

Electronic Supplementary Information

Analysis of temperature programmed desorption (TPD) data for the characterization of catalysts containing a distribution of adsorption sites

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The following pages show the results of some simulations on datasets containing different levels of noise, and differing numbers of data points.

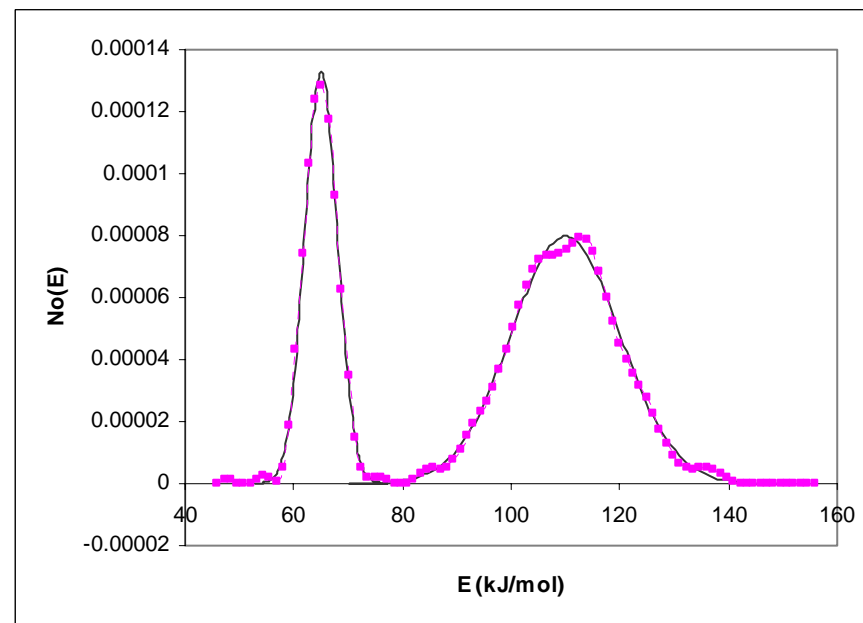
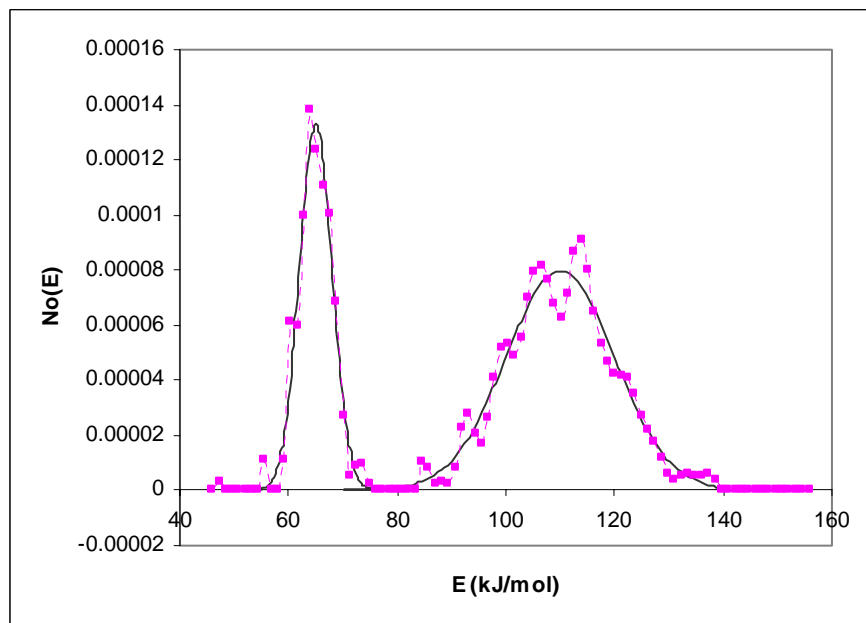
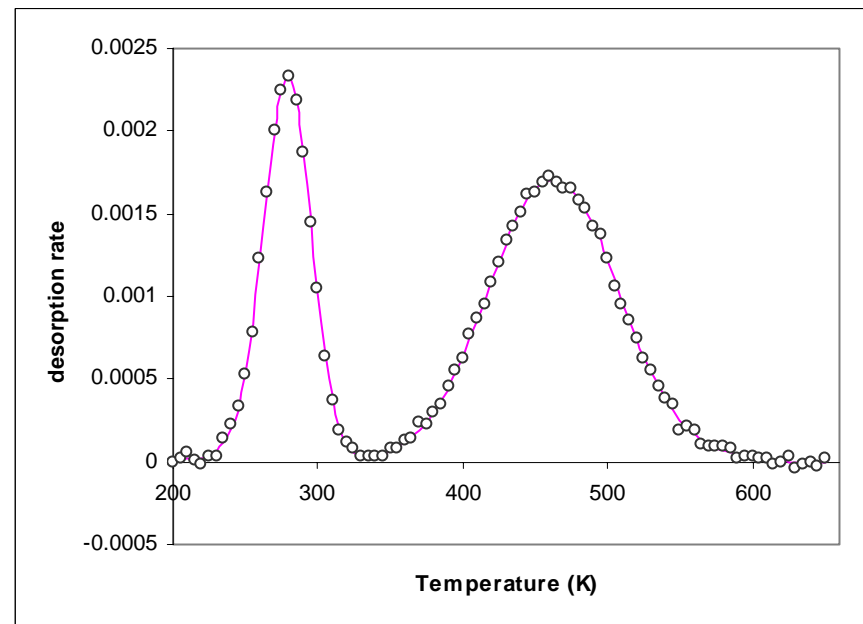
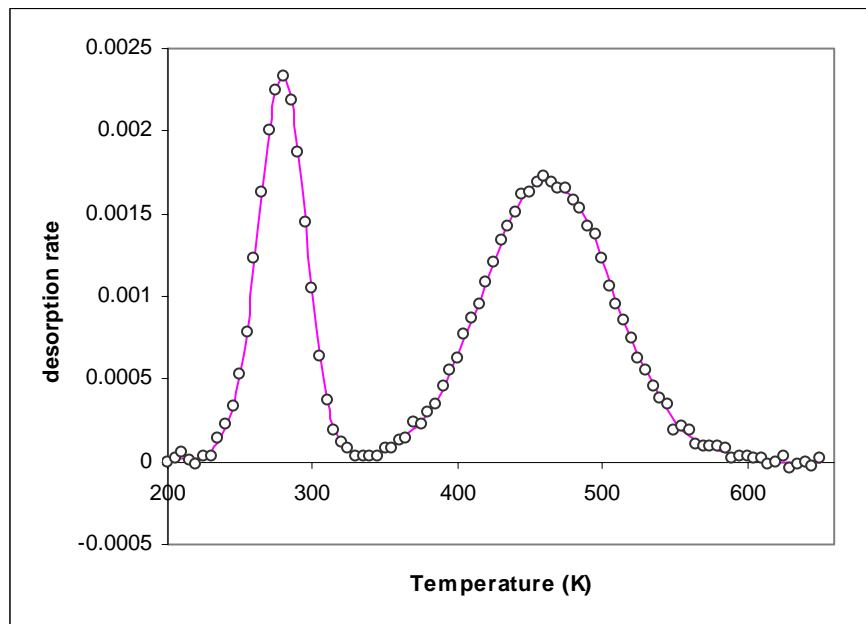
“Ideal” TPD data were generated for samples containing known activation energies for desorption. Different levels of Gaussian-distributed noise were added to the ideal TPD data. The noise level is quoted as the root mean square of the noise level divided by the peak intensity of the highest peak.

