DBCreate: A SUPCRT92-based Program for Producing EQ3/6, TOUGHREACT, and GWB Thermodynamic Databases at user-defined T and P

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Thermodynamic databases are critical for modeling geochemical processes associated with aqueous species, redox, mineral, and gas solubility reactions. The earliest thermodynamic databases were published in the late 1960s and 1970s (Robie and Waldbaum, 1968; Helgeson, 1969, 1978; Robie et al., 1979). The adequacy and accuracy of such thermodynamic databases directly affect the capability of geochemical models. Therefore, it is essential that the databases are continuously revised and maintained over time as more accurate or revised data become available. SUPCRT92 (Johnson et al., 1992) has served as the standard computational tool to achieve this task. It is a flexible program for calculating the standard thermodynamic properties of reactions among aqueous species, minerals, and gases at given temperature (T) and pressure (P). However, difficulties emerge in using it to produce thermodynamic databases for geochemical modeling programs such as

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the Geochemist's Workbench (GWB) (Bethke, 2006), EQ3/6 (Wolery et al., 1992), and TOUGHREACT (Xu et al., 2006). To generate the required databases for these programs using SUPCRT92, the conventional method is to first calculate all requisite data from SUPCRT92 via a user-interactive interface, then manually entering all data into the original database in the original format. This process is time-intensive and error-prone. To avoid these difficulties and facilitate efficient alteration and creation of geochemical thermodynamic databases, we have developed a software program, DBCreate, which rapidly (order of magnitude of minutes) produces geochemical databases at user-defined T and P. One example of the application of this program can be found in Tutolo et al. (in review). The DBCreate package, as well as the SUPCRTGRID (our modified version of SUPCRT92), can be found at *http://z.umn.edu/dbcreate*.

DBCreate is an interactive FORTRAN90/95 program that consists of two functions, one which generates a series of SUPCRT92-formatted reaction (RXN) files, and the other which produces an objective database (the user-required database). The RXN files, which have a *rxn* file-name extension, contain reactions from the source database (e.g., data0.dat formatted for TOUGHREACT and EQ3/6 or thermo.com formatted for GWB). The objective database contains newly calculated equilibrium constants from a series of SUPCRT92-formatted plot (PLT) files, 8-point P/T grids from a SUPCRT92-formatted CON file, and the standard thermodynamic data at 25°C and 1 *bar* from a SUPCRT92-formatted direct-access thermodynamic database (here and after, DPRONS.DAT). The flow of information between DBCreate and SUPCRT92 is schematically illustrated in Fig. 1. In order to

accelerate the process, we developed SUPCRTGRID, which is an automated, rapid-input/output revision of SUPCRT92, suited for DBCreate. The generic descriptions of CON, RXN, PLT files, and DPRONS.DAT can be found in Johnson et al. (1992).

The core of DBCreate contains four subprogram units: i) A reading module that reads aqueous species, minerals, and gases reactions from the source database and writes these reactions into the file *species.txt* which labels each reaction with a descriptive title, the species stoichiometry, and the species name; ii) A RXN-maker module that reads reactions from *species.txt* and only assembles those reactions, which exist in the user-defined DPRONS.DAT file, into a series of RXN files in SUPCRT92 format (an auxiliary file *spxNotFound.txt* is created at the same time to record those reactions which contain species that cannot be found in DPRONS.DAT); iii) A grid module that reads the equilibrium constants from all of the *kxy* files, and places these aggregate data into grid format in the file *logK.grid*; the values of the equilibrium constants are set as 500.0000 for those reactions which are beyond the P/T applicability range of SUPCRT92, and they are recorded in the file *logK.bynd*; and iv) A writing module that produces the objective database which contains the 8-point P/T grid from the CON file, all of the equilibrium constants from *logK.grid*, the standard thermodynamic data from DPRONS.DAT, and their references.

