

Manual

A program to calculate temperature-dependent thermodynamic parameters of chemical equilibrium in aqueous...

Exit Help About program Notepad Calculator

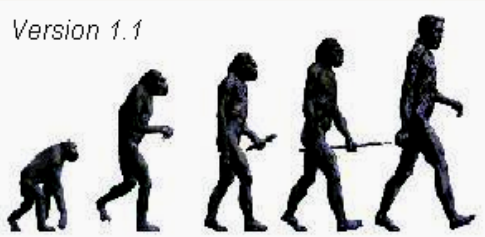
Title Calculate thermodynamic parameters Calculate equilibrium constants

A program to calculate thermodynamic parameters from stability constants over a range of temperatures in aqueous solutions

using:

- the Vant - Hoff equation,
- the isobar equation,
- the extended isobar equation,
- the Clarke - Glew equation,
- the extended Clarke - Glew equation,
- the DQUANT equation,
- the Valentinier equation,
- the Blandamer - Robertson - Scott equation

Version 1.1



from the simplest.....to a thorough quantitative treatment

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Introduction

Temp_effects is a program for fitting thermodynamic properties. It employs a large number of regression models (both linear and nonlinear) to represent input data in the most precise and convenient way. **Temp_effects** is designed to calculate the chemical equilibrium thermodynamic parameters: $\lg K_{298.15}^0$, $\Delta H_{298.15}^0$, $\Delta S_{298.15}^0$, $\Delta C_p_{298.15}^0$, $d(\Delta C_p_{298.15}^0)/dT$, $d^2(\Delta C_p_{298.15}^0)/dT^2$, their uncertainties and the statistical characteristics of regression experiments.

Temp_effects has been developed under the Windows 9x, and Windows NT/XP operating systems. The 32-bit version was built by Borland Delphi 5.0. The first version **Temp_effects** program was released on January 28, 2004 as version 1.0.

Temp_effects is composed of the following files:

- **Temp_effects.exe** – the **Temp_effects** program exe-file
- **samples input files**
- **Temp_effects.chm** – the help file

If you have any suggestions, or there is any regression model that you would like to see added to the repertoire, please send us an e-mail. We will gladly listen to your comments. We wish to continue development and support of this program.

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Using Temp_effects.exe

Temp_effects has an easy point-and-click interface and allows the user to:

- Calculate the thermodynamic properties ($\lg K_{298.15}^0$, $\Delta H_{298.15}^0$, $\Delta S_{298.15}^0$, $\Delta Cp_{298.15}^0$, $d(\Delta Cp_{298.15}^0)/dT$, $d^2(\Delta Cp_{298.15}^0)/dT^2$) from temperature dependence of equilibrium constant along with its uncertainties (two-sided 95% confidence limit)
- Choose from 8 built-in regression models
- Use the combined algorithm (modified pit-mapping algorithm with steepest descent) for robust nonlinear regression performance
- Support for uncertainties in each data point
- Use weighted and non-weighted schemes of robust nonlinear regression
- Use automated procedures in the Dixon Q-test to check and reject doubtful points
- Use residual plot to reflect serial correlation of residuals
- Terminate a computation at any time
- Calculate the dependence of chemical equilibrium constants on temperature
- Copy plots directly to the clipboard to use in another Windows application
- Save all results of calculation in a Rich Text Format file
- Read simple ASCII data files
- Use comments in input file and in final output
- Scale, translate, sort, remove and edit data set by hand similarly to a spreadsheet

The Temp_effects program has 2 main tabbed pages:

- ❑ **Calculate thermodynamic parameters**
- ❑ **Calculate chemical equilibrium constants**

