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THERMAL ANALYSIS, CALORIMETRY AND CHEMICAL THERMODYNAMICS — A REVIEW*

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ABSTRACT

An attempt is made to review the level of development of the subjects covered by the Swiss Society for Thermal Analysis and Calorimetry, namely thermal analysis, calorimetry and chemical thermodynamics.

A comprehensive presentation and elucidation of the stage of development of these subjects seems to be impossible because of the broadness of each of these subjects with respect to theoretical, methodological and instrumental aspects, and also because of the diversity of applied and basic research in this area. The discussion is therefore restricted to such aspects as definitions and the boundaries of these subjects. Furthermore, the importance of chemical thermodynamics in the application to thermoanalytical methods and to applied research is pointed out.

INTRODUCTION

The following paper was presented at the first scientific meeting of the Swiss Society for Thermal Analysis and Calorimetry which was held in Zürich in March 1976. The subjects, which were discussed there, are also of some importance to the German Society for Thermal Analysis. Therefore the paper will be repeated at this GEFTA meeting.

Within the title of this paper, there are several open questions, probably more than one would expect at first glance. These open questions arise from completely different reasons and are concerned with the following expressions: review, thermodynamics, chemical thermodynamics, thermal analysis and finally calorimetry. Particular details concerning these points will be discussed in the following sections.

DEVELOPMENT OF THERMAL ANALYSIS, CALORIMETRY AND CHEMICAL THERMODYNAMICS

An attempt will be made to review the present status of the subjects covered by the Swiss Society, namely thermal analysis, calorimetry and chemical thermo-

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dynamics. A comprehensive presentation and elucidation of the stage of development of these subjects however, seems at first to be impossible. This impression is based on the broadness of each of these subjects with respect to theoretical, methodological and instrumental aspects and also because of the diversity of applied and basic research in this area. Furthermore, the level of development for such a scientific field is constantly changing and therefore absolute criteria are not available for such a critical review. On the other hand, this broadness of subject matter is necessary to ensure the success of a scientific society over a period of one or two decades. This condition should be fulfilled in the case of our Swiss society.

It is generally accepted that an evaluation of technological progress is achieved more easily than an evaluation of the progress in research. Such an evaluation of subjects with many applications within technology, such as thermal analysis, calorimetry and chemical thermodynamics, should therefore be discussed in two separate parts: namely, with respect to basic and applied research. Hass delivered a paper[1] on the occasion of the presentation of the Perkin Medal Award in 1968 with the title *History never repeats*. He pointed to the problem which is sometimes called the research technology interface. Without further discussion of this relationship between university and chemical industry I quote from this excellent address: "Occasionally you hear the hoary fallacy that the store of scientific knowledge is continually being depleted by application to industry and so the reservoir must be refilled. This implies that if an idea is once used it can never be used again. The fact is exactly the contrary: when an idea is used it is always expanded, strengthened, and made more readily available than it was before. This can be seen if we take an example such as the wheel, it has been applied to tens of thousands of innovations and will doubtless be applied to hundreds of thousands in the future. As a result we have wooden wheels, wire wheels, steel disk wheels, plastic wheels, cog wheels, little wheels, and as I am reminded by looking at this audience—big wheels".

The interpretation of Hass' remarks can be extended to the further evolution of the fields of thermal analysis, calorimetry and chemical thermodynamics.

Thermodynamics was mentioned in the introduction as another point of discussion. Clausius introduced in his paper *Ueber die bewegende Kraft der Wärme und die Gesetze, welche sich daraus für die Wärmelehre selbst ableiten lassen* the second law of thermodynamics in 1850. Clausius' theories were based on the work of Carnot and Clapeyron. According to Gibbs[2] the fundamental studies of Clausius implied a new epoch in the history of physics and marked the beginning of the subject of thermodynamics as a science. This so-called conventional thermodynamics includes the macroscopic description of the phenomena of heat and temperature with the restriction to conditions of equilibria or to changes over a reversible pathway. The term thermodynamics is analogous to the terms hydrodynamics and electrodynamics. However, is this analogy really consistent for the subjects discussed? Physical phenomena associated with water and electricity are described as functions of time and space in hydrodynamics and electrodynamics. However, the systems which are described by conventional thermodynamics are independent of time and space. In other words, no differential equations with derivatives with respect to space and time exist in conventional thermodynamics. This inconsistency could be eliminated by changing the name of conventional thermodynamics to thermostatics. In this case the analogy to hydrostatics and electrostatics would be accurate.

