THERMODYN©

A simple Excel spreadsheet for the calculation of free reaction energies for actual conditions of activity and temperature

A product of the Woods Hole Microbial Diversity Courses 1996-1999; by Lars Riis Damgaard (Aarhus, Denmark) and Kurt Hanselmann (Zurich, Switzerland).

Thermodyn© is being improved and extended by swiss | i-research & training. Copies can be obtained on request from <i-research.training@hispeed.ch>

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The Excel spreadsheet Thermodyn© allows one to calculate free reaction energies (Gibbs Free Energy, ΔGr) and electrochemical potentials (Eh) for chemical and biochemical reactions and half-reactions, respectively, which commonly occur in microbial metabolisms and in a great variety of microbial ecosystems. Thermodyn is meant to be used as a learning tool to make applying thermodynamic laws in microbial physiology and geomicrobiology more understandable to the student. Comparing free reaction energies which are calculated for real conditions (activities, concentrations, pH, temperatures) make thermodynamics in many cases a more useful concept to understand processes in nature than if one has to rely on values calculated for standard states solely. In addition, the graphs will aid in quickly getting an idea on how changes will influence the outcome of a reaction.
The program can be adapted to the particular application of the user since new thermochemical values and those calculated for other physical states, may be added to the dataset anytime. The sources from which the original dataset was derived from are listed in the references given at the end of the database sheet (dBase).

Thermodyn© requires Excel installed on MacIntosh or on PC-Computers.

HOW TO PROCEED WHEN USING THERMODYN©
1. Define process of interest.
2. Write process as a stoichiometrically balanced equation (balance electrons, charges, masses).
3. Define boundary conditions, a variable and the range of applicability.
4. Enter equation number, substrates (s) and products (p), state, boundary conditions and other required values into the corresponding spreadsheet columns.
6. Run calculation and adjust scaling of graph coordinates if necessary.
7. Interpret graphs and vary conditions.

LAYOUT
The entire workbook consists of seven partially linked spreadsheets:
1. **Instructions**: Contains explanations about the architecture of the workbook and the individual spreadsheets as well as Operating Procedure, Conventions and References.

2. **Settings**: Allows the user to enter the number of calculations (up to 50) to be executed within the range chosen for the variable. Each calculation is presented as a dot in the plot. If you only want a line graph, choose 1 as a number of intervals; the plot will then show the 2 endpoints only. This sheet also explains the meaning of error messages.

3 & 5: **ΔG_values and E_values:** These are the actual user sheets, one for free Gibbs energies, the other for electron potentials. The calculation area (white) allows one to enter up to five reaction equations or a reaction with up to 30 reactants. Five reactions have been entered as example reactions with this copy of Thermodyn©. For reactions under varying temperatures Hf°-values must be available for all compounds involved in the reaction. For reactions run under standard temperature conditions (if Hf° is not available for all compounds), one has to put 298.15K into the temperature field below the calculation area. The table at the bottom displays pK for 25°C (standard) and for the chosen temperature. These values are calculated based on the free energies, enthalpies and entropies of the particular reactions. Since not all thermochemical values are consistent in a physical sense (different ways of measurement or calculation), we also list an uncertainty based on the two ways of how $\Delta Gr°$ can be calculated (see explanations under OPERATING PROCEDURES). One can choose different temperatures for plot 1 and plot 2 and hence will get the different pK values. Placing an "x" in the appropriate field allows one to display the plot of the corresponding reaction. The "x" at "log plot?" presents a logarithmic plot of the results. This is needed for ranges of variables over several orders of magnitude. Since pH must be converted to H(+) activity, $H(+) = 10^{-pH}$ or the corresponding number value must be inserted into the corresponding field in the activity column. The table at the bottom allows one to calculate these values. They are not automatically linked to the corresponding field, but must be inserted there manually, either as the calculated number value or in Excel code $=10^{-pH}$. In unprotected sheets, the plot axis can be altered by employing standard Excel code and plots can be exported as Excel linked files or pictures.