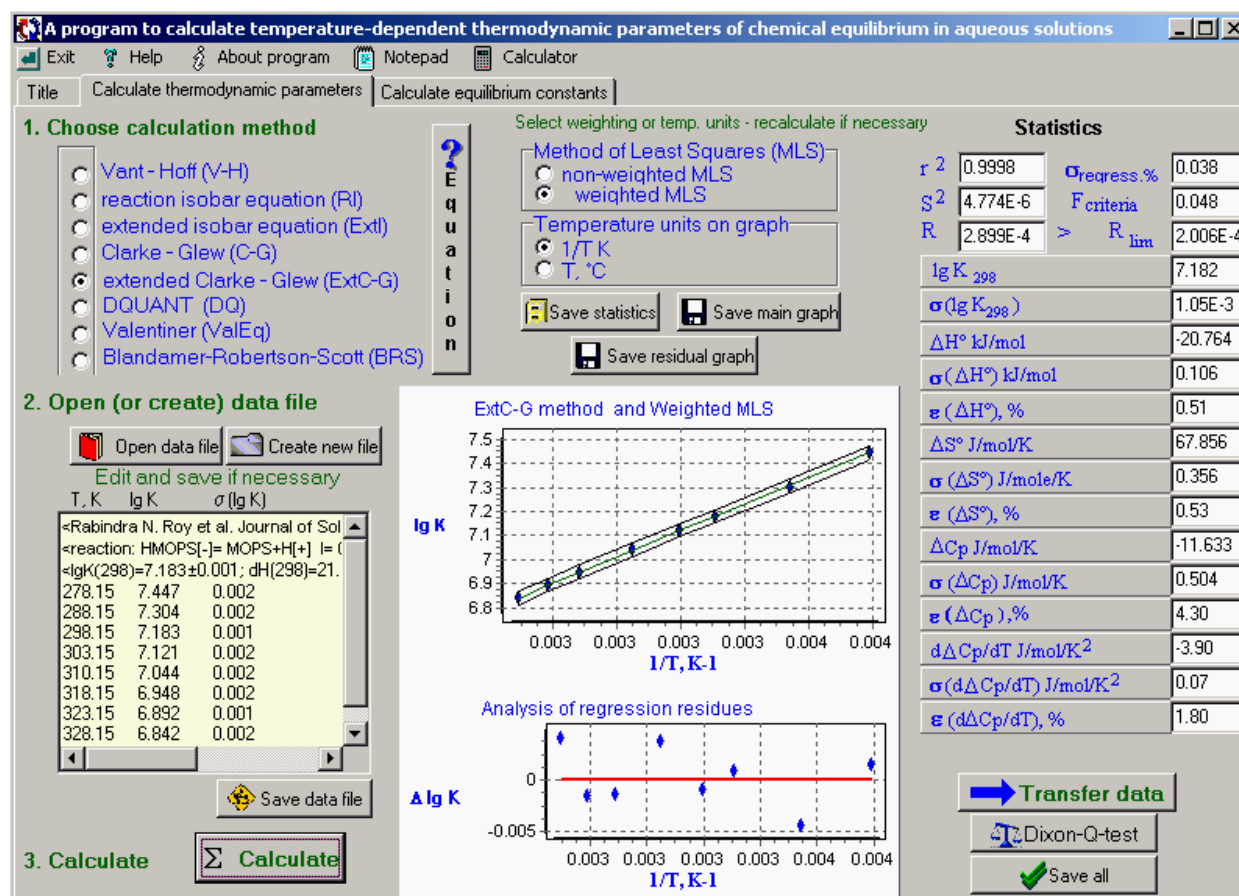
Like all Windows applications, you can also select items off of the menu bar to accomplish certain tasks.

The toolbar gives access to frequently used commands

- ✓ **Exit**
- ✓ **Help**
- ✓ **About program**
- ✓ **Notepad**
- ✓ **Calculator**

Calculate thermodynamic parameters

A typical window of the tabbed-page ‘Calculate thermodynamic parameters’ of [Temp_effects](#) is shown below:



Firstly, load sample data by clicking on the ‘Open data file’ button. When a file is selected the data will be displayed in the Data edit pane.

Data Edit Pane

This is the spreadsheet-like interface that occupies the left side of the window. It holds all of the data to be modeled. The first column of data is the temperature (in Kelvin). The second column holds the stability constant data, the third column holds uncertainties of stability constant. To edit a particular value, simply click the cell which holds it and type in the new value.

Chart Pane

The ranking chart can help to rank all of the valid regression models from best to worst. The standard error and correlation coefficient are used to determine these rankings.

Statistics

Contains the main statistical information, calculated thermodynamic parameters and their uncertainties.

Regression options

The regression options sets user preferences that control the regression and mathematical operations. In most cases it uses linearization of the equations to calculate the parameters of a linear and nonlinear least squares methods by the algorithm described in [80JON]

$$\lg K(T) - F(\text{linear}) = b_0 + b_1 \cdot f(T)$$

where the $F(\text{linear})$ term allows transformation of the model equation to a linearized one.

Minimization of the regression parameters is performed by a combined method - multivariate grid (pit-mapping) search and steepest descent with parabolic approximation for the acceleration of convergence [86SHA/ILL].

In the [Temp_effects program](#) both weighted least squares and non-weighted least squares methods are used. [Temp_Effects](#) implements weighted regression schemes, so that the user has an opportunity to reduce the contribution of doubtful data. Weighting allows the user to define the influence of each datum point on the final set of fitted parameters. A large weight denotes that a particular point influences the parameters more, and a small weight decreases its effect on the parameters.

[Temp_effects](#) can weight each point in the nonlinear regression progresses.

The non-weighted method may be used when the relationship between the variances of the data around the fitted curve and the stability constant values of the points is not known. However, in many experiments the uncertainty can be given a particular value. In this case, weighting of the points can prevent the larger scatter at higher stability constant from adversely affecting the regression model.

