last five are data files. Generally the user will need to edit only the instruction files. They are most conveniently prepared by modifying existing

files with a text editor. There are a number of site-specific operations for which no instructions can be provided; including file transport, storage and retrieval, editing and compilation. Problem setup and execution are relatively simple. The files that must be available on disk are PRODTIE, PRODTIK, PRODT2E, PRODT2K, PRODT3, REFS, and PROCON (compiled version of PROTOCOL: if not available PROTOCOL must be recompiled). An effort has been made to identify each variable in these files. A text editor can be used to change the values, but great care should be taken that each is correct and that all are consistent: only errors leading to computational failures are likely to be caught during input and execution. The normal procedure for running PROTOCOL can be summarized as follows:

1. The isothermal thermodynamic input file PRODT2E, if available, should require no modification. However it is suggested that all type 6 species be removed, since they occupy array positions. Use the preprocessor MANEQL if an update in the thermochemical file (PRODT2E) for the problem temperature is required.
2. Generate a rate function from experimental data, using terms from the existing menu:

$$\text{moles} = c_1 + c_2 + c_3 t^2 + c_4 t^{.5} + c_5 t^{-2} + c_6 t^{-1} + c_7 t^{c8}.$$
 If necessary, a new submodel can be created by additional coding in subroutine MASSES.
3. Set up the kinetic file (PRODT2K), using appropriate rate constants and waste form data.
4. Create a run instruction file (PRODTIK).
5. Create an initial system composition file in MINEQL format (PRODTIE).
6. Assemble the set of files on disk and run the compiled version of PROTOCOL (PROCON).
7. For graphics output, run the postprocessor, POSTP, with its instruction file, POSDT2, and the PROTOCOL output files PROSUMC, PRODTIK, and PRODT2K.

On initialization, PROTOCOL reads the kinetic file, computes waste form physical parameters, the resident water volume and flowrate. It then enters a nest of three loops in time, phase and component, where it remains until completion of the problem. In each element of the time loop a step length is

computed and a water equilibration is carried out. In each element of the phase loop are performed calculations for its individual components; rate functions and resulting mass fluxes and geometric changes. Finally, compositional changes due to water mixing and flow are determined and entries made in the output tables, completing the time step.

6.2 Files

Aside from specific instructions that direct the computations, the information in the files is organized on four levels. These pertain to the experimental or repository system, to the waste form, to the chemical phases in that waste form, and to the individual component elements in each phase. In outline form the following information is required:

System

- A. Temperature
- B. Water
 - 1. Volume flow rate
 - 2. Resident volume or film thickness
 - 3. Density
 - 4. Initial chemical composition

Waste Form

- A. Mass, surface area, density, physical dimensions
- B. Number of component phases

Phase

- A. Mass and density
- B. Number of components

Component

- A. Mass and density
- B. Formula weight and charge
- C. Leach rate data
- D. Thermochemical properties and formation reactions of species in other phases.

6.2.1 Thermochemical Instructions

The thermochemical instruction file (PRODTIE) is a slightly modified version of the MINEQL input component data set. It is a table of components in the system, listed by type. A value for the total analytical concentration of each component is required, and a guess for its final concentration at equilibrium. For each element that has a variable oxidation state, a redox couple must be available in the data base PRODT2E, and both members must be specified as components. In PROTOCOL/MINEQL, H^+ and e^- are also components, must be specified, and are used to fix the pH and P_{e^-} , respectively. The listing of components in PRODTIE for PROTOCOL is more extensive than that in MINEQL, since it must contain not only those components initially in the water, but also those that are to be leached for the solid. Although concentrations for the latter must be specified, initially they can be set at negligible values.

When entering data in PRODTIE, it should be noted that lines 3-7 are options that would significantly increase the length of the output files. For example, ISUBS will add about four hundred lines to PROOUT (depending upon the other input parameters). MATREL will increase PROOUT by about three thousand lines. Typos in the input data may not cause an error message to be displayed, but may significantly affect the output data. All the input files must be available for the program to run correctly. If one is missing, a system error will result during execution.

The variables read from PRODTIE are listed below with formats and descriptions, except ITMAX, EPS, ITER, THRSH, and XMU which are MINEQL variables.

KUTITS	I2	Causes rejection of unnecessary dissolved solids
KUTITC	I2	Causes rejection of trivial aqueous complexes
NOPRINT	I2	Value greater than 0 suppresses PROOUT print
ISUBS	I2	Value greater than 0 writes list of subroutine calls
ITIME	I2	Value greater than 0 writes time of entry into subroutines
ICMPLX	I2	Value greater than 0 writes complex molalities to PROSUMC
MATREL	I2	Value greater than 0 writes extensive matrix element diagnostics to PROOUT
IADS	I4	
AREA	E10.3	
ZEL	E10.3	

The succeeding records contain a component identification number, log of estimated final concentration, analytical concentration and chemical formula in an I5,3x,F6.2,E7.2,1x,A20 format.

6.2.2 Kinetic Instructions

PRODTIK is the run instruction and system parameter file. It provides most of the specifications of the physical system as well as time step and print instructions. The principal values to be specified are:

Waste Form:

- Geometry - cylindrical or irregular
- Interfacial area
- Initial mass

Time Step:

- Initial step size
- Increment factor
- Maximum number of steps
- Simulation time limit

Water

- Flow or static
- Volume
- Density
- Flow rate

Print

- Option for table of identification and stabilities of species considered

The variables read from this file are listed below with formats and descriptions.

ISYSTM	I3	Pointer to type of calculation: 1=exptl, 2=repository
ISFLOW	I3	Water flow pointer, 0=static, 1=flow, 2=change
ISCNUM	I3	Number of water change times in schedule
ITAB	I3	Flag to print ΔG^0 and reference tables, 0=omit, 1=print
SDINC	E10.4	Initial time increment, days
SINCR	E10.4	Time increment factor

STEMP	E10.4	Kelvin temperature
SWVOL	I3	Water volume resident with waste form, mL
SCTIME	E10.4	Water change time, days
SCFRAC	E10.4	Fraction of water changed
SVELO	E10.4	Linear water velocity, cm/year
POROS	E10.4	Fractional effective porosity of host formation
SPACE	E10.4	Canister spacing, cm
STMAX	E10.4	Maximum run time allowed, years
SIMAX	E10.4	Maximum number of time increments allowed
SAOV	E10.4	Ratio of interface area to water resident volume
SWDEN	E10.4	Water density, g/mL
NWIDN	I3	Waste form identification number
NWGEO	I3	Geometry pointer
WMASS	E10.4	Initial total mass, g
WAREA	E10.4	Surface area, if irregular shape
IPD	I3	Number of points for Guassian Quadrature
IETIMS	I3	1 adds set of very early times, 0 omits
SW	E10.4	Water flow rate, mL/day, if ISFLOW=2
SR	E10.4	Resident water volume, mL

6.2.3 Thermochemical Data

The publicly available MINEQL data file contains component identification numbers, stoichiometric coefficients and logarithms of the equilibrium constants for reactions at 298K. These reactions are for the formation of species from a basis set of species, or components at 298K. Sources of the data are unspecified.

