User's Guide for FREED

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FREED is a thermodynamic database program developed originally at the Department of Metallurgical Engineering, University of Missouri - Rolla, with support from the Center for Pyrometallurgy and the U. S. Bureau of Mines. Excel '97 version developed by Mr. Richard Luu, under the direction of Dr. Arthur E. Morris, Thermart Software. The reaction feature (converted from THERBAL by Semih Perdahcioglu) was added in January 2007 (Excel 2002) and updated to Excel 2016 in September 2018. FREED is free, but technical support is not. FREED is the database program for THERBAL, FlowBal, and other Thermart software products. FREED is one of several Excel-based computational programs developed by Thermart Software, as described on the Thermart web page **(www.thermart.net).**

Abstract

FREED (FRee Energy and Enthalpy Database) is a program in **Excel** for storing and managing thermodynamic data. It was developed originally for preserving and enhancing the U. S. Bureau of Mines thermodynamic database. In its present form, the database also includes about 50 species from USGS Bulletin #2131 and some from other sources. New databases can be created for the user's convenience, and subsets of any database can be created for use by other programs. This User's Guide contains information about FREED and its use. Help buttons will give hints during FREED use. Details about the program and the USBM database are in **Appendix A**. A description of examples is given in **Appendix B.** This guide is not intended to help with Excel. Users are assumed to have a basic understanding of Excel, physical chemistry, and chemical thermodynamics. **The reference pressure and temperature for FREED data is one atmosphere and 298.15 K.** FREED data is stored in units of gram-moles, the thermochemical calorie, and degrees Kelvin. FREED's tools can report the data in Celsius temperature and Joules.

Getting Started

FREED consists of 2 Excel files: (*FREED 11.0.xlsm* and *FREED Examples.xls*), plus this User's Guide, an rtf file. FREED contains a title and database worksheet, and has all the program subroutines and functions that manipulate the database. The special worksheet (PureElements) will be described later. FREED is installed by copying it to your PC. You are ready to use FREED when FREED is opened. FREED 11.0 is the version adapted to work in Excel 2016. There is no floating toolbar; instead, the toolbar icons are stored in the ribbon at the top of the worksheet. Click on Add-Ins, and you will see two icons in the upper left-hand corner of the ribbon.

Warning! If you already have an older version of FREED on your PC, you must delete it before trying to install the new files, *especially* Freed.xla, which may be located in the Excel Library folder. To be sure, do a search for any old Freed.* files, and *delete all of them*.

The workbook FREED Examples.xls contains several worksheets showing examples of the use of FREED. Each of these example worksheets has one or more comments that explain the point illustrated by the example. **Appendix B** in this guide gives a brief summary of the examples. Users are urged to examine these examples.

FREED is started in the same manner as any other Excel file. Open and you will see a Title page and some worksheets. The Add-ins toolbar contains 2 buttons: FREED and Exit (X). Normally, you should not need to make any changes in FREED itself; but if you do make any changes, you can save it with a new name. Add a comment to indicate the nature of the changes. Click on the Start FREED button to begin using the program.

A worksheet titled *Database* contains the preloaded database, which contains the entire USBM database, plus a number of species from several other databases. Data for approximately 2400 species are stored, mainly as coefficients describing heat content through several ranges of temperature, from which free energy of formation (dG*f*) coefficients are calculated. Worksheet *PureElements* is involved in this calculation, and should not be changed except by experts in thermodynamics. An index to the elements in the database and the meaning of the color codes are included as comments in cell D6

and D8. Use the index to help you navigate the database.

The data for each species occupies one row. Each species is characterized by its *formula*, *name*, and *descriptor*. The latter term is used to distinguish between species with the same name and formula, such as gaseous and liquid forms of the same species, or between metastable solids with a different crystal structure. Where available, a mineral name and density at 298.15 K are also listed. The elements colored light green in column A are the standard (reference) state elements. The other color coding (yellow, light turquoise, tan, rose and gray) are described in a comment at the beginning of the database, and in following sections of this Guide.

Species are listed in a certain order, depending on the formula. First is the monomer element, followed by species containing a parenthesis, then species with subscript amounts less than 1. Next are species containing more than 1 mole of the element. Last are species containing one mole of the initial element. However, note that a subscript like "12" precedes a subscript like "2". The ordering logic is illustrated best by examining the listing for the first few Ca-, Na-, and Fe-containing species. Of course, you may reorder the species any way you want using cut and paste. Insofar as possible, the Bureau's usage governed the selection of which element should be listed first and second in a formula. Care should be taken in searching for all species having certain elements. For example, OH is listed with the O-containing species. The formula could just as well be HO, and listed with the H-containing species. Other database vendors use different listing systems.

Columns G and H list the heat of formation from the elements and entropy at 298.15 K. The free energy of formation and all other thermodynamic functions are calculated from this information in a manner described later. (For simplicity, the number 298 will be used henceforth to designate 298.15, the basis temperature for FREED). Column I gives the maximum temperature for the species, and J gives comments about the phase changes for the constituent elements of the species and other useful information. Column K lists the reference from which the data was taken. More details on the contents of these columns, and a description of the data in the other columns is given in Appendix **A** to this Guide. You may search the database by pressing <Ctrl F> and typing in the formula of the species of interest. Excel's *filter* feature may also be

used.

For test purposes two imaginary elements and some species involving them were created and added to FREED: Jalium and Zymium. You may play around with species involving these elements or create new species from them for testing, without any danger of corrupting the database.

