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QUANTITATIVE THERMAL ANALYSIS, I

MATHEMATICAL PROBLEMS OF QUANTITATIVE DIFFERENTIAL THERMAL ANALYSIS

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A highly simplified method for calculating heat of phase transitions from DTA data is presented. Two DTA curves are needed to calculate the heat of transition and the specific heat of the sample: one is for the original sample and one is for a sample prepared by mixing the original sample with some unreactive diluent the specific heat of which is known. The data of the DTA curves used in the calculations are the peak area, the rate of heating and the deviation of the DTA curve from the base line.

The quantitative determination of thermal effects by differential thermal ana ysis (DTA) using normal apparatus is based on the well-known relation between the peak areas (S) and the heat (Q) absorbed or liberated by the substance investigated [1 – 5]. This relation is usually expressed mathematically by the equation

$$S = KQ \tag{1}$$

Owing to the extremely high number of factors determining the value of the coefficient K, it is practically impossible – at least at present – to give a full mathematical interpretation of K [6, 7]. Attempts to take these factors into consideration empirically have led to much valuable experimental material in respect to the dependence of the peak area on various experimental conditions and on the characteristics of the substance investigated, i.e. heat conductivity [8], heat capacity [9, 10], shape [11] and degree of dispersion [12] of the sample, rate of heating [13], rate of heat exchange between the sample and the medium [14], position of the junction of the thermocouple in the sample [4, 9], etc. It seems reasonable to assume that all mentioned and unmentioned factors are reflected in the geometry of the thermal curves. The aim of the present paper is to find a method for their simplified mathematical analysis.

Before passing to the mathematical treatment of thermal curves, it is necessary to discuss the effect of the thermophysical properties of the sample on the geometrical elements of the thermal curves.

A number of limitations assumed by various authors attempting the mathematic interpretation of thermal curves [7, 15] reflects that they accept the dependence of the geometry of thermal curves on the thermophysical properties of the sample.

Such a limitation is, e.g. the assumption that "the beginning and the end of the thermal effect are placed at the same level" [15].

Experimental data on the dependence of the geometrical elements on the thermophysical properties of the sample are very scarce [8, 10]. They show that the geometrical elements of thermal curves (viz. the deviation of the differential curve from the zero line as well as the peak area) depend on the thermal conductivity of the sample. A consequent mathematical analysis of these facts is found in the work of Piloyan [15] which is one of the most valuable contributions to the subject, both theoretically and practically.

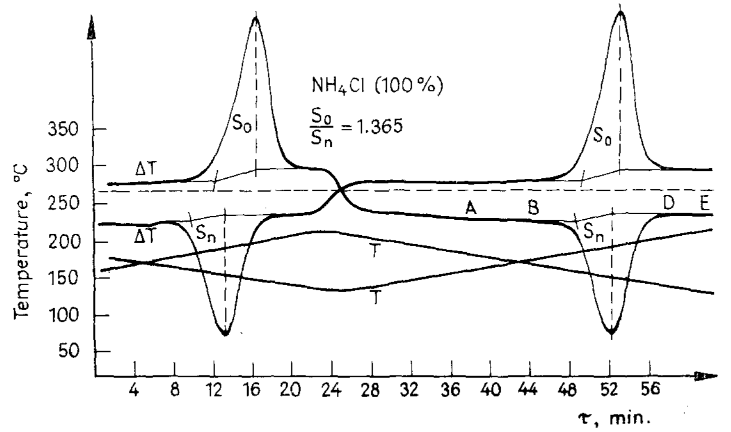

Fig. 1. Heating and cooling DTA curves of pure ammonium chloride

However, at the moment of transition, two phases of the sample are present, the starting phase and the final phase. No definite answer is given in the literature to the question whether it is the thermophysical characteristics of the starting phase or of the final phase which actually determine the shape and the parameters of the thermal curve. This is all the more important to decide since these characteristics often differ sharply (e.g. in the case of melting).

The effect of thermophysical characteristics is particularly impressive in thermograms of substances with reversible phase transitions. In this case all other factors can be easily kept constant: heating and cooling thermograms can be taken repeatedly in any required order of sequence without changing anything in the apparatus and the system can be strictly isolated from all external effects.