The thermodynamic data file that has been used in this project is an extended version under development at the Lawrence Livermore National Laboratory. Changes in component species have been made in *PROTOCOL* to reflect the present application to inorganic materials. Organic ligands have been removed and many actinide components have been added. The current components are listed in Table 1.

Table 1 Revised listing of MINEQL components

1. Ca^{2+}	26. Sn^{2+}	52. Bk^{3+}
2. Mg^{2+}	27. Sn^{4+}	53. Cf^{3+}
3. Sr^{2+}	28. La^{3+}	54. TcOOH^+
4. K^+	29. Ce^{3+}	55. Fm^{3+}
5. Na^+	30. Au^+	56. Tl^{3+}
6. Fe^{3+}	31. Th^{4+}	58. Ra^{2+}
7. Fe^{2+}	32. UO_2^{2+}	101. CO_3^{2-}
8. Mn^{2+}	33. Cu^+	102. SO_4^{2-}
9. Cu^{2+}	34. U^{4+}	103. Cl^-
10. Ba^{2+}	35. $\text{Zr}(\text{OH})_5^-$	104. F^-
11. Cd^{2+}	36. Pu^{3+}	105. Br^-
12. Zn^{2+}	37. Pu^{4+}	106. I^-
13. Ni^{2+}	38. PuO_2^+	108. S^{2-}
14. Hg^{2+}	39. PuO_2^{2+}	109. PO_4^{3-}
15. Pb^{2+}	40. U^{3+}	110. $\text{P}_2\text{O}_7^{4-}$
16. Co^{2+}	41. Np^{4+}	111. $\text{P}_3\text{O}_{10}^{5-}$
17. Co^{3+}	42. NpO_2^+	112. $\text{Si}_2(\text{OH})_4^-$
18. Ag^+	43. NpO_2^{2+}	118. $\text{B}(\text{OH})_4^-$
19. Cr^{3+}	44. Tc^{4+}	122. MoO_4^{2-}
20. Al^{3+}	46. Am^{3+}	123. WO_4^{2-}
21. Cs^+	47. Am^{4+}	124. AsO_4^{3-}
22. Li^+	48. AmO_2^+	125. HVO_4^{2-}
23. Be^{2+}	49. AmO_2^{2+}	127. NO_3^-
24. Sc^{3+}	50. H^+	135. IO_3^-
25. $\text{Ti}(\text{OH})_4^0$	51. Cm^{3+}	136. TcO_4^-

Missing numbers have not been assigned (or reassigned). Some components are available that are not required for the specific application to waste glass/repository/ground water systems. In addition to increases in the number of components and other species, the modified file now contains for each species S_0 , ΔH^0 of formation, ΔG^0 of formation, a literature reference number, chemical formula and mineral name, if any.

The MINEQL file was also extended linearly to accommodate data for elevated temperatures: each entry for a species at 298K is followed by similar line entries for higher temperatures. Data at any temperature can be accepted, and thermochemical properties can be entered in either Kcal or KJ. A flag is provided for the conversion of units. The master file is revised on a continuous basis. It presently contains 878 dissolved solids and 922 aqueous species.

The master and derivative isothermal files are supplied in the PROTOCOL package on an "as is" basis. As far as possible, data have been selected from reputable, well-reviewed tabulations. However, because of the number of species included, a critical review has not been possible, and no general statement concerning accuracy and self consistency can be made.

A dual identification number system was established because of the expansion of the master file. The species numbers used by MINEQL are temporary, because of the large number of insertions that are made. The permanent identification numbers are used for reference. References are generated for most data that are used in each simulation, and the user is advised to review values that are most important for the results of specific problems.

PRODT2E is an isothermal equilibrium thermodynamic file derived from the master file by the preprocessor. The variables read from this file are listed below, with their format and description.

Record 1	Column headings (not read)
Record 2	Blank
Record 3	1x,I5,A1,F7.2,4(I4,I3),I3,F7.1,16x,F9.3,I1,I3,11x,R5, 1x,R2,12A1,17R1

The record 3 format is repeated to the end of the file.

IN	I1	Field for flag written by MANEQL, not read by PROTOCOL
IDYT	I5	Temporary identification number
ITYPE	A1	Blank specifies that ΔG is in kcal, S indicates KJ/mole
GKT	F7.2	Log K
IDT	I4	Component identification number
IAT	I3	Stoichiometric coefficient
NWAT	I3	Number of water molecules in species formation reaction
TEMPER	F7.1	Kelvin temperature
DELTGSS	F9.3	ΔG zero of formation for a species at a selected temperature
IRE	I3	Reference for ΔG and S
JNUM	R5	Species permanent identification number
FORMUL1	R2	Species chemical formula
FORMUL2	A12	Species chemical formula
MINAME	R17	Mineral name or additional reference
ISC	I1	Flag for silicated components
NFLAG		Flag (.) to skip species

Successive equilibria involving solid solutions can be simulated with the appropriate rate functions and system parameters with a special data file which contains a set of silicated components and their saturated log K values. These "dissolved solids", in the MINEQL definition, precipitate individually according to their assigned stabilities and the activities of their components in solution.

When PROTOCOL is used to estimate such stability data, a flag is set for each silicated component included in the list of dissolved solids (type 5 species). The experimental solubility is inserted in E9.3 format in the field normally occupied by the ΔG_f^0 . All other dissolved solids are removed from the file.

6.2.4 Kinetic Data

The kinetic data input file (PRODT2K) has three levels of data, in which are specified properties of waste form, phase and chemical component. To accommodate complex waste forms, it can be extended linearly to any length consistent with the current dimensions of the arrays.

The waste form is characterized by an identification number, overall density, length/radius ratio (if cylindrical), and number of phases. Each phase has an identification number, initial mass and density, and number of components. Each component has an identification number, density, mass fraction of its phase, submodel pointer, and set of eight constants.