The data were analysed by least squares fitting using the two regularization penalty functions described in the paper. The first penalty function is based on the area of the distribution (equation 34), while the second penalty function is based on the square of the second derivative of the distribution (equation 35). The fits shown are those in which the regularization parameter λ was chosen by the L-curve method as described in the paper.

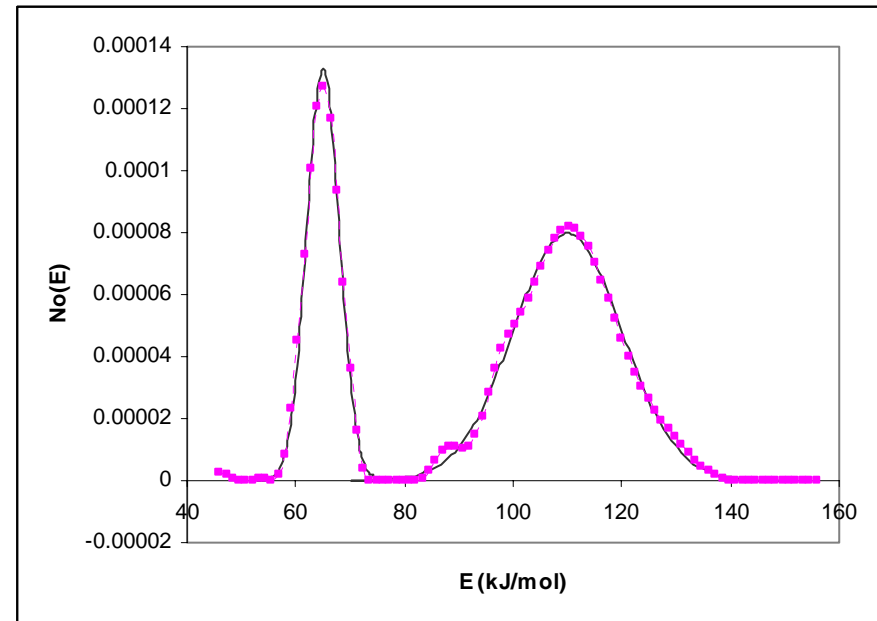
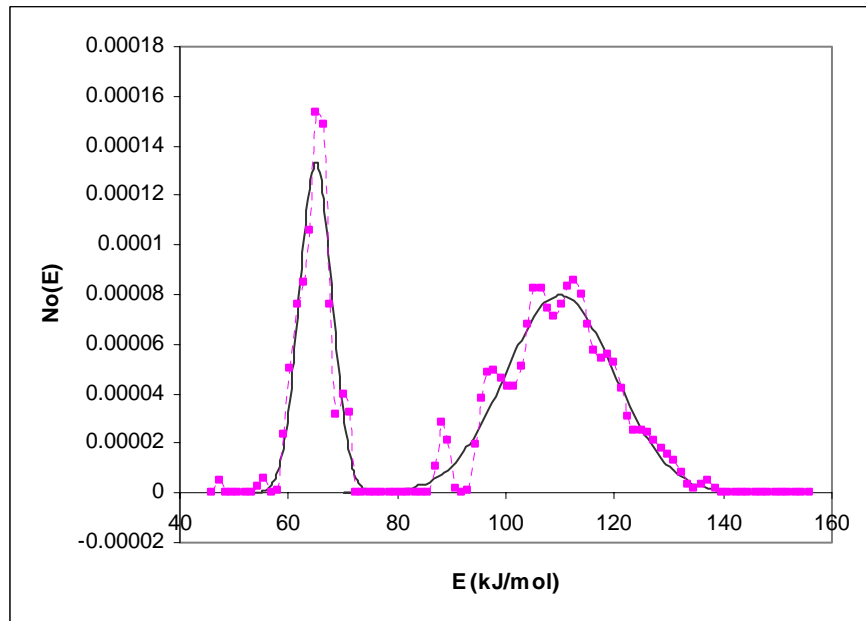
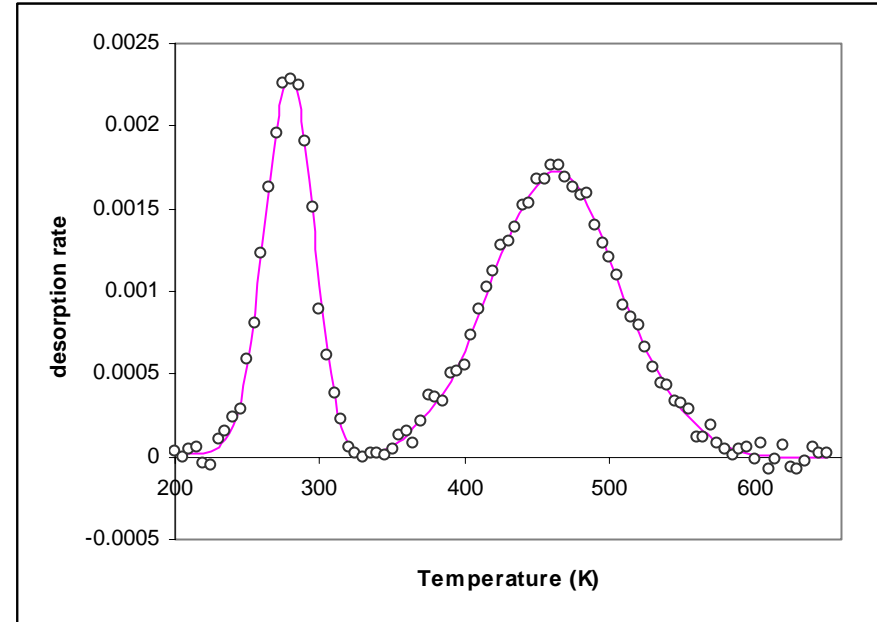
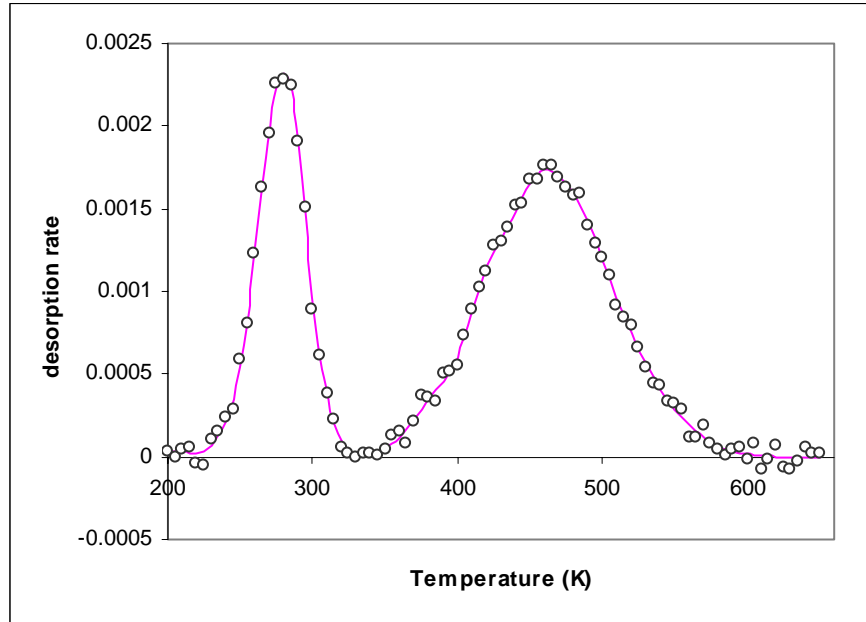
Datasets of type A correspond to a sample with two types of adsorption site, one with a relatively narrow distribution ($E_1 = 65$ kJ/mol; $\sigma_1 = 3$ kJ/mol) and the other with a relatively broad distribution ($E_2 = 110$ kJ/mol; $\sigma_2 = 10$ kJ/mol). The relative populations of the sites was 1:2. Both sites have pre-exponential factors $A = 10^{10} \text{ s}^{-1}$. The heating rate was 0.1 K/s. Datasets containing different levels of noise are presented.