Fig. 1 shows thermal curves for heating and cooling ammonium chloride in the temperature range of its reversible polymorphous transition. Although the peaks on the curves correspond strictly to the same value of the phase transition heat, the peak areas on the curves for heating and cooling are not the same. The peak area in the cooling diagram is almost 36% greater than that in the heating diagram.

In the literature dealing with the influence of various factors on the value of the peak area, two possible reasons are found which may cause the difference between the experimentally obtained area values: 1. a difference in the transition temperature, 2. a difference in the conditions of heat propagation in the directions towards the sample and away from the sample.

Differences in the transition temperature may – as shown earlier [8] – cause a sensible difference in the peak areas if they reach a substantial value. The higher the transition temperature, the less this difference is reflected in the peak area. It is easy to show [8] that these factors are able to change the ratio of the peak areas by approximately 2%.

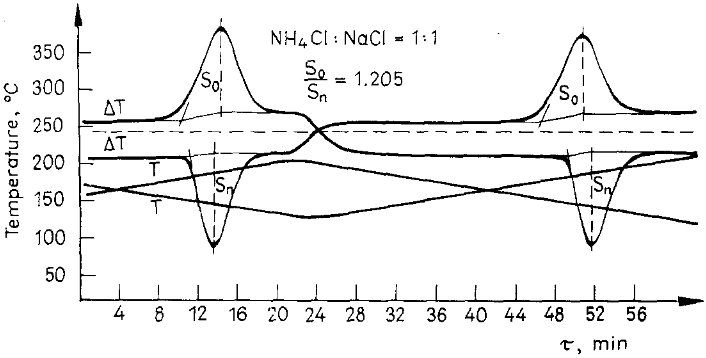

Fig. 2. Heating and cooling DTA curves of a mixture of ammonium chloride and sodium chloride (1 : 1 weight parts)

The effect of the second assumed reason is also small, although no quantitative evaluation of this effect could be found in the literature.

Finally, even if it were assumed that the above-mentioned reasons are responsible for the difference in the peak areas, they are absolutely unsatisfactory for explaining the experimental facts illustrated in Fig. 2. In this figure, heating and cooling curves of ammonium chloride diluted with an unreactive substance (sodium chloride) in a weight ratio of 1 : 1 are shown. As a result of the dilution, the transition temperature remains practically unchanged but the difference between the peak areas is sharply reduced from 36% to 20%.

In our opinion, the difference between the areas is due to the difference in the thermophysical characteristics of the starting and final phases.

Let us consider the position of the differential curve relative to the zero position (line A_1E_1) in the quasi-steady state (AB and DE, Fig. 1). It becomes obvious that the starting phase and the end phase are characterized by substantial differences in their thermophysical properties (thermal conductivity). (It should be mentioned that in these experiments air was used as a standard and not aluminium oxide as is often applied. Thus, this method, in its physical sense, is related closely to the "standardless thermography method" [17]).

The higher the thermal conductivity, the less the deviation from the zero line and the less the peak area.

The first of these statements is expressed mathematically by the well-known equation

$$\Delta t = \frac{VR^2}{Fa}$$

where V = rate of heating,
R = radius of the cylindrical or spherical sample,
F = shape coefficient,
a = thermal conductivity of the sample.

The second statement can be considered as confirmed experimentally in [8] and [10].

By comparing these statements with the data in Fig. 1 it can be concluded that the peak area depends on the thermophysical properties of the final phase.

The effect of the unreactive diluent consists in reducing the difference between the thermophysical properties of the sample before and after the transition and thereby reducing the difference between the peak areas (Fig. 2).

The above statements are confirmed by the analysis of the heat supply necessary for phase transformation. In fact, the peripheral layer of the sample in which the phase transition starts first receives heat only from the outside. The heat supply to this first layer is determined by the thermal resistance of the medium which separates the heating element and the surface of the sample. The second layer of the sample which lies deeper receives heat also only from the outside but the thermal resistance opposed to the supply of this and all following heat portions is composed of the thermal resistance of the separating medium and the thermal resistance of the transformed layer which has the thermal characteristics of the new, final phase, for temperatures near the transition temperature.