FREED can also contain substances that are mixtures of other species, but not chemically bonded. These are designated in the database with a tan color in column A. For example, air is listed as $N_{1.78}O_{.42}$ (1 mol of dry argon-free air), and is located at the beginning of the N-containing species. Summing appropriate data for each species created several copper concentrates (mixtures of various amounts of $CuFeS_2$ and FeS_2). The concentrates contain 34.9 to 39.0 %S, and 34.6 to 27.1% Cu. The dG_f of air was calculated by assuming ideal mixing of the elements, and for the series of copper concentrate species, the dH_f, S_f, and Cp values were the proportional sum of those for the constituent species (chalcopyrite and pyrite). Additional mixed-substance species may be created by the user, and used as needed, in a similar way. Mixed-substance species are for the convenience of the user as *entry*-species for FREED's Reaction option and other programs. They should **not be selected as possible <u>product</u> species in FREED's Reaction feature or the THERBAL equilibrium program!**

Other types of species in FREED are non-physical species intended to represent the thermodynamic properties of solution phases. For example, the species $Pb_{.25}Sn_{.75}$, $Pb_{.5}Sn_{.5}$, and $Pb_{.75}.Sn_{.25}$ can be used in simulating liquid solution behavior in the Pb-Sn system. Similarly, supercooled and superheated liquid species are listed (e.g., Pb(l) and Sn(l) for use in solution phase modeling, with a rose-colored cell. Finally, species that exist **only as solutes** have been created for use by THERBAL in dealing with non-ideal solutions. These are denoted by a gray fill in the formula cell, and a (d) in the descriptor cell to denote "dissolved". The dG_f and dH_f of these species have been set = 0 for use in **THERBAL only;** these species have no other use. More information on the creation of these special species is given in Appendix A.

FREED's *Main Menu* appears as a floating toolbar. Click on the help button for hints on using the Main Menu. The left side of the Main Menu is an index window displaying about 25 species and their descriptors. Search for species by typing in the

first letter of the species formula (such as P, which will take you to the first species containing Phosphorus). Typing <Ctrl Home> or <Ctrl End> takes you to the beginning and end of the index.

Except for the Reaction and Coefficients tools, species must be selected from this window in order to use the various features of FREED. Highlight one or more species (hold down the <Ctrl> key to highlight more than 1 species). Click the >> button to copy the species to the selection window. Pressing the << button removes a Selected species, and pressing <> clears the Selected List windo). You may select the same species more than once, which can be useful in creating a subdatabase for THERBAL. When the desired species have been copied to the selection window, select the desired action from the Options menu. As described below, certain options operate only on the first-listed species in the window.

If you have purchased THERBAL and have any trouble running FREED or using any of its features, please send an email to A. E. Morris (thermart@att.net) describing your problem. State the version of Excel and the Windows operating system you are using. There is no guarantee that help will be forthcoming.

Using the Features

FREED is more than just a database. It has several options for manipulating the database, making calculations with the data, and other things. In addition, all of Excel's powerful features can be used on the data (such as Goal Seek, Solver, Regression Analysis, and charting tools). The data can also be formatted in tabular form, and exported to documents. Advanced users can write macros to manipulate the data in other ways. The section below describes the various features of FREED.

The Main Menu window lists FREED's features : *Properties, Tables, Calculator, Datafiles, Graphics, Coefficients,* and *Reaction*. All but the Coefficients and Reaction features operate on the Selected List species. The results from operating a feature appear as worksheets. The results from operating some features erases the prior results and some do not; this is discussed in later paragraphs. The *Cancel* button returns you to the previous screen. A brief description of each option will appear when you rest your mouse cursor on any button for a moment. This type of descriptive text

generally appears anyplace where you have a choice of options. There are a couple of other features that are not displayed on the Options window; these are used only for managing the database.

As an introduction, FREED worksheets have been created in the main FREED workbook for some of the above features. Freed-xmpls.xls has additional worksheets. Each worksheet contains a comment to point out significant features. See **Appendix B** for more details about the example workbook.

The *Properties* feature calculates a summary of the thermodynamic data for a species in the form of atomic and weight composition and the coefficients of the Cp, H_T-H_{298}, dH_f and dG_f equations. Different units for temperature and energy can be chosen, but of course all equations require Kelvin for temperature units. The *Tables* feature shows tabular values for various thermodynamic properties of a species, and also contains the same information as the *Properties* feature. A major break in the table indicates a transformation in the species, and a dashed line in the table indicates a transformation in one of the constituent elements. Please refer to the entry for the elements making up the species for information about the transformations. The lower limit on any table is 298 K (25°C) regardless of the value entered in the minimum temperature window. Enter 300 (for K) or 100 (for °C) to get table entries in even 100-degree intervals.

The *Datafiles* feature is much like the Properties feature except that no value headings are given, and only degrees K can be used. The Datafiles format is designed to be used as an input file for other calculational programs that need thermodynamic data. The single digits in column B indicate the number of equations that follow. For all of these options, a list of the selected species will appear in column A of the worksheet produced.

The *Calculator* allows the user specify a value of a thermodynamic property, then to calculate the rest of them. Only the first species in the Selection List is active for the Calculator feature. If the value specified is at a phase change temperature or if there are an infinite number of solutions, an error message may appear. You are advised to use the *Table* feature to examine the source of multiple answers or any error messages. Be careful in changing the temperature unit to Celsius because the range of permissible

temperatures is different in Celsius than in Kelvin. If the specified value appears more than once over the data range, all values will appear as a result of the calculation. The calculator option also produces a set of H_T-H_{298} equation coefficients for the species, in the same equation format as the Properties tool. The *Graphics* feature produces a plot of a variable vs. temperature. The chart can be customized with the usual Excel tools. You may wish to use Excel's Trendline tool to develop an equation to represent the variable as a function of T. Quite often, a two-term equation gives a satisfactory fit over a 300 to 400 degree temperature span, or a quadratic equation over a 500 to 800 degree temperature span.

In some cases, it may be desirable to add a record for which tabular data is the only type available. This requires coefficients for H_T-H_{298}. These coefficients may be obtained by entering values of H_T-H_{298} for two or more temperatures using the *Coefficients* feature. The number of equation coefficients will be equal to the number of data points entered. Enter the temperatures and the H_T-H_{298} data in the appropriate boxes, in ascending T. Be sure that no phase change temperature is in the range. The results will appear as tables of H_T-H_{298} and Cp for the entered data, for temperature in K, and H_T-H_{298} in Calories or Joules, as appropriate. OR: you can enter data in degrees C. Coefficients will be listed as a, a', a'', etc., which will correspond to the coefficients for the various temperature terms selected. Further instruction on adding new species to FREED is given in the Appendix.