Datasets of type B correspond to a sample with a single type of adsorption site ($E = 100$ kJ/mol, $\sigma = 3$ kJ/mol, pre-exponential factor $A = 10^{10} \text{ s}^{-1}$). The heating rate is 0.1 K/s. Datasets containing a different number of data points are presented.

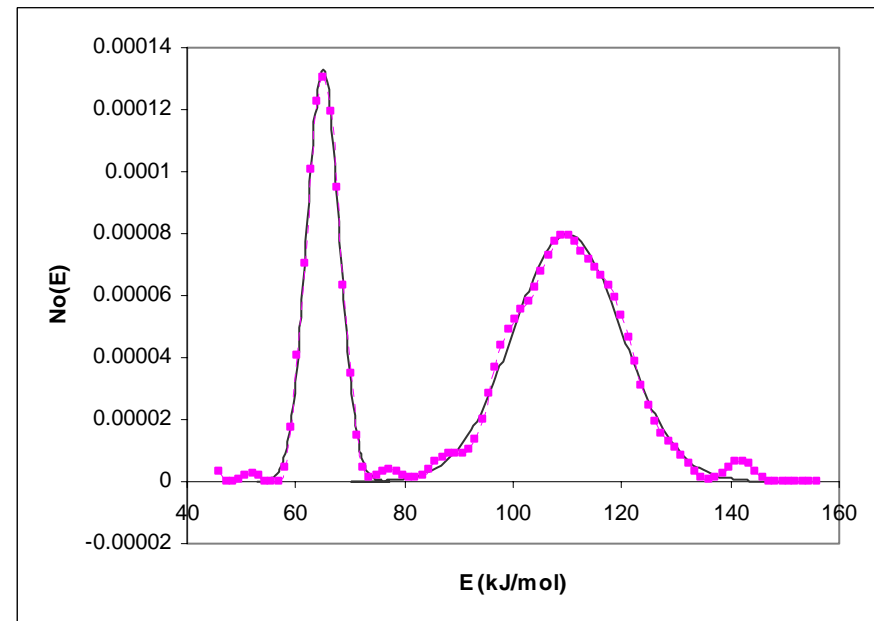
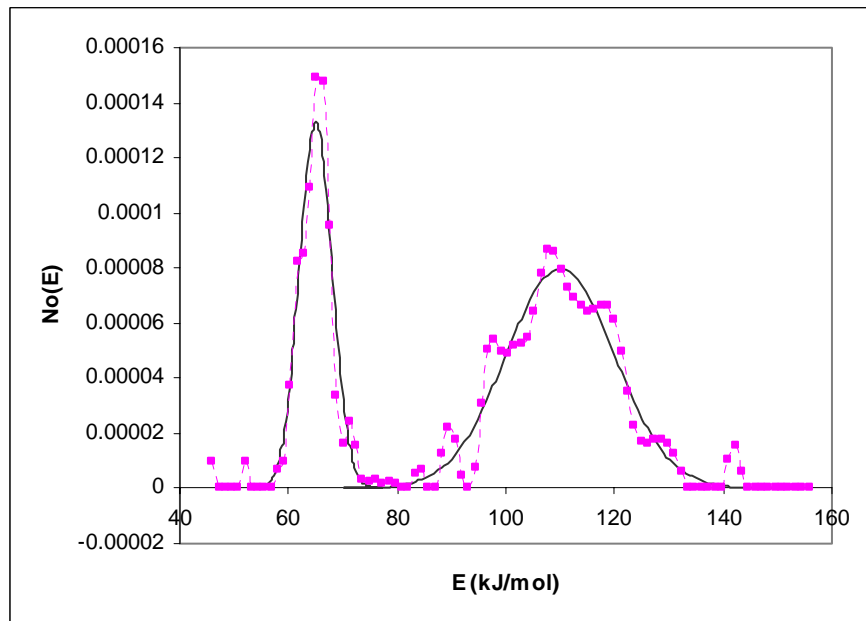
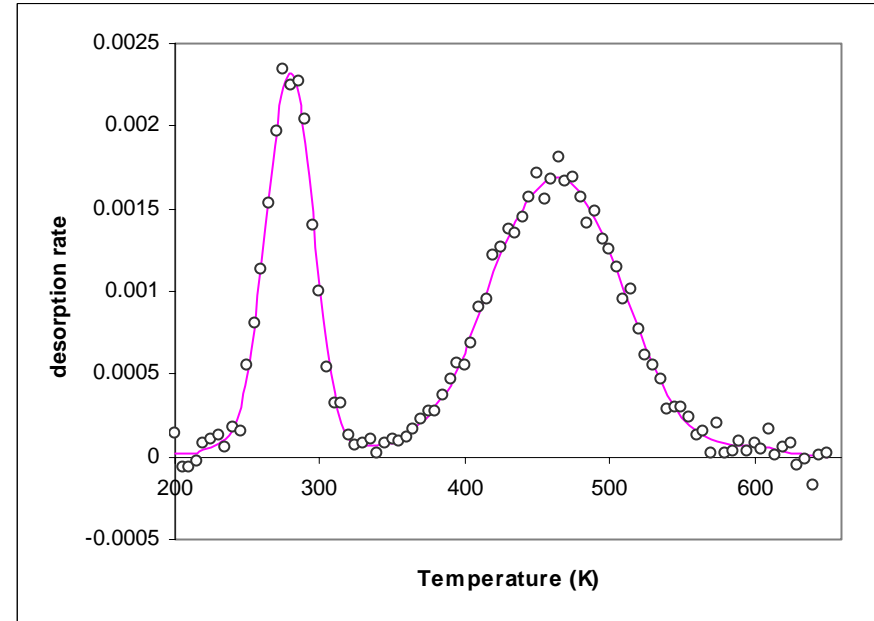
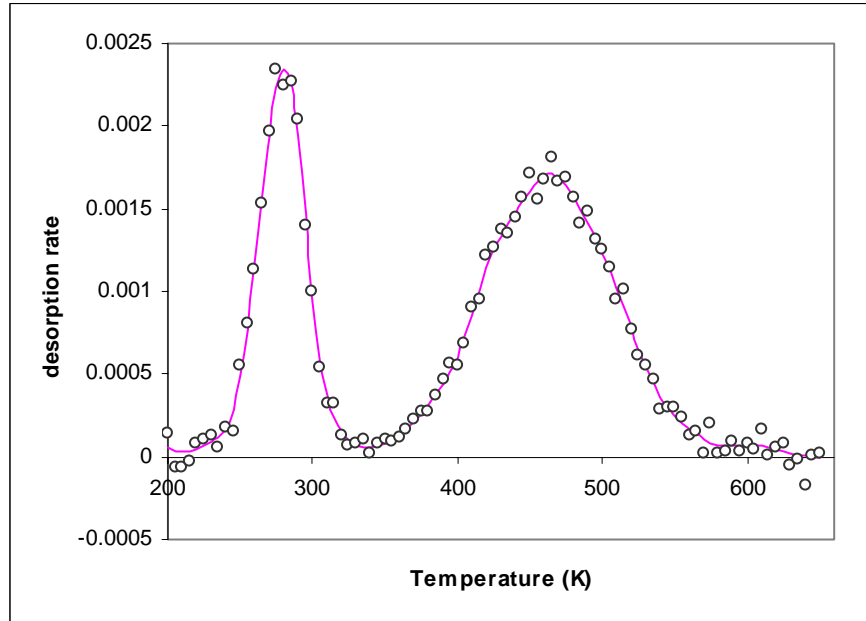
Dataset A1: noise level = 1%. Top = TPD data (points) and simulation (curve) ; bottom = energy distribution: actual (curve) and derived (points). Left-hand side = penalty function based on area (Eq. 34). Right-hand side = penalty function based on second derivative (Eq. 35).