Thus, it may be concluded that the peak area in the differential diagram is determined, apart from other factors, by the thermophysical properties of the substance in the final phase, near the transition temperature.

Passing now to the question of the mathematical relation between the geometrical elements of the thermal curves and the thermal effect, let us first examine the thermal curves in the case where no sample and no standard is present, i.e., when both junctions of the differential thermocouple are placed in empty test tubes. For the case of an "ideal" apparatus, the differential curve will give a straight line coinciding with the zero line A_1E_1 (Fig. 3). The temperature curve will give an inclined straight line passing through the points T_1 and T_4. These curves show that the heat supply to both junctions of the thermocouple is identical and no temperature gradient occurs between the junctions.

In the next experiment all thermal conditions are left unchanged and one of the test tubes is filled with the sample. In this case the thermal curves change and will take the form of ABCDE and $T_1T_2T_3T_4$.

The change of the differential curve in the quasi-steady range is interpreted physically in the following way: that junction of the thermocouple which is placed in the sample will always be colder since part of the heat flow is absorbed by the mass of the sample. The area limited by the line A_1E_1 and the curve ABCDE will depend on the quantity of heat absorbed by the sample [15, 16]. This can be expressed in a generalized form for the interval AB by

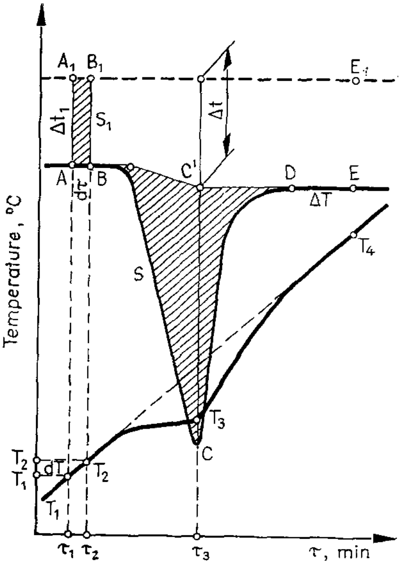

Fig. 3. Quantitative elements of the DTA curves

$$S_1 = K_1Q_1 \tag{2}$$

where S_1 = area A_1B_1BA, degree · minute
Q_1 = heat absorbed by the sample when heated from T_1 to T_2, kcal
K_1 = proportionality factor, degree · minute/kcal.

The factor K_1 is a highly complex function of a great number of variables including the thermophysical properties of the sample.

Since in the investigated interval AB no phase transition occurs in the substance and, therefore, heat is used up only for increasing the temperature of the sample by $dT = T_2 - T_1$, Q_1 can be expressed by

$$Q_1 = MC_1\,dT \tag{3}$$

where M = mass of the sample, g,
C_1 = specific heat of the sample, kcal/g · degree.

The area S_1 is equal to the product of Δt_1 and $(\tau_2 - \tau_1)$, i.e. for low values of $\tau_2 - \tau_1 = d\tau$

$$S_1 = \Delta t_1 d\tau \tag{4}$$

From Eqs (2), (3) and (4), substituting $\frac{dT}{d\tau} = V_1$ the following expression is obtained:

$$\Delta t_1 = K_1 M C_1 V_1 \tag{5}$$

Eq. (5) is valid for any interval of the differential curve where no transition occurs, provided that the values used are related to this interval. Thus, at the moment τ_3, presuming that in this moment the system is in a quasi-steady state and the differential curve passes along CE, Eq. (5) takes the form of

$$\Delta t = KMCV \tag{6}$$

The coefficients K in Eqs (1) and (6) expressing the thermal proportion of the area under the same conditions (both are related to heat transfer conditions through the final phase at temperatures near the transition temperature and to identical experimental conditions) can be taken as equal.

By solving Eqs (1) and (6) and substituting $Q = mq$, where q = specific thermal effect in kcal/g and m = mass of the thermoactive component in g, or the total mass of the investigated sample (for the case $M = m$), the following equation is obtained:

$$q = S\frac{V}{\Delta t} C \tag{7}$$

The specific thermal effect of the transition is equal to the peak area multiplied by the heating rate and the specific heat of the sample and divided by the deviation of the differential curve from the zero position.