Chemical thermodynamics was indicated as another point of discussion. The limits of this subject are not clearly defined. Chemical thermodynamics is restricted according to Münster[3] and Labhart[4] to the chemical aspects of thermostatics. However, according to Denbigh[5] chemical thermodynamics is extended to statistical thermodynamics, e.g., to thermodynamics in relation to the existence of molecules.

Unequivocal definitions of the boundaries of thermal analysis and calorimetry do not exist either. The methods of differential thermal analysis (DTA) and thermogravimetry (TG) are of great importance within the field of thermal analysis from a historical point of view. Calorimetric methods were introduced in thermal analysis with the development of calorimetric titration methods and differential scanning calorimetry (DSC). Moreover, the range of application of differential scanning calorimetry is practically identical with that of differential thermal analysis (DTA). A proper definition of thermal analysis should therefore closely relate the methods of DSC and those of DTA. It is a question of whether the boundaries of a subject of science shall be given by historical aspects or by a definition which is based on physical parameters measured and the methodology used. To achieve proposals for a definition of the limits of thermal analysis and calorimetry is one of the goals of our society.

Thermal analysis and calorimetry will be discussed in detail for the purpose of such a classification. The question is reexamined if it is possible to separate the thermoanalytical methods from the whole of physicochemical methods. According to a definition given by Wendlandt[6], thermal analysis is confined to those techniques in which some physical parameter of a system is determined as a function of temperature. Furthermore, this temperature function is generally restricted to a dynamic system with changes in a linear manner. A broader definition of thermal analysis is indicated in another chapter of Wendlandt's book[7] which states that "Almost all of the analytical techniques that produce temperature-dependent data may perhaps be classified as thermal techniques. This would include ultraviolet and visible spectroscopy, infrared spectroscopy, nuclear magnetic resonance, electron spin resonance, X-ray diffraction, electron diffraction, and many others".

METHODS OF THERMAL ANALYSIS

The lack of correlation between the historically important methods of thermal analysis is shown in the following section with a few examples of selected methods classified according to the thermodynamic parameters measured. The purpose of this discussion is to give a more rigorous definition of thermal analysis and calorimetry.

Let us begin with the DTA and the DSC methods. Qualitative DTA instruments are not considered because only quantitative DTA is amenable to reproducible caloric calibration. Temperature differences between a sample volume and a reference volume are measured with DTA instruments as a function of temperature or time. The DSC method on the other hand, provides a direct measurement of the difference in heat flow to the sample volume and to the reference volume, also as a function of temperature or time. The fundamental difference between the two methods is based on a thermodynamic property of the dependent, measured variable. The temperature difference measured with the DTA method is an intensive parameter whereas the parameter determined by the DSC method is extensive, namely the difference in heat flow. Intensive parameters, relating to properties such as temperature, pressure, density, etc., are those parameters which can be specified at any point in a system. All intensive properties are not additive and therefore are not related to the quantity of the sample. The extensive properties, such as enthalpies, volume and mass, are additive properties. The values of extensive properties are not defined for any of the points of a system but are related to the system as a whole.

From a practical point of view, however, such a classification is not satisfactory because the methods (DTA and DSC) are so closely related that upon appropriate calibration the same information can be obtained.

On the basis of the foregoing considerations, the following definition can be proposed:

Thermoanalytical methods allow the determination of any physical property as a function of temperature, including dynamic and isothermal measurements.

The thermoanalytical methods are divided into two groups, namely the calorimetric group and the group of thermoanalytical methods in a wider sense. These two groups of methods are defined in the following manner:

(1) Thermoanalytical methods in the narrow sense allow the determination of a caloric, dependent variable by a direct or indirect procedure.

(2) Thermoanalytical methods in the wider sense allow the determination of any physical property as a function of temperature, including dynamic and isothermal measurements.

This latter group of methods is defined in such a manner as to favour a broad development of methods of thermal analysis which today are not generally accepted as such. Thermoanalytical methods in a narrow sense, the so-called calorimetric group, consist of two subgroups. The methods of the first subgroup allow a direct measurement of calorimetric values as the dependent variable. The second subgroup consists of all methods which measure temperature or differences in temperature as the dependent variable. These methods are further restricted in that the measured values must be able to be reproducibly transformed into caloric data. Furthermore, the following facts must be stressed: (i) the definition of thermoanalytical methods in a wider sense includes all the thermoanalytical methods in a narrow sense; (ii) the definition of thermoanalytical methods in a wider sense is, in practice, restricted to a given number of conventionally accepted methods. Borderline methods which fall under this definition may not yet have become established as thermoanalytical methods, but may in future be accepted as such.