The interpretation of the constants depends upon the submodel that has been selected. If submodel 1 is used, for example, a wide variety of rate functions can be constructed by summing from a menu of terms in powers of time that is provided. If other terms are required, they can be added with minor code modifications. If dependences on parameters other than time are available, other submodels are easily added by redefinition of the input constants.

It should be noted that input rate functions for components of an element in different oxidation states may be modified in subroutine INPUT. Very large changes in the ratios of such components may take place during iteration, depending upon the specified oxidation potential. Considerable iteration time can often be saved by assigning oxidation state ratios for an element according to those determined in the previous increment, disregarding the input rate functions. The variables read from this file are listed below with their formats and description. In the file each variable is also accompanied by a definition.

Record 1	File name, descriptor
Records 2 & 3	Blank
Records 4-6	Heading, not read
Record 7	Blank
Record 8	I3,1x,I3,3x,I3,4x,I2,1x,E11.4,2x,I3,3x,A5,6x,A50. The format of record 8 is repeated to the end of the file. Dummy variables are read in, and normally assigned as follows:
NWNAM 50A1	Solid phase name
WDENS E11.4	Solid density, g/mL
WRAT1 E11.4	Initial 1/r
NPNAM 50A1	Phase name
PMASS E11.4	Total initial grams phase in cylinder
PDENS E11.4	Phase density,g/mL

HPCON	13	Value greater than 0 sets all components rates to congruency, based on component NPBAS
NPBAS	13	Identification number number of basis species for congruent dissolution rate option
NPCOM	13	Number of components in phase
NCIDN	13	Component identification number,
CDENS	E11.4	True initial component density in phase
CFRAC	E11.4	Component initial mass fraction of phase
CCONS	E11.4	Constant in dissolution rate function (repeated in following records)

6.2.5 Ionic Sizes

PRODT3 is the ionic size file.

Record 1-3 4012

Record 4 2012

IONZ	12	Component ionic charge
------	----	------------------------

6.2.6 References

REFS is a listing of references for species data:

Record 1-5 Blank

Record 6 F4.0,3x,110R1. Record 6 is repeated to the end of the file.

REFNO F4.0 Reference identification number

HAUTH 110R1 Reference

6.2.7 Output files

For each problem that is run, PROTOCOL writes summary tables of its instructions and data base, as well as the status of the waste form and the composition of the resident aqueous phase.

Species distributions are recorded in terms of the list of chemical components (basis species) defined in Table 1. During the computation, the

masses and concentrations of components, aqueous complexes and precipitated solids are stored in "attribute" arrays, which classify them as inflowing, leached, resident or released by outflow. In addition, separate arrays record the identification numbers, stoichiometric coefficients, and concentrations of the components of multicomponent species. As species are gained or lost in each time step by reaction or flow, all the appropriate arrays are debited or credited. The distribution of masses of components as a function of time are documented in several output files.

Output files

PROOUT - Chemical status output file
PROSUMW - Waste form summary output file
PROSBS - Storage file for subroutine calls and other debug data
PROSUMC - Chemical species summary output file PROSCP - Silicated component phase data
PRODEL - Output data of species deleted as trivial
PRONAM - Storage file for mineral names

Output Data Tables

File	Table	Data
PROSUMW	1	System and Run Parameters
PROSUMW	2	Waste Form Parameters
PROSUMW	3	Computed Leaching Functions
PROSUMC	4	Species Distribution and Release
PROSCP	5	Silicated Component Phase Data

6.2.7.1 Detailed Equilibrium Data (PROOUT)

The normal output of MINEQL is a detailed summary of the activities at equilibrium of all species that were considered in a single problem (Westall, Zachary and Morel 1976). In MINEQL, all chemical species are assigned to one of six types, summarized briefly as follows:

1. Components - basis set of soluble species, from which species of all other types are formed.
2. Complexes - all other soluble species.
3. Species at fixed activity - gases at fixed partial pressure, precipitated solids not allowed to dissolve, fixed pH or Eh, and redox reactants.
4. Precipitated solids subject to dissolution.
5. Dissolved solids subject to precipitation.
6. Species not to be considered, usually for kinetic reasons.

The format of this main output file PROOUT has been retained with little change as a description of intermediate states in the dynamic leaching process: one such tabulation can be generated for each time step. However, because of the large volume of output, an option has been made available to limit it to the first three steps. The output parameters in this tabulation are the component concentration C , $\log C$, $\log K$ for the species formation reaction, and the species formula expressed as sets of component identification number and stoichiometric coefficient.

6.2.7.2 Run Instructions, Kinetic Data and Waste Form Status Summary (PROSUMW)

The output file PROSUMW contains five tables. Tables 1 and 2 are verbatim records of instruction file PRODT1K (6.2.2) and kinetic data file PRODT2K (6.2.4.), respectively. A summary of output data relating primarily to the waste form is written into output Table 3. Values are tabulated in each time step for the following parameters for all components in each leached solid phase:

- Increment number
- Reaction time
- Phase and component identification numbers
- Mass corrosion rate
- Cumulative fraction mobilized
- Mass mobilized
- Cumulative mass remaining
- Cumulative depth depleted
- Cumulative water volume flowed

An annotation is also made in each time step of precipitated phases, including temporary and permanent identification numbers, chemical formula, and mineral name, if any. (Output Tables 6 and 7 are described in 6.2.7.5.)

6.2.7.3 Component Distribution and Release (PROSUMC)

The main summary of component distribution as a function of time is output Table 4 (file PROSUMC). It records all material in the system initially (external to the waste form), as well as all that has entered by water inflow and left by outflow. In each time step, a single line entry is written for each (MINEQL) component listing current values for the following parameters:

- Cumulative moles leached
- Resident plus cumulative moles added from inflowing water
- Initial (start of increment) cumulative moles lost to outflow
- Cumulative moles available for distribution
- Molality of distributed (uncomplexed) component
- Molality of distributed complex
- Total molality of component in complexes
- Molality of component in precipitated phase (individual and total)
- Current moles lost to outflow
- Final (end of increment) moles lost to outflow
- Cumulative fraction of component released

The individual activities of aqueous complexes in most time steps are not normally of interest. Since they require a large amount of printout space and are also available elsewhere (PROOUT), their inclusion in output table 4 has been made optional. For comparative purposes, entries are also included for the masses of precipitated phases, expressed as molalities.