In some cases, Cp data are available, but not H_T-H_{298} data. In that case, the Coefficients feature may be used to fit the Cp data to equations. An H_T-H_{298} equation can be derived from the Cp data by entering a single H_T-H_{298} data point (usually at the lowest T value). Also, Coefficients can fit dG_f data. Remember that a dG_f equation must not span a phase change temperature for the species OR any of the constituent elements. A 3-term dG_f equation (T, TlnT and a constant) is often adequate over a span of 800°. A word of warning: although the Coefficients feature is simple and quick, it isn't the best way to obtain equation coefficients from tabular data. Instead, it's better to use Excel's Regression tool, which obtains statistically-valid coefficients from all of the data. This tool is described in worksheet H-EqnFit.

The worksheets created by the Properties, Table, Calculator, Coefficients and

Datafile options are erased each time the option is used. The Graphics sheets are not. If you want to save any of the created worksheets for subsequent editing or printing, either rename them or copy selected cells to sheets in a separate workbook. The latter option allows you to answer "no" when asked if you want to save the changes in FREED when you close it. In any case, if you have changed the column widths or other worksheet formats in the FREED sheets created by the various options, **exit without saving these changes.**

Sometimes new free energy data becomes available for a species without corresponding new H_T-H_{298} data. FREED allows the user to enter free energy coefficients directly into the database by editing the free energy coefficients. This will also change the dH_f coefficients. However, the resulting record will not be internally self-consistent. Any record so altered should be indicated by adding a comment in column J. Some species were found to have errors in the tabular data, and were corrected in this manner. Such records are colored yellow in column A. Save the "custom" record by pressing <Ctrl S>. The *dGRestore* feature is used to create an internally-consistent FREED record for a newly-added species. Please see **Appendix A** (Adding a New Species) for correct use of this feature.

Finally, the *Reaction* tool allows you to determine the thermodynamic properties of a reaction of your choice. Clicking on the Reaction button brings up a dialog box that asks you to select the reactants and products from the main FREED Index. Entering a letter of the alphabet takes you to the first species beginning with that letter. You can enter a second letter to further refine the index list. Press <backspace> to cancel your letter choice(s). You must also specify a reaction name. Upon clicking OK, a new worksheet will appear with the reaction written on it. Help text viewed by clicking the Help button will tell you how to proceed. The two main options for the Reaction tool are *Calculator* and *Table*. It's best to start with the Table option unless you are quite familiar with the properties of your reaction system. In either case, be careful with the temperature limits when changing from Kelvin to Celsius units or the Calculator option may fail.

The Reaction Table tool includes a unique thermodynamic function called Overall Heat. In the *default* situation, *Overall Heat* is the sum of the heat of reaction at 298.15

K plus the sensible heats of the products above 298.15 K. For reactants entering above 298.15 K, enter the entry temperature for each reactant in row 16. **Do not enter any product temperature!** The initial reactant temperature does not affect the dHr, dGr or logKr values. It does affect the *Overall Heat* values by adding the enthalpy produced when (if) the reactants are cooled from their initial temperature to 298.15 K (this is always a negative number), reacted at 298.15 K, and then heated to the specified temperature.

You may use three different types of units in Reaction. If you use liters or grams, be aware that the reaction might not perfectly balance, in which case, a message to that effect will appear in row 26. Calculations will be made even if the reaction is not perfectly balanced. If the amount of misbalance is small, you may use the data with insignificant error. Otherwise, correct your values until the reaction balances. A useful feature of the Reaction tool are charts of selected results. You can use Excel's Trendline tool to obtain linear or polynomial equations to fit the data. The *Overall Heat* values are useful in indicating the adiabatic reaction temperature when reactants are initially at any specified temperature. Another use for the Reaction feature is to produce a set of data from which a Cp or H_T-H_{298} equation can be derived. Enter the same group of substances as reactants and products, and create a table. Use either Excel's Trendline tool on the chart, or the Regression tool on the data column to calculate the equation coefficients. Finally, the log(Krx) vs. 1/T chart is useful in obtaining a linear equation for the variables; temperature in detgrees K..

When you are finished using FREED, close it in the usual way by clicking on the small X box in the upper right-hand corner of the workbook. If you created tables and other worksheets, you might be asked if you want to save the changes you made in FREED. If you did not change anything, or if you do not want to save changes, answer "no" to the query. (It is better to save worksheets created by FREED in a *separate workbook* rather than clutter up FREED with these).

Using this Guide

This guide may be copied or removed from the title page and placed in some other convenient folder. Novice users should consult this Guide while using FREED. You can use the Find function <Ctrl-F> to seek information on a topic. Feel free to add your

own help text to this Guide, and save it. A suggestion: if cut and pasted elsewhere, configure your operating system to open this Guide as a WordPad document instead of as a Word document.

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2. Mr. Leslie McAdoo, Graduate Student in the Department of Statistics of the University of Missouri - Rolla was responsible for developing and implementing the statistical analysis of the USBM data set, and calculating the heat content equation parameters.

3. Mr. Richard Luu, Undergraduate Student in the Department of Chemical Engineering, University of California - San Diego, wrote all of the Visual Basic code for Excel, for both FREED and THERBAL. Mr. Luu is currently Chemical Engineer, General Atomics Company.

4. Mr. Semih Perdahcioglu configured and improved THERBAL's Reaction feature to operate in FREED, and made other valuable improvements.

5. Mr. Martin Alslaben reconfigured FREED to run smoothly in Excel 2016.

FREED Information

FREED is a copyrighted program developed by Dr. Arthur E. Morris (thermart@att.net), who should be contacted for information. See www.thermart.net for a description of other Thermart Software programs. Written correspondence should be sent to:

16925 Hierba Drive, #337, San Diego, CA 92128

There are other thermodynamic databases for sale, and NIST has thermodynamic data you can download from their site. A web search program may uncover other data sources. Also, see the online progcram FACT-Web, which also does simple eqjuilibrium calculations. For general information about thermodynamic functions and databases,

please look at the Wikipedia entry "Thermodynamic databases for pure substances", and the other Wikipedia entries referenced in that article. Owing to frequent additions to Wikipedia, new information may appear since this guide was written.