4 & 6: **dG_calc and E-calc**: These two sheets contain the calculations programs. Although the two sheets might be helpful, if one wants to extract particular numerical values one has to pay attention not to inadvertently destroy the programming codes.

7. **dBase**: The database is located in this sheet. It contains the available values in the order Gf° [molar free energy of formation in kilojoule/mol], Hf° [molar free heat (enthalpy) of formation in kilojoule/mol/Liter], S° [molar entropy in joule/mol/Liter/°Kelvin].

Cells intended for user input are generally white, while cells not intended for user modification are shaded. By default, the spreadsheet is password protected (password "**pass**") to prevent inadvertent changes of calculation formulas. Sheets and cells can be "unprotected" using the options command "unprotect sheet" in the "Tools" pulldown menu. Anytime you intend to make changes in a shaded cell, you will first have to "unprotect" the sheet. Please protect it again once you have made the changes. "Unprotection" and "protection" are not needed for making changes in "white" cells.
Be cautious when copying and pasting fields and make sure that you only copy the values and texts, NOT the underlying formula and links.

OPERATING PROCEDURES

To calculate the free energy change, ΔGr, of a reaction proceed as follows:

1. Figure out the balanced stoichiometry of the reaction(s) of interest.

2. Fill the proper values into the white cells in the calculation area.
   - Define the reaction number (1 to 5).
   - Define whether the compound is a substrate (s) or a product (p).
   - Enter the requested data for the compounds below the fields marked: "Stoichiometric coefficent", "Enter formula" (see Appendix A for details),
   - For "State" (physical aggregation state) and "Special remarks" *, check the entry in the dBase, if necessary.
   * In some cases a word must be entered in the field "Special remarks" (e.g. "dilute") for the spreadsheet to pick up the desired compound from the database; in the remaining cases, the field may remain blank.
   - "Activity": use activity corrected** concentrations in mol/liter for dilute solutes and dissolved gases or partial pressure in atm for gases.
       By convention, activity is set 1 for liquid H_2O and solids. Actual activities should always be used for properly calculating ΔGr values.
       ΔGr becomes ΔGr°, if all activities are 1.
   ** Activity corrections are values ≤ 1, but >0. Activity factors have to be calculated separately employing the proper activity correction concept for each compound in a particular environment (ionic strength, conductivity, salinity defined). The proper concept is chosen according to the ionic strength of the environment.

3. If the spreadsheet "recognizes" the compound in the database, the name of the compound will appear in the shaded "Compound" field, the corresponding formula in the "Formula" field. If your entry is not recognized or if more than one database entry matches a formula, an error message appears in red in the "Error" field. In appendix A we list a few hints on how you can solve error messages. The "Error" field furthermore displays error messages if you enter none or inappropriate entries in other fields. Errors must be corrected for the calculations to proceed.

4. The field "Note" displays information which should be considered when interpreting the result; e.g. "CALC!" means that the database value is obtained from a theoretical calculation and not from an experimental determination; "300K" means that the listed value is valid for 300°K and not for 298.15°K, which is the standard temperature for which most of the values are listed. Calculations are not corrected for this deviation in temperature and the calculated ΔGr values should only be taken as approximation.

5. Two parameters may be varied: activity corrected concentration and temperature. Entering "v" in the corresponding row of the column "Variable" denotes the activity which is being varied between minimal and maximal boundaries (see point 6). If you compare reactions it is essential that you chose the same or corresponding variables.

6. Enter the temperature and the maximum and minimum activity corrected concentration boundary conditions in the fields under "Plot". The Min. and Max. values define the range for which the calculated values will be plotted. When you define a pH range as boundary conditions, you must consider that acids and bases can be protonated or deprotonated at different pH values.

7. pH values are used as proton activity in the calculations. Recall that pH is defined as $-_{10}log$ [H⁺], the value to be entered for [H⁺] is thus 10^{-pH}, in Excel notation "=10^(-pH)". The proper value can be calculated with a pH converter and linked or entered manually into the proper cell. For all other values you can use the scientific notation option, e.g. 2e-3, which corresponds to 0.002.