6.2.7.4 Deleted Species

A tabulation is made (output file PRODEL) of all species that have been rejected in time steps 0 and 1. In this table are listed for each species the identification number, molality if aqueous, QMAX and QMAX/KEQ if a dissolved solid.

6.2.7.5 Species Identification and Stability (PROSUMM)

In the interest of quality assurance a self-referencing capability has been provided. An option is available which attaches to a simulation a record of the value and origin of every value of Gibbs free energy that was used. The tabulation is necessary because the data files are subject to frequent revision as described in section 8.1 and because PROTOCOL selects for each problem a potentially unique set of input data. The intent is to provide enough information with the problem output that a meaningful independent evaluation or recalculation could be carried out. Two documentation output Tables 6 and 7, can be automatically generated for every run, and are printed in output file PROSUMM.

Output Table 6 lists species that were selected from the isothermal data file and considered in the computation. For each species are tabulated its chemical formula, serial number, standard free energy of formation, mineral name (if any), and reference number.

Output Table 7 is a list of references for the free energy values, or for the information that was used to derive them. A listing of free energies is more meaningful than log K values for this purpose, since the latter refers to reactions written according to a specific set of rules and using a specific basis species component set (Table 1). These reactions are not stored in a readily retrievable form, and the basis set itself is subject to modification.

6.2.7.6 Terminal Output

PROTOCOL is designed to be run in a time sharing mode from a remote terminal. During simulation, the operations are directed by files, and interaction with the user takes place only if the online graphics option is exercised (6.2.7.7). Output to the terminal is a brief report of the course of the computations, and consists of the following information:

1. Increment number and seconds of computer time used at the end of each increment

2. Precipitation and dissolution of phases, reported by phase identification number
3. MINEQL standard error messages
4. PROTOCOL error messages, and MINEQL supplementary error messages, often including diagnostics or references to probable source locations in coding
5. Increment number and reason for termination if normal exit (such as exceeding allowed simulation time or number of increments)
6. Summary of computer time used if normal exit, including central processor, system and input/output times.

6.2.7.7 Graphics

Two types of graphics capabilities are available. The first is an online plotting option using GRAFLIB, a graphics library written in LRLTRAN (LLNL FORTRAN) for use on the Livermore time sharing system. Versions exist for the CDC-7600, and CRAY-1 machines. A package of 5 subroutines in PROTOCOL is used to plot data as they are generated during the simulation. The following operations are performed:

1. Selection of a plot option is requested (time function of component molalities, component molalities in complexes, component percent distribution in species, component mass in precipitates, or component release)
2. The available components are listed and the selection of a set of four is requested
3. A standard grid is drawn, labeled and titled
4. A key is written, associating plot symbols with components
5. Data are plotted as soon as they are calculated
6. Precipitating phases are listed by identification number in a separate key as they are formed.

For most other sites, the online graphics option cannot be used without translation for an available library. The option is also not available in the version for the CDC-7600 machine.

A postprocessor is also provided to plot data from the output file PROSUMC; for a full description of this program see the appendix, section 8.2.

6.3 Submodels

Submodels are expressions from external sources that describe the kinetics of leaching in terms of the chemical and physical parameters of a system. They are implemented in subroutine MASSES. They are designed to be modular, so that new ones can be added with a minimum of programming. However, some familiarity with the program variables will be required. Submodels are selected by setting the value of NCMOD in file PRODT2K. The assignment is very flexible: It is possible for each component of each phase to be supplied with an individual rate model. A component can be released from different phases at different rates and according to different models.

6.3.1 Submodel 1

Submodel 1 is a generalized leach function with leach rates expressed in cumulative moles per square centimeter and time in hours. It should be noted that in this submodel, the leach rate is a function of component surface area, not of water volume, and therefore not of concentration.

This submodel uses function FQ1, which calculates the cumulative moles per square centimeter of component leached and multiplies it by the area, to give cumulative moles of component leached. Submodel 1 stores a summary of component moles distributed, after leaching additions for the current increment have been made, but before the moles of the components in the groundwater have been added. The parameters that are stored are cumulative moles of component leached, cumulative moles of component added from inflowing groundwater, cumulative moles of component lost to outflow, and current moles of component available (to add to resident groundwater moles). The total cumulative moles of component lost to outflow, CLOST, which was calculated at the end of the preceding increment is used as a starting point for the new increment.

6.3.2 Submodel 2

Submodel 2 computes the net mass of silica dissolved from silica phases, using existing leaching rate functions (Rimstidt & Barnes (1980)). The rates of forward (dissolution) and reverse reactions are a function of temperature only. Interfacial area and water volume are used in the rate functions to compute net mass dissolved in each time step.

6.3.3 Submodel 3

Submodel 3 is a rate function of the type proposed by W. Kuhn (W. Kuhn 1982) in which the terms in the rate functions are associated with specific chemical and physical processes, and contain constants that are obtained by the investigator by fitting experimental data. For this submodel the input values of the array CCONS in file PRODT2K are redefined as noted by comments in the source listing.

6.4 Error returns

Error traps have been installed at points where usage has shown them most commonly to occur. Listed below are those most frequently encountered. The most common cause is incorrect or unwise specification in problem setup. In places where errors most frequently occur during execution, especially division by zero, messages are returned identifying the subroutine, variable and position of origin.

1. Skip of percent output - In subroutine OUTPUT if the variables V and T(J) go to zero a skip of percent will result in the summary file PROOUT. Some possible causes are an error in a stoichiometric coefficient for some species of the component or an incorrect ligand identification number.

2. T(J) is given a zero value in subroutine SOLVE - this may also be related to problem 1 above. Check the PROOUT input summary of dissolved solids, for unusually positive log K values. Check component identification numbers and stoichiometric coefficients.
3. Read error on input: one of the input files from which the program is trying to read is not available. Check that PRODT1E, PRODT2E, PRODT1K, PRODT2K, PRODT3, and REFS are available on disk.
4. The initial mass or surface area of the waste form has been set to zero. Check in file PRODT1K that WMASS or WAREA has been entered correctly (must be a nonzero value).

6.5 Common Blocks

A cliché PROCOM is used to transmit the common blocks to the subroutines without having to relist them. For compilers that do not have the cliché capability, some reorganization may be desirable.

