

The development and application of a raw signal database for heat flow

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Abstract: A digital heat flow database was newly introduced. The new database is the natural extension of and includes original data obtained by calorimeter for the digital age. Therefore, it enables a comparison of the calorimeter apparatus itself, a reaction kinetics calculation, a comparison of characteristics of the reactive substances and an evaluation of the characteristics extraction method. With the ordinary database, which is a list of extracted values such as exothermic onset temperature or heat of reaction that are noted on MSDS, etc., it is unavoidable to include some arbitrariness. Therefore, there are still problems in the safe handling of unstable substances. In this study, a differential scanning calorimeter is chosen for the apparatus and several basic treatment methods of the new database are introduced. A baseline recalculation and a simple chemical kinetics analysis are also performed as examples of application methods. The results show potentially hazardous risks.

Keywords: heat flow, database, DSC

INTRODUCTION

Use of a Differential Scanning Calorimeter, or DSC, is one of the most popular screening methods for thermal stability measurements. The basic DSC has only two heat flow sensors covered with a heater. In spite of the simple configuration, it can show many thermal physics features, such as onset temperature, decomposition heat, maximum exothermic acceleration, glass transition and so on. However, these specific values are influenced by chemical impurities, the temperature rise rate, the DSC apparatus and the scientists' experience. Therefore, it is not easy to compare values taken in different situations. For example, the onset temperature is one of the most important values for validating the thermal stability of chemical substances. It is well known that a lower temperature rise rate gives a lower onset temperature, but this is not the only critical influence on onset temperature. The onset temperature is the temperature at which a given heat flow curve detaches from the baseline. From this definition, 1) the baseline must be suitably chosen, 2) the detachment must be accurately detected, 3) for accurate detection, the S/N ratio must be understood for different situations having, for instance, different apparatus, sensors and sensor ages. Recently, DSC apparatus have semi-automatic data proceeding programs, so it seems that there is less meaning in discussing these problems. However, the issue is how to compare specific values that are processed by different apparatus and programs. The answer is to

show the raw data of the DSC itself. This was not historically possible in paper publications, but now the Internet can be used for such huge data storage and retrieval.

In 1988, the National Institute of Industrial Safety, Japan, formerly the National Institute of Occupational Safety and Health, Japan, published a DSC data book [1]. It has the heat flow curves and specific values of 470 chemical substances. In 2007, the National Institute of Occupational Safety and Health, Japan revised this data book as digital data of 456 chemical substances and opened it to the Internet [2]. In this report, the new DSC database is introduced and one example from the DSC database is given.

DATABASE AND APPLICATION

DATABASE

Figure 1 shows the new database of the DSC[2]. Basically, the database comprises only one table with the substance name in Japanese and English and links to pdf and csv file formats. The data can be searched for by search engines or a browser's search function. However, since the data is open to the Internet, AJAX technology developed not only by us will soon provide good search solutions.

The data is available in pdf and csv formats. The pdf data of o-Nitoracetanilide, which is just a scanned page of Ref. 1, is shown in Figure 2. The original paper based data book has measurement detail information and a constitutional formula, but no digital text data. The csv data is digitalized data of the

$$B(T) = (H(T_o) - \frac{\partial H}{\partial T} \Big|_{T=T_o} (T - T_o))(1 - \alpha(T)) + (H(T_e) - \frac{\partial H}{\partial T} \Big|_{T=T_e} (T - T_e))\alpha(T) \quad (1)$$

$$\alpha(T) = \int_{T_o}^T (H(\tau) - B(\tau))d\tau / \int_{T_o}^{T_e} (H(\tau) - B(\tau))d\tau \quad (2)$$

T_o and T_e indicate the onset and terminal temperatures respectively. α is the reaction progress. The baseline function and the reaction progress must be calculated iteratively. An initial baseline function is chosen as the line between the onset and terminal points. The convergence of this iteration is achieved immediately with an ordinary computer. When the converged baseline was higher than the heat flow, the onset and terminal temperatures are chosen to reduce the reaction range, i.e. the onset temperature was increased and the terminal temperature decreased. In this calculation, the error range around the reaction range edge was considered with dispersion values that calculated the difference between the linear estimation values and the heat flow values. Therefore thrice the square root of the calculated dispersion was used for