In [Temp_effects](#) the statistical weight of a data point is determined as [86SHA/ILL]:

$$\omega_i = 1/s^2(R_i) \approx 1/\sigma^2(R_i)$$

Using this method, weights are normalized so that the average weight is equaled to one

$$\omega_i^* = \omega_i / (N^{-1} \sum \omega_i)$$

Data file requirements

The program reads a plain ASCII text file (*.txt or *.dat), which consists of columns.

Three main commands may be used:

Open file - open input file

Save file - save changes to input file

Create the new file of data - create new data file

Statistical Information

In the program the following statistical criteria are used [77SEB, 78MOS/TUK, 81DRA/SMI, 82TAY, 86SHA/ILL]

- ☐ Fisher criterion F
- ☐ coefficient of multiple determination (square of multiple correlation coefficient) r^2
- ☐ root-mean-square regress error $\sigma_{(\text{regress})}$ %,
- ☐ Hamilton criterion (comparison of R and R_{lim} criteria),
- ☐ mean square about regression (residual sum of squares) S^2 (weighed and nonweighed)

Calculate the thermodynamic parameters

Thermodynamic parameters are calculated from the dependence of equilibrium constants on temperature

Open data file '**Open file**'

- ☐ Select the equation model
- ☐ Select the calculation method (**MLS**)
- ☐ Press the '**Calculate**' button

The temperature scale to be used can be selected:

- ☐ Celsius temperature $^{\circ}\text{C}$
- ☐ Kelvin temperature K

The automated procedure of the **Dixon Q-test** may be used [78BAR/LEVJ, 91ROR, 93MIL, 93MIL/MIL] at the 95% confidence level for data sets.

A warning message window is shown when a doubtful point is detected by the Q-test. The doubtful point is marked by red on the diagram.

This point is marked by italic bold type in **Data Edit Pane**. If possible, exclude such points and repeat the calculation.

Save results

The user can save

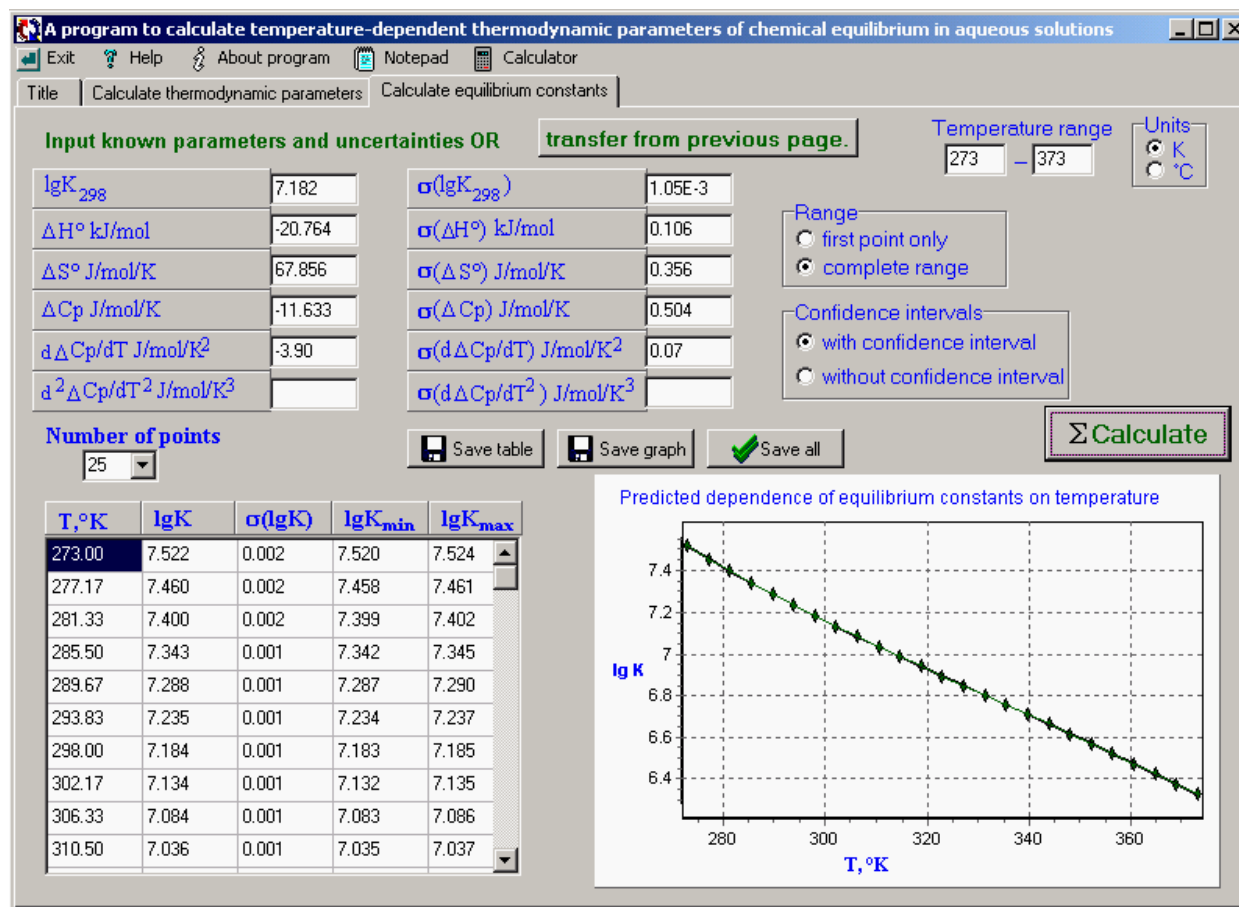
- ☐ the statistics and calculated thermodynamic parameters as a text file, to the clipboard or to both
- ☐ the main graph as a graphic file (**GraphCalc.bmp**) and to the clipboard simultaneously
- ☐ the residual graph as a graphic file (**GraphResidual.bmp**) and to the clipboard simultaneously
- ☐ all results together (table, diagram, comments) as a text file in RTF format.

