



DSC Curve Solutions®

Definitions of input parameters

Parameters employed in simulation of DSC Curve Solutions as shown in the figure below are defined as follows:

The screenshot shows the DSC Curve Solutions v3.0 software interface. The window title is "DSC Curve Solutions v3.0 Copyrights © 2007-2013 ... www.caotechnology.com.au". The menu bar includes File, Defaults, Run, View, Excel, and Help. The main window is divided into two main sections: "Sample properties" and "DSC experimental conditions".

Sample properties:

- Mass (mg): 10
- Specific Cp (J/gK): 1.5
- Temperature, Xc, Curing, Reaction Dependency: (dropdown menu)
- Glass transition:
 - ΔSpecificCp (J/gK): 0.15
 - From (°C): 60
 - To (°C): 75
 - Initial Xc (%): 20
- Enthalpy relaxation:
 - Relax. enthy (J/g): 3
 - Initial % of Relax'n: 0
 - k0 (1/Sec): 3
 - Ea (J/mol): 500
 - Exponent m: 0.5
 - Exponent n: 1.5
- Melting - Cryst'n:
 - M. Enthalpy (J/g): 30
 - Initial Xc (%): 20
 - Ultimate Xc (%): 80
 - Tpeak (°C): 270
 - HW-CSD, μm²: 250
 - Asymmetric Factor: 0
 - X Rate factor: 0.015
 - X Tmax (°C): 170
 - HW-CRC, μk²: 250
 - Avrami index, n: 4
- Curing:
 - Curing heat (J/g): -300
 - k10 (1/Sec): 0
 - k20 (1/Sec): 25000
 - Exponent m: 0.25
 - Initial curing (%): 0
 - Ea1 (J/mol): 60000
 - Ea2 (J/mol): 60000
 - Exponent n: 1.75
- Reaction:
 - React'n heat (J/g): 600
 - k10 (1/Sec): 1
 - k20 (1/Sec): 1
 - k30 (1/Sec): 10
 - Initial react'n (%): 0
 - Ea1 (J/mol): 30000
 - Ea2 (J/mol): 30000
 - Ea3 (J/mol): 30000
- Other thermal events / models: (dropdown menu)

DSC experimental conditions:

- Instrumental factors:**
 - Reference Cp (J/K): 0.04
 - TTC (Thermal Transfer Coefficient), ñ (J/Ks): 0.003
- Heating programs:**

Prog.	H. Rate (°C/min)	From (°C) min	To (°C)
<input type="checkbox"/> Prog. 1	5	20	340
<input type="checkbox"/> Prog. 2	0	10	340
<input type="checkbox"/> Prog. 3	-15	340	10
<input type="checkbox"/> Prog. 4	10	10	340
<input type="checkbox"/> Prog. 5	-20	340	20
<input type="checkbox"/> Prog. 6	10	20	340
<input type="checkbox"/> Prog. 7	-10	340	20
- Modulation:**
 - Sinusoidal Modulation:

Amplitude (°C)	Freq. 1	Freq. 2	Freq. 3
1	0	0	0
Period (Sec)	60	45	25
 - Saw-tooth Modulation:

Amplitude (°C/min)	Period A (S)	Period B (S)
1	120	120

Sample properties

Mass (mg) — sample mass in (mg)

Specific Cp (J/gK) — sample specific heat capacity in (J/gK)

Up to temp (°C) — the temperature until which the specific heat capacity of the sample in the above input box holds.

Glass transition:

ΔSpecificCp (J/gK) — change of specific heat capacity of the sample over T_g

From (°C) — the *temperature* at which the glass transition starts to occur.

To (°C) — the *temperature* at which the glass transition ends.

