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Survey of the effect of fill volume on the values for the enthalpy and rate constant derived from isothermal microcalorimetry: applications of a newly developed test reaction

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Abstract

A recent paper has reported the results of an inter/intralaboratory study into a test and reference reaction for isothermal microcalorimeters, the imidazole catalysed hydrolysis of triacetin. The values derived were $2.8\times10^{-6}\pm9.7\times10^{-8}$ dm^3 mol^{-1} s^{-1} and -91.7 ± 3 kJ mol^{-1} for the rate constant and enthalpy, respectively. This paper reports the findings of an investigation, using this test reaction, into the effect of ampoule fill volume on the recovery of the derived rate constant and enthalpy. Fill volume is likely to be of significance for all commercially available, heat conduction, isothermal microcalorimeters. Experiments, reported here, were performed in a thermal activity monitor (TAM, thermometric AB, Jarfalla, Sweden) operating in the batch mode, for 3, 4 and 20 ml glass ampoules and 4 ml stainless steel ampoules. It is shown that the rate constant can be accurately recovered at fill volumes greater than 50% but below 50% fill volume this accuracy diminishes.

Keywords: Triacetin; Volume study; Isothermal microcalorimetry

1. Introduction

The need for a chemical test reaction for the validation of microcalorimeters has been known for some time. Chen and Wadso first proposed the imidazole catalysed hydrolysis of triacetin in 1982 [1]. More recently, the imidazole catalysed hydrolysis of triacetin was subjected to an inter/intralaboratory investigation and subsequently accepted [2], as such a test reaction. The data derived were the enthalpy, *H*, and rate constant, *k*, for this second-order reaction.

The experimental data upon which the recommended values, for *k* and *H* are based were derived from experiments conducted in the ampoule (batch) mode, in commercially available, isothermal, heat conduction microcalorimeters (thermometric TAM, Setaram Micro DSC III, Setaram C80, DAK). In all instances the ampoules used [2] (volume range: 3–9 ml) were filled to their nominal fill volume with reaction medium.

However, the design of some of these instruments is such that the thermopile units do not completely surround the ampoules. The channels for the 3 and 4 ml ampoules, used in the thermometric thermal activity monitor (TAM, thermometric AB, Jarfalla, Sweden) are designed in such a way that the thermopiles only

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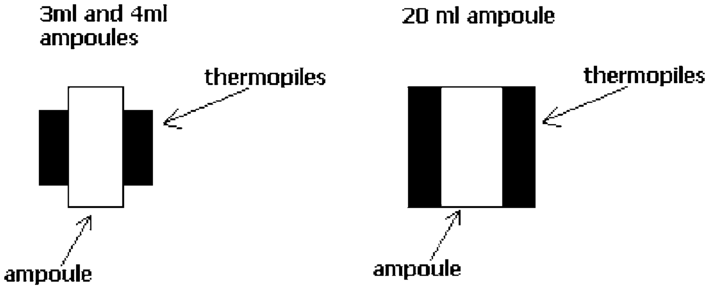

Fig. 1. Schematic of thermopile arrangements for the 3, 4 and 20 ml ampoules.

cover a percentage of the ampoule surface. There are areas at the upper and lower sides of the ampoules which are not covered. For such instruments, it is not known what effect ampoule fill volume will have on the recovered data. However, the channel for the 20 ml TAM ampoule is designed differently. In this case the thermal elements extend over the height of the ampoule and surround the ampoule, except for the top and base. (These arrangements are sketched in Fig. 1.) It might be expected that the values for *H* and *k* recovered from the extrema of fill volume for the 3 and 4 ml ampoules may be different from those of the 20 ml ampoule. Indeed this is considered by us to be an issue associated with use of all such commercially available isothermal, heat conduction microcalorimeters.

Knowledge of the values for *k* and *H*, for the test reaction, allows for performance testing of the calorimeter, training of new personnel and also for troubleshooting, i.e. correction of systematic errors. Hills et al. [3] have shown how it is possible to identify, and correct for, systematic errors such as drift in baseline or incorrect setting of upper calibration limits, etc. This paper reports investigations into the possibilities for use of this reaction in the study of experimental design for studies performed in isothermal microcalorimeters of this type.