Common Blocks

PARM1
LCMARAY1
LCMARAY2
LCMARAY3
GRAFIX
SPHASES
COMPON1
COMPON2

6.6 External Names

6.6.1 Subroutines

- MAIN - directs the program through input, calculation and output.
- MININ - reads the instruction section of input file PRODTIE.
- RELEASE - contains the time loop, in which switching between leaching and distribution is carried out.
- MINEQL - calculates the chemical equilibrium composition of the system. PROTOCOL incorporates a modified version of MINEQL (Westall 1976). The principle subroutines from MINEQL are ERROR, EXCOL, EXROW, INION, IONCOR, INPUT, INTYPE, OUTPUT, SIMQ, SOLID, SOLIDX, SOLVE.
- KINOUT - general purpose subroutine for input and output of kinetic data; reads PRODTIK instructions and PRODT2K rate functions and writes PROSUMC, PROSUMW and PROSCP.
- TIMER - calculates the length of the current time increment in years, (although experimentally derived rate functions may be in other units). TIMER sets up a master array of time steps which may have three components; a set of early times to detect the precipitations of very insoluble species, a set of scheduled water change times, and a main array of time steps.
- MASSES - computes mass and dimensional changes in multiphase, multicomponent solids due to leaching using input rate functions. It should be noted that all mass calculations for the waste form phase(s) are carried out in terms of elements in order to avoid uncertainties concerning their oxidation states and because some basis species contain hydrogen and oxygen.
- GQUAD - evaluates the numerical integral of the function $FQ(X)$ between the limits (A,B) using Gauss Quadrature with a polynomial of degree M (M+1 points), where M=1,2,3,4,5,9 or 14. GQUAD uses arrays ZQ which contains roots of the Legendre polynomials, WT which contains corresponding weight factors, NPOINT which selects the current (M+1) point formula, and KEY which supplies correct roots and weights for a given M.
- WATER - calculates the fraction of component released in moles. It uses the resident water volume, which was input from file PRODTIK, and a calculated volume flowed.

- ERROR - prints the standard MINEQL error messages. These include references to a possible reason for an error and a possible location in the coding.
- RESET - resets the MINEQL arrays to zero at the end of each time step, saving only the initial resident water composition and the component molalities that are bound in precipitates.
- EXCOL - MINEQL subroutine which exchanges columns in the IDX, A, X, SX, and T arrays.
- EXROW - MINEQL subroutine which exchanges rows in the IDY, A and K arrays.
- INION - MINEQL subroutine which reads ionic charge data and initializes the variables for IONCOR.
- IONCOR - MINEQL subroutine which performs ionic strength corrections according to the Davies approximation.
- INPUT - MINEQL subroutine which reads the data portion of PRODT1E. It inputs the components that are to be used in the computation, including an initial guess for their free concentrations, and their (total) analytical concentrations. INPUT also reads thermodynamic data file PRODT2E to select an appropriate set of species.
- RECYCLE - uses component activity from previous increment as an improved initial estimate for its current activity.
- INBAL - modifies the masses of some pairs of leached components in increments greater than zero. The masses are distributed into ratios reflecting those determined in the preceding increment. The purpose is to decrease the simulation time and promote convergence by eliminating unnecessary iterations.
- INTYPE - MINEQL subroutine which checks and assigns species types
- OUTPUT - MINEQL output subroutine which has been extensively modified to also compute and output cumulative species distribution data.
- SCPHAS - computes free energies of formation for silicated components from solubility data.
- SIMQ - MINEQL subroutine for the solution of n linear equations in n unknowns by Gaussian elimination and substitution.

- SOLID - MINEQL subroutine which modifies the A, K, and T matrices for the set of precipitated solids, issuing an immediate return if there are none. If there are precipitated solids, modification begins with the last type IV species as the pivotal species and works upward to the first type III species.
- SOLIDX - MINEQL subroutine which solves the chemical equilibrium problem for the amounts of solids, "unmodifies" the A, K, T, GX, and X matrices (i.e., restores the stoichiometry to reflect the original set of components) and dissolves or precipitates solids as necessary.
- SOLVE - MINEQL subroutine which solves the chemical equilibrium problem for soluble species.
- JACOB - MINEQL subroutine writes the Jacobian matrix .
- GIBTAB - tabulates Gibbs free energy data for all species that were considered in the current problem.
- REFERENS - writes a table of literature references, corresponding to the reference numbers associated with each species in GIBTAB.

6.6.2 Function Subprograms

- FQ1 - computes mass of a component released in a time increment from empirical rate data fit to a general form rate equation, and the cumulative moles released at time T.
- FQ2 - computes the mass of silica released from silica phases, from leaching rate functions (Rimstidt & Barnes 1980).
- IADY - MINEQL function which finds the storage location of species IDY in the K array; if species IDY cannot be found an error message is issued and execution is terminated.
- IADX - MINEQL function which finds the storage location of component IDX in the X, GX, and T arrays; if component IDX cannot be found, an error message is issued and execution is terminated.
- FSIN - sine function
- FCOS - cosine function

6.7 Program characteristics

6.7.1 Program Size

Two FORTRAN versions of PROTOCOL are maintained, for the CDC-7600 and the CRAY-1. The lengths are about 4,600 and 5,100 lines, respectively, and they are dimensioned for 49,000 words. The CRAY-1 version contains an additional set of subroutines for online graphics. The memory size required is greatly dependent upon the intended use. The program has been configured for present purposes to treat large and chemically complex systems. It currently accommodates a maximum of two waste form phases with 26 components per phase, 12 precipitated phases, 140 components in the basis set, 30 silicated component phases, and 600 total species. It should be noted that of the 140 basis species only 75 have actually been assigned. Current dimensioning is adequate for problems as large as 17 components.

6.7.2 Timing

Run time is dependent on the following variables; number and types of components in the system, size of the isothermal data file, number of time steps, quality of starting estimates, and volume of output requested. As a rough guide it has been found that a typical system of 17 basis set components with a thermochemical file of maximum size (298K and common elements) and normal output files but without large excursions in redox ratios, will require about 13 seconds for the initial equilibration (step 0) on the CRAY-1 and 5 seconds for each succeeding step.

6.8 Examples of Usage W/Machine Output

The following two examples consider the basic capabilities of PROTOCOL; the modeling of kinetic and steady state processes. In each case, properties of the solid product phases are known. It should be noted that if empirically-based dissolution rate functions are used without information on the kinetics of formation of solid products, anomalies may result. Metastable phases are often formed at early times, which convert to equilibrium phases at slow rates.