Transfer data for Calculation

Calculated thermodynamic parameters can be transferred to the [Calculate the chemical equilibrium constants](#) tabbed page to calculate (predict) chemical equilibrium constants as a function of temperature. Click on the '**Transfer data**' button.

Calculate (predict) chemical equilibrium constants

A 'Calculate equilibrium constants' window is shown below



Calculate and save results

To calculate the dependence of chemical equilibrium constants on temperature

- ❖ Select the calculation range - single point or range
- ❖ Indicate the number of point
- ❖ Indicate the temperature range
- ❖ Press the "Calculate" button

Note. The model equation chosen from previous window **Calculate thermodynamic parameters** is used.

The user can select the plot in various coordinates

- ❖ Celsius temperature °C
- ❖ Kelvin temperature K

The user can save

- ❖ the table of the calculated values as text file (**PredictTable.txt**) and to the clipboard simultaneously
- ❖ the diagram as a graphic file (**prediction.bmp**) and to the clipboard simultaneously
- ❖ all results together (table, diagram, comments) as a text file in RTF format.

Note. The **Temp_effects** program generates data tables on the basis of model. These tables contain of 5 columns:

- ❖ calculated values of equilibrium constants (**K**, **lg K**) corresponding to the range of temperature data points that you specify

- ❖ uncertainties of calculated equilibrium constants $\sigma(\lg K)$
- ❖ the highest and the least values of calculated equilibrium constants **$\lg K_{\min}$, $\lg K_{\max}$**

Regression Models

Recalculation of chemical equilibrium data from the reference temperature of 298.15 K (25°C) to any desired temperature is made by using the relationships provided by thermodynamics. The procedures are straight-forward provided that information is available for ΔH_m^0 or ΔS_m^0 at the reference temperature and for their temperature dependencies. Complete information of this kind is rarely available for formation reactions of chemical complexes in aqueous solution and it is therefore necessary to rely on approximation methods of various kinds.

As will be seen from the following text the different approximation methods used to describe the temperature dependencies of chemical equilibria constants.

The extrapolation of experimental values of $\Delta G_m^0(T)$ (or, conversely, equilibrium constants) to a reference temperature, generally 298.15 K, is usually done by using various modifications of the so-called second- and third-law methods. The third-law extrapolations require free energy functions and are generally the preferred method of calculation when long temperature extrapolations are required, particularly where the reactants and products are pure phases for which experimental heat capacities or relative enthalpies are available or can be accurately estimated. That is, third-law extrapolations should generally be used for equilibria between different phases at high temperatures. When extrapolations over relatively small temperature ranges are made, then second-law extrapolations can be used for accurate calculations, but this method requires experimental or estimated heat capacities around the temperature of interest. Second-law extrapolations should generally be used for aqueous equilibria.

van't Hoff equation [98PUI/RAR].

The simplest assumption to be made is that the heat capacity change of reaction is zero at all temperatures (*i.e.*, the standard molar enthalpy of reaction does not vary with temperature).

By combining the *Gibbs-Helmholtz equation*

$$\left(\frac{\partial \Delta_r G_m^0 / T}{\partial T} \right)_p = \frac{-\Delta_r H_m^0(T)}{T^2},$$

and the relation $\Delta_r G_m^0(T) = -RT \ln K^0(T)$, it is possible to obtain, for a given constant pressure p :

$$\frac{d \ln K_p^0(T)}{dT} = \frac{\Delta_r H_m^0(T)}{RT^2}$$

which is called the *van't Hoff equation*. In more perspective form:

$$\lg K(T) = \lg K_{298.15}^0 + \frac{\Delta H_{298.15}^0}{R \ln 10} \left(\frac{1}{298.15} - \frac{1}{T} \right)$$

For a temperature range $(T - T_0)$ equal or less than ± 10 K, the error introduced in $\log_{10} K^0(T)$ by this simplification will, in most cases, be well within its uncertainty limits.