To date this test reaction has only been used to determine the performance of isothermal heat conduction microcalorimeters operated in the ampoule (batch) mode. Moreover, these test reaction studies were performed with ampoules which were filled to their nominal fill volume with reaction medium. In some instances, the material under investigation might be scarce or, for practical reasons (e.g. in some solid state reactions) the sample may be spread thinly on the base of the ampoule and, therefore, it is impossible to have a complete fill of the ampoule. This paper reports investigations of, as an example, the performance of a thermometric TAM as a function of fill volume for 3, 4 and 20 ml glass ampoules and also a limited study of 4 ml stainless steel ampoules. The volumes studied range from ca. 10 to 100% of the nominal fill volume.

The test employed was to compare the values for the rate constant and enthalpy recovered from the experimental data at different fill volumes, with the reported values. The development of a new mathematical approach [4] allows direct determination of the thermodynamic and kinetic parameters of any chemical reaction whether it proceeds to completion or reaches equilibrium. The development and subsequent inter-intralaboratory-studies of a chemical test reaction, the imidazole catalysed hydrolysis of triacetin [2], has allowed the determination of recommended values for the rate constant, *k*, and the enthalpy *H* for this reaction. The published values are [2]: $2.8 \times 10^{-6} \pm 9.7 \times 10^{-8}\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$ and $-91.7 \pm 3\,\text{kJ}\,\text{mol}^{-1}$, respectively. The reaction can be shown to be second order in nature, over at least 100 days, and, given sufficient time, would proceed to completion, i.e. no equilibrium exists.

2. Experimental

The experimental protocol and conditions used for all experiments are outlined in [2]. The only variation being the range of fill volumes used. These volumes range from 100% down to approximately 10% of the nominal fill volume.

Table 1
Results of the 20 ml glass ampoule experiments

Parameter	Fill volume (ml)				
	20	15	10	5	2.5
H (mean; kJ mol^{-1})	86.5	89.5	88.2	87.6	85.4
S.D.	4.5	3.4	2.3	6.8	13.7
S.D. (%)	5.3	3.8	2.6	7.7	16.0
k (mean; dm^3 mol^{-1} s^{-1})	2.9E−6	2.7E−6	2.7E−6	2.6E−6	2.8E−6
S.D.	1.4E−7	1.2E−7	8.3E−8	1.9E−7	4.9E−7
S.D. (%)	5.0	4.3	3.1	7.3	17.7

Table 2
Results of the 3 ml glass ampoule experiments

Parameter	Fill volume (ml)					
	3	2.5	2.0	1.5	1.0	0.5
H (mean; kJ mol^{-1})	95.4	89.2	87.2	102.0	86.4	69.0
Range	–	–	–	174.4	3.6	30.1
k (mean; dm^3 mol^{-1} s^{-1})	2.8E−6	2.8E−6	2.8E−6	3.0E−6	2.6E−6	3.3E−6
Range	–	–	–	4.5E−7	8.6E−7	6.6E−7

Table 3
Results of the 4 ml glass ampoule experiments

Parameter	Fill volume (ml)						
	4	3.5	3.0	2.5	2.0	1.5	0.5
H (kJ mol^{-1})	90400	90500	90600	90200	88100	64500	91800
k (dm^3 mol^{-1} s^{-1})	2.8E−6	2.8E−6	2.9E−6	2.8E−6	3.0E−6	4.1E−6	3.5E−6

3. Results

The values obtained for k and ΔH, at each fill volume for the 20 ml ampoule are reported in Table 1.

The results for the derived values k and H, for the 3 ml glass ampoules, are reported in Table 2.

The results from the 4 ml glass and stainless steel ampoules are reported in Tables 3 and 4, respectively.

These results are more dramatically presented in Figs. 2–6.

It should be noted that for studies conducted in the 20 ml ampoule, five experiments were conducted at each fill volume except for the 2.5 ml experiments where only three were performed. For the 3 ml ampoule only single experiments were conducted in the 3–2 ml range and duplicates were performed for the remaining fill volumes. No repeat studies were performed on the 4 ml ampoules.

