
Version 6.2

FitAll

nonlinear regression analysis

Chemistry Functions Guide



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Introduction

This **FitAll™ Chemistry Functions Guide** describes the functions contained in the **Chemistry Functions Library** and has an appendix that explains how to get help from **MTR Software**.

[Function Reference](#) ³

[Appendix](#) ⁵¹

Function Reference

Overview

This section describes each of the functions in *FitAll's Chemistry Functions Library*.

In most cases, a graph of the function is shown. These graphs were created using "typical" parameter and constant values.

The actual appearance of a function depends on the parameter and constant values and may look quite different from the illustrations shown.

Equation

Gives the equation and its variations. The variations are listed in order of increasing complexity.

Constants

Lists the constants, K, that are used in the function. The default values for the constants also are given.

Parameters

Lists the parameters, P, that are used in the function.

Multi-Fits

Describes the Multi-Fit functionality of "Multi-Fit enabled" functions.

Sample Applications

Gives examples of some situations in which the function is known to be used.

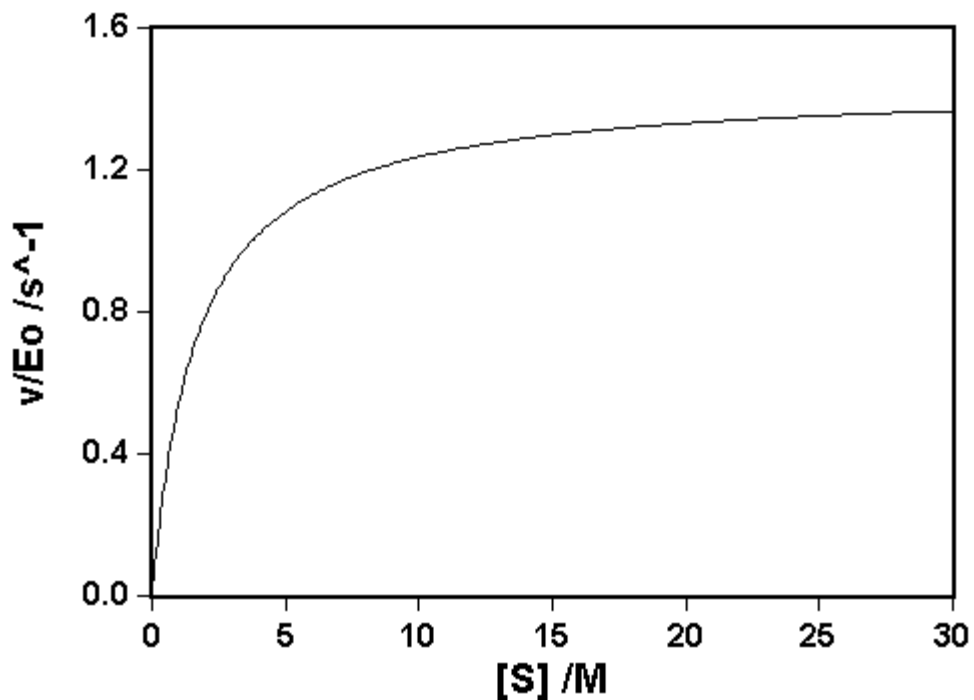
Remarks

Provides general comments and hints, and lists any known limitations or restrictions that should be observed when using the function.

Also see

Provides links or references to other related functions.

Ftn 0401: Michaelis-Menton Kinetics



Equation

Three variations of the function are available. For example:

$$Y = \frac{P1 * X}{(P2 + X)}$$

$$Y = \frac{P1 * X}{(P2 + X)} + \frac{P3 * X}{(P4 + X)}$$

$$Y = \frac{P1 * X}{(P2 + X)} + \frac{P3 * X}{(P4 + X)} + \frac{P5 * X}{(P6 + X)}$$

in which

- Y is the measured response.
- X is the independent variable, often the time in seconds.

Parameters

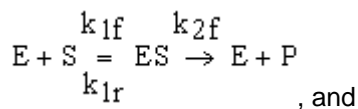
Parameter	Name	Comments
P1	k2	First order rate constant for the conversion of the

Parameter	Name	Comments
		enzyme-substrate complex, ES, of the first enzyme or isozyme to products.
P2	Km	Michaelis constant for the first enzyme (or isozyme).
P3	k2b	First order rate constant for the conversion of the enzyme-substrate complex, ES, of the second enzyme or isozyme to products.
P4	Kmb	Michaelis constant for the second enzyme (or isozyme).
P5	k2c	First order rate constant for the conversion of the enzyme-substrate complex, ES, of the third enzyme or isozyme to products.
P6	Kmc	Michaelis constant for the third enzyme (or isozyme).

Sample Applications

- Fitting initial rate data for the enzyme catalyzed conversion of a substrate, S, to a product, P

For one enzyme, the reaction scheme (mechanism) is:



$$K_M = \frac{(k_{1r} + k_{2f})}{k_{1f}}, \quad k_2 = k_{2f}, \quad Y = v/E_0, \quad X = [S], \quad E_0 \text{ is the initial (total) enzyme concentration (in moles/L) and } v \text{ is the initial rate of product formation (in moles/L/s).}$$

- When more than one enzyme (or isozyme) is present, the second and / or third variations of this function can be used.
- Binding of a ligand or substrate to a metal or receptor.

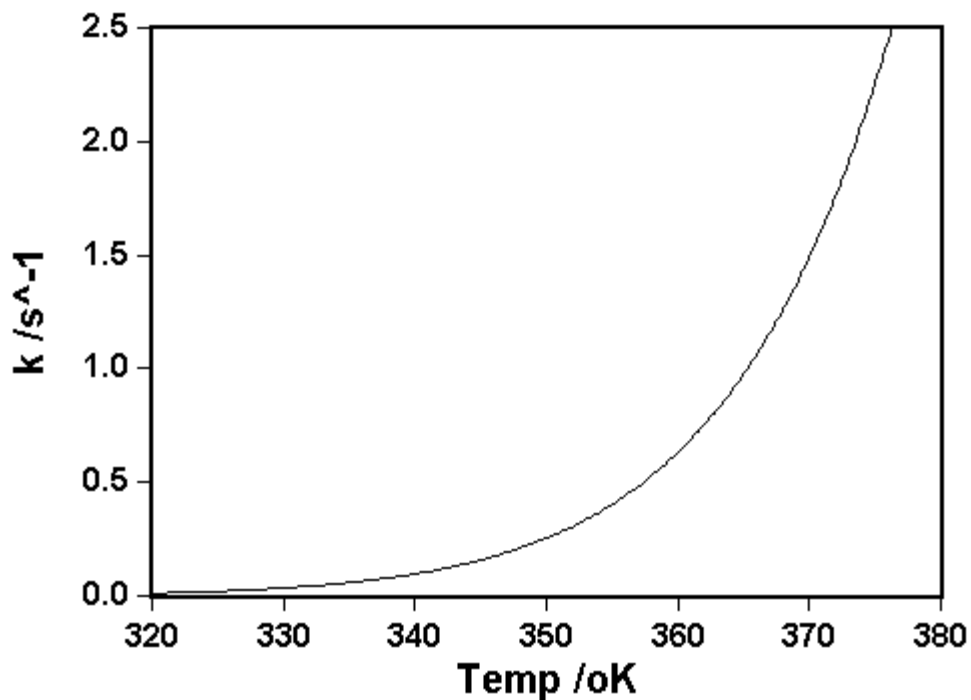
Remarks

This function is very similar to the saturation curve described by function 0205 in the **Binding Curves FitAll Function Library**. The only difference is that the parameters are defined in a slightly different way.

When automatic initial estimates are made, **FitAll** assumes that the data are sorted on column number 1; that is, the X-values.

Frequently, the best fitting strategy is to fit your data, or a segment of it, to one Michaelis-Menton curve before attempting fits with the more complicated forms of this function.

Ftn 0402: Arrhenius Activation Energy



Equation

$$Y = P1 * e^{\left[\frac{-P2}{(K1 * X)} \right]}$$

in which

- Y is the measured response, usually the rate constant
- X is the independent variable, the temperature in $^{\circ}\text{K}$.

Constants

Constant	Name	Comments
K1	R	Universal Gas Constant, $R = 8.3143 \text{ J}/^{\circ}\text{K}/\text{mole}$ or $R = 1.986 \text{ cal}/^{\circ}\text{K}/\text{mole}$ The default value is 8.3143.

Parameters

Parameter	Name	Comments
P1	A	Arrhenius pre-exponential factor.
P2	Ea	Arrhenius activation energy.

Sample Applications

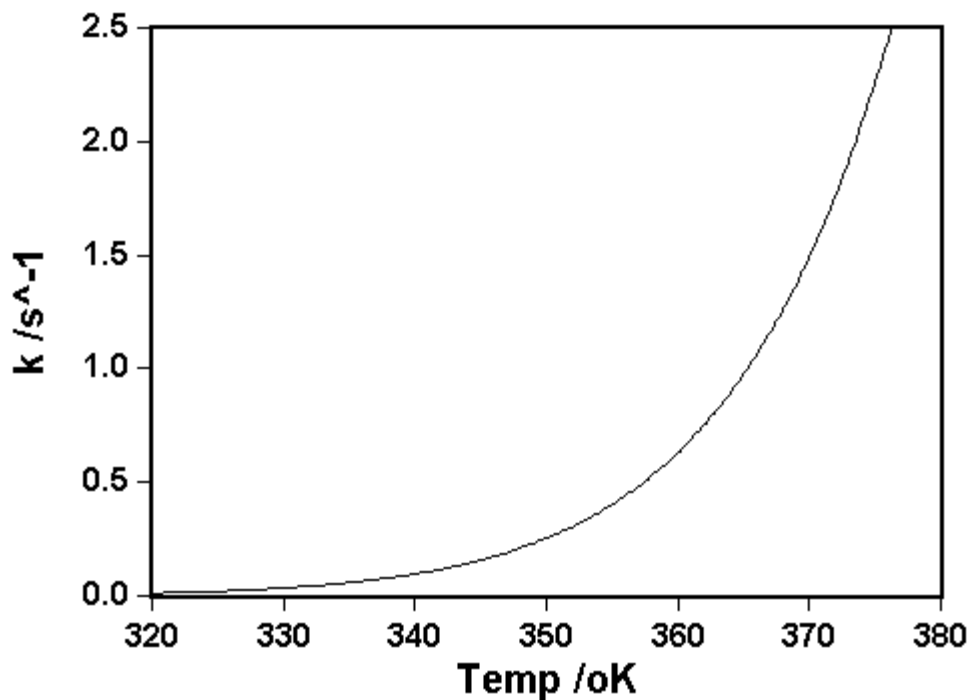
- Determining the Arrhenius activation energy, E_a , from the temperature dependence, X = temperature in $^{\circ}\text{K}$, of the rate constant, Y in s^{-1} .
- Determining the activation energy from the temperature dependence of the rate of a crystallization process.
- Determining the band-gap energy of a semi-conductor from the temperature dependence of the electrical resistivity.