Enthalpy Relaxation:

There are several models available in the open literature describing enthalpy relaxation on glass transition. They are:

- 1) The Cowie-Ferguson model (CF)

$$\Delta H(t_a, T_a) = \Delta H_\infty(T_a)(1 - \phi(t_a))$$

$$\phi(t_a) = \exp\left[-\left(\frac{t}{\tau}\right)^\beta\right]$$

- 2) The Petrie-Marshall model (PM)
The same equations as the Cowie-Ferguson model but $\beta=1$
- 3) The Tool-Narayanaswamy-Mohnihan model (TNM)

$$\frac{H(T_a, t) - H(T_a, \infty)}{H(T_a, 0) - H(T_a, \infty)} = \phi(t)$$

$$\phi(t_a) = \exp\left[-\left(\frac{t}{\tau}\right)^\beta\right]$$

$$\tau = A \exp\left[\frac{x\Delta h}{RT} - \frac{(1-x)\Delta h}{RT_f}\right]$$

- 4) The Adam-Gibbs model (Extended Scherer-Hodge model)
...

- 5) The Kinetic-rheological model

$$\frac{d\alpha}{dt} = k \alpha^m (1 - \alpha)^n$$

$$k = k_0 \exp\left(-\frac{E}{R(T - T_{g1})}\right)$$

$$dH = H_R^0 m_s d\alpha$$

Where: α — degree of relaxation (%).

k_0 — Kinetic constant (1/S).

m — exponent (=0.5).

n — exponent (=1.5).

E — Activation energy (J/mol).

T — Temperature.

T_{g1} — the starting temperature of glass transition.

R — the gas constant

H_R^0 — Relaxation enthalpy (J/g).

m_s — Mass of sample (g)

Relaxation Enthalpy (J/g) — Relaxation enthalpy in (J/g)

k_0 (1/S) — Kinetic constant (1/S)

Ea (J/mol) — Activation energy for the kinetic constant (J/mol)

Initial % of relaxation — Initial degree of relaxation in terms of percentage, must be in the range of 0 ~ 100. For a fully aged sample, it is 0, and for a quenched sample, it is 100.

Melting and Crystallisation:

M' Enthalpy (J/g) — ΔH_m^0 , melting enthalpy in (J/g)

Initial Xc (%) — X_{c0} , the crystallinity that the sample already has prior to DSC measurement.

Ultimate Xc (%) — $X_{c\infty}$, maximum crystallinity of the sample.

T_{peak} (°C) — the temperature at which the melting enthalpy reaches maximum.

HW-CSD, μm^2 — μ_m^2 , half width of the Gaussian crystallite size distribution curve

Asymmetric F — Asymmetric factor describing how asymmetry is the crystallite size distribution. For the Gaussian distribution it is zero,

X rate factor — A_K , the pre-exponential factor for the Gaussian crystallisation rate function

X Tmax (°C) — T_{max} , the temperature at which the crystallisation rate reaches maximum for the Gaussian crystallisation rate function

HW-CRC, μk^2 — μ_k^2 , half width of the crystallization rate distribution curve

Avrami index, n — n , the Avrami crystallization index.

Curing (autocatalytic model):

Curing heat (J/g) — ΔH_c^0 , curing heat in (J/g). The convention is endothermal is positive figures, exothermal negative figures

Initial curing (%) — α_0 , the initial degree of curing that the sample already has prior to DSC measurement.

k_{10} (1/Sec) — k_{10} , Arrhenius frequency factor for curing constant K_1 (S^{-1})

k_{20} (1/Sec) — k_{20} , Arrhenius frequency factor for curing constant K_2 (S^{-1})

Ea1 (J/mol) — E_{a1} , activation energy for curing constant K_1 (J/mol)

Ea2 (J/mol) — E_{a2} , activation energy for curing constant K_2 (J/mol)

Exponent m — m , exponent

Exponent n — n , exponent

Following equations show more details of these parameters

$$\frac{d\alpha}{dt} = (K_1 + K_2 \alpha^m)(1 - \alpha)^n$$

$$K_1 = k_{10} \exp\left(-\frac{E_a^1}{RT}\right)$$

$$K_2 = k_{20} \exp\left(-\frac{E_a^2}{RT}\right)$$

Where: α — degree of curing (%)
 k_{10}, k_{20} — frequency factors, E_{a1}, E_{a2} — activation energies (J/mol), m, n — exponents
 R — the universal gas constant
 T — temperature

Reaction (Differential rate laws, zero-order, first-order and second-order laws):

React'n heat (J/g) — ΔH_r^0 , reaction heat in (J/g). The convention is endothermal is positive figures, exothermal negative figures
 Initial curing (%) — α_0 , the initial degree of reaction that the sample already has prior to DSC measurement.