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Appendix A: Program Details

The USBM database contains all published and unpublished U.S. Bureau of Mines thermodynamic data, tabulated over a period of years by the Bureau's Albany Research Center. The vast majority of the data was published in four Bulletins. For the FREED project, the data was supplied by the Bureau in the form of computer disks containing tabular values for Cp, H_T-H_{298}, S, etc., in calories. Column K in the database lists a reference number for each Bulletin as follows:

1. Bulletin #672 (1982): Elements and Oxides
2. Bulletin #674 (1984): Halides
3. Bulletin #689 (1987): Sulfides
4. Bulletin #696 (1995): Carbides, Nitrides, etc.

In some cases, the data provided by the Bureau on disks corrected some errors in the original Bulletins, and extended Tmax. A few species were on the disks that were not in any of the Bulletins. Also, some species have been added to FREED from non-USBM data. In particular, all species in USGS Bulletin #2131 that **weren't in the USBM Bulletins** (about 50 species) were added to FREED. These are mainly complex mineralogical species. However, all species added from non-USBM sources are likely to be internally inconsistent, since the dG_f was calculated from USBM data on the elements (PureElements worksheet), plus other-source data for the species. The source of data for non-USBM species is indicated by a letter (J = JANAF, B for Barin, FACT for the FACTSage program, and HK for data published by Dr. Herb Kellogg), or a comment that briefly describes the source.

The original data sources contain considerable bibliographic and other information about the source of data used by the compilers. Persons interested in such information should consult the original source publications. You should always verify the FREED data for a species before using it for any critical application.

Thermodynamic data is stored in FREED as entropy and heat of formation at 298.15 K, coefficients describing the heat content vs. temperature, and temperatures and heats of transformation. Each species is described by three terms: *name, formula,* and *descriptor*. The reference pressure is one atmosphere. Species with the same name

and formula have a different descriptor. For example, if one wanted to add a new data record for zinc oxide ZnO, (c), a different descriptor would be required, such as (s).

Data Processing

The original data was supplied on computer disks as smoothed tabular heat content data. The data was generally the same as that printed in the USBM Bulletins, but minor changes were made in several species in order to fit the data across phase changes, or correct errors. The original Bulletins contained equation parameters for Cp, H_T-H_{298}, dH_f and dG_f, but these equations often failed to adequately reproduce the tabular values. This was because the equations in the Bulletins often contained fewer terms than was used originally by the Bureau to smooth the experimental data. Therefore the tabular data was analyzed statistically with the SAS program to obtain constants for the following equation:

$$H_T-H_{298} \text{ (calories)} = AT + BT^2 + C/T + DT^{1/2} + ET^3 + F. \qquad [1]$$

The statistical fitting technique forced $H_T-H_{298} = 0$ at 298, forced the calculated heat content to equal the tabulated values at transition temperatures, and forced the heat capacity (Cp) at 298 to equal the tabular value. One H_T-H_{298} equation is required for each species phase, and a plot of H_T-H_{298} vs. T is discontinuous at each phase change temperature. A few errors found in the tabular data were corrected. The fitting process selected the fewest number of parameters capable of giving an "adequate" correlation between the original tabular data and the values calculated by the equation. In all but a few cases, the calculated heat content differed from the table value by less than 0.1% and by less than 10 calories. In some cases, the heat content could not be adequately fit by one six-term equation over the entire span of temperature. This required the use of two or more equations, and is indicated in the database as a transition marked "Eqn Break". A particularly difficult region to fit was near a Curie point or a Lambda transformation. For example, see the record for nickel. The number of significant figures used for each parameter in Eqn. 1 was chosen to give a precision of ±1 cal. The liquid - gas transition temperature is based on a vapor pressure of 1 atm.

The upper temperature limit (Tmax, column I) on many of the species in the USBM database was below that desired for some calculations. Tmax for the datafiles for such

species was extended by taking the requisite data from the 3rd Edition of the JANAF Tables, and fitting it to a 2, 3 or 4-term H_T-H_{298} equation, such that the value of H_T-H_{298} at the former Tmax was the same (or virtually the same) as the USBM value. Species with an extended Tmax have the cell in column I tinted light turquoise. A letter J indicating such an extension is included in the reference cell (column K) for such each species. In some cases, near the USBM Tmax, the USBM and JANAF data deviated significantly. When there was a difference in the data for heats and temperatures of transition near or above the USBM Tmax, JANAF data were used. Accordingly, the extended data may not be the most accurate, and is intended solely for the convenience of the user in obtaining estimated values. The user is advised to use caution in using the extended data for any critical calculation, and to refer to the source data in that case.

The heat capacity (Cp) was calculated by taking the derivative of the H_T-H_{298} equation with respect to T, giving an equation of the type:

$$Cp = a + bT + cT^{-2} + dT^{-½} + eT^2 \qquad [2]$$

where a = A from Eqn. 1, b = 2B, c = -C, d = ½D, and e = 3E.

Cp is infinite at phase change temperatures, and is discontinuous at second-order transformations (like Curie points). The entropy (S) is calculated by integrating the Cp/T equation over each phase stability range, and adding the entropy of transformation at phase change temperatures. The constant of integration is obtained by using the value of S(298).

The heat of formation $dH_f(T)$ is calculated by taking the difference between the H_T-H_{298} for the product species and the constituent elements, plus $dH_f(298)$. Values of $dH_f(T)$ are discontinuous at phase change temperatures for the species and the constituent elements.