Remarks

Arrhenius activation energy is applicable only over very limited temperature ranges as E_a is also temperature dependent. A better fit of the temperature dependence of a chemical reaction's rate constant usually can be obtained using the equation derived from Absolute Rate Theory, [function 0403](#), to obtain the activation enthalpy, $dH^{\#}$, and activation entropy, $dS^{\#}$.

When automatic initial estimates are made, **FitAll** assumes that the data are sorted on column number 1; that is, the X-values.

Ftn 0403: Activation Enthalpy and Entropy



Equation

$$Y = K1 * X * e^{\left[\frac{-P1}{(K2 * X)} + \frac{P2}{K2} \right]}$$

in which

- Y is the measured response, usually the rate constant.
- X is the independent variable, the temperature in degrees K.

Constants

Constant	Name	Comments
K1	k/h	Ratio: Boltzmann's Constant / Plank's Constant = $2.0842 \times 10^{42} / \text{K/s}$.
K2	R	Universal Gas Constant, R = 8.3143 J/°K/mole or R = 1.986 cal/°K/mole. The default value is 8.3143.

Parameters

Parameter	Name	Comments
P1		Activation Enthalpy
P2		Activation Entropy

Sample Applications

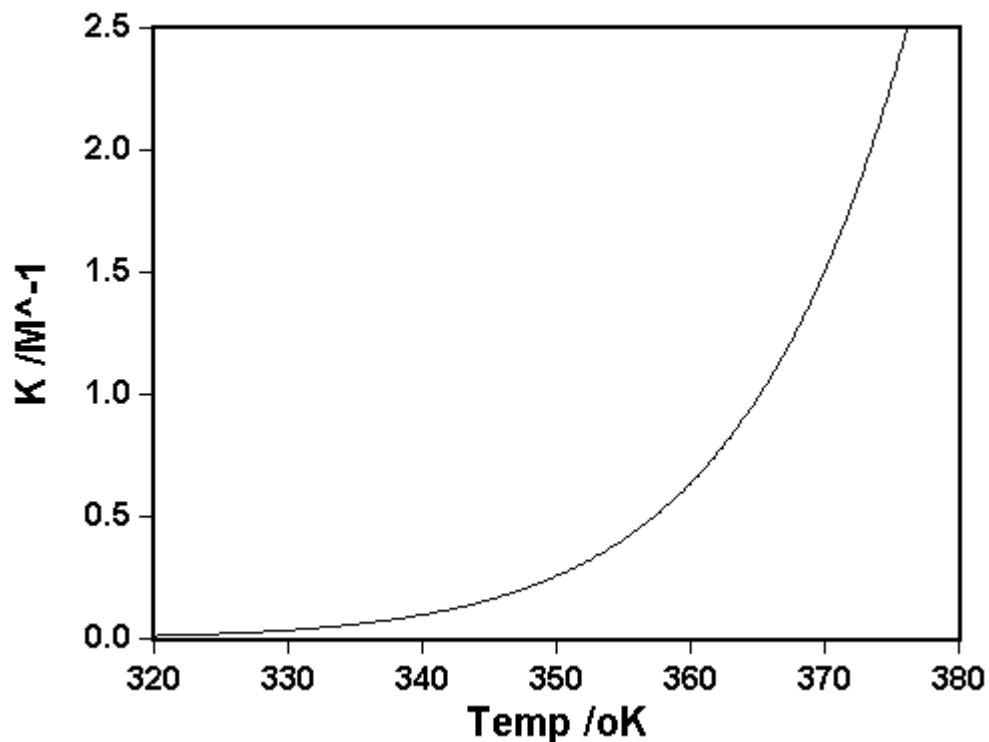
- Determining the activation parameters from the temperature dependence of a first order rate constant; that is, Y is the observed rate constant in s^{-1} and X is the temperature in $^{\circ}K$.

Remarks

The choice of value for $K2$, = R, determines whether the activation enthalpy, dH° , will have units of cal/mole or Joules/mole.

When automatic initial estimates are made, **FitAll** assumes that the data are sorted on column number 1; that is, the X-values.

Ftn 0404: Equilibrium Enthalpy and Entropy



Equation

$$Y = e^{\left[\frac{-P1}{(K1 * X)} + \frac{P2}{K1} \right]}$$

in which

- Y is the measured response.
- X is the independent variable, the temperature in degrees K.

Constants

Constant	Name	Comments
K1	R	Universal Gas Constant, R = 8.3143 J/°K/mole or R = 1.986 cal/°K/mole. The default value is 8.3143.

Parameters

Parameter	Name	Comments
P1	dH	Equilibrium Enthalpy
P2	dS	Equilibrium Entropy

Sample Applications

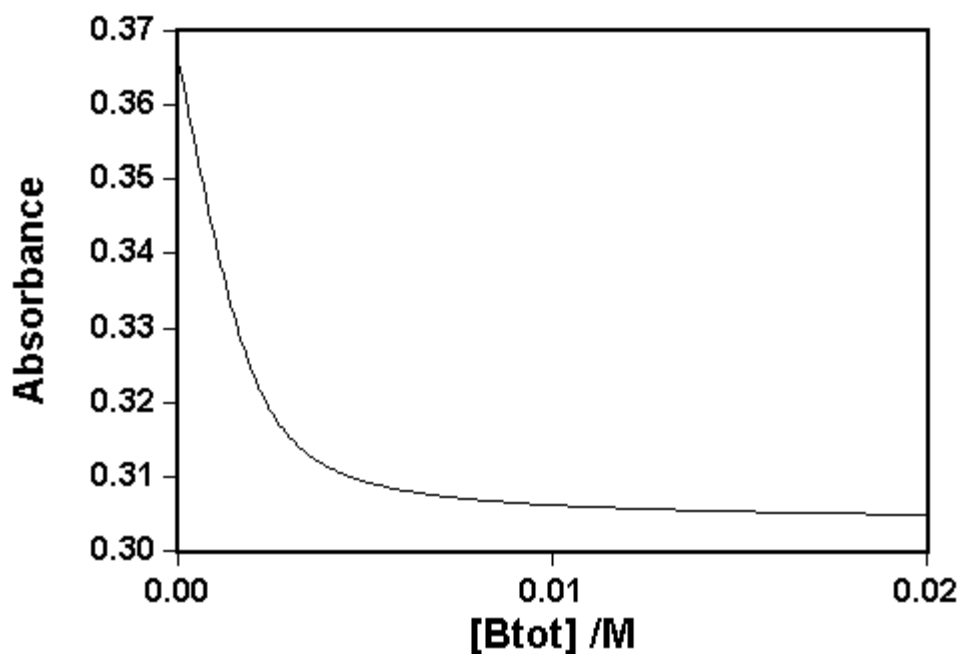
- Determining the Enthalpy, dH, and Entropy, dS, from the temperature dependence of an equilibrium or stability constant.

Remarks

The choice of value for $K1$, = R, determines whether the enthalpy, dH, will have units of cal/mole or Joules/mole.

When automatic initial estimates are made, **FitAll** assumes that the data are sorted on column number 1; that is, the X-values.

Ftn 0405: Reversible Chemical Equilibrium_1: A + B = C, X1 = Btot, K1 = Atot



Equation

Three variations of the function are available:

$$Y = P3 * K1 + P4 * X1 + (P2 - P3 - P4) * \left\{ \frac{P1 * (K1 + X1) + 1 - \sqrt{[P1 * (K1 + X1) + 1]^2 - 4 * P1^2 * K1 * X1}}{2 * P1} \right\}$$

$$Y = P3 * K1 + (P2 - P3) * \left\{ \frac{P1 * (K1 + X1) + 1 - \sqrt{[P1 * (K1 + X1) + 1]^2 - 4 * P1^2 * K1 * X1}}{2 * P1} \right\}$$

$$Y = P2 * \left\{ \frac{P1 * (K1 + X1) + 1 - \sqrt{[P1 * (K1 + X1) + 1]^2 - 4 * P1^2 * K1 * X1}}{2 * P1} \right\}$$

in which

- Y is the measured response.
- X1 is the total concentration of B, [Btot].

Constants

Constant	Name	Comments
K1	[Atot]	Total (constant) concentration of component A.

Parameters

Parameter	Name	Comments
P1	Q	Equilibrium (association or formation) quotient (constant) defined as: $Q = [C]/([A]*[B])$.
P2	Rc	Specific response factor for C; for example, the extinction coefficient, absorbtivity, or specific conductivity of C. Specific response factors, R, are assumed to be directly proportional to the concentration of the substance being monitored. For example, the response due to C, Yc, is given by: $Yc = Rc * [C]$.
P3	Ra	Specific response factor for substance A. In the third variation of this function it is assumed that $Ra = 0$.
P4	Rb	Specific response factor for substance B. In the second and third variations of this function it is assumed that $Rb = 0$.

Sample Applications

- Determining the equilibrium (stability or formation) constant for binding of a ligand or substrate to a metal ion or an enzyme.

Remarks

Alternate ways of expressing the same type of chemical reaction are:

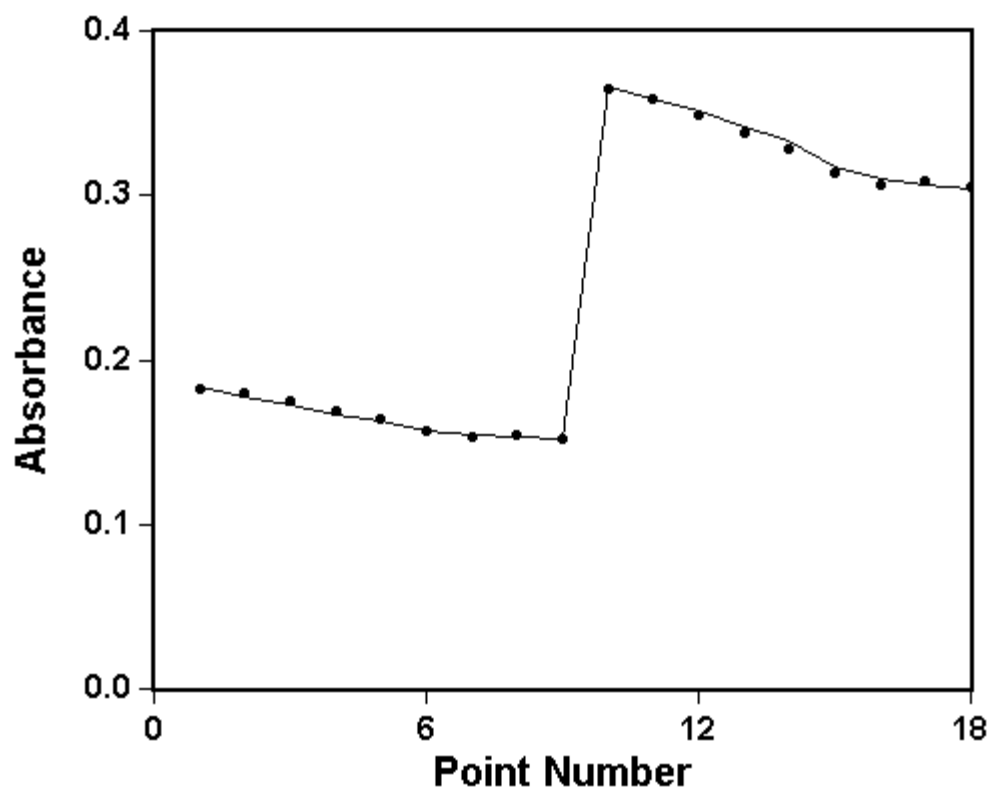
- $A + B = AB$
- $M + L = ML$
- $E + S = ES$

This function was derived assuming that:

- The total concentration of A, $[A_{tot}]$, is the same (constant) for all data points. If this is not the case, see [function 0406](#) ^[15].
- Initially no C is present. That is, all of the reaction product, C, is derived from the substances A and B that are admixed.
- The total concentrations of A and B may be of similar magnitude. That is, under some conditions the reaction of A with B may consume a significant amount of B.
- If the concentration of B is always much larger than that of A, $[B_{tot}] \gg [A_{tot}]$, the function can be simplified and closely approximated by a simpler saturation curve, see functions 0203 and 0206 in the **Binding Curves *FitAll* Function Library**.
- The reaction is reversible and its stoichiometry is 1:1:1.

