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PROBEN-ABHÄNGIGKEIT (PA) CURVES AND SIMPLE ANHYDROUS CARBONATE MINERALS

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Marked modifications to carbonate DTA curves are caused by variations in the partial pressure of CO_2 gas in the furnace atmosphere. Calcite is used to illustrate the curve configurational changes which may occur. Attention is drawn to the effects of variations in: thermal conductivity of the gases used as furnace atmospheres, the furnace access to the ambient atmosphere, the volume of the furnace "tube" and the size of the sample (and therefore the amount of self generated CO_2). These effects emphasise the care with which the constancy of DTA determination conditions must be maintained for content evaluation methods such as "Proben-Abhängigkeit" curves.

It is well established from DTA studies that in dehydration and in many decomposition reactions, the peak temperatures for individual minerals depend strongly on the amount of these minerals present in individual samples. From this follows the concept of "Proben-Abhängigkeit (PA)" curves (curves of sample amount dependence) as proposed and expanded by Smykatz-Kloss in 1967 and 1974 (see Smykatz-Kloss 1974). Such curves represent the plot of change in peak temperature *(t)* on a normal scale (ordinate) against the known sample content (in mg) of each mineral present, on a logarithmic scale (abscissa).

The application of peak temperature data from other samples, of equal weight, containing unknown proportions of minerals for which "Proben-Abhängigkeit" curves have been constructed (all data determined under identical DTA conditions), allows semi-quantitative mineralogical content determinations to be read off along the abscissa.

The opportunity is taken to utilise the differential thermal analysis data obtained in connection with other studies, to illustrate the extreme care with which content evaluation methods, such as Proben-Abhängigkeit curves, must be undertaken particularly with regard to simple anhydrous carbonate minerals of which calcite ($CaCO_3$) is taken as an example.

It must immediately be pointed out, that the originator of this Proben-Abhängigkeit curve concept, clearly states in his subsequent book, (Smykatz-Kloss, 1974), that the conditions of determination must be standardized and lists the conditions under which the DTA data for his Proben-Abhängigkeit curves were obtained.

Calcite decomposes on heating with the single simple reaction,

$$CaCO_3 \rightarrow CaO + CO_2$$

at a temperature which is dominantly controlled within finite limits by the pressure of CO_2 in the atmosphere immediately surrounding the sample which in DTA is a function of the furnace atmosphere.

Experimental

DTA curves were taken with a standard Du Pont 900 Differential Thermal Analyzer, equipped with a 1200° furnace and using platinum sample and reference cups with matched platinum/platinum-13% rhodium thermocouples.

Total sample size 40 mg, reference calcined alumina (40 mg), samples at -150 BSS and heated at a rate of 10°/min., with thermocouples calibrated against the α/β quartz inversion temparature.

Effects of carbon dioxide furnace atmospheres

The principle of greatly varying partial pressures of CO_2 in the furnace atmosphere from virtually zero to 1 atmosphere by using dynamic furnace atmospheres of N_2 and CO_2 respectively has been clearly demonstrated previously in connection with the improved detection and identification of carbonates in coal; Warne (1965 and 1975).

The overall result is that as the partial pressure of carbon dioxide gas which surrounds the calcite sample rises the dissociation reaction (see above) is progressively retarded owing to the increased partial pressure of this gas which has to be overcome before this reaction can occur. The dissociation reaction therefore starts late and more abruptly and occurs at higher temperatures with a greater reaction velocity. Thus comparing curves 5 and 1 or 6 and 2 in Fig. 1, determined in dynamic furnace atmospheres of nitrogen and carbon dioxide respectively, it may be seen that:

a) the peaks become very much more sharply attenuated and the peak height is greatly increased;

b) the complete individual peaks, including the *initiation*, *peak*, and *termination* temperatures move up scale to occur at considerably higher temperatures;

c) the detection limit and content evaluation potential is greatly increased (for a detailed study see Warne and Mitchell, in press).

Effects of variations in conditions of DTA

It is therefore felt that the vital concept of standardized and reproducible conditions for DTA is very well stressed and illustrated by drawing attention to the thermal behaviour of calcite. The decomposition of this mineral (which is notably relevant to other anhydrous carbonate minerals) is very sensitive to and greatly influenced by what may appear to be small or relatively unimportant changes in the furnace atmosphere conditions. Often however these changes greatly influence not only the temperature and speed at which the decomposition reactions take place but may also greatly alter the area of the peak representing a specific reaction on the resulting DTA curve.