TABLE 1

IMPORTANT THERMOANALYTICAL METHODS

Thermoanalytical methods in a narrow sense

- Differential thermal analysis
- Thermometric titrimetry
- Calorimetry
  - Differential scanning calorimetry
  - Reaction and solution calorimetry
  - Calorimetric titrimetry
  - Combustion calorimetry

Thermoanalytical methods in a wider sense

- Cryoscopic and boiling point methods
- Thermogravimetry
- Dilatometry and thermomechanical analysis
- Torsional braid analysis
- Vapor pressure methods
- Solubility methods
- Low resolution nuclear magnetic resonance

The essential differences between the above definition of thermoanalytical methods and those according to Wendlandt[6] and Mackenzie[8] are based on the following: (i) isothermal measurements which are widely used in thermal analysis are included; (ii) a broader consideration of calorimetric methods; (iii) the introduction of a well-defined calorimetric group and a rather open second group. It will be shown later that the formation of these two groups is also confirmed by thermodynamic considerations.

The methods which are today generally regarded as thermoanalytical methods are presented in Table 1.

CHEMICAL THERMODYNAMICS

Chemical thermodynamics is another area whose scientific and technological aspects shall be promoted by our society mainly with respect to applications to thermoanalytical problems. Let us begin the discussion with the question of the subjects which are normally included in chemical thermodynamics and with a remark about the general importance of chemical thermodynamics. Chemical thermodynamics is a part of physical chemistry. Consequently, the relations between chemistry and physical chemistry are also valid for chemical thermodynamics. The importance of physical chemistry lies in the application of appropriate physical methods to chemical problems.

Chemistry is an immense subject, because of the diversity of organic and inorganic substances. Therefore, the goals of physical chemistry in establishing general principles describing chemical phenomena are of such great importance.

As an example, physical chemistry may be subdivided according to the following scheme: chemical thermostatics, chemical kinetics, statistical thermodynamics,

TABLE 2

AREAS OF CHEMICAL THERMODYNAMICS

Chemical thermostatics	*Statistical thermodynamics*	*Chemical kinetics*	*Thermodynamics of irreversible processes*
Description of states of equilibrium quasi-static changes of state with axioms, e.g., laws of thermostatics under the following conditions: the atomic structure of substances is neglected macroscopic properties of substances are introduced with parameters Extension of the theory by Gibbs with the fundamental equations	Principle by Boltzmann entropy of a system related to the thermodynamic probability Subareas kinetic theory of gases thermodynamics of perfect crystals quantum mechanics	Kinetic theory of gases molecular motion by Brown Maxwell velocity distribution Reaction rate and mechanism Transition state theory	Balance of entropy Onsager reciprocal relationships

thermodynamics of irreversible processes, quantum mechanics and molecular spectroscopy. Several aspects favour the use of the subject chemical thermodynamics according to the interpretation of Denbigh^5, namely as the part of physical chemistry which includes the subjects chemical thermostatics, chemical kinetics and statistical thermodynamics. One could go another step further and divide physical chemistry into the main subjects of chemical thermodynamics, quantum mechanics and molecular spectroscopy. Chemical thermodynamics would then consist of the following subjects: (1) chemical thermostatics, (2) chemical kinetics, (3) statistical thermodynamics, and (4) thermodynamics of irreversible processes. These areas of chemical thermodynamics are summarized in Table 2.

SOME ASPECTS OF CHEMICAL THERMOSTATICS

Following these remarks about chemical thermodynamics, we will now discuss some aspects of chemical thermostatics in detail especially Gibbs thermostatics. Gibbs' fundamental equation describes the chemical potential of a substance in a given phase as a function of the state of the entire phase. The chemical potential of the substance i in phase α may be expressed as:

$$\mu_i^\alpha = -T^\alpha \left[\frac{\delta S^\alpha}{\delta n_i^\alpha}\right]_{U^\alpha,\, V^\alpha,\, y_j^\alpha,\, n_k^\alpha \neq i} \tag{1}$$

where T is the absolute temperature, S is the entropy, n_i is the number of moles of the substance i, U is the internal energy, V is the volume, y_j are the work co-ordinates, and n_k are the number of moles of all substances k which are present in the interior of phase α.

