Thermochimica Acta, 110 (1987) 141–144
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

INTRODUCTION AND CRITIQUE OF NON-ISOTHERMAL KINETICS

PAUL D. GARN

The University of Akron, Akron OH 44325 (U.S.A.)

ABSTRACT

The complexity of kinetics is analyzed suggesting that one should choose other methods either to obtain the data or to verify the conclusions from thermogravimetric measurements.

Twenty years ago I pointed out that the complexity of kinetics suggested that one should choose other methods either to obtain the data or to verify the conclusions from thermogravimetric data [1]. The statement was well supported by Gallagher and Johnson [2] who demonstrated that mere changes in sample size produced serious changes in the terms we call kinetic parameters. My serious thinking about the way we do kinetics began some years before; Berlin and Robinson [3] had reported that the activation energy of calcium carbonate decomposition varied from about 40 kcal mol^{-1} in nitrogen to about 210 kcal mol^{-1} in carbon dioxide. In the oral presentation [4], the speaker, in response to my question, admitted that the activation energy was a function of the sample holder! These variations are of course to be expected if the systems are examined closely.

Let us consider the expectations for a kinetic description:

First, the rate constant for a given process should be an intensive property, like density, rather than an extensive property such as mass. That is, it should not vary with sample size or shape or any external parameter not explicitly stated in the fundamental equation:

$$k = \mathrm{f}(T, a, b, c, \ldots)$$

Second, even apparently irrelevant parameters should be looked at with some suspicion. For example, some equipment manufacturers give different heat parameters for a helium atmosphere than for nitrogen or any other gas. Significant changes in rates or even processes can result from use of different atmospheres that are not even reactants or products. There are many reports that disclose these changes and many authors who accept them as real.

Thermal Analysis Highlights, 8th ICTA, Bratislava, Czechoslovakia.

0040-6031/87/$03.50

My voice has not been alone in warning of the traps awaiting the unwary. Lesser fractions of the kinetics papers in recent ICTA meetings than before have been repeating the errors of omission. Of the seven poster presentations in this assigned discussion group, even though apparent activation energies are often reported as firm values, nearly all reported the effect of some preparation or history on the measured rate parameters.

Taking the posters alphabetically, I will discuss first the poster by Barriga et al.: "Effect of Grinding on the Kinetics of the Transformation Vaterite–Calcite" [5]. The authors find from reduced-time plots "best fits" for three mechanisms from the models proposed by Sharp et al. [6]. But *many* reactions are already known to fit many of the forms, so delineation is difficult. Not very many authors take the next step in complexity, that of Selvaratnam and Garn [7]; I believe the principal reason is that most sets of data do not fit any model really well and the number of publications would be diminished quite drastically.

With regard to activation energy, which increased with grinding of the vaterite, this is the anticipated response. The apparent activation energy is a measure of the sharpness of the energy distribution peak that we assume for reactants. Any treatment that brings the particles more nearly into the same energy condition will certainly increase the activation energy that we calculate. Still, this report builds the knowledge we are developing concerning solid processes.

The next poster, by Bourrie and Filsinger [8], also demonstrated the precaution shown by Barriga et al., namely, using a second technique, in this case a non-dispersive infrared analyzer, to monitor the carbon monoxide as carbon was reacted with tantalum. The connection to the thermobalance chamber led to tailing of the CO signal because the product had to diffuse to the exit.

Another question arises here: why perform both experiments simultaneously when each can be done separately so easily? Certainly a simple heated reaction tube and the IR detector would avoid the tailing, and using a known pressure of carbon monoxide in the thermobalance could yield some useful thermodynamic as well as kinetic data. Doing the experiments together may save time and several kilowatts, but both sets of data are impaired.

Gruncharov et al. [9] studied the formation of phosphoric acid from mineral phosphates. They used carbon dioxide atmospheres, finding that the ratios of products, CaO and CaS, were controlled by the pressure of carbon dioxide. The thermodynamic control over Reaction 2 is easily perceived. Two questions arise: were there experimental verifications of quantitative formation of SO_2 in Reaction 1 and was sulfur dioxide ever tested to inhibit Reaction 1. It seems probable that CaO would be more marketable than CaS.

The decomposition of cupric chromate to yield CuO and $CuCr_2O_4$ was studied by Horvath and Hanic [10], using both TG and X-ray methods. For TG, the standard flowing nitrogen and static air were used for the reversible process. As we could expect, the oxygen, which inhibited the process, yielded a higher calculated activation energy than did flowing nitrogen, but a smaller value than in the static air X-ray method. The variation in sample exposure should be explained by the authors.

The popular compound, calcium carbonate, was studied by Maciejewski and Bałdyga [11]. Many papers have been written, mostly describing the heating in air, nitrogen or vacuum, from which results one may derive almost any conclusions. The present authors, however, recognize full well that the pressure of carbon dioxide plays a very important role. Not only is the initial evolution impeded by the presence of the reactant but diffusion of CO_2 from within the particle is inhibited. There is some major hazard, though, in treating the surface as the major concern. In cycling experiments done over 20 years ago [12] I found that the material took up less and less CO_2 on subsequent coolings. The internal annealling may be important.