The data presented in Figs. 2–5 are values of the rate constant and enthalpy as a function of fill

Table 4
Results of the 4 ml stainless steel ampoule experiments

Parameter	Fill volume (ml)						
	4	3.5	3.0	2.5	2.0	1.5	1.0
H (kJ mol^{-1})	94400	95700	89700	87900	102100	60500	135300
k (dm^3 mol^{-1} s^{-1})	2.7E−6	2.8E−6	2.8E−6	2.9E−6	2.8E−6	4.9E−6	2.9E−6

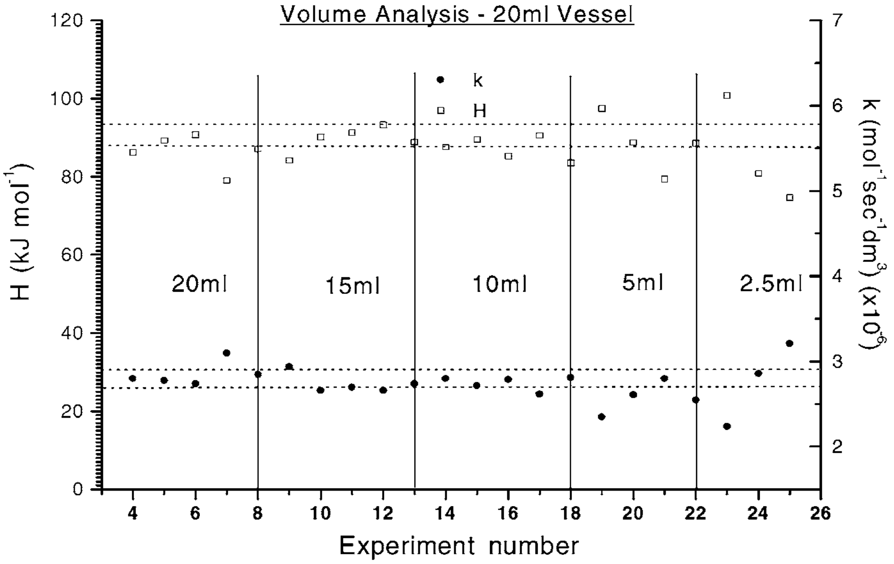

Fig. 2. Variation of k and H with fill volume for a 20 ml glass ampoule.

volume for the 20, 3 and 4 ml glass and stainless steel ampoules, respectively. The dotted lines represent the mean ± S.D. for the recommended data values [2]. For each of the Figs. 2–5, the upper set of dotted lines represent the maximum and minimum values for the enthalpy, the lower set of dotted lines represent the maximum and minimum for the rate constant.

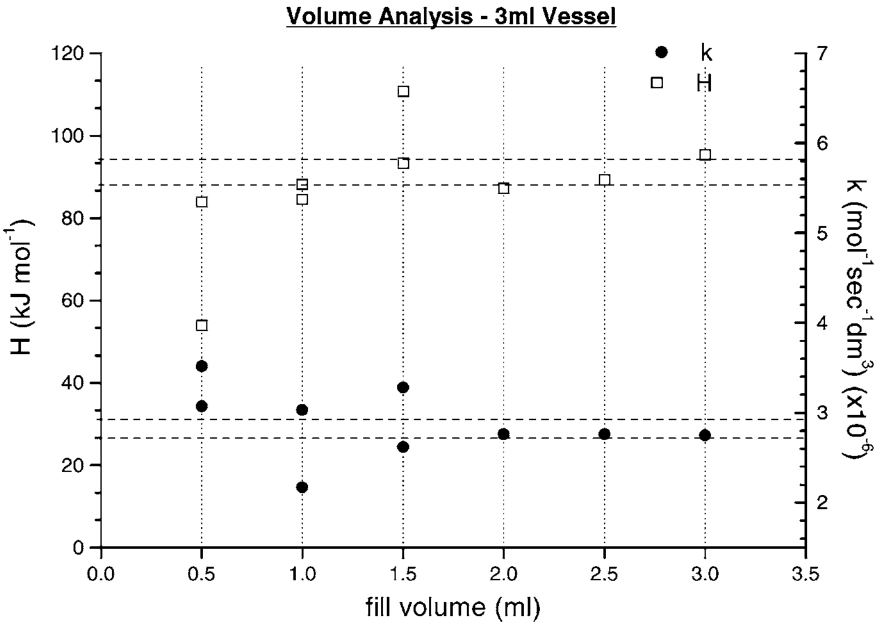

Fig. 3. Variation of k and H with fill volume for a 3 ml glass ampoule.