Following equations show more details of these parameters

$$\frac{d\alpha}{dt} = K_1 + K_2\alpha + K_3\alpha^2$$

$$K_1 = k_{10} \exp\left(-\frac{E_{a1}}{RT}\right)$$

$$K_2 = k_{20} \exp\left(-\frac{E_{a2}}{RT}\right)$$

$$K_3 = k_{30} \exp\left(-\frac{E_{a3}}{RT}\right)$$

Where : α — degree of reaction (%)
 k_{10}, k_{20} and k_{30} — frequency factors
 E_{a1}, E_{a2} , and E_{a3} — activation energies (J/mol)
 R — the universal gas constant
 T — temperature

Universal reaction model:

React'n heat (J/g) — ΔH_r^0 , reaction heat in (J/g). The convention is endothermal is positive figures, exothermal negative figures
 Initial curing (%) — α_0 , the initial degree of reaction that the sample already has prior to DSC measurement.

Following equations show more details of these parameters:

Universal reaction model:

$$\begin{aligned} \frac{d\alpha}{dt} = & k_{10} \exp\left(-\frac{E_{a1}}{RT}\right) \alpha^{m_1} (1-\alpha)^{n_1} [-\ln(1-\alpha)]^{p_1} + \\ & k_{20} \exp\left(-\frac{E_{a2}}{RT}\right) \alpha^{m_2} (1-\alpha)^{n_2} [-\ln(1-\alpha)]^{p_2} + \\ & k_{30} \exp\left(-\frac{E_{a3}}{RT}\right) \alpha^{m_3} (1-\alpha)^{n_3} [-\ln(1-\alpha)]^{p_3} \end{aligned}$$

Note, by selecting m , n and p exponents, one can re-derive the autocatalytic curing model and the n th order reaction model. Do not double select the same thermal event/model. If you do, interpret the results with care.

Where : α — degree of reaction (%)
 k_{10} , k_{20} and k_{30} — frequency factors
 E_{a1} , E_{a2} , and E_{a3} — activation energies (J/mol)
 R — the universal gas constant
 T — temperature
 $m_1, n_1, p_1, m_2, n_2, p_2, m_3, n_3, p_3$ — exponents

DSC experimental conditions

Instrumental factors:

Reference Cp (J/gK) — heat capacity of the reference cell in (J/gK)

TTC, λ (J/Ks) — λ , the thermal transfer coefficient in (J/Ks)

Reference Cp = mass multiplies specific heat capacity of the pan material.

Thermal Transfer Coefficient (TTC), λ , is an intrinsic instrumental factor that works for DSC.

It is determined by the designing and construction of a DSC instrument. And it is the key performance indicator of a DSC instrument:

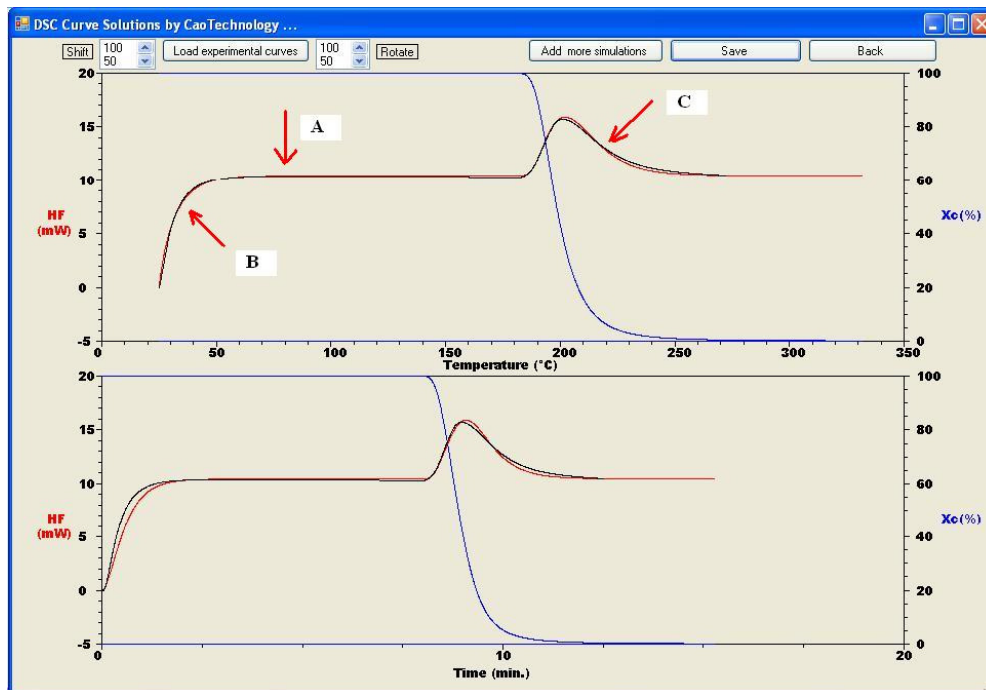
— the higher the λ , the better the DSC instrument is !