The basic thermodynamic data is stored in units of thermochemical calories. Columns A through J contain the basic information about each species, as discussed earlier in this guide. Column K is the reference to the Bulletin from which the data was taken. Columns L and M give the number of heat content (Ht) and free energy (dG_f) equations for the species, and columns N - S list the coefficients of the first H_T-H_{298} equation, from 298 to the first transition temperature (or Tmax if there are no transitions or equation breaks). Column T is an upper temperature limit (Tmax for the species, a

transition temperature or an equation break temperature) for the first H_T-H_{298} equation, column U is the heat of transformation, and column V contains a comment about the type of transformation. The term "Lambda" refers to any second-order transformation. The number of columns devoted to the H_T-H_{298} equation coefficients depends on the number of equations listed in column L. If L = 1, then 7 columns (N - T) are required. Nine columns are required for the first H_T-H_{298} equation if L>1 (N - S for the coefficients, T for the first transition temperature, U for the heat of transition, and V for a comment describing the type of transformation). This series of 7 or 9 columns is repeated for every H_T-H_{298} equation.

In some cases, the column may be too narrow to show all of the significant figures in parameters entered in numerical or scientific notation. Check to be sure by placing your cursor on the cell, and look in the formula bar. In any case, the complete cell values are used in calculations.

The column headings (like A*T, B*T^2, T1, etc.) refer specifically to the first H_T-H_{298} equation range. Column headings from W on are blank because the values in these columns do not necessarily refer to H_T-H_{298} equations, as described in the next paragraph. The H_T-H_{298} series termination is indicated by a **bold** temperature, which is also the same as the value of Tmax in column I. This indicates the end of the H_T-H_{298} equation parameter values.

The next series of columns are the parameters for the dG_f equations; note that elements in their standard state do not have dG_f equations. The parameters of the dG_f and dH_f equations are calculated from the $dH_f(298)$, S(298) and H_T-H298 equations according to standard procedures described in thermodynamics textbooks. This procedure assures that the heat content and free energy values are internally consistent as required by the laws of thermodynamics. As a reminder, this procedure uses data from the species AND the constituent elements (as listed in the PureElements worksheet) in making the $dG_f(T)$ and $dH_f(T)$ calculation, therefore, any changes in $dH_f(298)$, S(298) or H_T-H_{298} for the species or the constituent elements will result in a change in the $dG_f(T)$ and $dH_f(T)$ equation parameters. (Note--the data for the constituent elements is on the PureElements worksheet, and should not be changed without expert advice). Users wishing to modify the database should first have a clear understanding of how the various

functions are calculated. If there is any doubt, the program developer (Dr. A. E. Morris) should be contacted for further information.

The format of the $dG_f(T)$ equation is:

$$dG_f(T) = AT\ln(T) + BT + CT^2 + DT^{-1} + ET^{1/2} + FT^3 + G$$

(where the A, B, C, etc. values are <u>not the same</u> as the A, B, C, etc. values in the H_T-H_{298} equation). The $dG_f(T)$ function is not discontinuous at phase change temperatures of the species and constituent elements, but does undergo a change in slope at those points.

$dS_f(T)$ is not explicitly calculated for the species by FREED. At any temperature the following equation is valid:

$$dG_f(T) = dH_f(T) - TdS_f(T)$$

Seven columns are reserved for each set of the dG_f equation parameters, and these columns are bounded by columns listing the temperature range (except the first temperature, which is understood to be 298). The final dG_f equation terminates with the **bold** font temperature = Tmax.

After this, there are columns containing integers that relate to information about the constituent elements. The first number is the number of elements in the species (e.g., 3 for $CaCO_3$ and 2 for $CaCl_2$). The next number indicates the row in which the first element is located in the PureElements worksheet (this sheet should not be changed to avoid corrupting the database). The next number is the number of mols of the first element, and the next two numbers give the location of the second element and its number of mols. This sequence is repeated for all of the constituent elements.

The locations of the various equation parameters and other species information among the database columns can be confusing, since species have different transitions and numbers of H_T-H_{298} and dG_f equations. Any such confusion can be cleared up by comparing the values from the Properties worksheet with the values in the database row for the same species.

As mentioned earlier, the constituent elements in their reference (standard) states are involved in the calculation of $dH_f(T)$ and $dG_f(T)$. The reference elements are defined as those elemental phases that have a zero $dH_f(298)$. By definition, their dG_f is zero at all temperatures, hence a zero will appear in column M. These elements are colored

light green in column A, and are the elements listed in the PureElements worksheet. Note that the standard state for an element can be a defined state, rather than the most stable state, as in the case for P. Some thermodynamic compilations might have different standard states for the elements than those chosen by the Bureau of Mines, which is another good reason to take care in using thermodynamic data from multiple sources in process calculations. The standard state elements may have appropriate comments in column J for further clarification.

In a very few cases, some small errors or discrepancies were found during the statistical analysis of the USBM data. Most of these were corrected, and if the dG*f* values are not those created by FREED in the normal way, the species is designated yellow in column A, with a comment in column J. In several cases, it was not possible to determine which numbers were incorrect. Comments have been made in such cases, and the user may wish to refer to the original Bulletin.

A common inconsistency occurred during creation of the FREED record for the gaseous phase of a species when compared to the data for the reference state species at the boiling point. For example, a comparison of the data for Ca(c,l,g) above the boiling point to that of Ca(g) should show a value of zero for dH*f* and dG*f* of Ca(g), but in fact, the values were several calories. The cause could have been slight tabular errors in the data, the statistical residuals obtained during fitting of the tabular data to equations, or rounding off the boiling point to ±1°. Where this occurred, the dG*f* parameters for the gaseous species were set equal to zero in the database. The cell containing the species name was then set to yellow.

PureElements Worksheet

This worksheet contains necessary information about the elements in their standard (reference) state used in FREED's calculations. By definition, the standard (or reference) state for an element is that form having a zero value for the heat of formation at 298 K. That element is designated by a background color of light green in column A. Information from this sheet is used when the dGRestore option is activated, such as when adding a new species, or restoring internally self-consistent dG*f* data after altering the dG*f* data. If data for the reference state elements are changed on the Database worksheet,

there will be no effect when calculating the dG*f* of a species that contains that element. Only by changing data in the PureElements worksheet will there be an effect. For example, if the parameters for H_T-H_{298} of an element are updated in the PureElements worksheet, the changes in the element and all species containing that element are implemented *only by using dGRestore for that element and the associated species*. The sheet data should not be changed without obvious cause. Users who need to make changes in the PureElements sheet should contact an expert first to obtain proper advice.