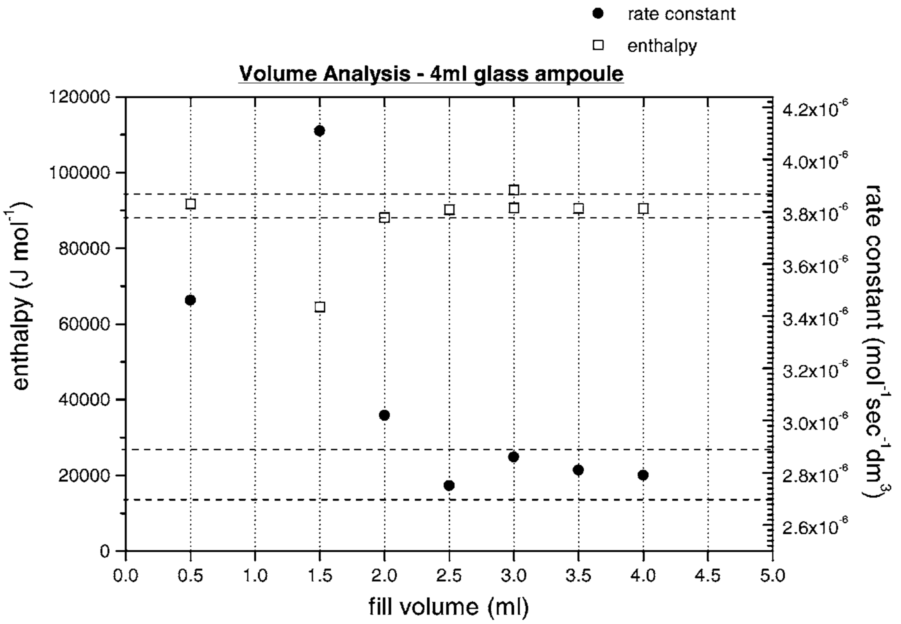

Fig. 4. Variation of k and H with fill volume for a 4 ml glass ampoule.

For the 20 ml ampoule, it is clear that the rate constant is consistently recovered across almost the whole volume range whereas the values recovered for the enthalpy appear to vary more significantly below 50% fill. It is also apparent from this simple statistical analysis, it is evident that all the values derived in this study overlap the accepted values for k and H, across the whole volume range. The reproducibility for fill

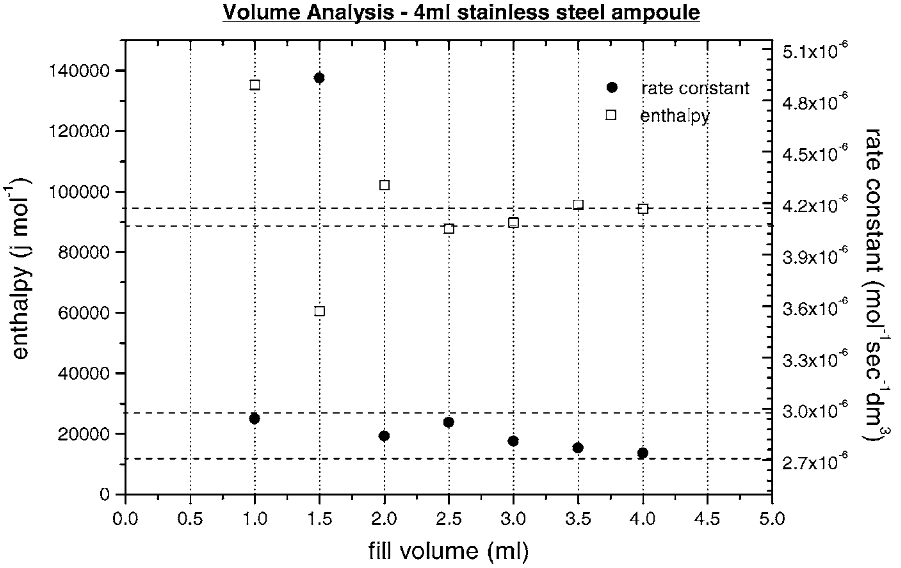

Fig. 5. Variation of k and H with fill volume for a 4 ml stainless steel ampoule.