How to determine Thermal Transfer Coefficient (TTC), λ :

Thermal Transfer Coefficient (TTC), λ , can be easily determined, as shown in the figure below, by

A) adjusts the specific heat capacity to match the plateau of DCS curves with that of DSC's;

B) tunes the thermal transfer coefficient, λ to fit the transient tail.



Heating programs:

H Rate (°C/min) — (underlying) heating rate in (°C/min)

From (°C) min, — the starting temperature of the program. In case of isothermal (underlying heating rate = 0, input the time in (min) for this box

To (°C) — the ending temperature of the program. In case of isothermal (underlying heating rate = 0, input the isothermal temperature here in (min)

DSC Curve Solutions has also provided the modulation functionality for helping instrumental research.

Sinusoidal modulation:

Amplitude (°C) — A_b , modulation amplitude in (°C)
Period (Sec) — p , modulation period in (second)

Saw-tooth modulation:

Amp (°C/min) — amplitude of modulation in (°C/min)
Period A (Sec) — modulation Period A in (second)
Period B (Sec) — modulation Period B in (second)
Period = Period A + Period B

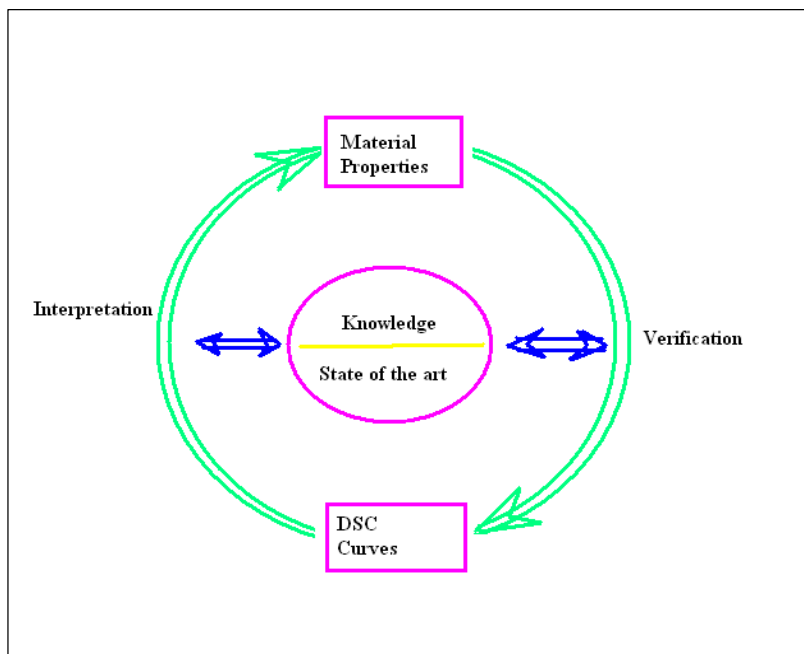
DSC Curve Solutions[®] (DCS)

— The world's first, the world's only —

Software DSC Curve Solutions[®] (DCS) represents a novel approach for thermal analysis that allows one to simulate full DSC curves vividly for experiments under any conditions for a range of thermal events; so that you can extract **all the relevant sample properties from any single DSC run**.

How can DCS be useful?