The work by Pacewska et al. [13] again demonstrates equilibrium between the solid surface and the surrounding atmosphere. The information in the abstract does not specify the starting material well enough; my handbook shows only $12H_2O$. It is easy to understand that these water molecules might be lost in two or three groups but the curves suggest equilibrium is only seldom reached. The appearance of a kinetic compensation plot was disappointing. That concept should have been thoroughly discredited by now [14–16].

Finally, the poster by Stoch [17] promises to be illuminating because it deals with a number of types of decomposition, classifying some into specific types. Some allocations seem too firm. For example, magnesium hydroxide does not appear to follow in practice the intracrystalline product grain description [18,19]. Even so, an examination of the several modes may save a lot of effort by later workers.

The basic problem is, of course, the use of the concepts of homogeneous kinetics to reactions that clearly do not meet the qualifications. The distribution of energies assumed in the Arrhenius equation is clearly not possible in a crystalline solid. Broad distributions are out of the question because the multiple interactions transfer energy too readily and the lowest energy—that of the perfect crystal — is surely the most probable [20].

My reporting task included two of my own contributions with A.-A. Alamolhoda. Both of these are improved data-taking for kinetics but neither extended abstract was submitted in time. One [21] was a derivation of an earlier paper describing the determination of Curie points of the ICTA Certified Reference Materials for Thermogravimetry [22]. The same device can be used for determinations of Curie points anywhere in the temperature range of the apparatus, hence on any paramagnetic material chosen by the user.

The other device [23] is a controlled atmosphere, supra- or sub-ambient pressure thermobalance. We have just finished the early testing, so all we could show is that we can make barium chloride 2/3 hydrate, a compound suggested by earlier experiments [24,25] from either the anhydrous material or the approximately monohydrate. Obviously, we can and will use it with other ligands that appear to have non-stoichiometric structures. One very important use will be the definition of conditions of temperature and pressure under which a particular compound is stable.

REFERENCES

1 P.D. Garn, Thermoanalytical Methods of Investigation. Academic Press, New York, 1965.
2 P.K. Gallagher and D.W. Johnson, Jr., Thermochim. Acta, 6 (1973) 67.
3 A. Berlin and R.J. Robinson, Anal. Chim. Acta, 27 (1962) 50.
4 National Meeting, American Chemical Society, New Nork, 1962.
5 C. Barriga, J. Morales and J.L. Tirado, Proc. 8th ICTA '85, Bratislava, Thermochim. Acta, 92 (1985) 211.
6 J.H. Sharp, G.W. Brindley and B.N.S. Achar, J. Am. Ceram. Soc., 49 (1966) 379.
7 M. Selvaratnam and P.D. Garn, J. Am. Ceram. Soc., 59 (1976) 376.
8 D.B. Bourrie and D.H. Filsinger, Proc. 8th ICTA '85, Bratislava, Thermochim. Acta, 92 (1985) 129.
9 Iv. Gruncharov, Pl. Kirilov, Y. Pelovski and Iv. Dombalov, Proc. 8th ICTA '85, Bratislava, Thermochim. Acta, 92 (1985) 173.
10 I. Horvath and F. Hanic, Proc. 8th ICTA '85, Bratislava, Thermochim. Acta, 92 (1985) 177.
11 M. Maciejewski and J. Bałdyga, Proc. 8th ICTA '85, Bratislava, Thermochim. Acta, 92 (1985) 105.
12 P.D. Garn, unpublished measurements, Bell Telephone Laboratories, Inc., 1962.
13 B. Pacewska, J. Pysiak and A. Klepańska, Proc. 8th ICTA '85 Bratislava, Thermochim. Acta, 92 (1985) 113.
14 P.D. Garn, J. Therm. Anal., 7 (1975) 191.
15 P.D. Garn, in F. Paulik (Ed.), Thermal Analysis, Vol. 1, Akademiai Kiado, Budapest, 1975, pp. 25–32.
16 P.D. Garn, J. Therm. Anal., 10 (1976) 99.
17 L. Stoch, Proc. 8th ICTA '85, Bratislava, Thermochim. Acta, 92 (1985) 97.
18 F. Freund and H. Nägerl, in R.F. Schwenker, Jr. and P.D. Garn (Eds.), Proc. 2nd Int. Conf. on Thermal Analysis, Worcester, MA, August 1968, Academic Press, New York, 1969, p. 1209.
19 H. Nägerl and F. Freund, J. Therm. Anal., 2 (1970) 387.
20 Paul D. Garn, J. Therm. Anal., 13 (1978) 581.
21 A.-A. Alamolhoda and P.D. Garn, Proc. 8th ICTA '85, Bratislava, Thermochim. Acta, 92 (1985) 831.
22 P.D. Garn and A.-A. Alamolhoda, in J.F. Johnson and P. S. Gill (Eds.), Analytical Calorimetry, Plenum Press, New York, 1983, p. 33.
23 A.-A. Alamolhoda and P. Garn, Proc. 8th ICTA '85, Bratislava, Thermochim. Acta, 92 (1985) 833.
24 Paul D. Garn, Anal. Chem., 37 (1965) 77.
25 M.-H. Chung, Dehydration–rehydration of barium chloride, Thesis, The University of Akron, 1984.