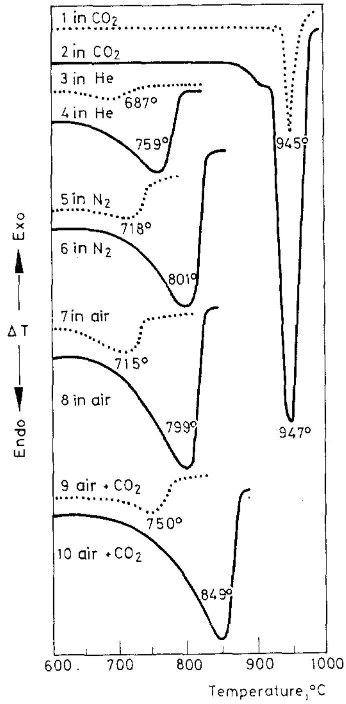

Fig. 1. DTA curves of mixtures of 7.5% (3 mg) and 50% (20 mg) calcite with 37 mg and 20 mg of alumina respectively, determined in the following furnace atmospheres: — curves 1 and 2 in dynamic CO_2, 3 and 4 in dynamic He, 5 and 6 in dynamic N_2, 7 and 8 in "static air" with the vertical furnace tube open at both ends to the room atmosphere and 9 and 10 in static air with the self generated gas component retained, by having only positive pressure equalisation with the room atmosphere through the lower end of the furnace tube. Dynamic gas flow rates: 100 ml per minute in all cases. ——— Samples with 50% calcite; · · · · · Samples with 7.5% calcite

To illustrate the statement immediately above, the following points should be considered with reference to Fig. 1. (This figure is composed of two sets of DTA curves, portrayed with full and broken line symbols which have been determined under standardized conditions.

The only exception being that the furnace atmosphere conditions differ as follows. The first set of curves, represented by the broken line symbol has been produced from samples all containing 3 mg (7.5%) calcite diluted with 37 mg of alumina while the other set portrayed with the unbroken lines represent samples all composed of 20 mg (50%) calcite with 20 mg alumina.

(1) With one exception, under all the furnace atmosphere conditions studied the peak temperatures very clearly fall with decreasing calcite content and therefore the Proben-Abhängigkeit curve concept is theoretically viable.

(2) The very important exception is the case of determination under dynamic conditions of carbon dioxide. Here the peak temperature remains remarkably constant over a calcite content decrease of from 50% to 7.5% and in fact over a much wider dilution range as has been shown elsewhere by the detailed data of Warne and Mitchell (in press). Thus if DTA curves are determined under these conditions, to increase, in particular, detection and content evaluation limits, the concept of Proben-Abhängigkeit curves cannot be applied.

(3) The actual peak temperatures and the magnitude of the peak temperature falls, which occur with dilution, in all the other cases are not the same. They are least in helium, more, in nitrogen or static air, which are similar to each other, and greatest in self generated carbon dioxide, Fig. 1, curves 3 to 10. The Proben-Abhängigkeit-curves resulting from determinations under these furnace atmosphere conditions will therefore be located in different positions and have different slopes on the resultant Proben-Abhängigkeit curve diagrams and are in no way interchangeable for purposes of content evaluation.

It is specifically this point which highlights so well the vital importance of the determination of DTA curves under strictly reproducible and standardized conditions, particularly with regard to carbon dioxide gas partial pressures, if the Proben-Abhängigkeit curve concept is to yield valid results.

(4) Extensive furnace atmosphere composition knowledge and control is therefore required to negate the variability of peak temperature movements between the extremes illustrated by curves 5 and 6 in (N_2) and 1 and 2 (in CO_2) and those where the self generated carbon dioxide furnace atmosphere is retained (often to different degrees dependent upon the type of equipment used), curves 9 and 10, Fig. 1.

Concerning this factor which is composed of (1) the degree of access with the outside room atmosphere, (2) the internal volume of the furnace tube (initially filled only with normal room air) and (3) the actual size of the carbonate sample under test. These are all variables which are capable of considerably influencing the resultant curve configurations. For example the greater amount or ratio of self generated carbon dioxide gas to the original volume of normal static air in the furnace tube surrounding the carbonate sample, may well be responsible for the greater peak temperature rise (50°) shown by curves 10 and 8, produced from samples containing 50% calcite, than that (35°) shown by curves 9 and 7 obtained from samples containing 7.5% calcite, see Fig. 1.