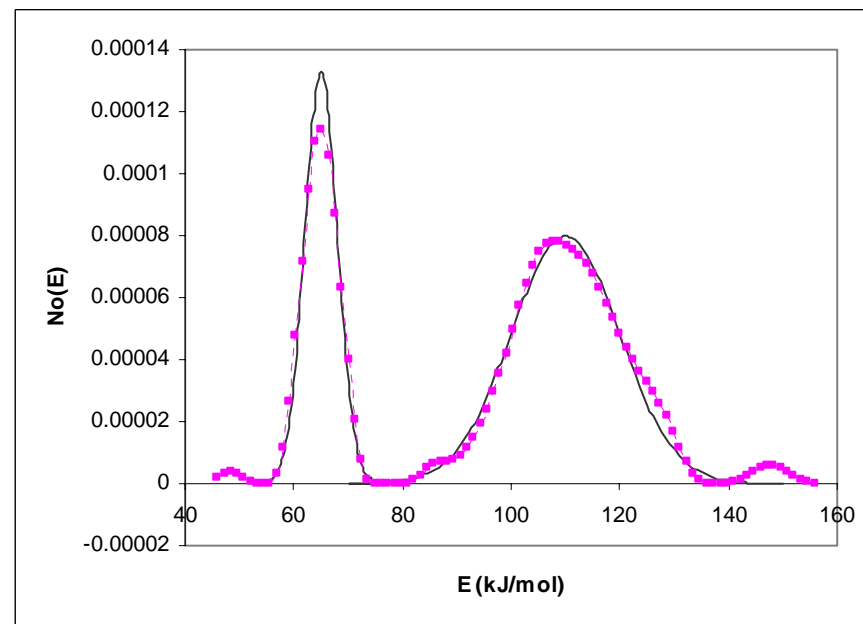
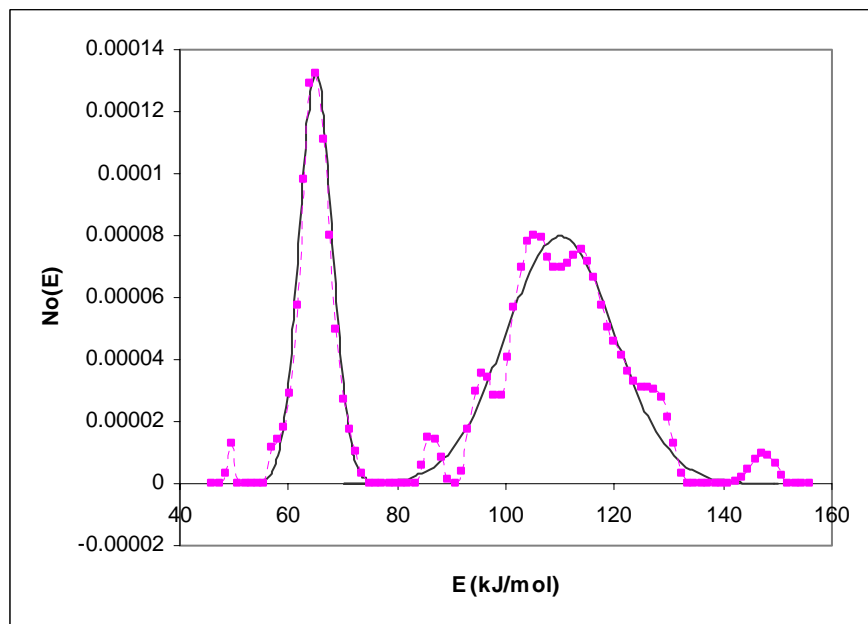
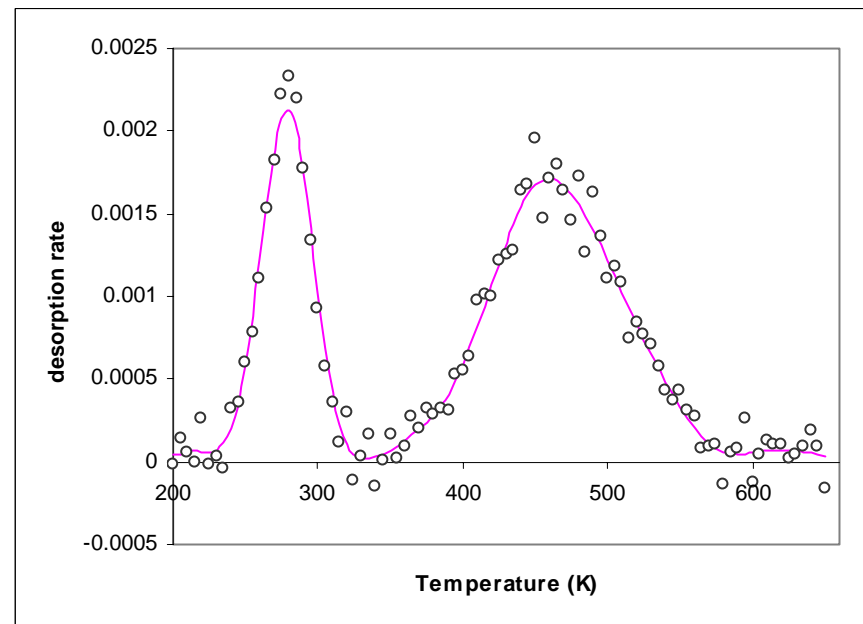
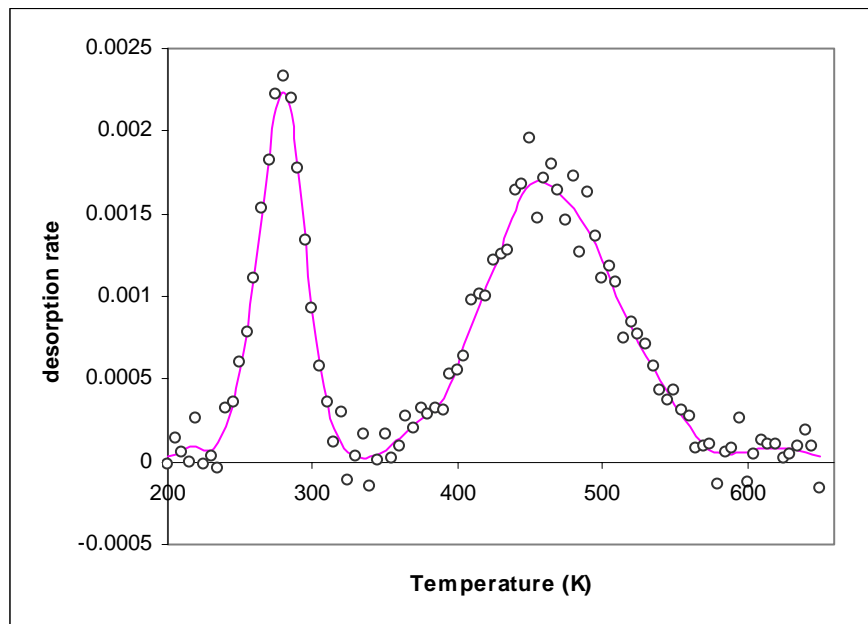
Dataset A2: noise level = 2%. Top = TPD data (points) and simulation (curve) ; bottom = energy distribution: actual (curve) and derived (points). Left-hand side = penalty function based on area (Eq. 34). Right-hand side = penalty function based on second derivative (Eq. 35).