Gibbs' fundamental equation is only valid if the internal state of a given phase is entirely determined by the chosen variables of state over the whole range of variation. Gibbs' fundamental equation is normally transformed for practical applications into other forms, namely into the so-called entropy and energy forms, respectively. These two equations shall be written omitting the phase index and with the further restriction that only volume changes are considered. For the entropy, we then obtain the following function written in a differential form:

$$\mathrm{d}S = \frac{1}{T}\mathrm{d}U + \frac{P}{T}\mathrm{d}V - \sum_{i=1}^{m} \frac{\mu_i}{T}\mathrm{d}n_i \tag{2}$$

and the analogous energy expression is:

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V + \sum_{i=1}^{m} \mu_i \mathrm{d}n_i \tag{3}$$

Both of these fundamental equations provide a complete thermodynamic description of a body in a given phase. Furthermore, these equations depend only on extensive parameters.

Each of the intensive parameters which are included in these fundamental equations can be expressed as a function of all the variables which are the extensive

TABLE 3

EQUATIONS OF STATE

From the entropy form		*From the energy form*	
$\frac{1}{T} = \frac{1}{T}(U, V, n_i)$	(4)	$T = T(S, V, n_i)$	(7)
$\frac{P}{T} = \frac{P}{T}(U, V, n_i)$	(5)	$P = P(S, V, n_i)$	(8)
$\frac{\mu}{T} = \frac{\mu}{T}(U, V, n_i)$	(6)	$\mu = \mu(S, V, n_i)$	(9)

parameters in the corresponding fundamental equation. These relations between the intensive dependent variables and the extensive independent variables are the so-called equations of state. The two sets of equations of state obtained from the fundamental eqns (2) and (3) are given in Table 3. Each of these equations of state describes only certain aspects of a thermodynamic system, i.e., it is not possible to calculate the thermodynamic equilibrium of a system with only one of these equations. As an example: for an entire thermodynamic description in the case of a one-component system only two equations of state are necessary because the third equation is obtained by applying the Gibbs–Duhem equation[9]. Two equations of state which are shown in Table 3 are known using a similar terminology as the caloric and thermic equations of state respectively. The caloric equation of state describes the internal energy as a function of temperature, volume and mole numbers of all the components of a system

$$U = U(T, V, n_i) \tag{10}$$

The thermic equation of state gives the dependence of the pressure of a system on the same variables

$$P = P(T, V, n_i) \tag{11}$$

The equations of state permit the description of certain aspects of thermodynamic systems as well as the definition of thermodynamic values. Examples of this are the molar heat capacity of a system at constant volume and the equation of isothermals. Expression (11) is already known as the explicit function of isothermals. Empirical constants which characterize the described substance must be introduced into this equation.

The heat capacity is defined by the total differential of the internal energy which is in the case of a one-component system given by

$$\mathrm{d}U = \left(\frac{\delta U}{\delta T}\right)_{V,n} \mathrm{d}T + \left(\frac{\delta U}{\delta V}\right)_{T,n} \mathrm{d}V + \left(\frac{\delta U}{\delta n}\right)_{V,T} \mathrm{d}n \tag{12}$$

The molar heat capacity of a system at constant volume is obtained from eqn (12) by introducing the internal energy per mole $u = U/n$ as

$$c_V = \frac{\mathrm{d}u}{\mathrm{d}T} = \left(\frac{\delta u}{\delta T}\right)_{V,n} \tag{13}$$

Many further examples in which these equations of state are applicable could be outlined.

Let us discuss now the relation between the dependent variable measured with thermoanalytical methods and the thermodynamical values calculated from these experimental results. Caloric values are measured by the thermoanalytical methods in a narrow sense. These methods enable a direct determination of thermodynamic values such as heat capacities, enthalpies, energies and entropies. In contrast, thermoanalytical methods in a wider sense yield experimental values of physical properties other than calorimetric, as a function of temperature. These experimental results can be used for a calculation of caloric data by the application of appropriate thermodynamic relations. The separation of all the thermoanalytical methods according to the dependent variable, namely in two groups which measure caloric and non-caloric values, respectively, is also supported by the different mathematical treatments which are necessary to obtain characteristic thermodynamic values from thermoanalytical data.

CONCLUSIONS

It may be concluded that chemical thermodynamics in its broad definition consisting of chemical thermostatics, statistical thermodynamics, chemical kinetics and the thermodynamics of irreversible processes, enables further applications within thermoanalytical methods, namely: (i) the evaluation of experimental data on a thermodynamic level which is independent of the methods and the instruments applied, (ii) the application to the development of methods, and (iii) the theoretical basis of experiments performed in the elucidation of chemical systems. Undoubtedly, the use of chemical thermodynamics is accentuated in the area of applied research. The development of chemical thermodynamics itself is the goal of physical chemistry.

As a final remark, it shall be emphasized that by itself applied research of chemical systems covers an immense area. In the future, chemical thermodynamics and thermoanalytical methods may also have a great impact in solving problems which are related to the field of applied research.

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