We generate a series of RXN files because SUPCRT92 only accepts a maximum of 50 reactions in a single RXN file. DBCreate monitors the number of reactions in each RXN file to assure that it does not exceed 50. Currently, DBCreate only supports Type-D CON file (see Johnson et al. (1992)). How-

ever, it is easy to extend the code to include other types of CON files. The user can also produce an objective database using DBCreate without a CON file if the classical EQ3/6 8-point P/T grid is used: 0.01, 25, and 60°C at 1.01322 bars and 100, 150, 200, 250, and 300°C along the H_2O vaporization curve. If this is the case, the option of "T-P-D grid & option switches" in the *kxy* files will be automatically specified as "file not saved" by SUPCRT92. Once DBCreate identifies this keyword, it will insert this 8-point P/T grid into the objective database by itself.

DBCreate is designed to keep interactive sessions to a minimum. Warnings, suggestions, and progress information are provided on the screen where appropriate. In the following listing, to extract RXN files for SUPCRT92, follow the sequence of square-bracketed prompts marked by an E superscript. To produce an objective thermodynamic database, follow the sequence of prompts marked by a G superscript.

$[1.0]^{E,G}$ Choose one of the above applications (1 or 2).

Respond as indicated with '1' or '2'. Specifying '1' indicates that RXN files are to be extracted from an existing thermodynamic database (proceed to [2.0]); Specifying '2' indicates that a new thermodynamic database is to be produced based on *kxy* files (proceed to [2.0]).

$[2.0]^{E,G}$ Choose one of the above databases (1 or 2).

Respond as indicated with '1' or '2'. Specifying '1' indicates that the following operations are to be performed on a thermodynamic database in EQ3/6 format (proceed to [2.1]); Specifying '2' indicates that the following operations are to be performed on a thermodynamic database in GWB format (proceed to [3.0]).

[2.1]^E Specify file name of source thermodynamic database:

Enter the appropriate file name of the EQ3/6- or GWB-formatted source database. If the specified file does not exist in the current folder, "The file does not exist! Try again..." will appear and query [2.1] will be repeated; otherwise, the extraction process will start; proceed to [2.2].

[2.2]^E Specify direct-access thermodynamic database:

Enter the appropriate file name of the direct-access database. If the specified database exists and is in the required format, the extraction will proceed to completion and the list of the output RXN files will be printed on the sreen. If the database exists but is in an inappropriate format, the program will terminate abnormally. If the database does not exist, query [2.2] will be repeated, and "The specified direct access thermodynamic database <*filename*> does not exist. Try again..." will appear.

[3.0]^G Enter file name of the source thermodynamic database on which the reactions are based:

Respond as indicated. If the specified file exists, proceed to [3.1]; otherwise, "The file does not exist! Try again..." will appear and query [3.0] will be repeated.

[3.1]^G Enter file name for the objective thermodynamic database:

Respond as indicated. Before the program proceeds to transfer equilibrium constants from all of the *kxy* files to a *logK.grid* file, it will first check the existence of the reqiured CON file and the direct-access thermodynamic database, as well as the matches of option switches among *kxy* files and the CON file. If the required checks go well, the execution will complete; otherwise, follow the given instructions to correct the errors, e.g., the lack of

required files and/or inconsistency of option switches among *kxy* files and the CON file.

There are two minor issues with the DBCreate package: a) using the *system* function which is system-dependent and environment-dependent to rename/delete a file or perform a directory listing; and b) leaving users to fulfill the references copying from the corresponding sequential-access version of the direct-access database to the newly produced objective database. The former issue can be resolved by passing the appropriate command to the *system* function according to the operating system. The latter issue is a result of accepting the direct-access file DPRONS.DAT option in SUPCRT92. Nonetheless, the DBCreate package itself facilitates the production of pressure-, temperature-, and problem-specific geochemical thermodynamic databases in a convenient and fast way while it minimize the possibility of introducing typo errors. It should be noted that producing an objective thermodynamic database at user-defined P/T without DBCreate is labor-intensive, time-consuming, and tedious.

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Figure 1: Schematic dataflow through the DBCreate software package. DBCreate extracts reactions from the source databases and assembles them into a series of RXN files. The RXN files, as well as user-defined CON and DPRONS.DAT files (indicated by dotted boxes), are input files for SUPCRTGRID. DBCreate takes all of the *kxy* files (PLT files from SUPCRTGRID outputs), together with the CON and DPRONS.DAT files to produce objective databases. Follow dashed arrows to generate RXN files, and solid arrows to produce the objective database.