When automatic initial estimates are made, ***FitAll*** assumes that the data are sorted on column number 1; that is, the X-values.

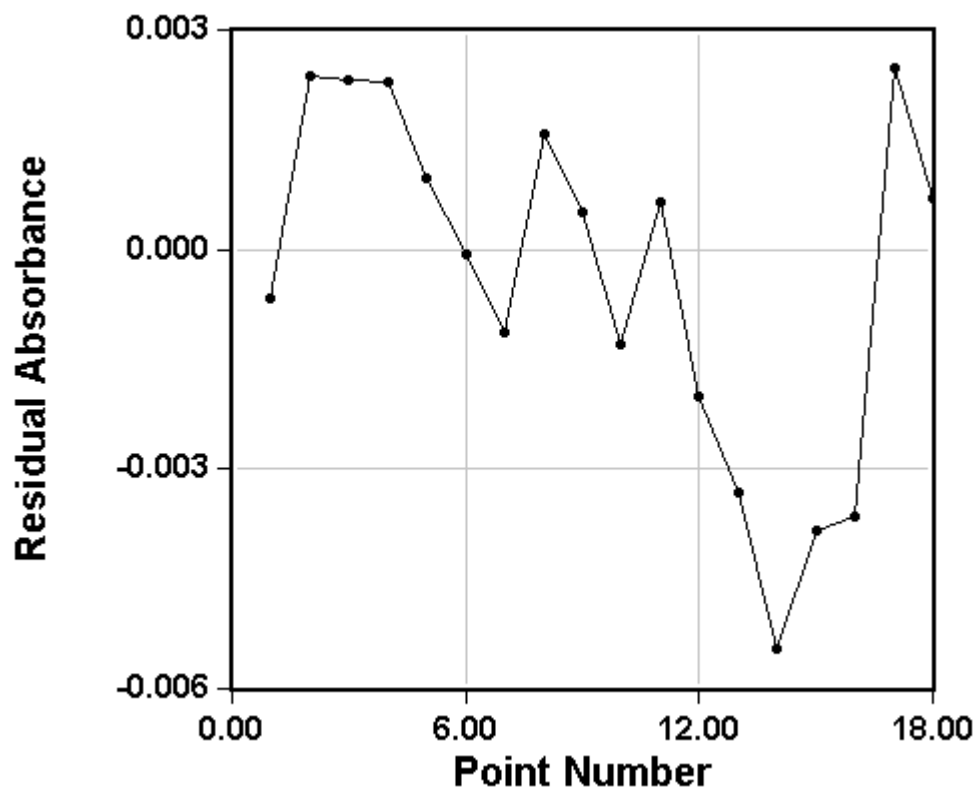
Ftn 0406: Reversible Chemical Equilibrium_2: $A + B = C$, $X1 = B_{tot}$, $X2 = A_{tot}$



NOTE:

This function has two independent variables, A_{tot} ($X2$) and B_{tot} ($X1$). The only way to plot a meaningful fit graph in this situation is to plot Y versus the "Point Number" rather than the value of the independent variable, X .

The best way to get a visual indication of the quality of the fit is to view the residuals graph, such as the one shown below.



Equation

Three variations of the function are available:

$$Y = P3 * X2 + P4 * X1 + (P2 - P3 - P4) *$$

$$\left\{ \frac{P1 * (X2 + X1) + 1 - \sqrt{([P1 * (X2 + X1) + 1]^2 - 4 * P1^2 * X2 * X1)}}{2 * P1} \right\}$$

$$Y = P3 * X2 + (P2 - P3) *$$

$$\left\{ \frac{P1 * (X2 + X1) + 1 - \sqrt{([P1 * (X2 + X1) + 1]^2 - 4 * P1^2 * X2 * X1)}}{2 * P1} \right\}$$

$$Y = P2 * \left\{ \frac{P1 * (X2 + X1) + 1 - \sqrt{([P1 * (X2 + X1) + 1]^2 - 4 * P1^2 * X2 * X1)}}{2 * P1} \right\}$$

in which

- Y is the measured response.
- X1 is the total concentration of B, [Btot].
- X2 is the total concentration of A, [Atot].

Parameters

Parameter	Name	Comments
P1	Q	Equilibrium (association or formation) quotient (constant) defined as: $Q = [C]/([A]*[B])$.
P2	Rc	Specific response factor for C; for example, the extinction coefficient, absorbtivity, or specific conductivity of C. Specific response factors, R, are assumed to be directly proportional to the concentration of the substance being monitored. For example, the response due to C, Yc, is given by: $Yc = Rc * [C]$.
P3	Ra	Specific response factor for substance A. In the third variation of this function it is assumed that $Ra = 0$.
P4	Rb	Specific response factor for substance B. In the second and third variations of this function it is assumed that $Rb = 0$.

Sample Applications

- Determining the equilibrium (stability or formation) constant for binding of a ligand or substrate to a metal ion or an enzyme.

Remarks

Alternate ways of expressing the same type of chemical reaction are:

- $A + B = AB$
- $M + L = ML$
- $E + S = ES$

This function was derived assuming that:

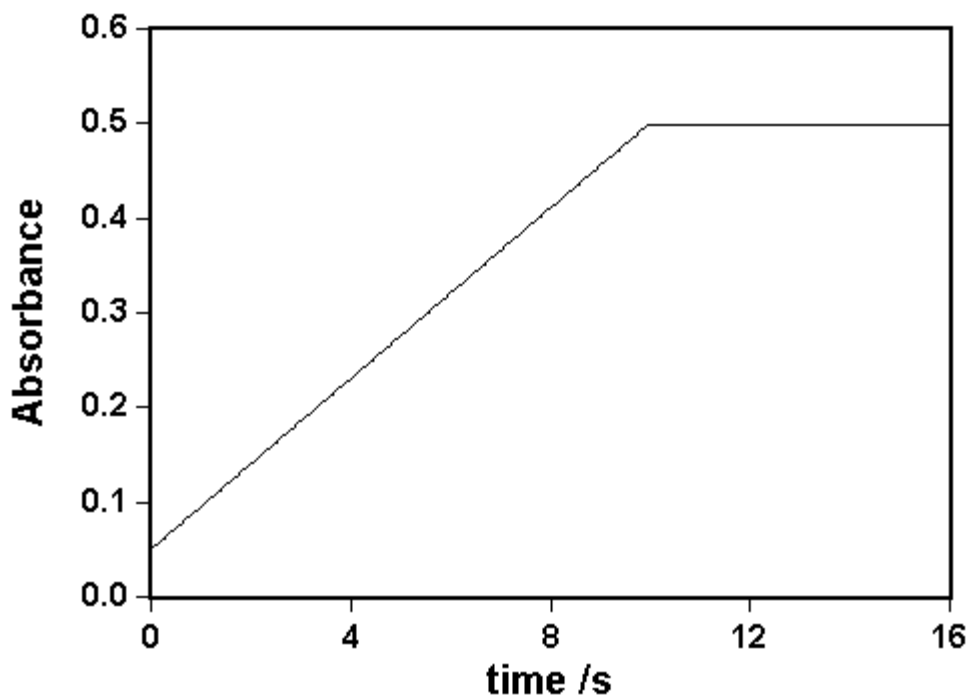
- Initially no C is present. That is, all of the reaction product, C, is derived from the substances A and B that are admixed.

- The total concentrations of A and B may be of similar magnitude. That is, under some conditions the reaction of A with B may consume a significant amount of B.
- The reaction is reversible and its stoichiometry is 1:1:1.

Because this function has two independent variables, X1 and X2, there is no convenient way for **FitAll** to automatically calculate the initial parameter estimates.

In some cases, you can obtain these estimates by fitting part of the data to [function 0405](#)¹². When you do this, choose an analysis range over which the X2-values are (reasonably) constant and assign K1 a value equal to the average of these X2-values.

Ftn 0407: Chemical Kinetics: Zero-Order Rxn: $A \rightarrow B$, $-dA/dt = k$



Equation

Two variations of the function are available:

$$Y = \begin{cases} P2 * K1, & \text{for } X < 0 \\ P2 * K1 + (P3 - P2) * P1 * X, & \text{for } 0 \leq X \leq \frac{K1}{P1} \\ P3 * K1, & \text{for } X > \frac{K1}{P1} \end{cases}$$

$$Y = \begin{cases} P2 * K1, & \text{for } X < 0 \\ P2 * (K1 - P1 * X), & \text{for } 0 \leq X \leq \frac{K1}{P1} \\ 0, & \text{for } X > \frac{K1}{P1} \end{cases}$$

in which

- Y is the measured response.
- X is the independent variable, often the time in seconds.

Constants

Constant	Name	Comments
K1	Ao	Total (initial) concentration of component A. Default value is 1.0.

Parameters

Parameter	Name	Comments
P1	k	Rate constant.
P2	Ra	Specific response factor for A; for example, the extinction coefficient, absorbtivity, or specific conductivity of A. Specific response factors, R, are assumed to be directly proportional to the concentration of the substance being monitored. For example, the response due to A, Ya, is given by: $Y_a = R_a * [A]$. If the analysis is done using the default value of K1 (= 1.0), the resolved value of P2 corresponds to $R_a * A_o$.
P3	Rb	Specific response factor for substance B. If the analysis is done using the default value of K1 (= 1.0), the resolved value of P3 corresponds to $R_b * A_o$. In the second variation of this function it is assumed that $R_b = 0$.

Sample Applications

- Determining the rate constant for a zero-order decomposition of a chemical substance or enzyme.