Reaction isobar equation [81RYZ].

By combining the *Gibbs equation*

$$\Delta_r G_m^0(T) = \Delta_r H_m^0 - T \Delta_r S_m^0$$

and the relation $\Delta_r G_m^0(T) = -RT \ln K^0(T)$, it is possible to obtain next equation, for a given constant pressure p :

$$\lg K(T) = -\frac{\Delta H_{298.15}^0}{R \cdot T \ln 10} + \frac{\Delta S_{298.15}^0}{R \ln 10}$$

Extended Reaction isobar equation [81RYZ].

Another approach, when the extrapolation extends over a temperature range larger than about 20 K, is to assume that the heat capacity of the reaction does not vary with temperature. Alternatively, partial molar heat capacities at 298.15 K are sometimes considered to be constant with temperature. This assumption is based on the fact that although values for ionic heat capacities generally increase with temperature, they usually also have a maximum around 325 to 375 K and then begin to decrease

$$C_{p,m}^{\infty}(T) \approx C_{p,m}^{\infty}(T_0)$$

[98PUI/RAR]. Therefore setting $C_{p,m}^{\infty}(T) \approx C_{p,m}^{\infty}(T_0)$ may be a valid simplification in the temperature range between 273 and 373 to 423 K depending on the nature of the reaction [67HEL]. However, using the heat capacity at the average temperature $C_{p,m}^{\infty}(\frac{T+T_0}{2})$ may be an even better approximation over some temperature intervals.

$$\lg K(T) = -\frac{\Delta H_{298.15}^0}{R \cdot T \ln 10} + \frac{\Delta S_{298.15}^0}{R \ln 10} + \frac{\Delta C_{p,298.15}^0}{R \ln 10} \left(\frac{298.15}{T} + \ln \frac{T}{298.15} - 1 \right)$$

Clarke-Glew equation [66CLA/GLE] is analog of extended **van't Hoff** equation

$$\lg K(T) = \lg K_{298.15}^0 + \frac{\Delta H_{298.15}^0}{R \ln 10} \left(\frac{1}{298.15} - \frac{1}{T} \right) + \frac{\Delta C_{p,298.15}^0}{R \ln 10} \left(\frac{298.15}{T} + \ln \frac{T}{298.15} - 1 \right)$$

Extended Clarke-Glew equation [66CLA/GLE]:

$$\begin{aligned} \lg K(T) = & \lg K_{298.15}^0 + \frac{\Delta H_{298.15}^0}{R \ln 10} \left(\frac{1}{298.15} - \frac{1}{T} \right) + \frac{\Delta C_{p,298.15}^0}{R \ln 10} \left(\frac{298.15}{T} + \ln \left(\frac{T}{298.15} \right) - 1 \right) \\ & + \frac{298.15 \cdot d(\Delta C_{p,298.15}^0)/dT}{2 R \ln 10} \left(\frac{T}{298.15} - \frac{298.15}{T} - 2 \ln \frac{T}{298.15} \right) \end{aligned}$$

DQUANT equation [67HEL, 98PUI/RAR]

The DQUANT equation was proposed by Helgeson [67HEL] and it has been used by several researchers, for example by Haas and Fisher [76HAA/FIS], Helgeson's group [85JAC/HEL], Smith, Popp and Norman [86SMI/POP], *etc.*, although the authors [76HAA/FIS, 86SMI/POP] used additional terms for the non-electrostatic contributions to the heat capacity.

Furthermore, the EQ3/6 geochemical computer program package [88JAC/WOL] uses the DQUANT equation to calculate high-temperature equilibrium constants of dissociation for neutral inorganic complexes.

The "DQUANT" name appears to have its origin in the name of a computer program which was used earlier at the Laboratory of Theoretical Geochemistry, University of California, Berkeley.

Assuming that the temperature dependence of the heat capacity change of a dissociation reaction is proportional to the temperature dependence of the electrostatic contribution, Helgeson [67HEL, his Eqs. (21) and (22)] obtained the expression:

$$\lg K(T) = \frac{\Delta S_{298.15}^0}{R T \ln 10} \left\{ 298.15 - \frac{\theta}{\omega} \left[1 - \exp \left(\exp(b + aT) - c + \frac{T - 298.15}{\theta} \right) \right] \right\} - \frac{\Delta H_{298.15}^0}{R \cdot T \ln 10}$$

where $b = -12.741$; $a = 0.01875 \text{ K}^{-1}$; $\theta = 219 \text{ K}$; $c = \exp(b+aT_0) = 7.84 \times 10^{-4}$; $\omega = (1+ac\theta) = 1.00322$; $\phi = a\theta = 4.106$.