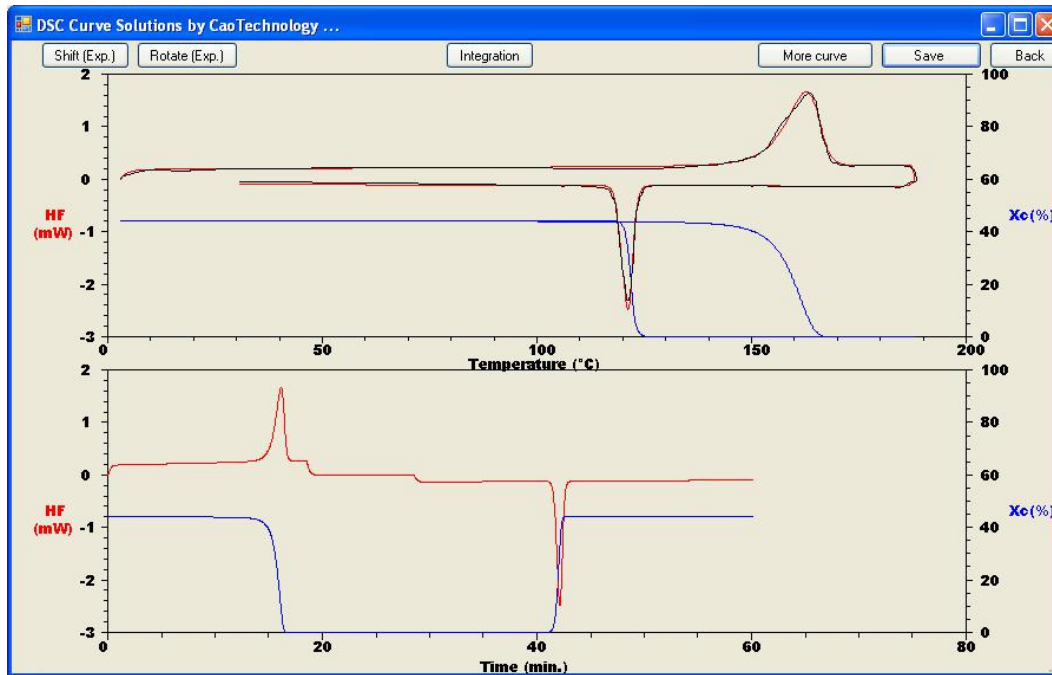
- It obtains sample thermal properties by fitting DSC curve with DCS curve - interpretation and verification, fused as one;
- It extracts more thermal properties than any conventional DSC analysis methods do; e.g. determine curing/crystallisation kinetics from a single non-isothermal DSC run;
- It covers a range of thermal events *i.e.* heat capacity, glass transition, enthalpy relaxation, melting and crystallisation, curing and reactions; furthermore its multi-component function allows you to deconvolute complicated DSC curves readily;
- It resolves your headache when observing a "shifting" "baseline" before and after a thermal event. DCS tells you why the "baseline" "shifts" and how to fit the "baseline".
-



- It covers DSC runs under any experimental conditions e.g. linear heating, sinusoidal (one or more freq.) and/or saw-tooth modulation if wished;
- It is a perfect aid to learn and teach DSC and polymers – you'll have a better understanding of the both.
- No training, no tutorial and no help is needed, you'll be an instant expert of DCS.

Examples of DCS applications

An iPP sample was heated from 5°C to 185°C at 10°C/min, stayed isothermally for 10 min, followed by a cooling at 5°C/min to 30°C, with its DSC experimental curve being shown in the black line in the figure below (digitised from Fig.2, Cao and Sbarski, *Polymer* **47**, 27-31(2006)). Now, simply key in all these known experimental conditions into DCS, we obtain simulated DSC curves shown in the red line. After several trial-and-error tuning reiterations, we fit the DSC curve with DCS curve to our satisfaction, leading to determination of following parameters from just a single DSC run:



Specific heat capacity, $c_p = 1.10$ J/Kg at 0°C, ramping linearly towards 1.66 J/Kg at 200°C;