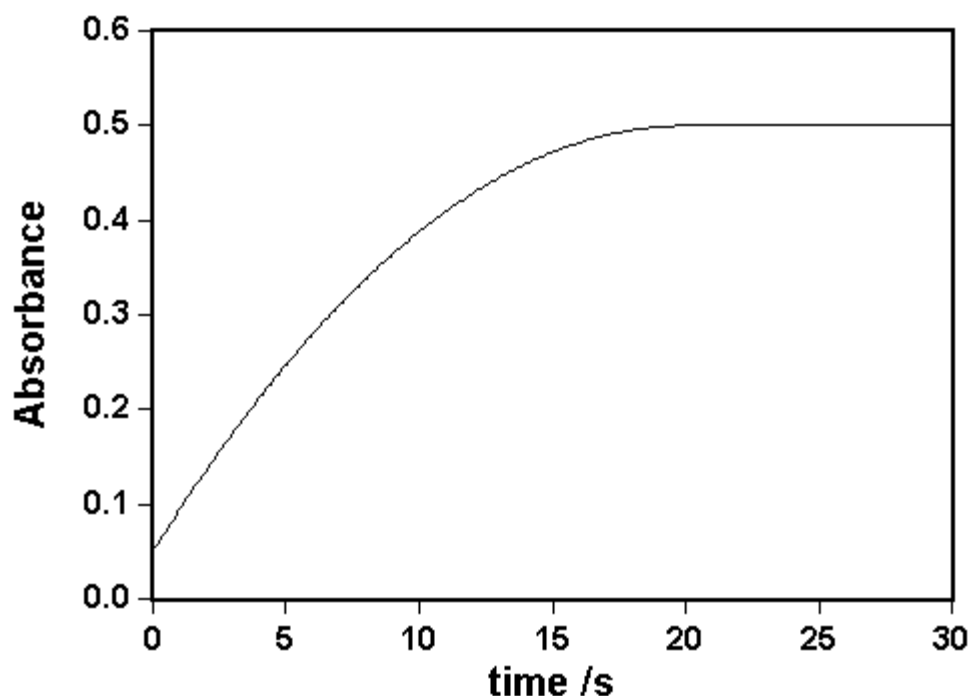
Remarks

This function was derived assuming that:

- The reaction stoichiometry is 1:1.
- Initially, no B is present. That is, all of the reaction product, B, is derived from A.
- The reaction is irreversible; that is, it goes to completion.
- The reaction rate is given by: $d[A]/dt = k$.

When automatic initial estimates are made, **FitAll** assumes that the data are sorted on column number 1; that is, the X-values.

Ftn 0408: Chemical Kinetics: Half-Order Rxn: A → B, $dA/dt = k \cdot A^{(1/2)}$



Equation

Two variations of the function are available:

$$Y = \begin{cases} P2 * K1, & \text{for } X < 0 \\ P2 * K1 + (P3 - P2) * P1 * X * \frac{4 * \sqrt{K1} - P1 * X}{4}, & \text{for } 0 \leq X \leq \frac{2 * \sqrt{K1}}{P1} \\ P3 * K1, & \text{for } X > \frac{2 * \sqrt{K1}}{P1} \end{cases}$$

$$Y = \begin{cases} P2 * K1, & \text{for } X < 0 \\ P2 * \left[K1 - P1 * X * \frac{4 * \sqrt{K1} - P1 * X}{4} \right], & \text{for } 0 \leq X \leq \frac{2 * \sqrt{K1}}{P1} \\ 0, & \text{for } X > \frac{2 * \sqrt{K1}}{P1} \end{cases}$$

in which

- Y is the measured response.

- X is the independent variable, often the time in seconds.

Constants

Constant	Name	Comments
K1	Ao	Total (initial) concentration of component A. Default value is 1.0. An appropriate value must be assigned to K1 if meaningful results are to be obtained.

Parameters

Parameter	Name	Comments
P1	k	Rate constant.
P2	Ra	Specific response factor for A; for example, the extinction coefficient, absorbtivity, or specific conductivity of A. Specific response factors, R, are assumed to be directly proportional to the concentration of the substance being monitored. For example, the response due to A, Ya, is given by: $Y_a = R_a * [A]$. If the analysis is done using the default value of K1 (= 1.0), the resolved value of P2 corresponds to $R_a * A_o$.
P3	Rb	Specific response factor for substance B. If the analysis is done using the default value of K1 (= 1.0), the resolved value of P3 corresponds to $R_b * A_o$. In the second form of this function it is assumed that $R_b = 0$.

Sample Applications

- Determining the rate constant for a half-order decomposition of a chemical substance or enzyme.

Remarks

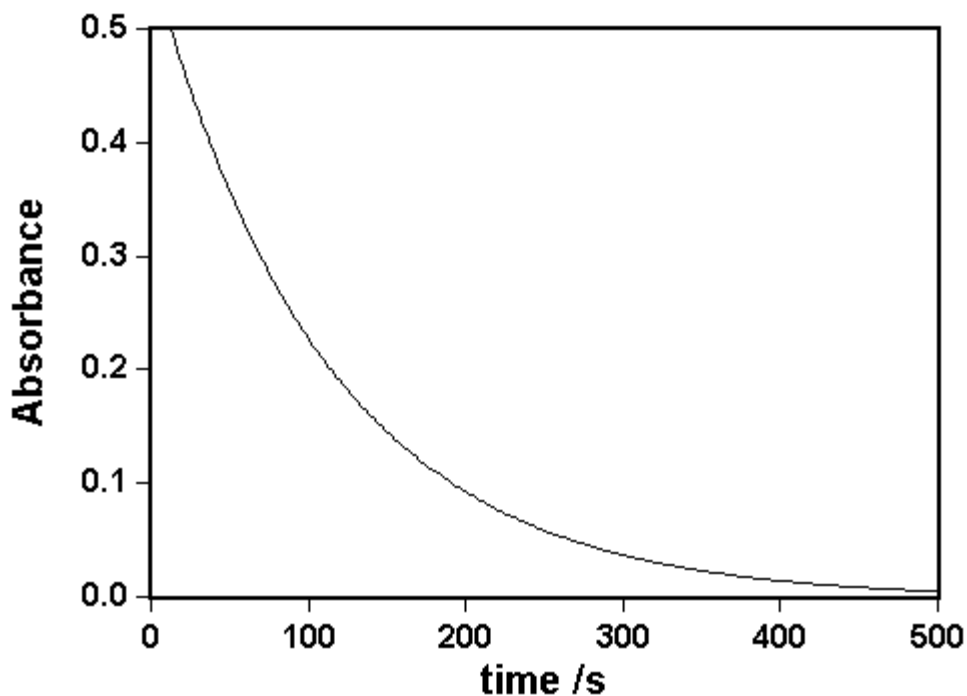
This function was derived assuming that:

- The reaction stoichiometry is 1:1.

- Initially, no B is present. That is, all of the reaction product, B, is derived from A.
- The reaction is irreversible; that is, it goes to completion.
- The reaction rate is given by: $d[A]/dt = k[A]^{1/2}$.

When automatic initial estimates are made, **FitAll** assumes that the data are sorted on column number 1; that is, the X-values.

Ftn 0409: Chemical Kinetics: First-Order Rxn: $A \rightarrow B$, $dA/dt = k \cdot A$



Equation

Two variations of the function are available:

- $Y = K1 * [P2 + (P3 - P2) * (1 - e^{-P1 * X})]$
- $Y = K1 * P2 * e^{-P1 * X}$

in which

- Y is the measured response.
- X is the independent variable, often the time in seconds.

Constants

Constant	Name	Comments
K1	Ao	Total (initial) concentration of component A. Default value is 1.0.

Parameters

Parameter	Name	Comments
P1	k	Rate constant.
P2	Ra	Specific response factor for A; for example, the extinction coefficient, absorbtivity, or specific conductivity of A. Specific response factors, R, are assumed to be directly proportional to the concentration of the substance being monitored. For example, the response due to A, Ya, is given by: $Y_a = R_a * [A]$. If the analysis is done using the default value of K1 (= 1.0), the resolved value of P2 corresponds to $R_a * A_o$.
P3	Rb	Specific response factor for substance B. If the analysis is done using the default value of K1 (= 1.0), the resolved value of P3 corresponds to $R_b * A_o$. In the second form of this function it is assumed that $R_b = 0$.

Sample Applications

- Determining the rate constant for a first-order decomposition of a chemical substance or enzyme.

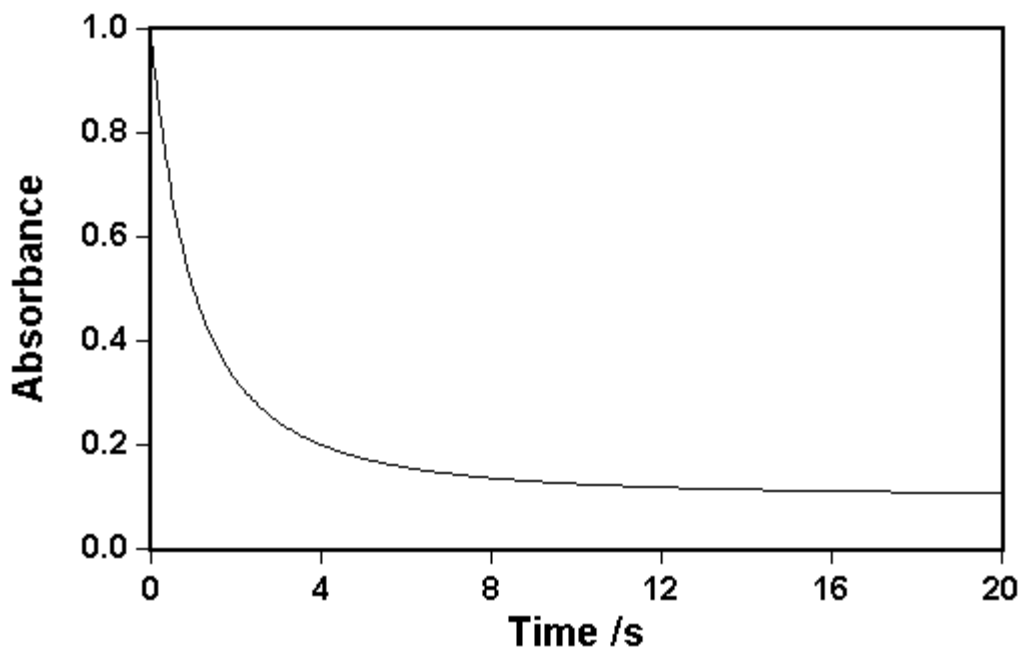
Remarks

This function was derived assuming that:

- The reaction stoichiometry is 1:1.
- Initially, no B is present. That is, all of the reaction product, B, is derived from A.
- The reaction is irreversiblereversible; that is, it goes to completion.
- The reaction rate is given by: $d[A]/dt = k*[A]$.

When automatic initial estimates are made, **FitAll** assumes that the data are sorted on column number 1; that is, the X-values.