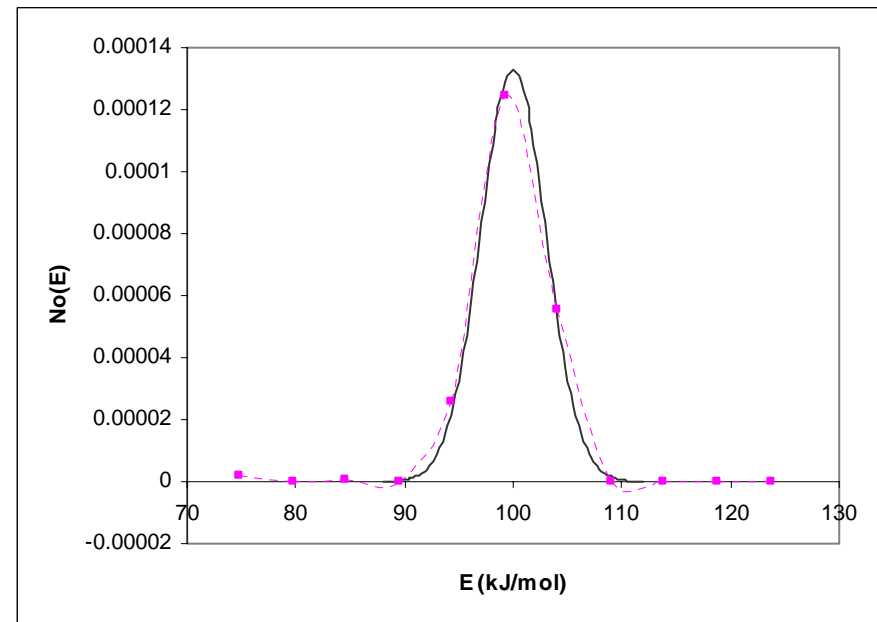
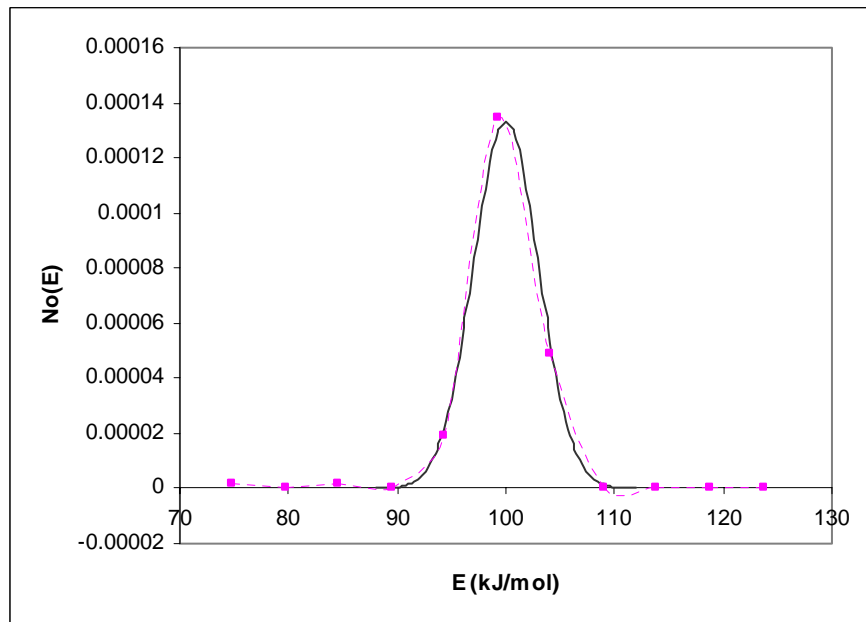
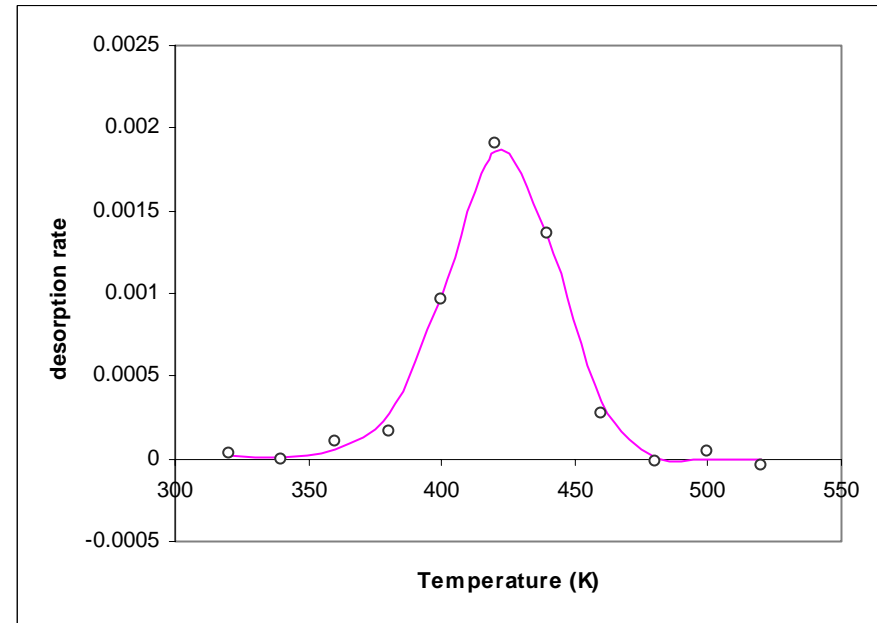
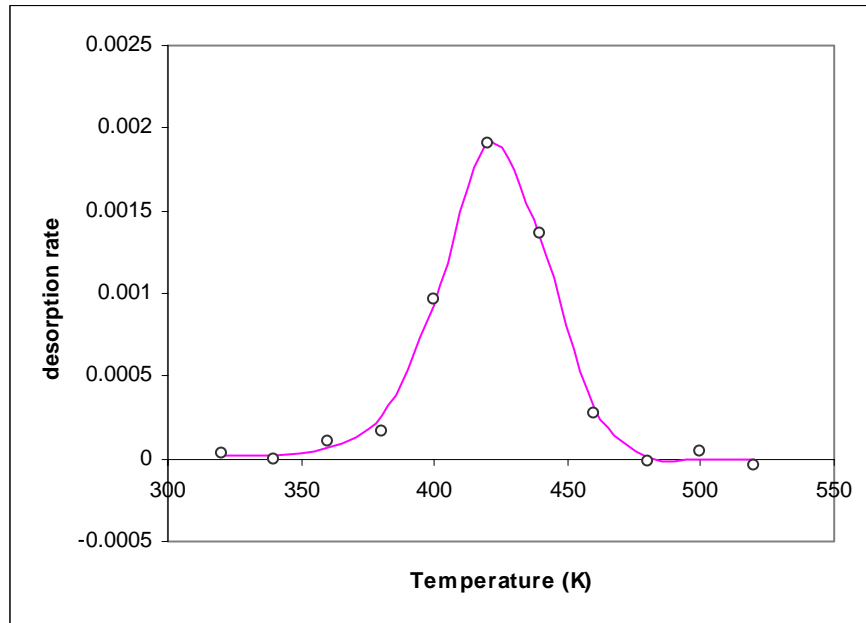
Dataset A3: noise level = 3%. Top = TPD data (points) and simulation (curve) ; bottom = energy distribution: actual (curve) and derived (points). Left-hand side = penalty function based on area (Eq. 34). Right-hand side = penalty function based on second derivative (Eq. 35).