6.8.1 Example 1. Silica dissolution

Variations were run on a leaching problem in which 10 grams of amorphous silica were dissolved into 100 ml of neutral water. Some results of these computations are shown in Figures 2 through 6. Note that concentrations in the resident water volume have been plotted, not the total mass of silica lost by leaching. Values for parameters were varied in the following ranges:

Temperature, 313-363K. Rates increase appropriately with increasing temperature, and precipitation and constant molality are achieved at progressively earlier times (Figure 2).

Water flow rate, 0-1 ml/day. Minor effects of flow rate on the concentration in solution of H_4SiO_4^0 were found. Changes in molality as a function of time and flow rate are plotted in Figure 3.

Interface area. The effects are shown of varying this parameter between 10^{-1} and $10^1 \text{ m}^2\text{g}^{-1}$ (Figure 4).

Initial concentration of silica, 10^{-4} to 10^{-20} molal (Figure 5). The inhibiting effect of an initial concentration in the water of the species being leached is shown clearly. It is also clear that in an experimental context, the magnitude of the effect would depend very strongly on when measurements were taken.

Sensitivity to thermochemical stability data. The ΔG_f^0 at 313K for H_4SiO_4 has been used as a variable (Figure 6), not because of actual uncertainty in this value, but to simulate a reaction in which the stability of a species that might be formed is not well known.

6.8.2 Example 2. Waste glass dissolution

Table 2 is an example of steady state data for a defense waste glass (Jackson 1984). In this example solubility data have been used to estimate values for the stabilities of silicated components. These, in turn, are used to compute release as a function of time at a volume flow rate of water of 0.1 L/D. The resulting functions are shown in Figures 7 and 8. In Figure 9 is shown the estimated release function for Ca extended to higher flow rates. Such steady state release functions form plane surfaces in time/flow/release space because of the simplicity of the saturation - controlled dissolution. These figures were generated by the post processor POSTP, using a data file listing solution concentrations.

Table 2. Estimated Free Energies of Formation for Oxide Components of Leached Residues from DWRG Glass, kJ/mole. Concentration data from Mendel (1984), deionized water leachate.

T	S/V	Tres	pH	SiO ₂	B ₂ O ₃	Al ₂ O ₃	Na ₂ O	CaO	SrO	CsO	Li ₂ O	Fe ₂ O ₃	UO ₃
363	10	4	9.04	-866	-1279	-1683	-694	-695	-708	-762	-755	-661	-1121
363	81	4	9.67	-861	-1274	-1681	-674	-685	-698	-743	-736	-665	-1117
363	88	4	9.84	-861	-1276	-1685	-671	-684	-697	-740	-732	-665	-1118
363	157	4	9.46	-861	-1273	-1679	-679	-689	-702	-746	-739	-662	-1118
363	266	4	9.87	-860	-1274	-1681	-668	-683	-696	-738	-729	-662	-1115
363	291	4	9.77	-861	-1275	-1682	-672	-684	-697	-741	-733	-662	-1115
363	970	4	9.83	-860	-1274	-1681	-669	-683	-696	-740	-730	-661	-1115
363	1940	4	9.91	-860	-1274	-1682	-667	-682	-695	-738	-728	-660	-1114
363	10	28	9.05	-862	-1272	-1679	-688	-691	-704	-758	-748	-661	-1119
363	81	28	9.70	-860	-1273	-1682	-673	-683	-697	-743	-732	-664	-1116
363	88	28	10.39	-860	-1279	-1692	-660	-677	-690	-733	-719	-673	-1113
363	157	28	9.58	-859	-1271	-1679	-673	-685	-691	-747	-729	-655	-1115
363	266	28	10.00	-859	-1273	-1682	-666	-679	-692	-738	-725	-662	-1114
363	291	28	20.01	-859	-1274	-1682	-666	-679	-692	-738	-725	-663	-1114
363	970	28	10.26	-858	-1274	-1685	-659	-677	-690	-734	-718	-669	-1113
363	1940	28	10.34	-858	-1274	-1685	-656	-676	-688	-733	-716	-673	-1112

7 References

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8 Appendices

8.1 Preprocessor, MANEQL

The thermochemical data base (MASTER file) that has been developed for PROTOCOL is maintained by a preprocessor program (MANEQL, MANager for Equilibrium data). This is necessary because of the number of species in the file and the additional entries for elevated temperatures (1800 species, 5000 total entries).

The preprocessor has two files, a brief instruction file and a data file (Figure 10). The data file contains literature references and values of standard free energy of formation for the set of basis species (components) at 298K and at 50K intervals from 323K to 723K. Nearly all the data at 623K and above are estimates, with high uncertainties. The instruction file contains a list of options for processing data files. These options control master file revision, isothermal file generation and basis species switching.

8.1.1 Features and Options

8.1.1.1 Master Thermochemical File Revision

The preprocessor revises the master thermochemical file as required by changes in the data. It computes equilibrium constant values for every species in the file that has a value for its free energy of formation. The revised entry is written into a storage file (NEWMAST). An instruction directs the program to either retain the temporary species identification numbers or to renumber. If renumbering is to be done, another instruction specifies the interval between successive numbers.

Changes that are processed are of three types: standard free energy of formation of a component, standard free energy of formation of another type of species and a value of $\log K$ for the species formation reaction. A change in the standard free energy of formation for a component will be propagated throughout the data file, changing values for a large number of species in which it appears. A change of standard free energy of formation for a species of any other type will be reflected in a single change in its value for $\log K$. Interpolations are carried out as required to obtain the necessary values from the component data file. If a $\log K$ value is changed and no free energy is listed, the latter will be calculated and written in the appropriate field in the storage file.

If the user does not wish to write out the species formation reaction, an option is available for interactive data input, with semiautomatic balancing. If the first component field for an entry is empty, MANEQL prompts for 4 components, bound H and O in the species, and water of hydration.

In each case where a significant change in a $\log K$ value has been made, the old entry is rewritten and is followed by the new entry, identified by an asterisk in column 1 of the data line. The purpose of this is to allow the user to see exactly where changes in the data have resulted, and their magnitudes.

A scan is made of the new storage data file to count the number of species of the five types. During this scan, if only a single entry for 298.1K for a species is listed, a Van't Hoff estimate for 373K will be attempted to provide

data for the temperature region 298.1K to 373K. Finally, data from the storage file are rewritten into a new MASTER file with their appropriate type segment headings.

When new species are added to the master file, it is advisable to examine their computed log K values for anomalies. The most common error for data input is in values for stoichiometric coefficients. These are likely to result in unusually large or small values for log K.

