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CONCLUDING REMARKS ON ESTAC 4

MODERN DEVELOPMENTS IN CALORIMETRY AND DIFFERENTIAL SCANNING CALORIMETRY

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As chairmen of the Calorimetry task group, we would like first to give a summary of the calorimetric section of the Jena Symposium, and then some proposals for initiating and informal discussion and further activities.

A little more than sixty papers were related to calorimetry and differential scanning calorimetry. These represent only 25% of the whole scientific programme. Differential thermal analysis is always strongly represented in ESTAC, as in the national meetings.

To summarize, we can say that about fifteen communications were concerned with C_p measurements, and twenty with thermodynamic or kinetic studies of mixing, solution, adsorption, wetting, immersion or phase change processes, or with the study of the thermal stability of polymeric materials. About thirty contributions reported on various processes in the field of inorganic chemistry.

In each of these three classes, the authors have described either new techniques or new applications of well-known techniques and the interpretation of their results.

Since the scientific programme indicates that our concluding remarks should be related to selected topics, we shall speak on new techniques and methods only. We sincerely apologize for any omission.

In the field of C_p measurements, we find, for example:

— a new low-temperature scanning calorimeter;

— a new automatic adiabatic calorimeter for the very low-temperature range (heating or cooling of samples is possible);

— a fully automated differential isoperibolic scanning microcalorimeter developed for routine C_p determination on mg samples over an extended temperature range;

— a new DSC–TG sample carrier which is able to operate up to 1700°;

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— another DSC–TG technique which is particularly suited for the investigation of polymeric materials.

Many authors have reported on measurements of the temperature-dependence on the heat capacity, in order to obtain standard thermodynamic properties of pure substances, as well as to get information on their behaviour in a particular range of temperature and to derive structural data. Measurements are sometimes carried out under extremes of physical or chemical conditions. Other measurements concern more complex systems.

As we have already pointed out, about twenty communications have dealt with the thermodynamics or kinetics of various kinds of processes. In many of these, the authors reported on new techniques, on new methods of investigation or on the use of standard reference materials for calibrating instruments or checking the reliability of their results. For example, we find:

— new instruments and methods for solution calorimetry, and particularly for rapid quality tests on solid samples such as cement, lime, fly ashes or solid wastes;

— a new liquid flow adsorption system connected to a commercially available heat conduction calorimeter (allowing the study of the processes of adsorption of surfactants from solutions);

— a new membrane cell for measuring heats of immersion;

— a new calorimetric technique for measuring the wetting heats of rocks (having small specific areas) by water or liquids of very high viscosity;

— a new photocalorimetric cell;

— new developments in solution, mixing and solid-solid phase transition calorimetry, as a result of the recent improvements of deconvolution techniques in heat conduction calorimetry of differential scanning calorimetry (the first plenary lecture of the scientific programme reported on these topics);

— contributions relating to the use of flow calorimeters for kinetic studies;

— a test certification for a potassium chloride sample as a standard reference material for solution calorimetry.

By using modern data-processing techniques, we can apply calorimetry and differential scanning calorimetry to a field which is continuously expanding. The panel and the high quality of the scientific program of ESTAC 4 fully illustrate the now powerful versatility of both techniques.

In some cases, we report test measurements for checking the reliability of new techniques or applications. Often, however, only experimental results are reported, without critical comment on methods or techniques.

Unfortunately, the instrumentation is standardized in only a limited number of applications (as in combustion calorimetry). In most cases, we use our own or commercially available apparatus connected to a very sophisticated data-

processing system (which is often a black box for us). As a result, the precision of our measurements is always high, but their accuracy is sometimes questionable.

In calorimetry and differential scanning calorimetry, as in any other technique, obtaining a high precision (that is a high reproducibility or repeatability) sometimes means that we precisely repeat the same systematic errors.

This can be done, for instance, by incorrect calibration of the instruments (which happens frequently in solution or mixing calorimetry), or by using software which produces systematic errors in both thermometric and calorimetric calibration in differential scanning calorimetry for C_p measurements.

In many applications, it can happen that very powerful instruments are underemployed with regard to the accuracy of their results. During this meeting, a limited number of contributions reported on the computer data-processing and the quantitative reliability of heat flux differential scanning calorimetry, as well as on the influence of experimental parameters and the properties of the substances.

As a result of recent improvements of theoretical models in thermodynamics and kinetics, we need high-quality data. It would be paradoxical not to get such results by using very sophisticated instruments and data-processing systems.

It would then be interesting to identify problems and to promote collaborative studies to investigate such problems, for example in the fields of:

— solution calorimetry (from room to high temperature);

— C_p measurements (from low to high temperature);

— kinetics studies, by comparing results given by many techniques applied to the same sample or process. We must keep in mind that a convolution of the signal often happens in both sample and calorimetric system. We then have to be very careful in any kinetic study, even if the calorimetric signal is corrected for the instrumental inertia.

During recent years, such international cooperation has proved to be very useful for solving similar problems in calorimetry (as, for example, in checking the reliability of deconvolution techniques for heat-conduction calorimetry).

Other task groups could promote discussion on other topics or questions, for example:

— What is necessary and what is possible in calorimetry and differential scanning calorimetry?

— How can we get calorimetric data relating to industrial processes?

For calorimetry, we should try to organize meetings with contributions concerning the calorimetric methods or data-handling, or about results which are of common interest. At a calorimetry conference, the results should be, more or less, a documentation of the usefulness of the methods.

Our proposal is to organize such meetings in the future, for example on:
— C_p measurements: problems and possibilities for reliable results.
— Applications of computers for data-acquisition and data-processing.
— New applications of calorimetric methods, etc.

Such meetings will lead to intensive and fruitful discussion and to some progress as regards the development of calorimetry.