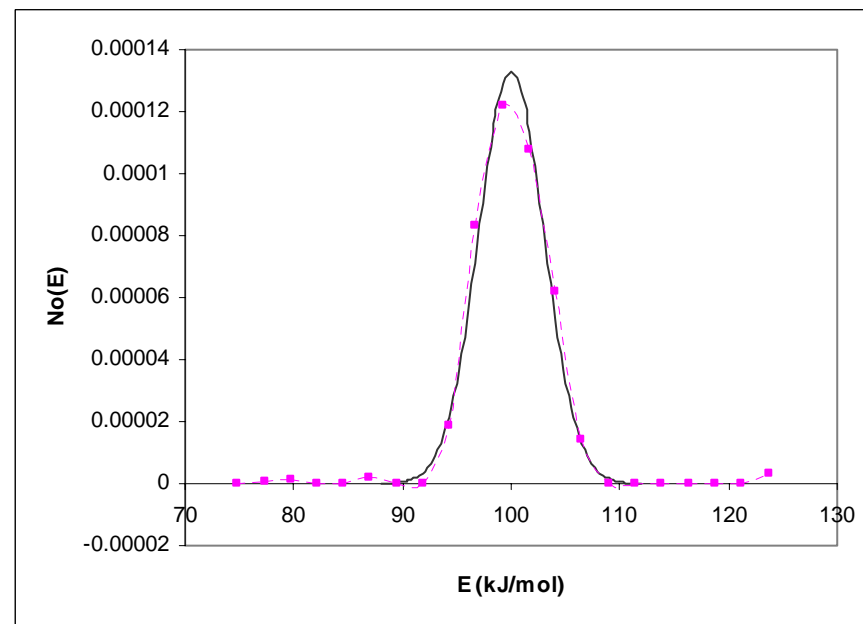
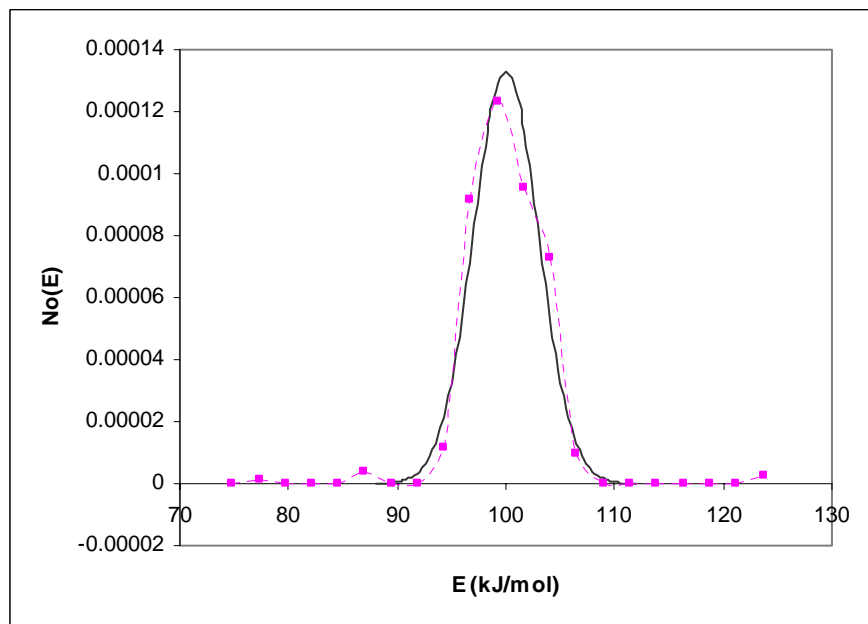
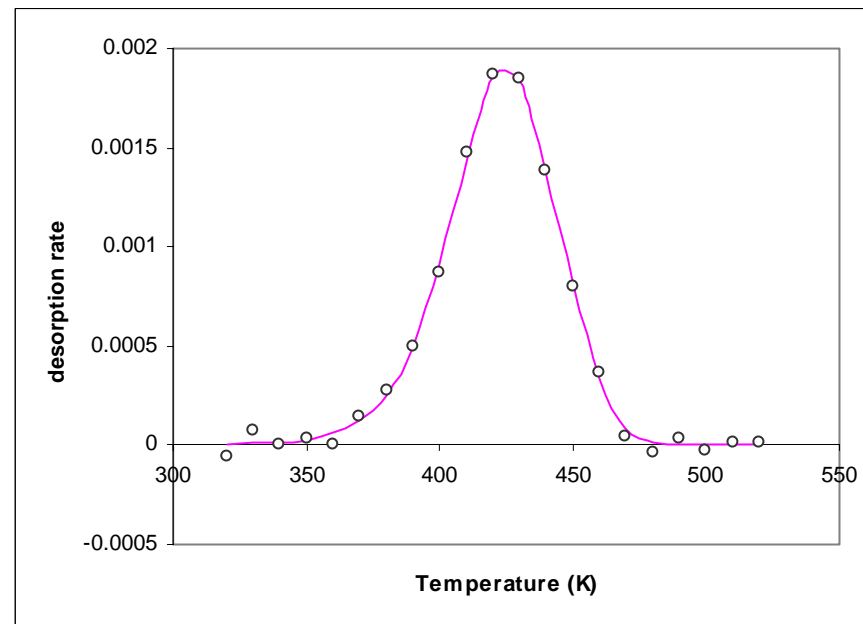
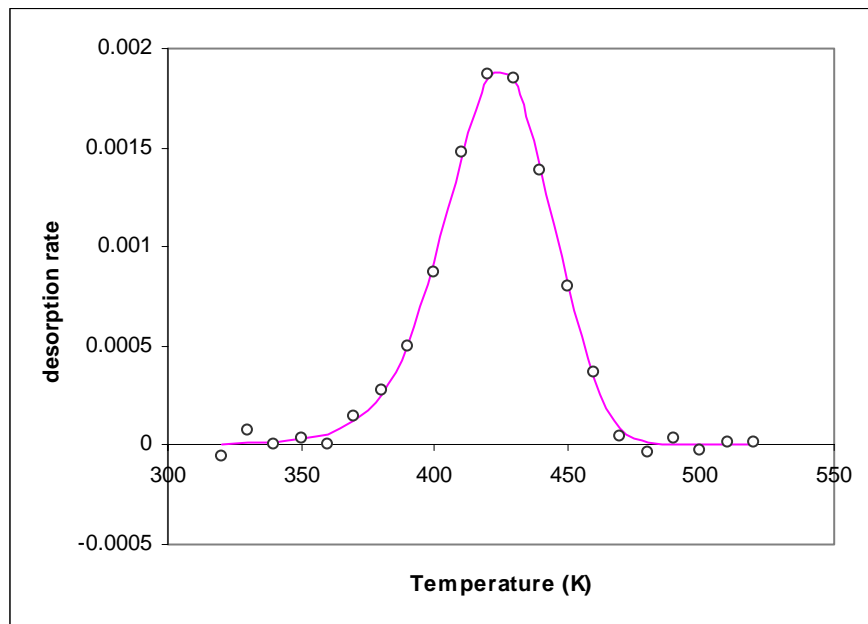
Dataset A4: noise level = 5%. Top = TPD data (points) and simulation (curve) ; bottom = energy distribution: actual (curve) and derived (points). Left-hand side = penalty function based on area (Eq. 34). Right-hand side = penalty function based on second derivative (Eq. 35).