8. The five reactions can be plotted in two different semi-logarithmic graphs (Plot 1 and Plot 2) by marking the desired reaction in the corresponding "Plot" field (Show react...). For very narrow ranges of activities, you might want to use a linear plot; just remove the "x" in the field after "Log plot?".

9. ΔGr-values are calculated from the energies of formation (Gf°) according to $\Delta Gr° = \sum Gf°(Products) - \sum Gf°(Substrates)$ and within the defined boundary conditions for $\Delta Gr = \Delta Gr° + R*T*ln\ Q$ (Q being the actual activities of products and substrates.

10. The number of points presented in the graph can be defined in the shaded fields in the sheet "Settings". You may choose up to 50 calculation points. ΔGr is plotted in the graph for each reaction with the number of data points defined. Moving the cursor to a particular point in the graph displays the activity corrected concentration and the corresponding ΔGr-value in a small cursor window. The first number is the exponent to the base 10 of the activity corrected concentration, the second is the ΔGr value in kJoule / Mol of reactant as written in the reaction equation. See Appendix C for limitations in calculating ΔGr°, ΔGr or Eh.

11. You may choose up to five curves for plotting by marking the corresponding field with an "x".

12. Temperature can be defined in Centrigrades, which will be converted into degree Kelvin.

13. The standard Gibbs free energy change (ΔGr°), the standard Enthalpy change (ΔHr°) for 298.15 K and the standard Entropy change (ΔSr°) are listed for each reaction in the light grey fields at the bottom. These values are needed to calculate temperature corrected equilibrium coefficients (K(T1) and K(T2)).

14. pK(T1) and pK(T2) values are based on the relationship $Keq = 10^{(-\Delta Gr°/2.3026\ R\ T)}$ for plots 1 and 2 respectively. pK(298) is the negative logarithm of the equilibrium value Keq for standard temperature (298.15 K); pK(T1) is the negative logarithm to the base 10 of the equilibrium coefficient at "Temp Plot 1" in Kelvin degrees; pK(T2) is the equilibrium coefficient at "Temp Plot 2" in Kelvin degrees.

15. With the aid of ΔSr° the sheet calculates ΔGr° via the relationship $\Delta Gr° = \Delta Hr° - T* \Delta Sr°$ and compares the value with ΔGr° calculated from $\Delta Gr° = \sum Gf°(Products) - \sum Gf°(Substrates)$. The ΔGr° % column lists the uncertainty expressed from the difference between the two modes of calculating ΔGr° in % of ΔGr° calculated from $\sum Gf°(Products) - \sum Gf°(Substrates)$. The ΔGr° value used for calculating actual ΔGr is always based on $\Delta Gr° = \sum Gf°(Products) - \sum Gf°(Substrates)$.

Appendix A

If a compound is not recognized by the spreadsheet the message "#VALUE" appears in the compound name field and the "Error" field displays in red "Not listed or duplicate!". This may be due to one of the following reasons:

1. The compound formula is 'misspelled' (according to the rules mentioned in Appendix B) in either your entry or in the database. Seek the compound of interest manually in the first or second column of the database (mark the corresponding columns and use Formula/Find... command) and correct the 'misspelling'.

2. The compound is not included in the database. You may add it to the database by unprotecting the spreadsheet and inserting a line anywhere in the database. The database will automatically accommodate any number of new entries as long as they are inserted within the database limits (Headings at top and "database bottom line" at bottom). Kurt Hanselmann will be happy to hear about additional data which could broaden the usefulness of the dataset.

If the message "#NUM" appears in the compound name field, several records match your entry. Find all places in which the compound appears in the database and differentiate or delete duplicate records, e.g. $CaCO_3$ can be Calcite or Aragonite; one must clarify in the "Special Remarks" column which one of the two species the program is supposed to use.

