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REPORT ON THE WORKSHOP ON KINETICS HELD AT ICTA-9

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This Workshop on Kinetics was held at the Ninth International Congress on Thermal Analysis in Jerusalem, Israel, on the 24th of August, 1988. Its format was modeled after the very successful Workshop on Kinetics held at ICTA-8 in Bratislava, Czechoslovakia, in 1985 which has been previously reported (1). The workshop moderators (Joseph Flynn, Michael Brown, Eugen Segal and Jaroslav Šesták) were assisted by a panel of the other members on the ICTA Kinetics Committee who were present -- Jose Criado (Spain), David Dollimore (U.S.A.), Paul Garn (U.S.A.) and Takeo Ozawa (Japan).

The moderators, panel and over 40 workshop participants held over two hours of discussion on kinetics problems. The workshop opened with a brief review by the Chairman, J.H. Flynn, of the history of the ICTA Kinetics Committee. Short introductory statements were given by many of the moderators and panelists. The remainder of the workshop consisted of a discussion period during which the attendees offered their own comments and directed questions to the panel members. Although the workshop was recorded on tape, portions of it were not understandable so only a short edited version of the above statements and discussions, based upon the tapes and notes prepared by Dr. Michael Brown, are the basis for this report.

The Chairman, J.H. Flynn, introduced the moderators and panel of Kinetics Committee members and detailed the progress which this committee had made since its establishment in Bratislava in 1985. Documents have been produced on recommended kinetics symbols (Šesták); recommended practices for kinetics investigations (Garn) and suggestions for kinetics tutorial programs (Dollimore). The possibility of preparation of single crystals also has been discussed. Committee meetings were held at ESTAC-4 in Jena, DDR and at NATAS-16 in Washington, USA. Dr Flynn also reported on his meeting with the IUPAC Commission on Chemical Kinetics.

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The workshop continued with presentations of comments by several members of the panel.

Professor Criado deplored the uncritical quotation of activation energy values, obtained through the use of commercial software, without careful control of the experimental conditions and without any attempt to determine a reaction mechanism. He also believed that in most experiments, the experimental errors are greater than any errors introduced by the use of the Arrhenius equation. (The question of noise in real curves was also raised by Professor Kirsh (Israel).) Professor Criado recommended the use of constant-rate thermal analysis technique developed by J. Rouquerol as it allows better discrimination of reaction processes, as well as avoiding self-heating and self-cooling effects if the sample mass is kept small. Professor Criado concluded by putting the onus on journal referees to try to improve the quality of kinetics papers.

Professor Dollimore emphasized that, although there is a need for general educational workshops and tutorials on kinetics, there is a greater need for conferences in which a panel of specialists may concentrate their attentions and discussions upon a few selected areas. He then commented on the overemphasis of the importance of interpreting kinetics with computer programs, especially those based solely upon the geometry of a hypothetical reaction interface. He suggested that for many systems this interface may be a diffuse region or zone rather than a sharp interface. More emphasis should be given to what the kinetics means rather than to using computers to define what the kinetics are. Professor Dollimore developed many of these latter concepts in greater detail in his Du Pont Award lecture at this congress (2).

Professor Garn drew attention to his view of the use of the Arrhenius equation which was covered in his invited lecture (3). He also stressed the amount of work needed to get reliable kinetics information.

Dr Ozawa discussed the results of round-robin tests using kinetics data from TG, DSC and DTA to predict the thermal life of polymeric materials conducted by the Japanese Institute of Electrical Engineers. These test methods were found not to be suitable mainly because of the large difference between processes operating at the higher temperatures of thermal analysis and those operating in practical applications such as in the long term operation of an electrical motor at lower temperatures. (This aspect was also stressed by Dr. P. K. Gallagher (USA)). Dr Ozawa suggested that the disparity between the kinetics results for test and service use also was due in part to differences in the gaseous atmosphere for the two cases. Thermal life prediction methods in Japan are tending toward step-wise isothermal methods at lower temperatures -- about one hundred and five degrees Celsius for polymers. He drew attention to the wide applicability of the Freidman differential method and made a strong plea for the formulation of criteria for publication of kinetics methods. He also pointed out that most of the models apply to single processes, but many real reactions involve several processes, e.g. nucleation and growth. Dr. G. Hakwoort (Neth) added a comment later that mass and heat transfer were also very important, especially in solid-gas reactions.

Professor Segal drew attention to his paper (4) dealing with kinetics parameters which are dependent upon the degree of conversion. He also commented on the problems of minimizing the difference between the sample temperature and the furnace temperature, for accurate kinetics measurements.

Dr. Šesták commented that there was no real crisis in kinetics, but that workers tended to follow one of two schools: a formal approach or a mechanistic approach. He suggested the introduction of an "accommodation coefficient", h(alpha), which would allow for the factors which make heterogeneous reactions differ from their homogeneous counterparts. The traditional function, f(alpha), would then be written as

$$f(\alpha) = (1 - \alpha)\, h(\alpha)$$

where h(alpha) might be 1 - alpha for homogeneous reactions, or - ln(1 - alpha) for nucleation and growth processes, or even alpha to the nth power as an additional possibility. He then went on to suggest how data could be analyzed in the form of plots of d(alpha)/dt against alpha. In ideal systems, the interface area can be related to an apparent "order", but in real systems there are complications owing to polydispersion and non-regular shapes, and statistical methods have to be applied. These concepts were developed in greater detail in his Bodenheimer Award Lecture presented at this congress (5).

As in most kinetics discussions, there were speakers for and against the use of the Arrhenius equation with a notable lack of positive recommendations for an alternative approach. Dr. Flynn pointed out that a test of the usefulness of the Arrhenius equation is whether it can successfully predict rates at higher or lower temperatures than those used for the original experiments.

Professor B. Wunderlich (USA) stressed the importance of irreversible thermodynamics and recommended that models should start from the simplest possible assumptions and be developed gradually. The chairman concluded by recommending this concentration on simple models, together with careful control of reaction conditions.

This workshop, as was the case for its predecessor (1), did not produce any new and significant developments in the field of thermal analysis kinetics, but it did produce among the participants a better understanding of one another's points of view. This may permit the development of more constructive dialogues concerning the real problems in the modeling of complex kinetics systems. As usual time ran out and the discussion had to be terminated.

References:

1) J.H. Flynn, M. Brown and J. Šesták, Thermochimica Acta, 110 (1987) 101-112.
2) D. Dollimore, Thermochimica Acta, 135 (1988).
3) P.D. Garn, Thermochimica Acta 137 (1988) 71-77.
4) E. Urbanovici and E. Segal, Thermochimica Acta 135 (1988) 193-198.
5) J. Šesták, Thermochim. Acta, this issue.