Helgeson [67HEL, 69HEL] claimed agreement of **DQUANT** equation with experimental values for most reactions in the temperature range 273 to 423 or to 523 K, with the upper temperature limit depending on the reaction. The errors at 473 K were of the order of 1 to 9 % of $\log_{10} K_{-T}$ [67HEL, p.3131] but increased with temperature. Note, however, that for some dissociation reactions whose $\Delta H_{298.15}^0(T_0)$ and $\ln S_m(T_0)$, and/or the heat capacity of dissociation are positive, the use of **DQUANT** equation is not recommended [67HEL, pp. 3131–3132]. **DQUANT** equation is of interest because it does not require any knowledge of the heat capacity change of a reaction and therefore described temperature dependencies of chemical equilibria constants more rather in comparison with **van't Hoff** and **Reaction isobar** equations.

For neutral inorganic species in aqueous solution, except for a few simple dissolved gases, there are no known methods to estimate the standard molar heat capacities. Therefore, **DQUANT** equation is of special interest to estimate high-temperature equilibrium constants for dissociation of neutral species.

Valentiner equation [07VAL, 39EVE/WYN, 76IVE/MOS]

$$\lg K(T) = \frac{A}{T} + C \ln T + B$$

$$\Delta H_{298.15}^0 = 19.145(A - CT)$$

$$\Delta S_{298.15}^0 = -19.145(B + C + C \ln T)$$

$$\Delta Cp_{298.15}^0 = -19.145C$$

Blandamer-Robertson-Scott equation [80BLA/ROB]

$$\ln K(T) = a_1 + a_2(T - 298.15) + a_3(T - 298.15)^2 + a_4(T - 298.15)^3,$$

where

$$a_1 = \ln K_{298.15}^0$$

$$\Delta H_{298.15}^0 = R \cdot 298.15^2 \cdot a_2$$

$$\Delta Cp_{298.15}^0 = R \cdot 298.15 \cdot (2a_2 + 2a_3 \cdot 298.15)$$

$$d(\Delta Cp_{298.15}^0)/dT = R \cdot (2a_2 + 8a_3 \cdot 298.15 + 6a_4 \cdot 298.15^2)$$

$$d^2(\Delta Cp_{298.15}^0)/dT^2 = R \cdot (12a_3 + 36a_4 \cdot 298.15)$$

The “? Equation” button allows you to look at desired equation.

The used equations to calculation of confidential intervals of chemical equilibrium constants

Whenever data are converted or recalculated, or other algebraic manipulations are performed that involve uncertainties,

the propagation of these uncertainties has to be taken into account in a correct way.

A detailed outline of the propagation of errors is given by Bevington [69BEV]

van't Hoff equation

$$\sigma(\lg K(T)_{V-G}) = \sqrt{\sigma^2(\lg K_{298.15}^0) + \frac{\sigma^2(\Delta H_{298.15}^0)}{(R \ln 10)^2} \left(\frac{1}{298.15} - \frac{1}{T} \right)^2}$$

Reaction isobar equation

$$\sigma(\lg K(T)_{Isobar}) = \sqrt{\frac{\sigma^2(\Delta H_{298.15}^0)}{(R \cdot T \ln 10)^2} + \frac{\sigma^2(\Delta S_{298.15}^0)}{(R \ln 10)^2}}$$

Extended Reaction isobar equation

$$\sigma(\lg K(T)_{ExtIsobar}) = \sqrt{\frac{\sigma^2(\Delta H_{298.15}^0)}{(R \cdot T \ln 10)^2} + \frac{\sigma^2(\Delta S_{298.15}^0)}{(R \ln 10)^2} + \frac{\sigma^2(\Delta Cp_{298.15}^0)}{(R \ln 10)^2} \left(\frac{298.15}{T} + \ln \frac{T}{298.15} - 1 \right)^2}$$

Clarke-Glew equation

$$\sigma(\lg K(T)_{Clarke-Glew}) = \sqrt{\frac{\sigma^2(\lg K_{298.15}^0) + \frac{\sigma^2(\Delta H_{298.15}^0)}{(R \ln 10)^2} \left(\frac{1}{298.15} - \frac{1}{T} \right)^2}{+ \frac{\sigma^2(\Delta Cp_{298.15}^0)}{(R \ln 10)^2} \left(\frac{298.15}{T} + \ln \frac{T}{298.15} - 1 \right)^2}}$$