On the basis of Eq. (7), thermal effects can be determined even without comparison with thermal effects of standard materials if the specific heat of the investigated substance is known. However, this value is unknown in many cases [6].

In such cases, since the physical interpretation of Δt and C have been given by the analysis of the heating and cooling curves, viz. that these values correspond to the final phase of the sample for temperatures near the phase transition temperature, it is possible to derive equations for calculating the specific heat of the substance investigated.

The equation for the specific heat is derived on the basis of Eq. (7) which is written in a more generalized form (without the condition $M = m$):

$$q = S\frac{V}{\Delta t}\,\frac{M}{m}\,C \quad \text{kcal/g thermoactive substance} \tag{8}$$

For the case when the initial sample is diluted with some indifferent diluent, Eq. (8) takes the following form:

$$q = S_2\frac{V_2}{\Delta t_2}\,\frac{M_2}{m_2}\,C_2 \quad \text{kcal/g thermoactive substance} \tag{9}$$

where all symbols with the subscript *2* correspond to the mixture of the initial sample and the diluent, and m and m_2, are the masses of the thermoactive component in the samples M and M_2, respectively.

Starting from the rule of additivity for the heat capacity of physical mixtures, C_2 can be expressed by the heat capacity of the initial sample C and the heat capacity of the diluent C_d if the weight ratio of the initial substance in the mixture (n) is known:

$$C_2 = nC + (1 - n)C_d \tag{10}$$

By substituting Eq. (10) into Eq. (9), solving Eqs (9) and (8) and carrying out some simple algebraic transformations in which M, M_2, m and m_2 are eliminated by introducing n, an equation is obtained for calculating the specific heat of the original sample:

$$C = \frac{S_2V_2\Delta t}{SV\Delta t_2 - S_2V_2\,\Delta t}\,\frac{(1 - n)}{n}\,C_d \tag{11}$$

Eq. (11) shows that the values for the thermal effect of the phase transition and the percentage of the thermoactive component are not indispensable to determine the specific heat of the original sample. On the contrary, by introducing the value of C calculated by means of Eq. (11) into Eq. (7), the specific thermal effect is obtained in kilocalories per gram of the original sample.

It is interesting to note that this procedure allows not only the specific heat of the substance undergoing a phase transition to be calculated but also that of the unreactive diluent. In this case the diluent and the substance investigated change places and C_d is the unknown in Eq. (11). The specific heat of the unreactive substance at the phase transition temperature of the thermoactive "diluent" can be determined:

i) by means of a single thermogram if the thermal effect of the phase transformation and the specific heat of the "diluent" are known:

$$C_d = \frac{\Delta t_2}{S_2V_2}\,qC\,\frac{n}{(1 - n)} \tag{12}$$

ii) by means of two thermograms, namely that of the pure diluent and that of the mixture if a) the thermal effect of only the thermoactive diluent is known, or b) only the specific heat of the final phase of the thermoactive "diluent" at the transition temperature is known. For case a),

$$C_d = \left(\frac{\Delta t_2}{S_2V_2} - \frac{\Delta t}{SV}\right)\frac{n}{(1-n)}q, \tag{13}$$

for case b),

$$C_d = \left(\frac{SV\Delta t_2}{S_2V_2\Delta t} - 1\right)\frac{n}{(1-n)}C \tag{14}$$

In these equations S, V, Δt, q and C, as in all previous equations, correspond to the thermoactive sample; S_2, V_2 and Δt_2 correspond to the mixture, and n is the weight ratio of the thermoactive substance in the initial sample.

Eqs (12) - (14) are obtained simply by writing the result of solving Eqs (8) – (10) in various forms.

Thus, the thermal effect of the phase transition can be calculated by using the data of two thermograms: the thermogram of the original sample and the thermogram of a sample obtained by diluting the original sample in a known ratio with an unreactive diluent the specific heat of which is known. For the calculations, three data of the thermal curves are needed: the peak area, the rate of heating and the deviation from the zero line.

When deriving the equations, an "ideal" apparatus has been assumed. Under practical conditions, this would be a very cumbersome task which in many cases could not be approximated satisfactorily. It can be shown that neither an "ideal" apparatus nor the use of air as a standard are indispensable conditions but can be dealt with by means of a single "adjustment" thermogram.