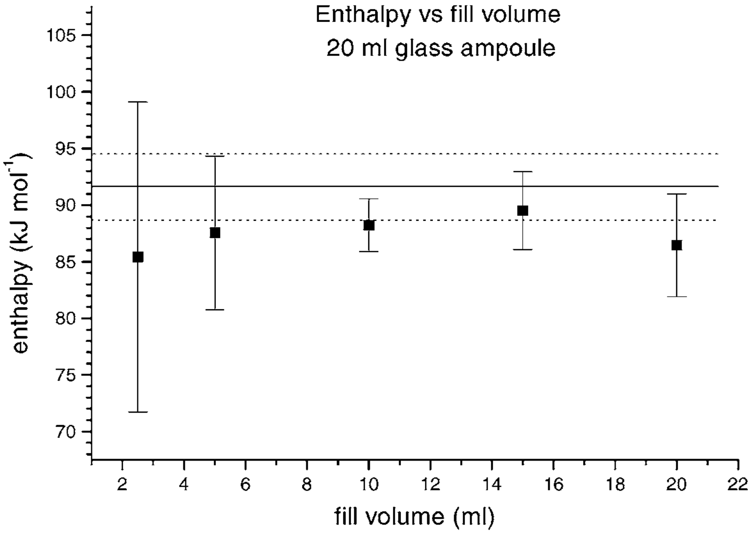

Fig. 6. Enthalpy vs. fill volume for the 20 ml glass ampoule. The dotted lines represents the accepted maximum and minimum values for the enthalpy, the solid line represents the accepted mean value for the enthalpy.

volumes between 10 and 15 ml is very good and for these volumes the statistical deviation expressed as a percentage of the overall value is similar to that for the published values for *k* and *H*. At the extrema of fill volumes, i.e. 20, 5 and 2.5 ml this reproducibility diminishes and indeed gets progressively worse as fill volume decreases. There is also an interesting trend observed in the magnitude of *H*. It appears that the mean value for *H* decreases with fill volume (with the exception of the 20 ml value). This may be related to the changes in heat conduction pathways involving the sides, base and lid of the ampoule. At the higher fill volumes, the thermal pathway through the lid may be more significant. Likewise at lower fill volumes the signal may be subject to more error as a more significant proportion of the heat flow will be through the base. However, it should be noted that the error limits, at the upper and lower end of the fill volume range, are such that even though the mean is not the accepted value it still falls within the accepted range because of the high values for the standard deviation. This is more readily seen in Fig. 6.

There are not enough data at present for a similar analysis of the 3 and 4 ml ampoule studies. However, it is clear that the recovered mean values for *k* and *H* are less reliable as the fill volume decreases below 50%.

4. Conclusions

It is apparent that for fill volumes greater than 50% of the total nominal volume, the enthalpy and rate constant can be satisfactorily recovered for the 20, 3 and 4 ml vessels. Below 50% fill volume, the reproducibility of these values is lower especially for that of the enthalpy.

Microcalorimetry allows for non-destructive examination of samples of materials. Such investigations can be made on heterogeneous, complex systems (solids [5], sequential reactions [6], parallel reactions [7], gas/solid systems [8], etc.) without the need for ancillary information to aid data evaluation. Solid state reactions, notoriously difficult to study [9,10] provide good examples for the utility of the microcalorimetric, method and for the need to understand the importance of experimental design (here the fill volume) in determining reliable, validated and traceable results, for *k* and *H*, for unknown systems. Only a limited statistical analysis has been included for the results reported here, since data recovery values are likely to be specific to individual calorimeters.

There are some important points to note with the studies conducted thus far and reported here. Many repeats will be required for each experiment before any statistical analysis can be performed, i.e. mean values for each fill volume and their associated statistical deviation. Once these values are established then it may be possible to calculate correction factors using similar methods to those outlined in [3]. In conjunction with the test reaction, and noting the implications of the results reported here, alternative ampoule designs could now, in principle, be investigated. For instance an insert which effectively raises the base of the ampoule to a level covered by the thermopiles, by means of a "shelf", could be investigated for performance, that is an exploration of position versus volume outcomes could be made. Such a design would be relatively simple for samples in the solid state however factors such as increased heat capacity and altered heat conduction pathways caused by the insert would have to be considered and thoroughly investigated.

The data and the observations presented in this paper indicate the need for caution when reporting the values for thermo-kinetic parameters derived from isothermal microcalorimetry where experiments are conducted with small sample sizes.

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