It is also noteworthy that these three variables, particularly the first two are not normally taken into account when the standardisation of conditions for DTA determinations are being considered or enumerated. They may however be of considerable importance particularly as far as carbonate minerals are concerned.

(5) A comparison of curve 3 with curves 5, 7 or 9 or curve 4 with curves 6, 8 or 10 (Fig. 1) shows a marked decrease in peak area when samples of equal calcite content are determined in helium (curves 3 and 4) compared to determinations in other furnace atmosphere gases.

This phenomena is considered due to the much greater (approximately 6 times) thermal conductivity of helium compared to either nitrogen, carbon dioxide or air which have different but comparable thermal conductivities. Thus although all these gases may be used to produce inert atmospheres, a new reference Proben-Abhängigkeit curve must be made, particularly if helium or any of the other noble gases are to be used*. Failure to do this will result in considerable variation in content evaluations and the detection limits are also likely to vary considerably and be not nearly as good when determined in helium, compare curves 3 and 5, Fig. 1.

Conclusions

For the valid application of content evaluation methods such as Proben-Abhängigkeit curves, the DTA curves involved must be determined with the utmost care being directed towards the standardization and reproducibility of analysis conditions. Of these, the furnace atmosphere plays a major role and is particularly important in the cases of carbonates and other minerals where the accumulation of their gaseous decomposition products around the sample under test affects the temperature and speed of the decomposition reactions involved (compare for example in the case of carbon dioxide and calcite, curves 7 with 9 or 8 with 10, in Fig. 1).

Determinations in such cases are not suitable for the Proben-Abhängigkeit curve method, i.e. where a dynamic furnace atmosphere of the same gas as that which is evolved from the mineral decompositions in question is used.

Under dynamic furnace atmosphere conditions the effects of variations in the thermal conductivity of the different purge gases used is of considerable importance and must be taken into consideration if valid content evaluations under different furnace atmosphere conditions are to be undertaken and compared.

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* The thermal conductivity of the noble gases has a large range; from several times less, to several times greater than nitrogen, with argon having a value approximately 2/3 that of nitrogen.

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Résumé — Les variations de pression partielle du gaz CO_2 dans l'atmosphêre du four entraînent des modifications importantes des courbes ATD des carbonates. La calcite est prise comme exemple pour illustrer les changements de forme des courbes qui peuvent avoit lieu. On attire l'attention sur les effets des paramètres suivants: la conductibilité thermique du gaz utilisé dans l'atmosphère du four, la communication du four avec l'atmosphère ambiante, le volume du tube-laboratoire du four et la taille de l'échantillonn (et par suite, la quantité de CO_2 dégagée par celui-ci). Ces effets montrent l'importance des précautions nécessaires pour maintenir constantes les conditions expérimentales lors de l'utilisation de l'ATD comme méthode de dosage. Ceci est illustré par les courbes montrant l'influence de la prise d'essai ("Proben-Abhängigkeit" (PA)).

Zusammenfassung — Bedeutende Veränderungen der DTA-Kurven von Karbonaten werden durch die Änderungen des CO_2-Partialdruckes in der Atmosphäre des Ofens verursacht. Calcit wird zur Veranschaulichung der Konfigurationsänderungen der Kurve, die stattfinden können, angewandt. Es wird auf die Wirkungen der Änderung folgender Variablen aufmerksam gemacht: Wärmeleitfähigkeit der als Ofen-Atmosphäre eingesetzten Gase, Zutritt des Ofens zur umgebenden Atmosphäre, Volumen der "Ofenröhre" und Probengrösse (und dadurch die Menge des selbst entwickelten CO_2). Diese Wirkungen betonen die Sorgfalt, mit der die Bedingungen der DTA-Bestimmungen für Inhalt-Auswertungsmethoden wie "Proben-Abhängigkeits"-(PA)-Kurven konstant gehalten werden müssen.

Резюме — Заметные изменения ДТА кривых карбоната обусловлены изменением парциального давления CO_2 газа в атмосфере обжигательной печи. Для иллюстрации изменения внешнего вида кривых, которое может происходить, был использован кальцит. Внимание было сосредоточено на таких эффектах изменения как термическая проводимость газов, используемых в качестве обжигательной атмосферы, печной проход к обычной атмосфере, объем печной „трубы" и размер образца и следовательно количество получаемого CO_2. Эти эффекты подчеркивают тщательность, с которой должно поддерживаться постоянство условий определения ДТА для методов оценки содержания таких как кривые "Proben-Abhängigkeit".