Adding a New Species

A new species can be added to the "Databases" worksheet by carefully following a few steps. The species data should be entered into the last row of the database and the results checked by printing a table. Once the data are deemed valid, the row can be cut and pasted to the proper location in the sheet. In order for the new species to be properly used, the following data must be entered for the new species:

- *Chemical formula* (column A) is entered in the conventional chemistry textbook format; however, the mol amount of a constituent element need not be in subscript format. Examine the existing formula format for use of parentheses for complex species.
- *Descriptor* (column B) is put inside parentheses. If the chemical formula is the same as an existing species, the descriptor **must** be different. For example, to enter data for Fe_3O_4 from a non-USBM source, the new descriptor must be different than the existing descriptor for Fe_3O_4.
- *Name* and *Mineral Name* (columns C & D) are optional.
- *Density* (column F) in g/cm^3 unit is optional.
- *Comment* and *Reference* (columns J & K) are optional.
- *Enthalpy of formation from the elements* (column G) at 298.15 K ($dH_{298.15}$) in Calories unit.
- *Entropy* (column H) at 298.15 K ($S_{298.15}$) in Calories unit.
- *Tmax* (column I) in K unit.
- *Number of equations of H_T-H_{298}* (column L).

- For each H_T-H_{298} equation in a temperature range, starting with the initial temperature, enter up to six coefficients (*a, b, c, d, e* and *f as* described for H_T-H_{298} in Data Processing section above), ending temperature, and transition enthalpy. The transition description may be entered. The temperature in the first equation should not to be entered; it is understood to be 298.15 K in the database. The ending temperature in the last equation must be equal to Tmax.
- If the source of the data is tabular, it will be necessary to derive values of the coefficients from the tabular data. A simple way is to use the coefficients feature in FREED to fit either H_T-H_{298} or Cp. A minimum of 2 temperature - H_T-H_{298} data points are required, which indicates a constant Cp. If Cp is nearly linear with T, select a third data point for T^2. In general, an examination of the non-linearity of Cp indicates how many terms will be needed to develop a satisfactory H_T-H_{298} equation. Also, the greater the temperature span, the more terms are needed for a satisfactory fit. If Cp is highly non-linear or shows multiple slope changes, the temperature span may be divided into two regions, with separate H_T-H_{298} equations. A better way is to use the statistics tool in Excel (regression analysis). The tabular data can be weighted towards the lower temperature data, since that is likely to be the most accurate. In some cases, it is very difficult to develop a set of H_T-H_{298} equation parameters that give an adequate fit to the tabular data. See the Freed-xmpls.xls worksheet for examples of obtaining equation parameters.

Do not enter any other information than listed above. Move the cursor to a blank cell elsewhere on the worksheet. Examine the Main Menu and search for the newly-added species. Select that species to the list, and use dGRestore to create the FREED record. Test the results by printing a table.

Remember that if a new species is added, the resulting dG*f* record will be based partly on data from the PureElements worksheet, and partly on data for the species. If the original new species data is based on reference element data that is different from the U. S. Bureau of Mines reference element data, the dG*f* values will be some hybrid of the

two sets of data. In other words, the dG*f* data for the new species will *not be internally consistent*. It can be made so by replacing the dG*f* values calculated by FREED with values calculated by the user from tabular dG*f* values from the original source of new species data. Users are urged to consult the developer (Dr. A. E. Morris) if they have questions about the ramifications of the validity of new species data.

Creating New Databases

A new database may be created by taking data from another source, and entering it appropriately in the proper columns. Each new database requires a separate copy of FREED. An empty FREED is obtained by deleting the contents of all rows that contain species data. A new PureElements worksheet may also be needed. The information in this Guide should be sufficient for knowledgeable users to create a new database, providing the existing PureElements worksheet needs no changes.

Creating Non-standard Species

It is often useful to have thermodynamic data for species in non-standard states, either outside their normal temperature range, or in their dissolved state. In the first case, it is useful for example, to have the properties of liquid iron below the normal melting point (<1811 K), and above the normal boiling point (>3135 K), and the properties of gamma iron above and below its transition temperature to alpha iron (<1185 and >1667 K). Records for non-standard species were created by extrapolating the H_T-H_{298} and S data from the stable temperature range to 298 K to obtain a fictional value for dHf and S at 298 K. This procedure results in increasing uncertainty the farther one departs from the temperature limits for the standard state. Non-standard state species are designated with rose-colored cells.

In the second case it is useful to have a datafile for a species in a unique dissolved state. For example, oxygen and other diatomic gases dissolve in metals as atoms, hence records were created for atomic species O, N,. S, H, and P by dividing the diatomic gas data by 2. These species are to be used only as dilute solute species in the Bale-Pelton non-ideal formalism or in free-form activity coefficient equations. Since both dG*f* and dH*f* of a solute is solvent-specific, both were set = 0. Dissolved state species

are indicated by gray-colored cells. A unique set of species were created to model the wustite solid solution phase: FeO (d), $FeO_{1.5}$ (d), and Fe_3O_4 (d). Further discussion of the use of non-standard state species in equilibrium calculations is discussed in the User's Guide to THERBAL.

Color Coding

As previously mentioned, certain cells are color coded to indicate special characteristics of the species. The meaning of the colors is indicated by a comment in cell D6. Formula cells colored light **green** refer to Reference State elements. **Yellow** refers to species where dG_f has been corrected to show 0 after transitions to standard states, or where other corrections were made in dG_f. **Tan** refers to mixed-substances species, which should not be used as product species in THERBAL EQM calculations (but can be used as input species). **Rose** refers to liquid species whose temperature range extends to 298.15 K, and above the normal b.p. **Gray** refers to species created for use in non-ideal solutions. These species represent solutes in the Bale-Pelton formalism or other unique solution phases, and may be used by THERBAL.