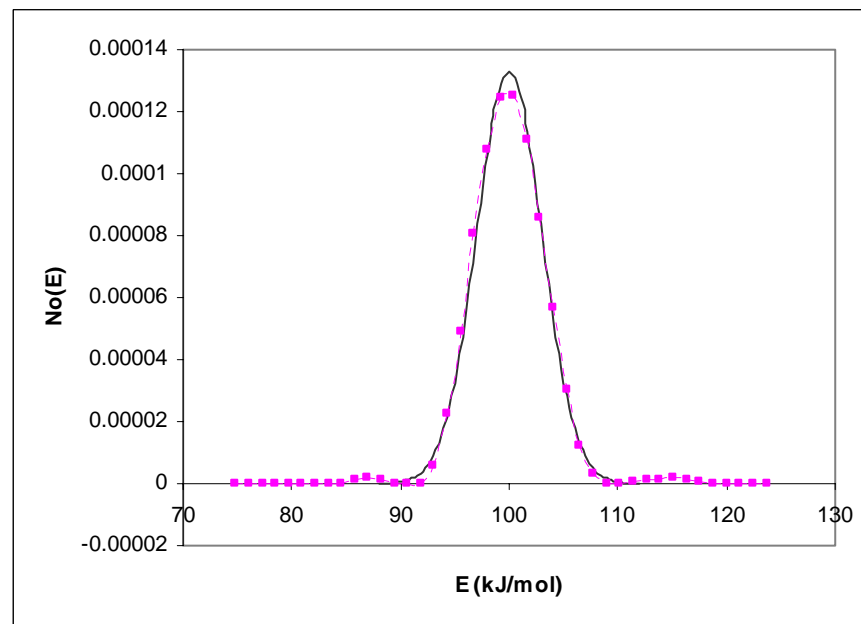
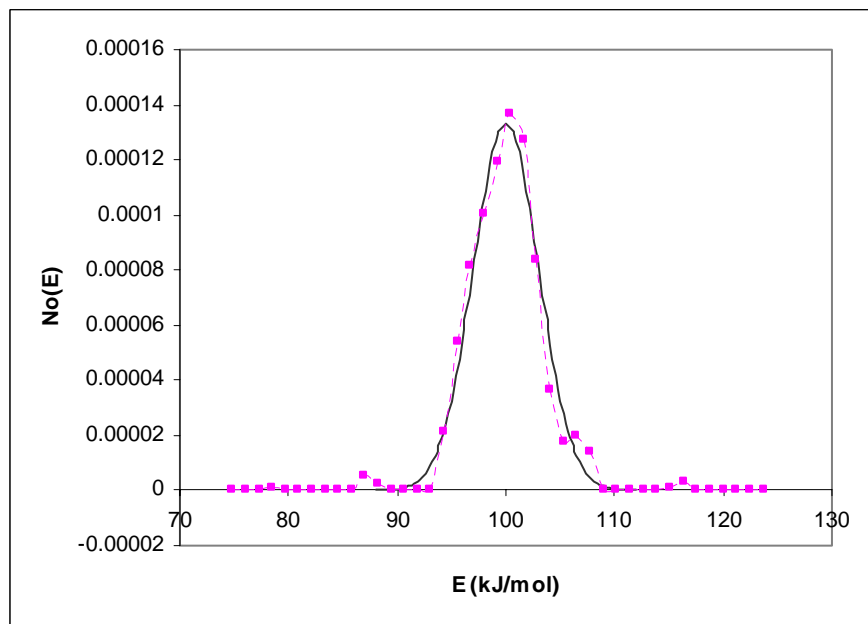
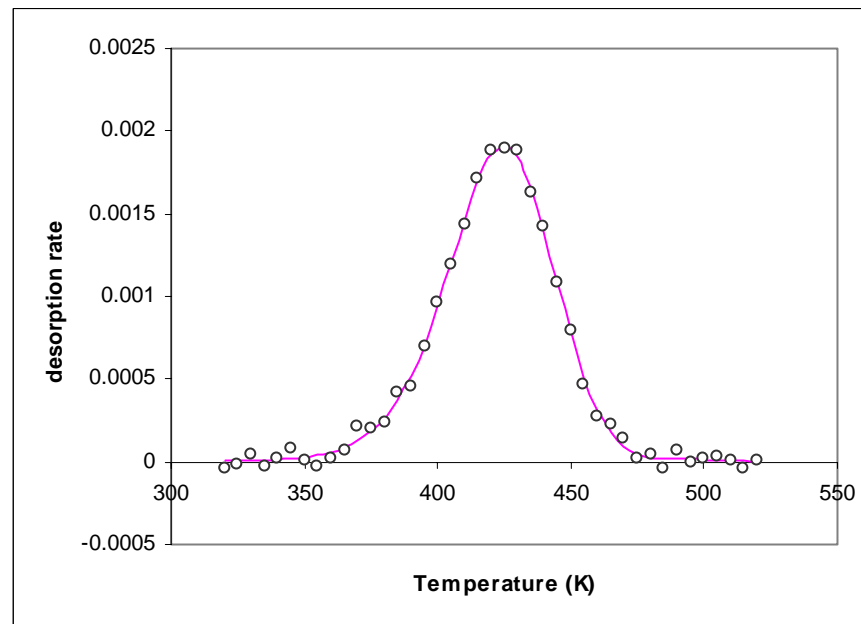
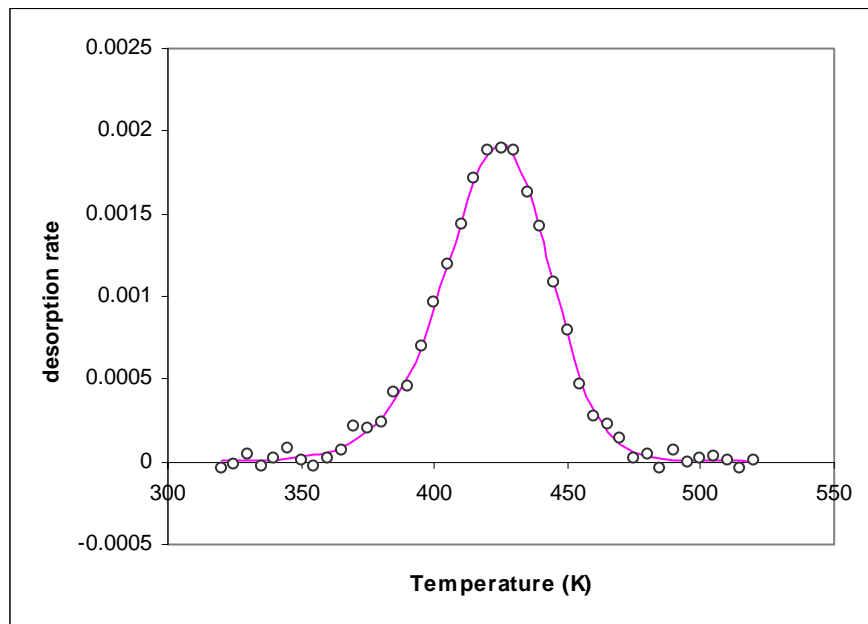
Dataset B1: 20 K between points. Noise level = 2%. Top = TPD data (points) and simulation (curve) ; bottom = energy distribution: actual (curve) and derived (points). Left-hand side = penalty function based on Eq. 34. Right-hand side = penalty function based on Eq. 35.



Dataset B1: 10 K between points. Noise level = 2%. Top = TPD data (points) and simulation (curve) ; bottom = energy distribution: actual (curve) and derived (points). Left-hand side = penalty function based on Eq. 34. Right-hand side = penalty function based on Eq. 35.



Dataset B3: 5 K between points. Noise level = 2%. Top = TPD data (points) and simulation (curve) ; bottom = energy distribution: actual (curve) and derived (points). Left-hand side = penalty function based on Eq. 34. Right-hand side = penalty function based on Eq. 35.



Dataset B4: 2.5 K between points. Noise level = 2%. Top = TPD data (points) and simulation (curve) ; bottom = energy distribution: actual (curve) and derived (points). Left-hand side = penalty function based on Eq. 34. Right-hand side = penalty function based on Eq. 35.