Ftn 0410: Chemical Kinetics: (3/2)-Order Rxn: A -> B, $dA/dt = k \cdot A^{(3/2)}$



Equation

Two variations of the function are available:

- $$Y = K1 \cdot P2 + (P3 - P2) \cdot K1 \cdot \left(1 - \frac{4}{(2 + P1 \cdot \sqrt{K1} \cdot X)^2} \right)$$

- $$Y = K1 \cdot P2 - P2 \cdot K1 \cdot \left(1 - \frac{4}{(2 + P1 \cdot \sqrt{K1} \cdot X)^2} \right)$$

in which

- Y is the measured response.
- X is the independent variable, often the time in seconds.

Constants

Constant	Name	Comments
K1	Ao	Total (initial) concentration of component A. Default value is 1.0.

Parameters

Parameter	Name	Comments
P1	k	Rate constant.
P2	Ra	Specific response factor for A; for example, the extinction coefficient, absorbtivity, or specific conductivity of A. Specific response factors, R, are assumed to be directly proportional to the concentration of the substance being monitored. For example, the response due to A, Ya, is given by: $Y_a = R_a * [A]$. If the analysis is done using the default value of K1 (= 1.0), the resolved value of P2 corresponds to $R_a * A_o$.
P3	Rb	Specific response factor for substance B. In the second form of this function it is assumed that $R_b = 0$.

Sample Applications

- Determining the rate constant for a (3/2)-order decomposition of a chemical substance or enzyme.

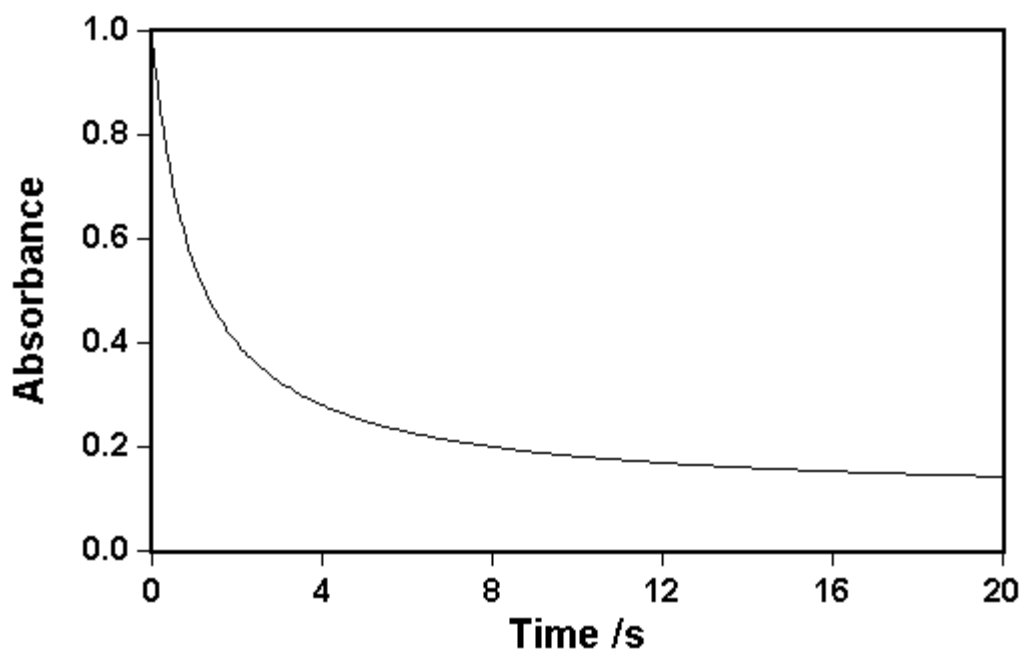
Remarks

This function was derived assuming that:

- The reaction stoichiometry is 1:1.
- Initially, no B is present. That is, all of the reaction product, B, is derived from A.
- The reaction is irreversiblereversible; that is, it goes to completion.
- The reaction rate is given by: $d[A]/dt = k*[A]^{3/2}$.

When automatic initial estimates are made, **FitAll** assumes that the data are sorted on column number 1; that is, the X-values.

**Ftn 0411: Chemical Kinetics: Second-Order (equal) Rxn_1: A
 -> B, $dA/dt = k \cdot A^2$**



Equation

Two variations of the function are available:

- $$Y = K1 \cdot P2 + \frac{(P3 - P2) \cdot P1 \cdot K1^2 \cdot X}{(1 + P1 \cdot K1 \cdot X)}$$

- $$Y = K1 \cdot P2 - \frac{P2 \cdot P1 \cdot K1^2 \cdot X}{(1 + P1 \cdot K1 \cdot X)}$$

in which

- Y is the measured response.
- X is the independent variable, often the time in seconds.

Constants

Constant	Name	Comments
K1	Ao	Total (initial) concentration of component A. Default value is 1.0. An appropriate value must be assigned to K1 if meaningful results are to be obtained.

Parameters

Parameter	Name	Comments
P1	k	Rate constant.
P2	Ra	Specific response factor for A; for example, the extinction coefficient, absorbtivity, or specific conductivity of A. Specific response factors, R, are assumed to be directly proportional to the concentration of the substance being monitored. For example, the response due to A, Ya, is given by: $Y_a = R_a * [A]$.
P3	Rb	Specific response factor for substance B. In the second form of this function it is assumed that $R_b = 0$.

Sample Applications

- Determining the rate constant for a second-order chemical reaction.

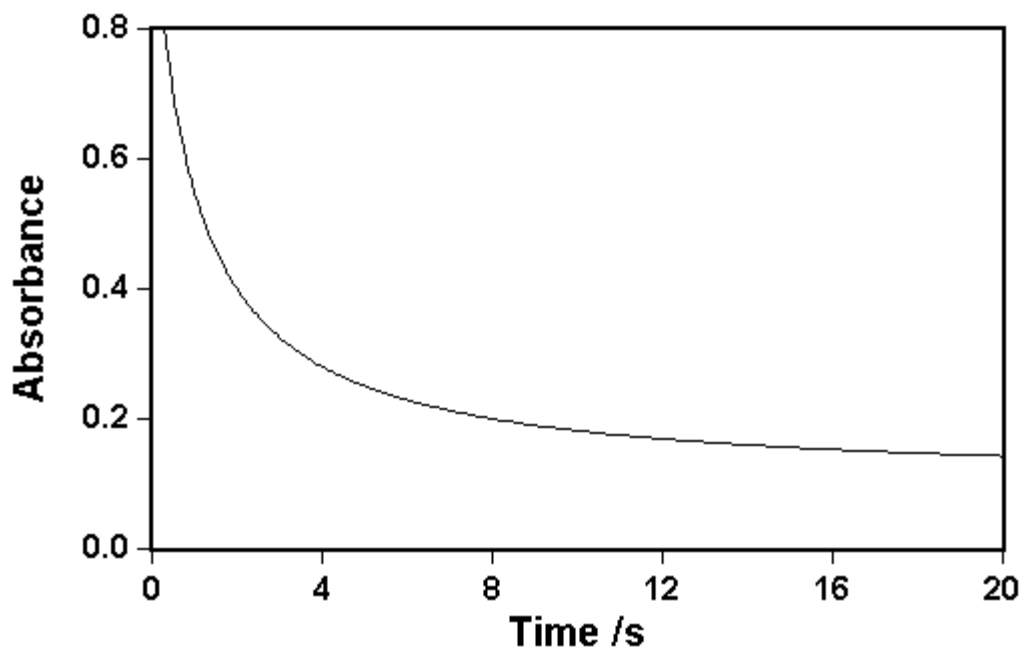
Remarks

This function was derived assuming that:

- The reaction stoichiometry is 1:1.
- Initially, no B is present. That is, all of the reaction product, B, is derived from A.
- The reaction is irreversiblereversible; that is, it goes to completion.
- The reaction rate is given by: $d[A]/dt = k*[A]^2$.

When automatic initial estimates are made, **FitAll** assumes that the data are sorted on column number 1; that is, the X-values.

Ftn 0412: Chemical Kinetics: Second-Order (equal) Rxn_2:
2A -> B, $dA/dt = k \cdot A^2$



Equation

Two variations of the function are available:

- $$Y = K_1 \cdot P_2 + \frac{\left(\frac{P_3}{2} - P_2\right) \cdot P_1 \cdot K_1^2 \cdot X}{(1 + P_1 \cdot K_1 \cdot X)}$$

- $$Y = K_1 \cdot P_2 - \frac{P_2 \cdot P_1 \cdot K_1^2 \cdot X}{(1 + P_1 \cdot K_1 \cdot X)}$$

in which

- Y is the measured response.
- X is the independent variable, often the time in seconds.

Constants

Constant	Name	Comments
K1	Ao	Total (initial) concentration of component A. Default value is 1.0. An appropriate value must be assigned to K1 if meaningful results are to be obtained.

Parameters

Parameter	Name	Comments
P1	k	Rate constant.
P2	Ra	Specific response factor for A; for example, the extinction coefficient, absorbtivity, or specific conductivity of A. Specific response factors, R, are assumed to be directly proportional to the concentration of the substance being monitored. For example, the response due to A, Ya, is given by: $Y_a = R_a * [A]$.
P3	Rb	Specific response factor for substance B. In second form of this function it is assumed that $R_b = 0$.

Sample Applications

- Determining the rate constant for a second-order chemical reaction.

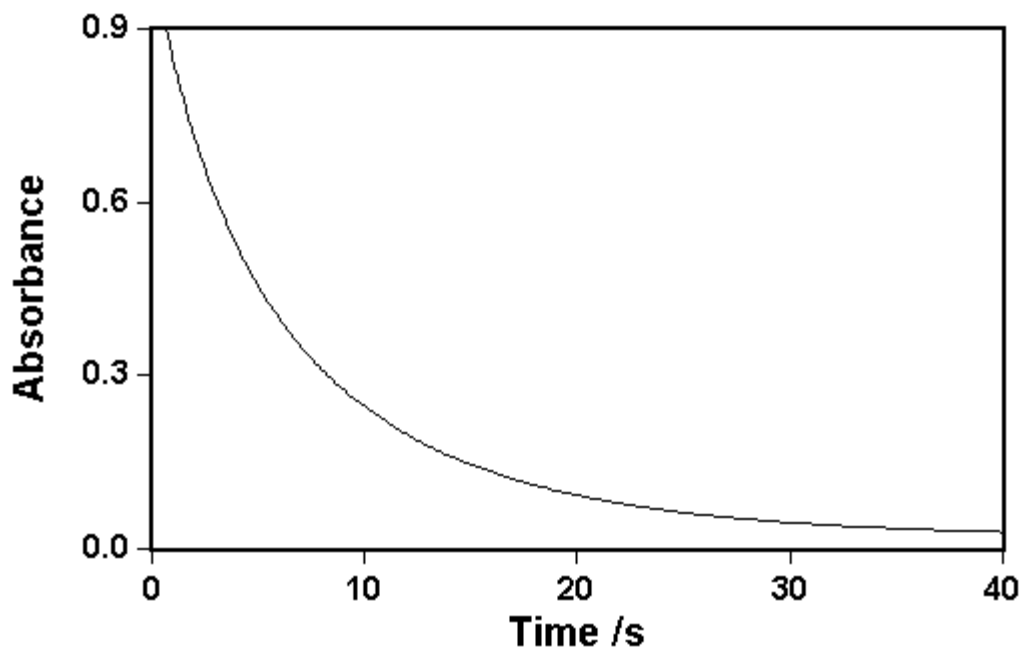
Remarks

This function was derived assuming that:

- The reaction stoichiometry is 2:1.
- Initially, no B is present. That is, all of the reaction product, B, is derived from A.
- The reaction is irreversiblereversible; that is, it goes to completion.
- The reaction rate is given by: $d[A]/dt = k*[A]^2$.