It should be remarked that the equations obtained need further improvement in some respects, particularly with regard to a more argued choice of the measuring points for the divergence of the differential curve from the zero line, for the rate of heating (if this rate is not constant) and possibly also with regard to the limiting of the areas. For this reason, the present paper should be regarded only as an attempt at a highly simplified mathematical treatment of the determination of thermal effects by differential thermal analysis, needing further improvement and development.

References

1. F. G. Kracek, J. Phys. Chem., 34 (1930) 225.
2. L. G. Berg and V. Ya. Anosov, Zh. Obshch. Khim., 12 (1942) 31.
3. S. Speil, Techn. Paper No. 664, Bureau of Mining (1945).
4. L. G. Berg, Vvedenie v termografiyu, Izdatelstvo Akademii Nauk SSSR, Moscow, 1961.
5. E. Deeg, Ber. Deut. Keram. Ges., 33 (1956) 321.
6. A. I. Cvetkov and G. O. Piloyan, Sovremennye tendencii razvitiya differencialnogo termicheskogo analiza, Itogi Nauki, Seriya Geologii, Moscow, 1965, 159.

7. S. L. BOERSMA, J. Amer. Ceram. Soc., 38 (1955) N8.
8. L. G. BERG and L. A. BORISOVA, Dokl. AN SSSR, 137 (1961) 631.
9. YU. V. SEMENTOVSKY, Trudy 1. soveshchanii po termografii, Izdatelstvo AN SSSR, Moscow—Leningrad, 1955, 67.
10. L. G. BERG and M. SH. YAGFAROV, Trudy 1. soveshchanii po termografii, Izdatelstvo AN SSSR, Moscow – Leningrad, 1955.
11. K. G. KUMANIN and N. S. KALNEN, Zh. Phys. Khim., 7 (1936) 405.
12. A. I. CVETKOV and G. O. PILOYAN, Fizicheskie metody issledovaniya mineralov osadochnykh, Izdatelstvo Nauka, Moscow, 1966, 53.
13. I. PROKS, Silikaty, 5 (1961) 114.
14. M. REY and V. KOSTOMAROFF, Silicates Industriels, 24 (1959) 603.
15. G. O. PILOYAN, Vvedenie v teoriyu termicheskogo analiza, Izdatelstvo Nauka, Moscow 1964.
16. D. J. DAVID, Anal. Chem., 36 (1964) 188.
17. L. G. BERG and E. E. SIDOROVA, Trudy 2. soveshchanii po termografii, Kazan, 1961.

RÉSUMÉ — On décrit une méthode simple pour calculer les chaleurs des transitions de phase à l'aide des données d'analyse thermique différentielle. Il est nécessaire de connaître la chaleur spécifique et les thermogrammes de l'échantillon pur et en mélange avec une substance indifférente, de chaleur spécific connue. Pour les calculs, on se sert des données suivantes: surface des pics d'A. T. D., vitesse de chauffage et déviation de la courbe d'A. T. D. par rapport à la ligne de base.

ZUSAMMENFASSUNG — Eine einfache Methode zur Errechnung der Werte der Phasenübergangswärme aus den DTA Daten wird besprochen. Die Kenntnis der spezifischen Wärme der betreffenden Substanz und zwei Thermogramme sind hierzu nötig, jenes der Originalprobe und jenes einer Mischung der zu prüfenden Substanz mit einem indifferenten Stoff von bekannter spezifischer Wärme. Die notwendigen DTA Daten sind die Spitzenflächen, die Erhitzungsgeschwindigkeit und die Abweichung der DTA Kurve von der Nullinie.

Резюме. — Дан максимально упрощенный математический метод для расчета значений тепловых эффектов фазового превращения по данным дифференциального термического анализа (ДТА). Теплота фазового превращения и теплоемкость исследуемого образца могут быть рассчитаны по данным дифференциального термического анализа (ДТА) чистого исходного вещества и образца, разбавленного любым индифферентным разбавителем с известной теплоемкостью. Для расчетов достаточно иметь следующие данные: площадь пика, скорость нагрева и отклонение дифференциальной кривой (ДТА) от нулевой линии.