Extended Clarke-Glew equation

$$\sigma(\lg K(T)_{ExtC-G}) = \sqrt{\frac{\sigma^2(\lg K_{298.15}^0) + \frac{\sigma^2(\Delta H_{298.15}^0)}{(R \ln 10)^2} \left(\frac{1}{298.15} - \frac{1}{T} \right)^2 + \frac{\sigma^2(\Delta Cp_{298.15}^0)}{(R \ln 10)^2} \left(\frac{298.15}{T} + \ln \left(\frac{T}{298.15} \right) - 1 \right)^2}{+ \frac{298.15 \cdot \sigma^2(d(\Delta Cp_{298.15}^0)/dT)}{2 R \ln 10} \left(\frac{T}{298.15} - \frac{298.15}{T} - 2 \ln \frac{T}{298.15} \right)^2}}$$

DQUANT equation

$$\sigma(\lg K(T)_{DQUANT}) = \sqrt{\frac{\sigma^2(\Delta S_{298.15}^0)}{(R \cdot T \ln 10)^2} \left\{ 298.15 - \frac{\theta}{\omega} \left[1 - \exp \left(\exp(b + aT) - c + \frac{T - 298.15}{\theta} \right) \right] \right\}^2}{+ \frac{\sigma^2(\Delta H_{298.15}^0)}{(R \cdot T \ln 10)^2}}$$

Valentiner equation

$$\sigma(\lg K(T)_{Val}) = \frac{\sigma^2 \Delta H_{298.15}^0}{(19.145 \cdot T)^2} + \frac{\sigma^2 \Delta S_{298.15}^0}{(19.145)^2} + \frac{\sigma^2 \Delta Cp_{298.15}^0}{(19.145)^2} \cdot (2 \cdot (\ln T)^2 + 2 \ln T + 2)$$

Blandamer-Robertson-Scott equation

$$\sigma(\lg K(T)_{BRS}) = \sqrt{2.3026^2 \cdot \sigma^2(\lg K_{298.15}^0) + \sigma^2(a_2) \cdot (T - 298.15)^2 + \sigma^2(a_3) \cdot (T - 298.15)^4 + \sigma^2(a_4) \cdot (T - 298.15)^6}$$

$$\sigma(a_2) = \frac{\sigma(\Delta H_{298.15}^0)}{(R \cdot 298.15^2)}$$

$$\sigma(a_3) = \sqrt{\frac{\sigma^2(\Delta Cp_{298.15}^0) + \sigma^2(a_2) \cdot R^2 \cdot (298.15^2 \cdot 4)}{(2 \cdot R \cdot 298.15^2)^2}}$$

$$\sigma(a_4) = \sqrt{\frac{\sigma^2(d^2(\Delta Cp_{298.15}^0)/dT^2) + \sigma^2(a_2) \cdot R^2}{(36 \cdot R \cdot 298.15)^2}}$$

Statistics

As a rule it is necessary to present the set of stability constant data points as a model parametric equation (**conjectured model**) and then calculate thermodynamic parameters. This model equation (**conjectured model**) can be anything. It can range from a simple Vant - Hoff equation to an extremely complex model with many parameters. When selecting an appropriate model an important consideration is the law of data distribution. Optimally the model should be chosen to reflect that law so that the parameters in the fit of the model curve have a physical interpretation and meaning.

The standard deviation from the mean describes the scatter of the data set around the average (the higher the standard deviation, the more the scatter)

$$\sigma = \sqrt{\frac{\sum_{i=1}^n (y - \bar{y})^2}{n - 1}}$$

For a regression curve fits the error is assessed using the standard error and correlation coefficient. These tools are not perfect, but they give a helpful evaluation of the performance of the fit of the curve. The standard error of the estimate is defined as

$$\sigma = \sqrt{\frac{\sum_{i=1}^n (y - \bar{y})^2}{n - 1}},$$

where \bar{y} denotes the value calculated from the regression model, y_i denotes the data points, and n is the number of parameters in the particular model (so that the denominator is the number of degrees of freedom). Note that this error function is very similar to, but not the same as, the chi-square function discussed in the Theory section. The standard error of the estimate quantifies the spread of the data points around the regression curve. As the quality of the data model increases, the standard error approaches zero.

Another measure of the "goodness of fit" is the correlation coefficient. To explain the meaning of this we must return to the data points and define the standard deviation, which quantifies the spread of the data around the mean:

$$S_t = \sum_{i=1}^{n_{\text{points}}} (\bar{y} - y_i)^2$$

where the average of the data points (\bar{y}) is simply given by

$$\bar{y} = \frac{1}{n_{\text{points}}} \sum_{i=1}^{n_{\text{points}}} y_i$$

The quantity S_t considers the spread around a constant line (the mean) as opposed to the spread around the regression model. This is the uncertainty of the dependent variable prior to regression. We also define the deviation from the fitting curve as

$$S_y = \sum_{i=1}^{n_{\text{points}}} (y_i - f(x_i))^2$$

Note the similarity of this expression to the standard error of the estimate given above; this quantity likewise measures the spread of the points around the fitting function. Thus, the improvement (or error reduction) due to describing the data in terms of a regression model can be quantified by subtracting the two quantities. Because the magnitude of the quantity is dependent on the scale of the data, this difference is normalized to yield

$$r \equiv \sqrt{\frac{S_t - S_r}{S_t}}$$

where r is defined as the correlation coefficient. As the regression model better describes the data, the correlation coefficient will approach unity.