When automatic initial estimates are made, **FitAll** assumes that the data are sorted on column number 1; that is, the X-values.

Ftn 0413: Chemical Kinetics: Second-Order (unequal) Rxn: A + B -> C, $dA/dt = k \cdot A \cdot B$



Equation

Two variations of the function are available:

$$Y = K1 \cdot P2 + K2 \cdot P3 + \frac{(P4 - P3 - P2) \cdot K1 \cdot K2 \cdot [1 - e^{(K2 - K1) \cdot P1 \cdot X}]}{K1 - K2 \cdot e^{(K2 - K1) \cdot P1 \cdot X}}$$

$$Y = K1 \cdot P2 + K2 \cdot P3 - \frac{(P3 + P2) \cdot K1 \cdot K2 \cdot [1 - e^{(K2 - K1) \cdot P1 \cdot X}]}{K1 - K2 \cdot e^{(K2 - K1) \cdot P1 \cdot X}}$$

in which

- Y is the measured response.
- X is the independent variable, often the time in seconds.

Constants

Constant	Name	Comments
K1	Ao	Total (initial) concentration of component A. Default value is 1.0. An appropriate value must be assigned to K1 if

Constant	Name	Comments
		meaningful results are to be obtained.
K2	Bo	Total (initial) concentration of component B. Default value is 2.0. An appropriate value must be assigned to K2 if meaningful results are to be obtained.

Parameters

Parameter	Name	Comments
P1	k	Rate constant.
P2	Ra	Specific response factor for A; for example, the extinction coefficient, absorbtivity, or specific conductivity of A. Specific response factors, R, are assumed to be directly proportional to the concentration of the substance being monitored. For example, the response due to A, Ya, is given by: $Y_a = R_a * [A]$.
P3	Rb	Specific response factor for substance B. In the second form of this function it is assumed that $R_b = 0$.

Sample Applications

- Determining the rate constant for a second-order chemical reaction.

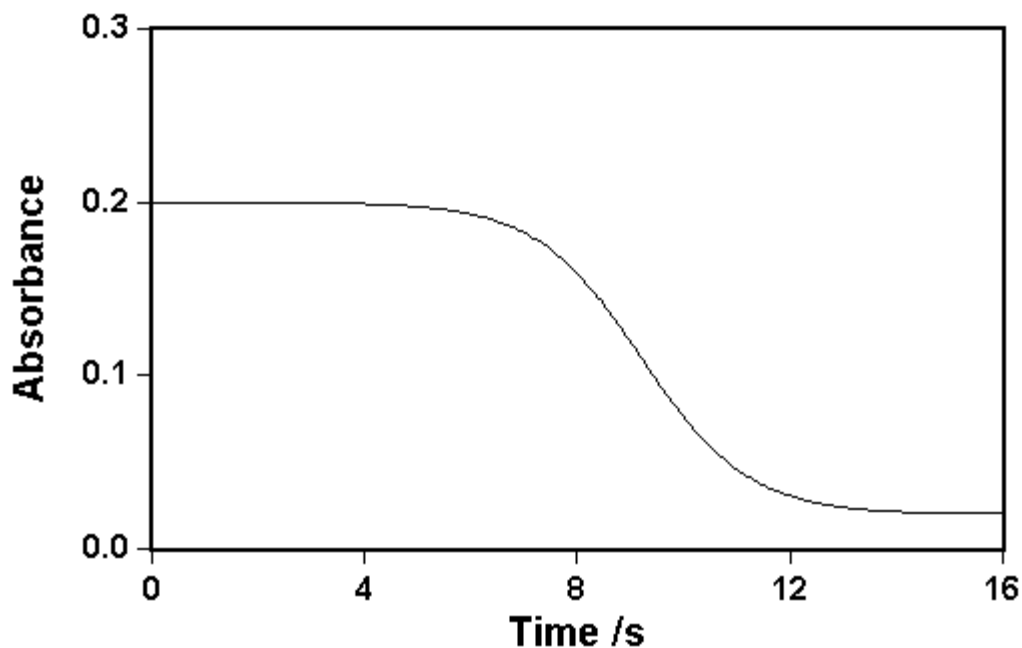
Remarks

This function was derived assuming that:

- The reaction stoichiometry is 1:1:1.
- Initially, no B is present. That is, all of the reaction product, B, is derived from A.
- The reaction is irreversiblereversible; that is, it goes to completion.
- The reaction rate is given by: $d[A]/dt = k*[A]*[B]$.

When automatic initial estimates are made, **FitAll** assumes that the data are sorted on column number 1; that is, the X-values.

Ftn 0414: Chemical Kinetics: Autocatalysis_1: A → B, $dA/dt = k \cdot A \cdot B$, B_0 Known



Equation

Two variations of the function are available:

$$Y = K_1 \cdot P_2 + K_2 \cdot P_3 + \frac{(P_3 - P_2) \cdot K_1 \cdot K_2 \cdot \left(1 - e^{-(K_2 - K_1) \cdot P_1 \cdot X}\right)}{K_2 + K_1 \cdot e^{-(K_2 - K_1) \cdot P_1 \cdot X}}$$

$$Y = K_1 \cdot P_2 - \frac{P_2 \cdot K_1 \cdot K_2 \cdot \left(1 - e^{-(K_2 - K_1) \cdot P_1 \cdot X}\right)}{K_2 + K_1 \cdot e^{-(K_2 - K_1) \cdot P_1 \cdot X}}$$

in which

- Y is the measured response.
- X is the independent variable, often the time in seconds.

Constants

Constant	Name	Comments
K1	Ao	Total (initial) concentration of component A. Default value is 1.0. An appropriate value must be assigned to K1 if meaningful results are to be obtained.
K2	Bo	Total (initial) concentration of component B. Default value is 1.0×10^{-4} . An appropriate value must be assigned to K2 if meaningful results are to be obtained.

Parameters

Parameter	Name	Comments
P1	k	Rate constant.
P2	Ra	Specific response factor for A; for example, the extinction coefficient, absorbtivity, or specific conductivity of A. Specific response factors, R, are assumed to be directly proportional to the concentration of the substance being monitored. For example, the response due to A, Ya, is given by: $Y_a = R_a \cdot [A]$.
P3	Rb	Specific response factor for substance B. In the second form of this function it is assumed that $R_b = 0$.

Sample Applications

- Determining the rate constant for an auto-catalytic chemical or biochemical reaction which has been "spiked" with a (small) known amount of the product, B, to initiate the reaction.

Remarks

This function was derived assuming that:

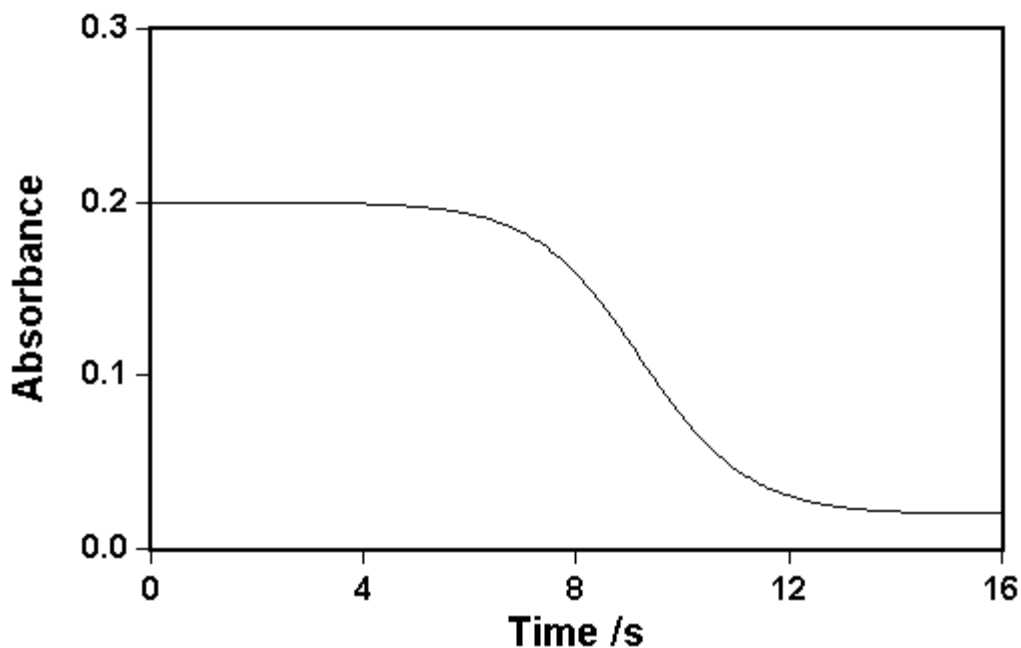
- The reaction stoichiometry is 1:1.
- Initially, there is a (small) known amount of B is present.
- The reaction is irreversiblereversible; that is, it goes to completion.

- The reaction rate is given by: $d[A]/dt = k[A][B]$.

If the reaction is initiated by the spontaneous decomposition of a very small (unknown) amount of A, [function 0415](#) 38 should be used to analyze the data.

When automatic initial estimates are made, **FitAll** assumes that the data are sorted on column number 1; that is, the X-values.

Ftn 0415: Chemical Kinetics: Autocatalysis_2: A -> B, dA/dt = k*A*B, Bo UnKnown



Equation

Two variations of the function are available:

$$Y = K1 * P3 + P2 * P4 + \frac{(P4 - P3) * K1 * P2 * \left(1 - e^{-(P2 - K1) * P1 * X}\right)}{P2 + K1 * e^{-(P2 - K1) * P1 * X}}$$

$$Y = K1 * P3 - \frac{P3 * K1 * P2 * \left(1 - e^{-(P2 - K1) * P1 * X}\right)}{P2 + K1 * e^{-(P2 - K1) * P1 * X}}$$

in which

- Y is the measured response.
- X is the independent variable, often the time in seconds.

Constants

Constant	Name	Comments
K1	Ao	Total (initial) concentration of component A. Default value is 1.0. An appropriate value must be assigned to K1 if meaningful results are to be obtained.

Parameters

Parameter	Name	Comments
P1	k	Rate constant.
P2	[B]o	Total (initial) concentration of component B.
P3	Ra	Specific response factor for A; for example, the extinction coefficient, absorbtivity, or specific conductivity of A. Specific response factors, R, are assumed to be directly proportional to the concentration of the substance being monitored. For example, the response due to A, Ya, is given by: $Y_a = R_a * [A]$.
P4	Rb	Specific response factor for substance B. In the second form of this function it is assumed that $R_b = 0$.