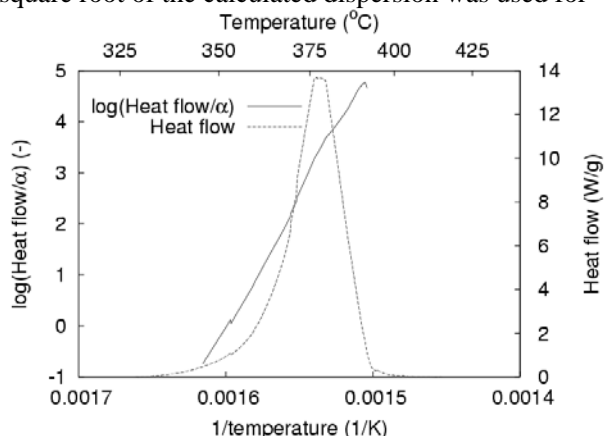


Fig. 4 Chemical kinetics analysis of *o*-Nitroacetanilide.

the determination of the heat flow and baseline comparison. The obtained baseline is also shown in Figure 3. The reaction heat was 394 cal/g = 1.65 kJ/g in the original data, but here it was calculated as 1.56 kJ/g. In the earlier study, a straight line between the onset and the terminal points was used for the reaction heat calculation. The onset temperature was 323 °C whereas here it is 326 °C. It is said that T_a , the cross point temperature of the tangential line of the onset point and the maximum heat flow derivative point, has less arbitrariness than the onset temperature[1,4]. It was 364 °C in the earlier study and is 363 °C here.

A chemical kinetic analysis was performed and is shown in Figure 4. In the figure, the heat flow / α is taken as the reaction rate. Therefore a first order reaction was assumed. Because of the error range and the too strong condition that the heat flow equals the baseline at the onset and the terminal temperatures for the reaction rate calculation, the reaction analysis was performed from 0.01 to 0.99 of the reaction progress. The logarithm of the reaction rate and the inverse of the absolute temperature have high linearity. The activation energy and frequency factor can be easily calculated for the reaction rates and it is therefore not important to include these values with the raw signal database. The activation energy and frequency are important when the extrapolation values are needed. From this data, anyone can calculate a given thermal reaction package with a given environment thermal history as the first step of screening without time consumption instead of taking a measurement. The 10 substances with the highest correlation of the reaction analysis with the first order model are summarized in Table 1. The table does not indicate that the decomposition reactions are really first order reactions, but they can be analyzed with the first order model. 53 of the 456 substances have good correlations with the reaction analysis by the first order reaction model with a correlation coefficient more than 0.98. These correlation coefficients of the reaction analysis

Table 1 Chemical substances of a high correlation coefficient with the first order reaction analysis.

	Correlation coefficient(-)	Decomposition heat (J/g)	Onset (°C)	Terminal (°C)
Benzalazine	0.9967	964	272	389
Benzoylhydrazine	0.9987	963	206	404
N-(2,3-Epoxypropyl)phthalimide	0.9911	323	272	396
4-Methoxybenzoyloxycarbonylazide	0.9985	622	113	197
Hydrazobenzene	0.9968	336	138	252
4-tert-Butylphenylthiophosphonic dichloride	0.9931	215	160	245
Dicumylperoxide	0.9970	634	116	213
n-Amylnitrite	0.9954	649	180	249
2,5-Dimethyl-2,5-di(tert-butylperoxy)hexane	0.9913	720	128	221
<i>o</i> -Nitroacetanilide	0.9934	1558	326	417

calculation ensure that the baseline calculations are suitable.

CONCLUSION

The raw signal database of the DSC was opened to the Internet for anyone to use freely. A reaction analysis was shown as an example of its application. Using computer software, it is easy to extract the specific values without any arbitrariness with this data. The recent development of AJAX will allow a greater variety of applications using the data. The National Institute of Occupational Safety and Health plans to

open the DSC data book and promote data collection from all over the world.

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