Appendix B

1. Since not all versions of Excel can accommodate sub- and superscripts, compounds are listed as atom followed by number of atoms, then number of charges and (+) or (-) for the charge sign. Parentheses are applied e.g. Proton = H(+) is H^+, Nitrate ion = NO3(-) is NO_3^-, Tetrathionate ion = S4O6(2-) is $S_4O_6^{2-}$, Ferric dihydroxy ion = Fe(OH)2(+) is $Fe(OH)_2^+$ vs. Ferric hydroxy ion = Fe(OH)(2+), which is $Fe(OH)^{2+}$. Ion pairs are marked with a terminal "(0)", e.g. Fe(OH)3(0), which is $Fe(OH)_3^0$ listed as "aq", which is different from the solid $Fe(OH)_3$. S, without brackets, is elemental sulfur, S^o, which is listed in several different forms (see "Special remarks" in the dBase).

2. Elements and atoms are listed first in the particular compound group; they are identified by "element" in the column "Special remarks". If crystal water is part of the molecule, it is listed after a dash (-): CaHPO4-2H2O is $CaHPO_4$ $2H_2O$. Furthermore, to list some compounds (e.g. most amino acids) list the compound name as formula copied from the dBase and put its name into the column "Special remarks". If you are unsure of the way a compound should be entered, search for it in the dBase, copy it with the "copy" command and paste it into the "Formula" field and, if necessary, add the "Special remark".

Appendix C

1. The calculation assumes that ΔH and ΔS are constant within the temperature range for microbial life. ΔGr^o is corrected for temperature according to the Gibbs-Helmholtz equation.

2. The influence of the ionic strength of the aqueous matrix is accounted for by the activity coefficient $0 < \gamma \leq 1$. The value 1.00 is only valid for very dilute solutions (activity = concentration). Ionic strength corrections (=activity coefficient ≤ 1) must be calculated in a separt sheet and be considered when calculating the values in the "Activity" column of the spreadsheet (= activity corrected concentration).

3. Chemical speciation, e.g. the ratio of species that need to be entered into the stoichiometric equation for a given pH or pe may be calculated with an independent speciation software. Some examples for conditions in oceans can be calculated by **AciBa**, the speciation learning workbook based on Thermodyn.

4. A number of values calculated with GAMESS for intermediates of major metabolic pathways are included at the end of the database. In order to distinguish them from the experimental values they are labelled m- for model compound. The list will be extended. With these values, Thermodyn will become useful for thermodynamic studies of metabolic reactions. For the moment, these values have not been tested in combination with values from the rest of the database. Results obtained with the values must be interpreted with caution.

5. If you search the database (dBase) with the Excel sheet search option, you may either use the group name, e.g. Element Nitrogen, the compound name or the formula written in the way as defined in Appendix B. Entries into the dBase are made in the following order:

> **Electron and Proton**
>
> **Inorganic compounds**
> Element Hydrogen
> Element Oxygen
> Element Carbon
> Element Nitrogen
> Element Phosphorus
> Element Arsenic
> Element Sulfur
> Elements Halogens
> Element Iron
> Element Manganese
> Element Calcium
> Element Magnesium
> Element Barium
> Element Strontium
> Element Sodium
> Element Potassium
> Element Aluminum
> Element Copper
> Element Lead
> Element Silicon
> Element Boron
> Elements

Organic compounds
Hydrocarbons & derivatives
O-containing aromatics
Carboxylic acids, aldehydes, ketones, ethers, esters
Alcohols
Carbohydrates
N-containing organic compounds
       AMINO ACIDS
       PEPTIDES
S-containing organic compounds
Halogenated hydrocarbons and precursors
Metabolic intermediates (in preparation)
       Coenzymes
       Glycolysis
       Citric acid cycle, Krebs cycle, tricarboxylic acid cycle
       Calvin-Benson-Bassham cycle, reductive pentose phosphate cycle
Model compounds calculated with GAMESS

Model biomass

Periodic Tables containing element data and Pauling's electronegativity values

REFERENCES FOR THERMOCHEMICAL DATA:

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Today, many of the data compiled in the dBase can be obtained from various online databases:
CRC Handbook of Chemistry and Physics, e.g. 93rd edition, 2012-2013, Section 5: Thermochemistry, Electrochemistry, and Kinetics
http://www.hbcpnetbase.com/

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