Sample Applications

- Determining the rate constant for an auto-catalytic chemical or biochemical reaction which has been "spiked" with a (small) unknown amount of the product, B, to initiate the reaction. The B initially present may have resulted from the spontaneous decomposition of A or it may have been present as an impurity in the reagents.

Remarks

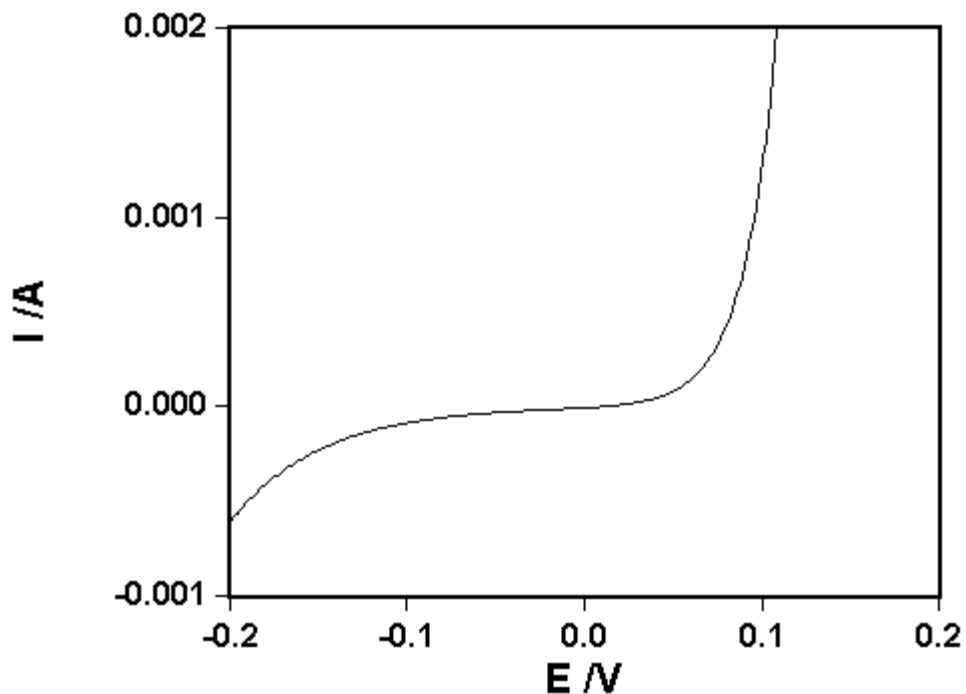
This function was derived assuming that:

- The reaction stoichiometry is 1:1.
- Initially, there a (small) unknown amount of B is present.
- The reaction is irreversible; that is, it goes to completion.
- The reaction rate is given by: $d[A]/dt = k*[A]*[B]$.

If the reaction is initiated by the spontaneous decomposition of a very small known amount of A, [function 0414](#) should be used to analyze the data.

When automatic initial estimates are made, **FitAll** assumes that the data are sorted on column number 1; that is, the X-values.

Ftn 0416: Current - Over Potential



Equation

Two variations of the function are available:

$$Y = P1 * \left\{ e^{\left[\frac{K1 * (X - P4)}{P2} \right]} - e^{\left[\frac{-K1 * (X - P4)}{P3} \right]} \right\}$$

$$Y = P1 * \left\{ e^{\left[\frac{K1 * (X - P4 - Y * P5)}{P2} \right]} - e^{\left[\frac{-K1 * (X - P4 - Y * P5)}{P3} \right]} \right\}$$

in which

- Y is the measured response, the current in amperes.
- X is the independent variable, the applied voltage in volts.

Constants

Constant	Name	Comments
K1	Ln(10)	Default value is 2.30258509.

Parameters

Parameter	Name	Comments
P1	Io	Exchange current or current density (in A or A/cm ²). In corrosion studies, the corrosion current or current density. Note: The sign convention used is: Anodic currents and voltages are positive. That is, positive voltages result in positive currents. Cathodic currents and voltages are negative. That is, the sign of the current, Y, is opposite to that often used in polarography.
P2	ba	Anodic Tafel constant (in V). In electrochemistry, this is equal to: $\frac{2.3RT}{\alpha nFT}$
P3	bc	Cathodic Tafel constant (in V). In electrochemistry, this is equal to: $\frac{2.3RT}{(1 - \alpha nFT)}$
P4	Eo	Equilibrium potential (in V).
P5	Ru	Uncompensated solution resistance (in ohms or ohm.cm ²). When doing a fit, it is often advantageous to limit the value of Ru to values greater than or equal to zero. These are the only physically meaningful values of Ru.

Sample Applications

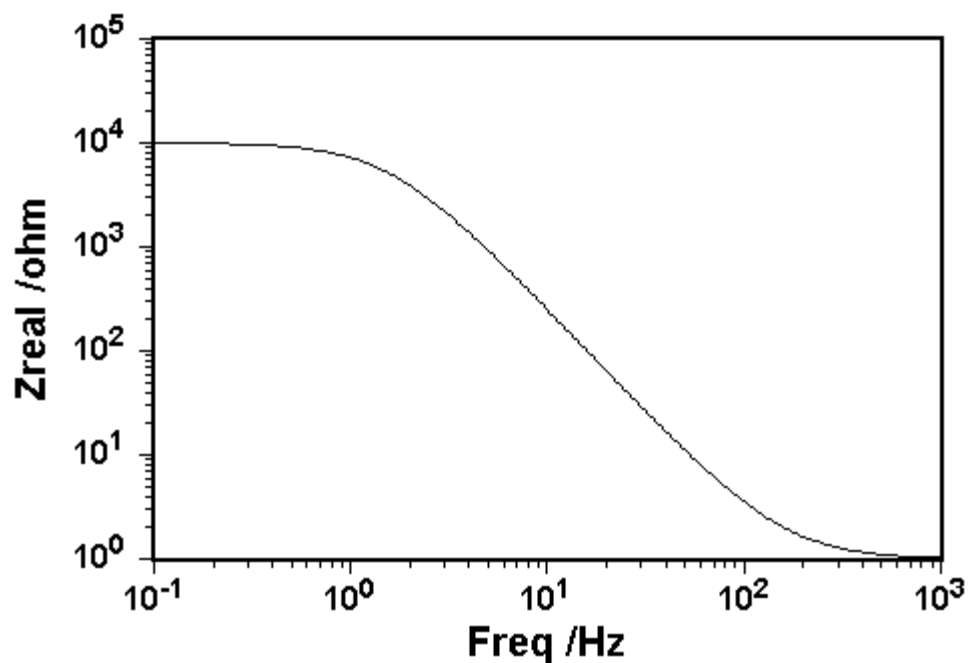
- Characterizing the current - over potential behaviour of a reversible electrochemical reaction.
- Characterizing the current - over potential behaviour of a corrosion reaction.

Remarks

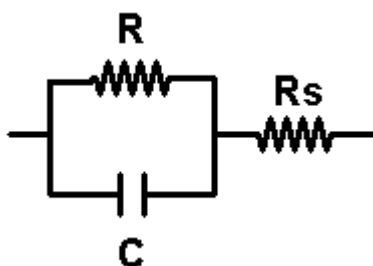
In most cases the current, Y , data will span a wide range of values, for example, three or four orders of magnitude. Because of this, it is strongly advised that you weight the data using a weighting factor of $1/(\text{Sigma}Y)^2$ or $1/(0.1Y)^2$.

When you plot the fit, plot $\text{Log}[Y]$ vs. X so that you will be able to see the deviations at low Y -values as well as at high Y -values.

Ftn 0417: Real Impedance of a Parallel RC+Rs Circuit



Equivalent Circuit



Equation

Two variations of the function are available:

- $$Y = \frac{P1}{\left[1 + (2 * \pi * P1 * P2 * X)^2\right]}$$

- $$Y = \frac{P1}{\left[1 + (2 * \pi * P1 * P2 * X)^2\right]} + P3$$

in which

- Y is the measured response, the "in-phase" or "real" component of the impedance, Zre (in ohm or ohm.cm).

- X is the independent variable, the frequency, f, in Hertz (cycles per sec).

Parameters

Parameter	Name	Comments
P1	R	Resistance or resistivity of the resistor, R.
P2	C	Capacitance of the capacitor, C.
P3	Rs	Resistance or resistivity of the series resistor, Rs. This is the limiting value of the impedance at high frequencies.

Sample Applications

- Determining the resistance and capacitance of a parallel RC circuit that is in series with a resistor, Rs, from the frequency dependence of the "real" or "in-phase" component of the impedance. The impedance measurements are frequently made using a Frequency Response Analyzer or similar instrument.
- Determining the polarization resistance of an electrochemical (or corrosion) reaction from the frequency dependence of the impedance.

Remarks

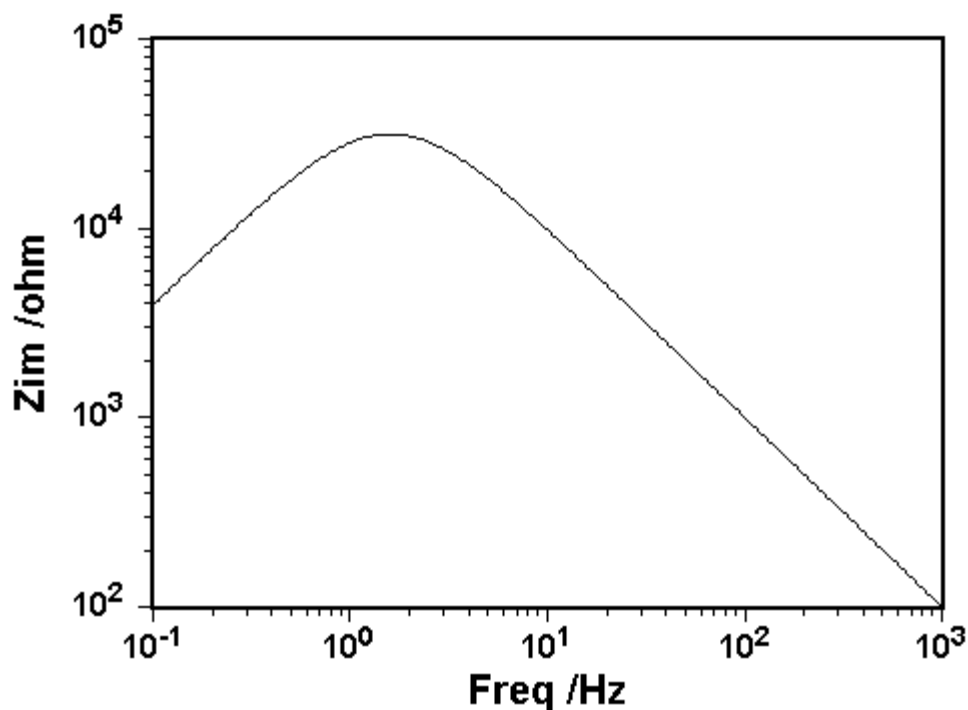
Because impedance measurements are made over a wide range of frequencies, X, it is normally advisable to use a weighting factor of $1/(\text{Sigma}Y)^2$ or $1/(0.01Y)^2$ when doing the fit.