Melting enthalpy, $\Delta H = 95.2$ J/g,

Melting peak temperature, $T_m = 161.5^\circ\text{C}$,

Half width of the Gaussian crystallite size distribution, $\mu_m^2 = 65$,

with its asymmetric factor of the Gaussian crystallite size distribution = -0.06,

Crystallisation rate factor, $A_k = 0.024$,

Maximum crystallisation rate temperature $T_{\max} = 118.5^\circ\text{C}$;

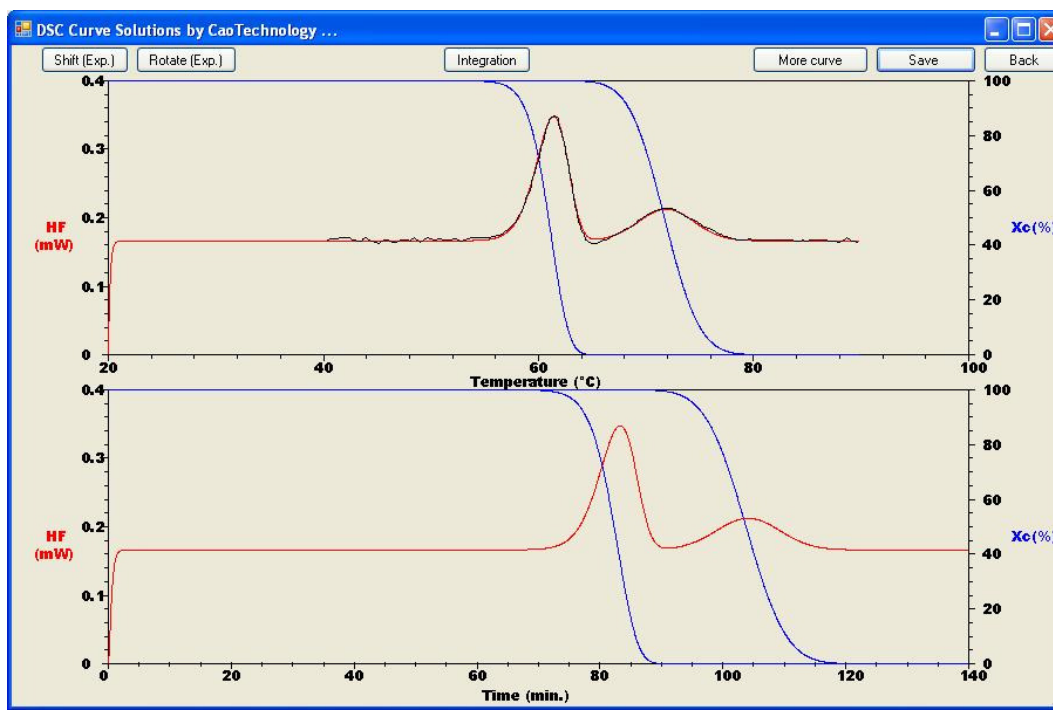
Half width of the crystallisation rate distribution, $\mu_k^2 = 120$,
and Avrami index, $n = 4$.

Given that the melting enthalpy for 100% crystallised iPP is 207 J/g,
we obtain the crystallinity curve as well (the blue curves)



Just from a single DSC run, we have fully determined all the relevant properties, in particular, the melting and crystallisation properties of the sample.

DSC curve deconvolution



Experimental DSC curve for a multi-domain immunoglobulin G (IgG) protein shows two denaturations (melting) endotherms slightly overlapping (curve in black); this is compared with the theoretical curve simulated using DCS v3.0. They are fitting very well. The DSC curve is readily deconvoluted and following parameters are obtained:

- Domain 1:** denaturation enthalpy, $\Delta H = 12.5$ J/g;
 peak temperature, $T_m = 61.2^\circ\text{C}$,
 half width of the Gaussian distribution, $mm2 = 12$;
 asymmetric factor of the Gaussian distribution = -0.065,
- Domain 2:** denaturation enthalpy, $\Delta H = 5.4$ J/g;
 peak temperature, $T_m = 71.7^\circ\text{C}$;
 half width of the Gaussian distribution, $mm2 = 37$;
 asymmetric factor of the Gaussian distribution = 0.