For a perfect fit, the standard error of the estimate will approach $S_r=0$ and the correlation coefficient will approach $r=1$.

In the program the following statistical criteria are used

Fisher criterion F [78MOS/TUK, 81DRA/SMI]

$$F = \frac{MS_R}{S_{rv}^2}$$

where MS_R - average square of error, which is caused by regress

$$MS_R = \frac{(\sum w_i X_i Y_i - (\sum w_i X_i)(\sum w_i Y_i)/n)^2}{(\sum w_i X_i^2) - (\sum w_i X_i)^2/n}$$

S^2 - average square of error, which is caused by residual variation

$$S_{rv}^2 = \frac{\sum w_i Y_i^2 - (\sum w_i Y_i)^2/n - MS_R}{n-2}$$

Coefficient of multiple determination (square of multiple correlation coefficient) r^2 [78MOS/TUK, 81DRA/SMI]

$$r^2 = \frac{\sum w_i (Y_{calc} - \bar{Y})^2}{\sum w_i (Y_i - \bar{Y})^2}$$

Mean square about regression (residual sum of squares) S^2 [77SEB, 82TAY, 86SHA/ILL]:

$$S^2 = \sum_{i=1}^n w_i (Y_i - Y_{calc})^2$$

Root-mean-square regress error $\sigma_{(regress)}$ for n - number of data points and p - number of minimized parameters

$$\sigma_{(regress), \%} = 100 \cdot \sqrt{\frac{1}{n-p} \left(\frac{Y_i - Y_{calc}}{Y_i} \right)^2}$$

Hamilton criterion (comparison of R and R_{lim} criteria)

$$R = \left[\frac{\sum_{i=1}^n w_i (y_i^{pass} - y_i)^2}{\sum_{i=1}^n w_i (y_i)^2} \right]^{0.5}$$

$$R_{\text{lim}} = \left[\frac{\sum_{i=1}^n \varpi_i \sigma^2 y_i}{\sum_{i=1}^n \varpi_i (y_i)^2} \right]^{0.5}.$$

The hypothesis is satisfactory, if $\mathbf{R} > \mathbf{R}_{\text{lim}}$ [\[64HAM\]](#)

Input files

Temp_effects contains the following sample input files:

- Al(OH)4⁻+2F⁻.txt
- Ca²⁺+HMal⁻.txt
- Ca²⁺+Mal²⁻.txt
- Nd³⁺+1CH₃COO⁻.txt
- Nd³⁺+2CH₃COO⁻.txt
- protonation H3Cit.txt
- protonation HF.txt
- protonation H2F.txt
- protonation MOPS.txt
- protonation THAM.txt
- UO₂²⁺+Mal²⁻.txt

The program reads a plain ASCII text file (*.txt or *.dat), which consists of columns.

The first column of data is the temperature (in Kelvin), while the second column holds the log (stability constant) data and the third column holds the uncertainties in log (stability constant) for each data point.

These text files may be produced by hand, by spreadsheet, or any other method that can produce three columns of data.

Note that the type of delimiter in the data file is immaterial. To separate the columns any non-numeric character may be used, e.g. either tab or space.

Comments may be interspersed freely within the data files provided they are placed between '<' and '>' symbols.

As an example:

Nd³⁺+1CH₃COO⁻.txt

<S.A. Wood et al. Chemical Geology, 2000, № 167, p.231-253>

<reaction: Nd³⁺+CH₃COO⁻=NdCH₃COO²⁺ 0.1m NaCl>

<lgK=2.10±0.13; dH=7.27±5.42;dS=60±20;dCp=250±40>

298.05	1.82	0.05
298.15	2.06	0.01
298.15	2.08	0.01
322.65	2.06	0.05
322.95	2.23	0.009
322.95	2.19	0.01
323.05	2.19	0.03
347.85	2.37	0.01
348.05	2.37	0.01
369.55	2.57	0.004
372.35	2.58	0.008
372.95	2.55	0.01
393.15	2.73	0.01
418.25	3.01	0.008
421.75	3.08	0.006
422.35	3.02	0.008
422.95	3.16	0.005
423.15	3.12	0.008

447.85	3.28	0.01
471.15	3.87	0.006
471.35	3.78	0.004
472.65	3.72	0.03
496.45	4.45	0.04
497.55	3.68	0.13
497.85	3.97	0.08

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