8.1.1.2 Isothermal File Generation

This option is called with a Kelvin temperature specification: a ready-to-use isothermal data file is generated in a two step process for any temperature to the nearest .1K from 298.1K to 700K. MINEQL reads the master file and, wherever the data permits, writes entries into a new isothermal file for the temperature requested. This is done either by selecting the appropriate entry from MASTER, or by interpolating between free energy of formation values for higher and lower temperatures.

After completion of this process, a scan is made of the new data file, counting the number of species of types 2-6. These sums and the segments containing the five species types are then written into a revised file. No data revisions or species numbering are carried out in the generation of isothermal files.

8.1.1.3 Basis Species Switching

In most cases the original MINEQL basis species were the simplest aqueous ions of the elements. It often happens, especially with cations, that these are not the only major species and are occasionally present in concentrations low enough to cause difficulties in convergence. The problem can often be resolved by switching to a major species as the basis for computation. However, manual switching for a large data base is prohibitive in terms of time and effort required. The alternative is to designate a set of auxiliary basis species and create the required logic to exchange them as required.

The status of this feature for PROTOCOL is that the switching has been set up as an option in MANEQL, exercised by setting a flag in the instruction file and specifying the identification number of the species to be switched. A subroutine is called that makes the required changes in log K values, component identification numbers, stoichiometric coefficients, free energy values, reference numbers, and chemical formulas.

The feature is a prototype in the sense that it is at this point able to do the switch for a single component at 298K, that is, from the basis species Fe^{3+} to FeOH^{2+} . The option has been tested and it generates a new isothermal data file with all the necessary data changes correctly made. Most of the logic for other component changes is therefore in place, and the feature can readily be extended as required. There are other components for which the option should prove very useful, such as uranium and silicon. For example, the silicon basis is $\text{SiO}_2(\text{OH})_2^{2-}$, which should for most purposes be converted to H_4SiO_4^0 .

8.1.2 Main Program Description

The basic functions of MAIN are to input the list of requested options (temperature, renumbering, file generation directions, basis switching) Gibbs free energies for components and water, and to call the required file generation subroutines.

8.1.2.1 Macroscopic Flow

The same technique is used in this summary as was used for PROTOCOL (section 5.1).

/ = Return to caller

> = The routine listed in boldface calls the one to the right of the arrow or when followed by a slash (/), command is returned to the routine which called it.

```
1  CLOCK    > /
2  EXIT     > /
3  SWITCH   > /
4  POZERO   > /
5  INTERCOM > /
6  BALANCE  > /
7  VANTHOFF > /
8  REWIND   > /
9  INTERPOL > 4 > /
10 POSTPASO > 8 > /
11 POSTPASM > 8 > 7 > /
12 REDT2    > 5 > 4 > /
13 REMAST   > 4 > 6 > 9 > 9 > /
```

Main Program > 13 > 1 > 11 > 1 > 12 > 10 > 1 > 2 > end

8.1.3 Input Files

8.1.3.1 MANDT1

MANDT1 is a an instruction file which contains the values, names and definitions of the input variables used to control MANEQL. The variables in this file are listed below.

TEMPIN F5.1 calculation temperature, kelvins
 IWRITE I3 - 1 revises MASTER, 2 writes NEWDT2 for MINEQL/PROTOCOL, 3
 switches a basis species
 IDS I3 Identification number of basis species to be switched
 IEDIT I3 NEWMAST edit option, 0 terminates, 1 removes corrected lines, 2
 removes both corrected lines and asterisks from NEWMAST.
 IRENUM I3 0 retains species numbers, 1 renumbers
 INTERV I3 Species intervals for renumbering

8.1.3.2 MANDT2

MANDT2 is the component data file used by MANEQL. In it are stored the component number and abbreviated symbol, valence, S_{298K}^0 , $\Delta G_{f,298K}^0$ and ΔG_f^0 at 50K intervals from 323K to 723K. The variables read from this file are listed below.

Record 1 column headings, (not currently read)
 Record 2 I3,I4x,I0F9.3 Component identification number and values for $\Delta G_{f,T}^0$
 Record 3 Reference for S_{298}^0 and $\Delta G_{f,T}^0$ (not currently read)
 Records 2 and 3 are repeated to the end of the file.

INDX 3 Component identification number
 (COMPONENT NAME) R7 (not currently read)
 (S_{298}^0) F7.2 (not currently read)
 DTIDEL F9.3 Component Gibbs free energy
 (REFERENCE) I3 (not currently read)

8.1.4 MANEQL Variables

TABTEMP - array of temperatures at which ΔG_f^0 of water and of the MINEQL basis species (components) are tabulated; 298.1K and 323K to 723K at 50K intervals
 DELWAT - ΔG_f^0 water at TABTEMP

- DELTA G_f^0 - ΔG_f^0 for a component at the selected temperature
NCOMPON - number of PROTOCOL/MINEQL components
IDS - identification number of a component to be replaced

8.1.5 Subroutines

- REMAST - implements the option to revise MASTER. REMAST generates a new master data file called NEWMAS T , which contains recalculated entries. The processing of corrections is as specified by the value of IEDIT, defined above in the input file MAND T 1 in column 1. Old entries identified by asterisks can be examined and removed manually using a text editor.
- RED T 2 - constructs an isothermal file for species, carries out component interpolations, and creates a list of component stabilities to be attached to PRODT2E. Component basis switching is also called from this subroutine.
- SWITCH - substitutes $FeOH^{2+}$ for Fe^{3+} in the basis set, which requires a change of one H^+ and one H_2O for each ferric atom in other species. Modifications will be required for switching other components.
- POZERO - converts negative values to zero for the set of component identification and species formation reaction numbers, resets the entropy at 298K, the enthalpy and free energy of formation to the replacement patterns 222.22, 333.33, and 1111.11 respectively.
- INTERPOL - carries out linear interpolations as necessary to obtain ΔG_f^0 values for four possible components at a specified temperature. INTERPOL is called from REMAST and is used in constructing a new MASTER file.
- INTERCOM - carries out linear interpolations as necessary to obtain ΔG_f^0 values for (NCOMPON) possible components at the specified temperature. INTERCOM is called by RED T 2 and is used in the construction of isothermal files. A table of the component stabilities that were calculated and used is also attached to the new isothermal file.

- BALANCE - performs an optional interactive semi-automatic balance of the formation reaction for a new species, prompting the user for H, H₂O, and O. The completed new record is then written into the master file.
- POSTPASD - reads NEWDT1 and rewrites it into file NEWDT2 with the added segment lengths for each species type.
- POSTPASM - edits NEWMAST, removing entries that have been recalculated, with an option to also remove the asterisks.
- VANTHOFF - estimates log K and ΔG_f^0 values for a species at 373K, if values of S_{298}^0 and $\Delta H_f^0, 298K$ are available.