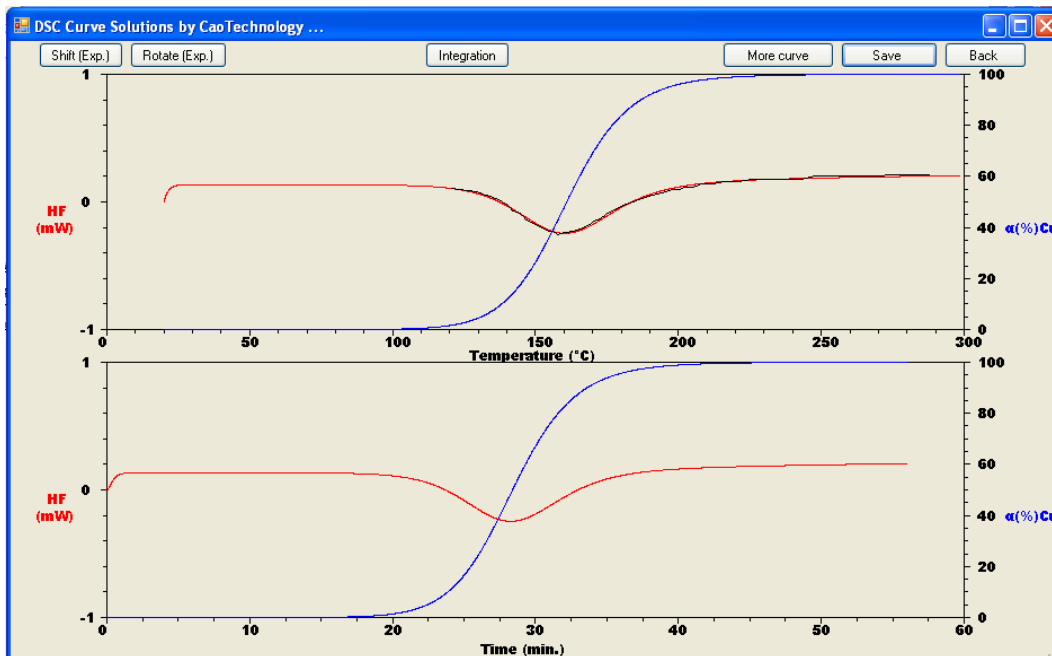
Non-isothermal kinetics and DCS

We need to know not only the activation energy, E_a , and pre-exponential factor, A , but also all the relevant parameters as well as the reaction model so that we can calculate the degree of reaction for any given thermal history - the usefulness of a methodology lies in its predictive power !

With DSC Curve Solutions® (DCS), one can determine all the kinetic parameters from any single DSC run for any given model.

Example of non-isothermal epoxy curing

Following example shows how DCS can be employed to study non-isothermal curing kinetics for epoxy resins. The black curve in the figure below is the exotherm of a DSC run at 5°C/min for an epoxy resin. Using the autocatalytic model shown below, we determine the kinetic parameters of the epoxy resin by simply fitting this single run DSC curve (black) with DCS curve (red) to satisfaction:



Autocatalytic model:
$$\frac{d\alpha}{dt} = \left[k_{10} \exp\left(-\frac{E_{a1}}{RT}\right) + k_{20} \exp\left(-\frac{E_{a2}}{RT}\right) \alpha^m \right] (1 - \alpha)^n$$

Kinetic parameters determined are:

Curing enthalpy, $\Delta H = -205$ J/g,
Frequency factor $k_{10} = 0$;
(Activation energy, E_{a1} can be any in this case);
Frequency factor, $k_{20} = 12200$ s⁻¹;
Activation energy, $E_{a2} = 51450$ J/mol;
Exponent, $m = 0.60$;
Exponent, $n = 1.45$;



i.e:

$$\frac{d\alpha}{dt} = 12200 \times \exp\left(-\frac{51450}{RT}\right) \alpha^{0.6} \times (1-\alpha)^{1.45}$$

This equation is what exactly what we need, no more no less — the resin's curing behaviour is fully described. With this equation, one can calculate the curing degree of the resin under any thermal history or curing conditions.

In addition, this DCS approach is a more accurate and better way for determination of thermal properties of a sample, because the intrinsic instrumental deformation of DSC curves have been compensated in the DCS simulations.