Light **turquoise** in the Tmax column refers to species whose upper temperature limit has been extended beyond Tmax in the Bureau of Mines tables. Reference State Species with extended Tmax are also indicated with a turquoise cell in column B near row 2400.

Future Developments

FREED development has ceased. No further pdates are contemplated.

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Appendix B: FREED Examples

The workbook *FREED Examples.xls* contains several worksheets that give additional information about FREED, and illustrate its use. Each worksheet is described briefly below. Comments on each worksheet can be read by positioning the cursor on the specified cell.

Many more examples of the use of FREED data can be found on the CD disks that are included with 3 textbooks:

J. W. Evans and L. C. De Jonghe, *The Production and Processing of Inorganic Materials*, 2nd Edition, TMS, Warrendale, PA (2002).

D. R. Gaskell, *Introduction to the Thermodynamics of Materials*, 5th Edition, Taylor and Francis, New York (2007).

A. E. Morris, G. H. Geiger, and H. A. Fine, *Handbook on Material and Energy Balance Calculations in Materials Processing*, Wiley/TMS, 2011.

Additional texts using FREED may appear in the future. Please check www.thermart.net.

Datafiles

This worksheet was prepared to show how the equation parameters for Cp, H_T-H_{298}, dH_f, and dG_f for $AlO_2H(g)$ are arranged on the sheet. The parameters are not labeled, which means the equation parameters can be read without stripping away text. This makes the datafile useful as an input data array for other thermodynamic programs.

Properties

This worksheet gives basic information about the species $AlO_2H(g)$, plus equation parameters and formats. The Properties worksheet is basically an annotated Datafiles worksheet, and thereby helps the user interpret the Datafiles file format.

Tbl&LogK

This worksheet shows a table of data for AgCl(c,l) in the standard USBM format. A subset of the Table data (yellow cells) was created for use by Excel's Charting option to

show the relationship between log(K_f) and 1/T. A two-term equation was developed from the data. This example shows how convenient it is to use Excel's data processing tools on FREED data.

Graphics-dG*f*

FREED contains a built-in macro to create plots of various functions vs. T. This worksheet shows a plot of dG_f of CaO. The original FREED plot was then modified and enlarged to better illustrate the result. The graphics function of FREED is particularly useful in visualizing data trends, and in preparing graphs of data for reports. Excel's Trendline tool can be used to develop equations from the chart.

Graphics-Cp-1 and Graphics-Cp-2

These worksheets show examples of how Cp for a species varies with T. Obtaining a satisfactory fit to the tabular data often requires two equations. The worksheet for Al_2(g) shows a comparison between the actual tabular values, and those obtained from the statistical fitting.

Graphics-Heq

FREED's H_T-H_{298} equations have several terms in order to fit the data over a large temperature span. In some cases, it is handy to have a two or three-term equation that can give an adequate fit over a shorter temperature span. This worksheet shows the enthalpy data for CH_4(g) over an 800 degree temperature span and the corresponding chart. Excel's Trendline tool was used to fit the data to a quadratic equation, which shows a coefficient of regression R value of 1.000. The Trendline equation is superimposed over the smoothed chart line. The number of significant figures in the Trendline equation was increased by reformatting the data labels/number. (The Trendline tool equation often fails to display a correct number of significant figures.) A value of R above about 0.999 indicates that the equation faithfully represents the data. Try fitting a linear heat content equation to the data (after deleting the quadratic Trendline) and see the difference.

Coeffs

In some cases, the data may not justify a regression fit to obtain equation parameters. In that case, FREED's Coefficients feature can be used to obtain equation parameter values for an H_T-H298 equation. An equation with as many terms as data points is obtained. This worksheet shows such an equation for $AlHO_2$(g). Further examples on using FREED's Coefficient feature to fit thermal data is shown on the H-EqnFit worksheet.

Another use for the Coefficient feature is to generate a dG_f equation from tabular dG_f data, where either new dG_f data is obtained without new H_T-H_{298} data, or where there are no H_T-H_{298} data. A 3-term dG_f equation (T, TlnT and a constant) is often quite adequate up to a range of 1000°. An example of fitting a 3-term dG_f equation for NiO is shown on this worksheet.

H-EqnFit

Adding a new species requires equation parameters for the H_T-H_{298} equation. Excel has a *Regression* tool for this purpose. This worksheet shows an example for CH_2Cl_2, with data obtained from JANAF, 3rd Edition. The data was weighted at the lower temperatures. A nice feature of the Regression tool is that it will plot the Residuals, as shown in this worksheet. However, H_T-H_{298} is not forced to = 0 at 298 K with this tool, so the intercept must be adjusted as described in the worksheet comment. The results show that a 6-term H_T-H_{298} equation is required over a 4000 degree range, because of the rapid change in Cp with T between 300 and 1300 K. Also shown on this worksheet is a comparison of the fitting procedure using FREED's Coefficients feature. Again, owing to the rapid change in Cp at lower temperatures, the Coefficients feature (naturally) does not do as good a job in fitting the data as does Excel's Regression tool. Regression can also be performed on a chart of data with Excel's *Trendline* tool.

V-Press

The tables generated by FREED can be used to calculate the vapor pressure of any species In this example, the tables for NaCl(c,l) and NaCl(g) were generated, and the difference between log(K_f) of each species was calculated. The resulting column of

data is the log of the vapor pressure of NaCl. The results are shown as a table, a plot, and an equation for the log of the vapor pressure vs. 1/T for NaCl(g) in equilibrium with NaCl(l). Excel's Regression tool was used to determine the equation parameters.

GbstCalcine

Alumina is produced by calcining Gibbsite, $Al(OH)_3$, in a rotary kiln. This example examines the heat balance for the process as a function of a number of process variables, such as water content of the Gibbsite, % excess air for combustion, air preheat, etc. The heat balance formulas were linked, so that if one input variable is changed, a series of calculations is automatically made to calculate output variables. Excel's Trendline tool was used to calculate the parameters of an equation relating certain variables.