If the series resistor, Rs = P3, is not present, the "real" impedance is described by the first equation.

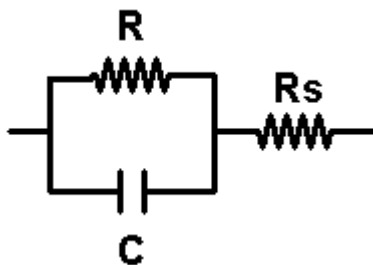
At low values of the frequency, X, the in-phase impedance, Y, approaches a limiting value of (R + Rs).

When automatic initial estimates are made, **FitAll** assumes that the data are sorted on column number 1, that is, the X-values.

Ftn 0418: Imaginary Impedance of a Parallel RC or RC+Rs Circuit



Equivalent Circuit



Equation

$$Y = \frac{-(2 * \pi * P1)^2 * P2 * X}{1 + (2 * \pi * P1 * P2 * X)^2}$$

in which

- Y is the measured response, the "out-of-phase" or "imaginary" component of the impedance, Z_{im} (in ohm or ohm.cm).
- X is the independent variable, the frequency, f, in Hertz (cycles per sec).

Parameters

Parameter	Name	Comments
P1	R	Resistance or resistivity of the resistor, R.
P2	C	Capacitance of the capacitor, C.

Sample Applications

- Determining the resistance and capacitance of a parallel RC circuit that is in series with a resistor, R_s , from the frequency dependence of the "imaginary" or "out-of-phase" component of the impedance. The impedance measurements are frequently made using a Frequency Response Analyzer or similar instrument.
- Determining the polarization resistance of an electrochemical (or corrosion) reaction from the frequency dependence of the impedance.

Remarks

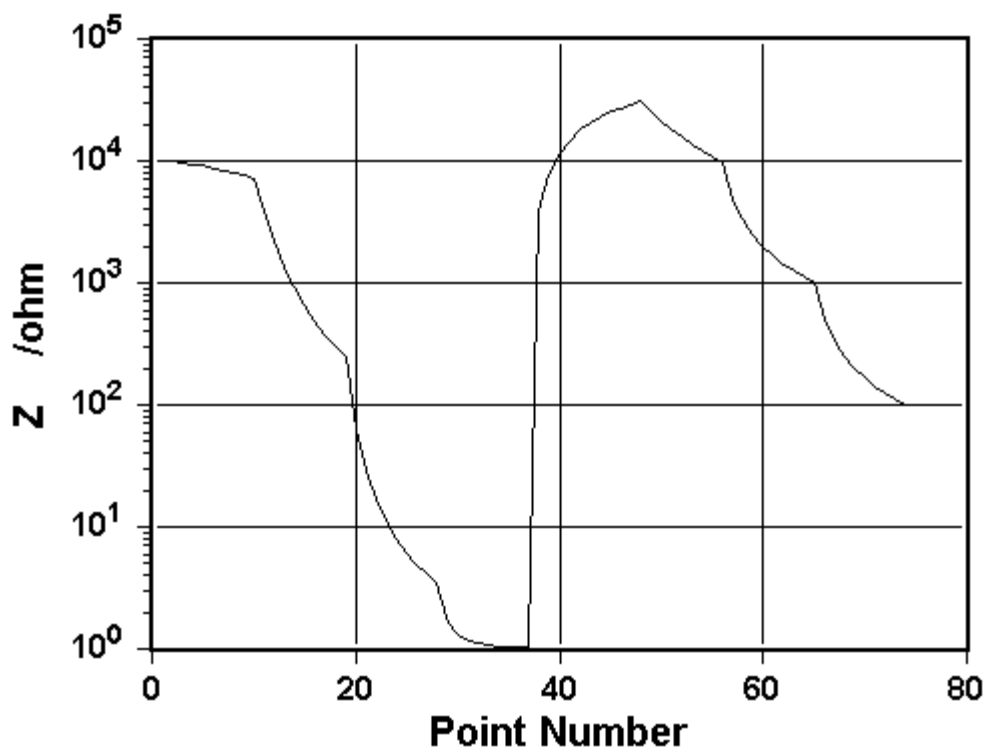
Because impedance measurements are made over a wide range of frequencies, X , it is normally advisable to use a weighting factor of $1/(\text{Sigma}Y)^2$ or $1/(0.01Y)^2$ when doing the fit.

The out-of-phase, imaginary, impedance is independent of the value of the series resistance, R_s .

At low values of the frequency, X , the in-phase impedance, Y , approaches a limiting value of $(R + R_s)$.

When automatic initial estimates are made, **FitAll** assumes that the data are sorted on column number 1, that is, the X -values.

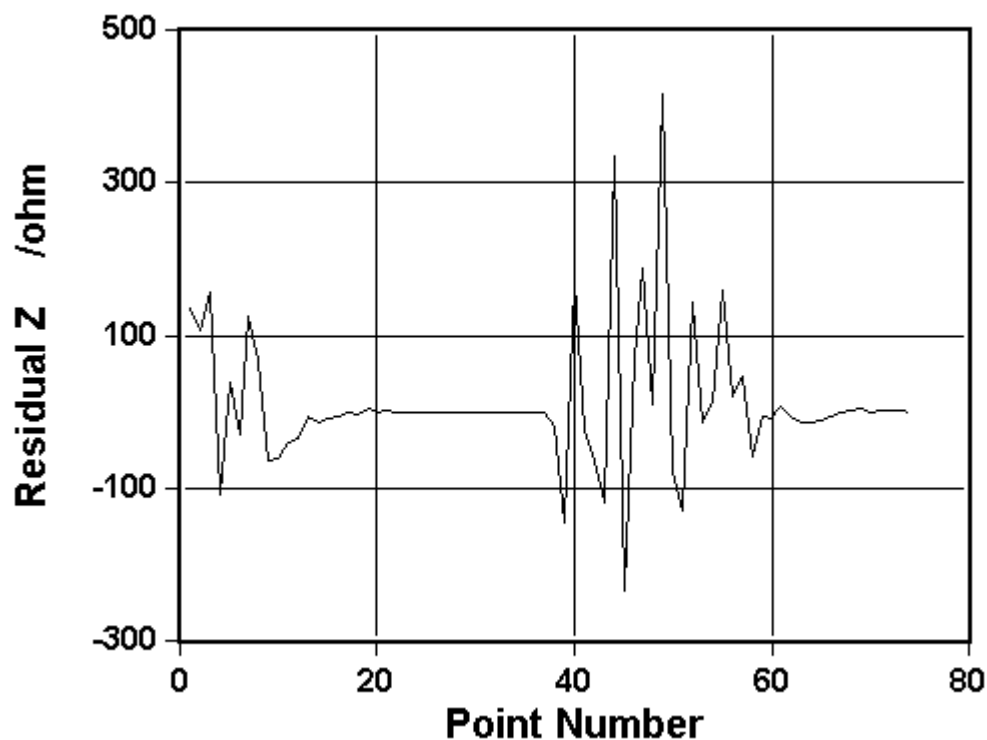
Ftn 0419: Real and Imaginary Impedance of a Parallel RC+Rs Circuit



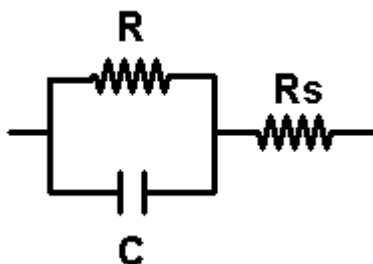
NOTE:

This function has two independent variables, X1 (the frequency) and X2 (a selector that indicates whether the Y-value is Zre or Zim). The only way to plot a meaningful fit graph in this situation is to plot Y against the "Point Number" rather than the value of the independent variable, X1.

The best way to get a visual indication of the quality of the fit is to view the residuals graph, such as the one shown below.



Equivalent Circuit



Equation

$$Y = \begin{cases} \frac{P1}{[1 + (2 * \pi * P1 * P2 * X1)^2]} + P3, & \text{for } X2 = 0 \\ \frac{-(2 * \pi * P1)^2 * P2 * X1}{[1 + (2 * \pi * P1 * P2 * X1)^2]}, & \text{for } X2 \neq 0 \end{cases}$$

in which

- The dependent variable, Y, is the "real" or "imaginary" component of the impedance, Zre or Zim , (in ohm or ohm.cm) depending on the value of X2.

- The independent variable, X1, is the frequency, f, (in Hz).
- The independent variable, X2, is a "selector" that, when zero indicates that Y is the "real" component of the impedance and, when non-zero that Y is the "imaginary" component of the impedance.

Parameters

Parameter	Name	Comments
P1	R	Resistance or resistivity of the resistor, R.
P2	C	Capacitance of the capacitor, C.
P3	Rs	Resistance or resistivity of the series resistor, Rs. This is the limiting value of the impedance at high frequencies.

Sample Applications

- Determining the resistance and capacitance of a parallel RC circuit that is in series with a resistor, Rs, from the frequency dependence of the "real" or "in-phase" and the "imaginary" or "out-of-phase" components of the impedance. The impedance measurements are frequently made using a Frequency Response Analyzer or similar instrument.
- Determining the polarization resistance of an electrochemical (or corrosion) reaction from the frequency dependence of the impedance.

Remarks

Because impedance measurements are made over a wide range of frequencies, X, it is normally advisable to use a weighting factor of $1/(\Sigma Y)^2$ or $1/(0.01Y)^2$ when doing the fit.

At low values of the frequency, X, the in-phase impedance, Y, approaches a limiting value of (R + Rs).

When automatic initial estimates are made, **FitAll** assumes that the data are sorted on column number 1, that is, the X-values.

Appendix

[Getting Help](#)  52

[Adding Functions to FitAll](#)  53

Getting Help

To get technical or other assistance from MTR Software you can:

Visit the FAQ page on MTR Software's web site at:

www.fitall.com

Email MTR Software at:

support@fitall.com

Write to MTR Software at:

MTR Software

77 Carlton Street, Suite 808

Toronto ON Canada

M5B 2J7

Telephone MTR Software at:

416-596-1499

Describe your problem or difficulty as completely as you can. We will try to answer your query quickly and completely.

You should also include your email address as well as your daytime, evening and weekend telephone numbers.

Adding Functions to FitAll

There are three ways to add your own specialized functions to *FitAll*.

1. You can contact **MTR Software** to get a quotation on the cost of creating a custom **FitAll Function Library** for you.
2. The *FitAll* Programmer's Guide, which is included with **FitAll Research Edition**, explains:
 - how to modify the supplied source code for the User Defined **FitAll Function Libraries** and
 - how to compile them using Borland Delphi version 5, 6, 7, 2005 and 2006.
3. You can contact **MTR Software** and request that the function be added to one of *FitAll*'s **Function Libraries**.

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