Available online at www.sciencedirect.com

SCIENCE DIRECT

Thermochimica Acta 417 (2004) 185–186

thermochimica acta

www.elsevier.com/locate/tca

Note

New calculational techniques for the elucidation of thermodynamic and kinetic parameters from isothermal calorimetric data: application to second order (and higher orders) reactions studied by flow calorimetry

M.A.A. O'Neill*

Medway Sciences, Natural Resources Institute, University of Greenwich at Medway, Medway Campus, Central Avenue, Chatham Maritime, Kent ME4 4TB, UK

Received 10 July 2003

Available online 27 February 2004

This laboratory has been concerned for some time with the development of novel calculational methods for the direct determination of thermodynamic and kinetic parameters from isothermal microcalorimetric data [1–6]. We have shown that it is possible to determine values for the rate constant, k, enthalpy, H, order of reaction, n, equilibrium constant, K, activation energy, E_a, and the quantity of material undergoing reaction, A, in a model free fashion (save that there is conformity with the van't Hoff isochore). Our early efforts were concentrated on the development of these techniques for the study of solution phase reactions examined using static/batch type calorimeters [1,2]. These techniques have been refined to incorporate methods for analysing solution phase flow calorimetric data [5,6] (for first order reactions) and solid state calorimetric data [4]. Whilst we are confident that we can calculate accurate values for the parameters of interest (for all reaction orders) from static/batch calorimetric data and for first order reactions studied by flow calorimetry, until now no consideration of higher order reactions studied by flow calorimetry has been addressed.

Note that for the calculation of the parameters of interest, from flow calorimetric data, it is required that accurate values for the rate constant of reaction can be found. This is trivial for first order reactions since the rate constant is merely the negative slope of the line from a ln(output) versus time plot. However, this is not the case for higher orders of reaction.

For reaction orders >1, it is necessary to identify the reaction order through a data pairing technique recently developed and reported by Willson and Beezer [3]. This technique examines the relationship between pairs of data points along a calorimetric curve and identifies the reaction order through the ratio of the two points. Once the order is known, then the appropriate calorimetric equation (previously published by O'Neill [7], Hills [8], Gaisford [9] and Willson [10]) can be applied. For the purposes of this demonstration, we will deal solely with a second order reaction for a reaction studied by flow calorimetry.

The equation which describes a second order reaction [7], studied by flow calorimetry, is given in Eq. (1):

$$\phi = \frac{-kHV_c[A_0]^2}{\tau[(1+k(t+\tau)[A_0])(1+kt[A_0])]} \tag{1}$$

where ϕ is the calorimetric output (J s^{-1}), k the rate constant ($mol^{-1}\,s^{-1}\,dm^3$), H the enthalpy (kJ mol^{-1}), V_c the thermal volume (dm^3) (for further discussion of this term see [5]), $[A_0]$ the initial concentration of reagent ($mol\,dm^{-3}$), t the time (s), and τ the residence time (s).

Note that the rate constant, k, and the enthalpy, H, appear as a product function and therefore cannot be separated by simple algebra. In order to calculate one, it is necessary to obtain an accurate value for the other. Also note that the calorimetric output is dependent upon the terms τ and V_c, these are related to the flow rate of the reaction solution and the physical dimensions of the calorimetric cell, their values can be found through the application of a test and reference reaction, the base catalysed hydrolysis of methyl paraben [5,11].

By taking the ratio of Eq. (1) for two data points at times t_1 and t_2, the top line of Eq. (1) "disappears" to leave an

---

* Tel.: +44-1634-883-362; fax: +44-1634-883-044.