8.2 Postprocessor, POSTP

POSTP is a postprocessor program for graphical displays of data from the PROTOCOL species distribution output file PROSUMC. For portability, this program uses the widely available CRAY-1 DISSPLA 9.0 graphics library. Since this library is publicly available, the description of the DISSPLA routines will not be presented here. It can be used on machines with 4,5,6,8 or 10 character words. Data is read from PROTOCOL files PRODT1K, PRODT2K, PROSUMC, and from its own instruction file POSDT2.

8.2.1 Features and Options

POSTP is an interactive plotting program: It displays options and instructions. The user defines the graph as follows:

1. A list of 14 parameters for ordinate and abscissa is displayed, two to be selected.
2. A list of the four combinations of log arithmetic and linear scales is displayed, one to be selected.
3. A list of available components is displayed, any number to be selected.

The program checks the selections for compatibility with the data in file PROSUMC. Values for each component are compared with the succeeding component's values. If the variation in data is too large to plot on the selected scale, the incompatible component is displayed along with a deletion option. After compatibility checking is completed, an automatic axis

scaling option is offered. If automatic scaling is not chosen, starting and ending points and interval width are read from file POSTDT2. The program checks the selected scale type for compatibility with data and changes it, if inappropriate. Whenever a scale change is made, a message indicating the change is displayed.

8.2.2 Program Description

8.2.3 Input Files

8.2.3.1 POSTDT2

POSTDT2 is the instruction file which controls the postprocessor. The following features are currently available and can be requested by text editing of the input file.

- Arbitrary plot size and orientation

- Specifiable title, frame, grid, ticks and connecting lines

- Automatic legend write

- Fourteen character styles, some with shading options

- Nineteen symbol options

- Segmenting of curves for arrays with zero values

- Multiple curves on each plot

- Sorting option to arrange abscissa values in monotonically increasing order.

8.2.3.2 PROSUMC

PROSUMC is described in section 6.2.7.3. POSTP has been dimensioned to read up to 100 increments, 100 components, and 12 parameters. PROSUMC may also contain precipitated solids listed by identification number. These are not currently read by the postprocessor.

8.2.3.3 PRODT1K

POSTP reads PRODT1K to determine NCOMP, the number of components written into PROSUMC (record 17, I3 format).

8.2.3.4 PRODT2K

POSTP reads PRODT2K to determine NSIMAX, the maximum number of increments (record 17, I1 format).

8.2.4 Data and Control Variables

NSEGH	I2	plot segment number
LHED1	A80	character string for first line of plot heading
LHED2	A80	second line of heading
ABSCI	E9.3	abscissa, variable to be plotted on the x axis
ORDIN	E9.3	ordinate, variable to be plotted on the y axis
IPLST	I1	list of variables to be plotted
MKDEF	I4	instruction; identification number of symbol to be plotted
NSRTA	I2	flag to sort abscissa values into monotone sequence
NACTV	I2	flag to plot current subsegment
NDRCT	I2	1 directs subroutine input to segment read, 2 to subsegment
LALPH	I2	pointer to alphabet
IFRAM	I2	value greater than 0 enhances plot frame
NTIXX	I2	number of ticks per division on x axis
NTIXY	I2	number of ticks per division on y axis
NHEDN	I2	number of lines of heading
IMARK	I2	pointer to connect plotted points
ICONL	I2	pointer to type of connecting line: solid, dot, dash
ISCLE	I2	scale pointer: 1=linlin, 2=loglin, 3=linlog, 4=loglog
XSTRT	E9.3	x axis starting value
XNTRV	E9.3	x axis interval
XFINI	E9.3	x axis end value
YSTRT	E9.3	y axis starting value
YNTRV	E9.3	y axis interval

YFINI E9.3 y axis end value
 XCYCL E9.3 number of cycles in x if log plot
 YCYCL E9.3 number of cycles in y if log plot
 NSTYL I2 character style pointer
 IFILL I2 pointer to fill shaded character styles (for NSTYL >7)
 SIZEX F5.2 page size, x direction
 SIZEY F5.2 page size, y direction
 HEIGH F5.2 character height, inches
 AR2DX F5.2 x distance for area2d call
 AR2DY F5.2 y distance for area2d call
 GRARG F5.2 grace margin, inches
 NPLTS I2 number of plots on each graph
 NSIMAX I2 number of time increments
 NCOMP I3 number of components
 YY E9.3 dummy variable, to check record for noncomponent
 INCRNO I2 current increment number
 YEARS E9.3 current time
 LWN A4 component chemical formula
 ZZ E9.3 numerical component data entry
 KKK I2 abscissa variable
 JJJ I2 ordinate variable
 NLINS number of curves on a plot: required for legend
 NCNTR counter for number of points in a plot segment
 ISEGM flag to indicate whether a segment is waiting to be plotted
 MARKR segment plot symbol
 ENDAT marks end of segment data input
 LMENT chemical element for which output data is to be plotted

8.2.5 Subroutines

MAIN - The site dependent linkages have been grouped in a block of coding for easy replacement when necessary.
 INPUT - reads the general run instructions and data segments
 SETUP - writes plot headings and sets up scaling
 PLOTT - constructs curve segments from variable arrays, draws the segments, and writes the legend

Figure 1 PROTOCOL Files

Figure 2 Computed Aqueous Silica Concentrations
as a Function of Temperature. Amorphous Silica
in Contact with Static Water at pH = 6.

Figure 3 Computed Changes in Dissolved Silica Concentrations as a Function of Flow Rate. Amorphous Silica at 313K and pH = 6.

Figure 4 Computed Effects of Surface Area on Dissolved Silica Concentrations. Amorphous Silica in Static Water at 313K and pH = 6.

Figure 5 Computed Effect of Initial Silica Concentration on Dissolved Concentrations. Amorphous Silica in Static Water at 313K and pH = 6.

Figure 7 Estimated Steady-State Releases of Species
from DWRG Surface Phase. Flow = 10 ml/day, T = 373K

Figure 8 Estimated Steady-State Releases of Species
from DWRG Surface Phase. Flow = 10 ml/day, T = 373K

Figure 9 Release Surface for Calcium from DWRG
Surface Phase, Function of Flow Rate. $T = 363K$

Figure 10 Preprocessor Files