HofComb

This example shows how Excel's various tools can be used to make a heat balance for combustion, and to carry out a simultaneous equilibrium and heat balance. The first part of the example shows how the AFT for combustion of CO with excess air is calculated. Tables for CO, CO_2, N_2, and O_2 were generated by FREED, and used for the calculations. A graphical approach is used to develop Trendline equations for the net heat effect vs. amount of air used. The AFT is seen as the point where the Trendline crosses the net heat = 0 line. The AFT values are then plotted vs. % excess air, and an equation is developed for AFT vs. % excess air. Formulas were written in cells such that if the amount of air is changed, an entire new heat balance is calculated.

The second part of the example shows how the temperature of a burner is calculated. Air and carbon are burned such that the combustion gas has an aC = 1. The heat balance depends on the composition of the combustion gas, but the composition of the combustion gas is a function of T. Since the gas composition is a quadratic equation, the quadratic formula was used to calculate it, and the results plotted. A heat balance was then made for each data point, and also plotted. A polynomial Trendline was obtained that allowed the burner temperature to be calculated.

The extensive use of Excel's charting tools allows the user to obtain a visual appreciation of the functionality of variable relationships. The Trendline tool can fit

points to different equation types, and display the equation on the chart.

Air+SO2

This example illustrates the use of Excel's Goal Seek tool to calculate the extent of oxidation of SO_2 to SO_3 by air. First, FREED data for SO_2 and SO_3 were used to obtain an equation for log(Krx) for:

$$2SO_2 + O_2 ==> 2SO_3$$

as a function of 1/T. Then, 4 equations were written to express the stoichiometry, total pressure, and Keq expressions to define the system. Since one of the equations was a cubic, the solution was obtained by using Excel's Goal Seek tool. Several amounts of air were put in per mol of SO_2, at 3 temperatures, and the results plotted. The results were converted to % SO_2 converted vs. amount of air added, and a second plot made.

This example shows how a very complex set of equations can be solved for a large number of input values, which would be impossible using a hand-held calculator. Excel's charting tools are valuable in illustrating the trends in the results. Multiple solves can be made by using Multigoal, an Excel add-in developed by Thermart Software.

GasComp

The C-O system has several important variables, such as pO_2, activity of C, pCO, and pCO_2. The relationships between these variables was calculated over a large temperature span. This required 3-term log(K_f) equations for the formation of CO and CO_2, which were obtained by using Excel's Regression tool. Formulas were written to express each of these variables as functions of T and P_{total}. Where certain non-linear relationships existed, Excel's Goal Seek tool was used to solve the equations. A template was set up in such a way that the user enters values of certain variables, and the rest are calculated. A similar calculation template was prepared for the C-O-N system, for the special case of burning of carbon with air.

Mo-O-C Diag

The phase relations between the gas and condensed phases was calculated and plotted. The data was well-represented by 2-term log(K_f) equations calculated from

FREED data, and the charting tool used to indicate the unstable region for each 2-condensed-phase equilibria. A final phase stability diagram was drawn, and the T-P relationship calculated and plotted for the 3-condensed phase equilibria.

CndsdTbl

The format of the FREED Table feature has a default column width that makes it difficult to print more than one legible table to a page. This worksheet has been formatted to fit up to 3 tables per page. The Table worksheet values are copied to this worksheet with narrower columns. But beware--in some cases, significant figures may be truncated to fit the available space.

Heq-rxt

FREED's Reaction feature provides a convenient way to calculate an enthalpy (or Cp) equation for a mixture of substances. Here a process gas containing several species is used as both the reactant and product species, but of course since no chemical reaction occurs, all of the columns Overall Heat are zero. The Heat column represents the heat content of the process gas between 25° and 1000°C, in J/mol of process gas. If the heat balance problem has a somewhat uncertain heat loss, a linear H_T-H_{298} equation may be adequate. Excel's Trendline tool was used to develop such an equation, as shown on the legend box. The difference between a linear H_T-H_{298} equation and the table data is shown in column H. A better fit is obtained with a quadratic equation.

Sulfox-rxt

This worksheet illustrates the use of the Reaction tool for the oxidation of SO_2 to produce SO_3. Please see the earlier worksheet Air + SO2 for orientation on this example. The Table shows four thermodynamic functions at 50°C intervals between 400 and 1500°C. Note that log(Kr) becomes zero between 750 and 800°C (as does dGr) , and the overall heat becomes zero between 1350 and 1400°C. The Calculator tool was used to determine the exact temperature where log(Kr) = zero: 780.3°C. A value of 500 was entered for T1 and 1000 for T2. The default chart produced by this tool can be enhanced, and Excel's Trendline tool used to obtain an equation that adequately fits the

data.

NGBurn-rxt

This example illustrates the use of the Reaction tool to explore the heat produced by the combustion of one mole of a certain natural gas. Here, the upper T record for C_2H_6 is 1000 K (726.85 °C). This explains the truncation of all but the Heat column at this temperature. However, the Heat column values do not depend on the high temperature heat data for C_2H_6, so the heat column values extend to the upper temperature limit of the *product* species.

A combustion reaction like the one written for this example is not a standard reaction, where products and reactants are in equilibrium with each other at a certain temperature. Therefore, the values of dGrx and logKrx have no meaning.

DBHeadings

This worksheet contains a table to help use FREED's Database. The headings for H_T-H_{298} equations should be printed for use when adding new species.

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Disclaimer

An extensive effort has been made to faithfully reproduce the USBM and other datafiles. However, errors may exist, and the author assumes no responsibility for damages caused by the use of any data or results obtained by using FREED. For critical calculations, the user should refer to the original USBM Bulletins, or to other reliable sources of thermodynamic data. For data from non-USBM sources, the values of dG_f may be internally inconsistent, and the user is urged to consult the source for critical calculations. Please report any errors to the developer.