E-mail addresses: moneill27@tiscali.co.uk, moneill27@hotmail.com (M.A.A. O'Neill).

doi:10.1016/j.tca.2003.12.012

equation in terms of only one unknown, k (Eq. (2)):

$$\frac{\phi_1}{\phi_2} = R = \frac{(1 + kt_2[A_0] + k\tau[A_0])(1 + kt_2[A_0])}{(1 + kt_1[A_0] + k\tau[A_0])(1 + kt_1[A_0])} \tag{2}$$

Eq. (2) can be rearranged to give a quadratic equation in terms of k (Eq. (3)):

$$\begin{aligned} &k^2(Rt_1^2[A_0]^2 + Rt_1\tau[A_0]^2 - t_2^2[A_0]^2 - t_2\tau[A_0]^2) \\ &\quad + k(2Rt_1[A_0] - 2t_2[A_0] + R\tau[A_0] - \tau[A_0]) \\ &\quad + (R - 1) = 0 \end{aligned} \tag{3}$$

This quadratic equation is now readily solved for k using standard procedures. As always with a quadratic equation two roots will be returned, clearly the real rate constant will be given by a positive root. Once a value for k is found, it can be used in Eq. (1) to find the enthalpy and from there all other parameters can be found.

This calculational method has been scrutinised through its application to simulated data. It can be shown that the correct value for k is returned for simulated data where the value of k ranges from 4×10^{-8} to $4 \times 10^{-3}\,\mathrm{s}^{-1}$ and enthalpies ranging from 50 to $150\,\mathrm{kJ\,mol}^{-1}$ assuming that the order of reaction (second order in this case) is known from ancillary sources. If the reaction order is not known prior to the experiment, then the data pairing technique for the calculation of n, noted earlier, must be employed. In this case, the range of accessible k and H are constrained by the limitations of the method for determining n.

This example describes the derivation of the equations necessary for the determination of the rate constant (and hence the enthalpy) from data obtained for second order reactions, although the derivation for third order reactions has not been attempted, it is anticipated that it could be achieved by a similar technique to that described earlier.

It is now possible to calculate accurate thermodynamic and kinetic information for all integral ordered, solution phase reactions studied by static/batch and flow calorimetry and from solid state reactions (assuming that the reaction conforms to the Ng equation [12]) directly from the calorimetric data free from assumption as to the mechanism of reaction.

References

[1] R.J. Willson, A.E. Beezer, J.C. Mitchell, W. Loh, J. Phys. Chem. 99 (1995) 7108.

[2] A.E. Beezer, A.C. Morris, M.A.A. O'Neill, R.J. Willson, A.K. Hills, J.C. Mitchell, J.A. Connor, J. Phys. Chem. 105 (2001) 1212.

[3] R.J. Willson, A.E. Beezer, Thermochim. Acta. 402 (2003) 75.

[4] M.A.A. O'Neill, A.E. Beezer, A.C. Morris, K. Urakami, R.J. Willson, J.A. Connor, J. Therm. Anal. Calorim. 73 (2003) 709–714.

[5] M.A.A. O'Neill, A.E. Beezer, G. Vine, C. Labetoulle, L. Nicolaides, R.B. Kemp, D. Olomolayie, P.L.O. Volpe, D. Oliveira, Thermochim. Acta 413 (2004) 193–199.

[6] M.A.A. O'Neill, A.E. Beezer, J.C. Mitchell, J. Orchard, J.A. Connor, Thermochim. Acta 417 (2004) 187–192.

[7] M.A.A. O'Neill, Ph.D. thesis, University of Greenwich, 2002.

[8] A.K. Hills, Ph.D. thesis, University of Kent at Canterbury, 2001.

[9] S. Gaisford, Ph.D. thesis, University of Kent at Canterbury, 1997.

[10] R.J Willson, Ph.D. thesis, University of Kent, 1995.

[11] M.A.A. O'Neill, A.E. Beezer, C. Labetoulle, L. Nicolaides, J.C. Mitchell, J. Connor, J. Orchard, R.B. Kemp, D. Olomolaiye, Thermochim. Acta 399 (2003) 63.

[12] W.L. Ng, Aust. J. Chem. 28 (1975) 1169.