

EFFECT OF DILUENT AND ATMOSPHERE ON DTA PEAKS OF DECOMPOSITION REACTIONS

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A study has been carried out of the influence of sample dilution, the nature of the gas atmosphere, and the static or flowing conditions of this, on the DTA curves resulting from the thermal decomposition of solids. The results obtained seem to indicate that only the reversible reactions of solid thermal decomposition are seriously affected by such factors.

Differential thermal analysis has been widely used in the study of the kinetic and thermodynamic aspects of decomposition reactions of solids. A serious drawback to this technique is the lack of reproducibility of the DTA curves provided by the literature [1] for analogous substances. According to the Committee of Standardization of the International Confederation for Thermal Analysis (ICTA), the discrepancies must in great part stem from variations in the experimental conditions from one publication to another. This is difficult to establish, however, because of the lack of experimental detail that has so far characterized the DTA literature.

Investigation of the influence of the experimental conditions on the DTA curves of solids is therefore of great interest. Studies of the effect of dilution of the sample on its DTA curve were carried out earlier [2, 3], and it was concluded that dilution affects only the DTA peaks due to thermal decomposition reactions, causing a lowering of the peak temperature. Warne and Mackenzie [3], studying the thermal decomposition of alkaline-earth carbonates, think that such a phenomenon could be explained by the effect of dilution on the CO₂ pressure around the sample of the CO₂ resulting from decomposition of the salt.

In the present paper, a simultaneous study has been carried out of the effects exerted on the DTA curves of reversible and irreversible decompositions of solids, by the dilution of the sample and by the nature and flow rate of the gas flowing over the sample.

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Experimental

Materials. CaCO_3 (d'Hemio A. R.) and $\text{Ni}(\text{COOH})_2 \cdot 2 \text{H}_2\text{O}$ (Probus A. R.), previously dehydrated at 130° , were used.

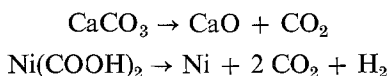
Differential thermal analysis. An AMINCO 4.4442 A thermoanalyzer, provided with a 1000° furnace, nichrome sample holders and chromel-alumel thermocouples, were used. The heating rate was $16^\circ/\text{min}$ and all experiments were performed with Al_2O_3 as reference material. Sample and reference weights were about 200 mg.

Static and dynamic atmospheres were used at a total pressure of 1 atm. When flowing gases were required, a flow rate of $60 \text{ cm}^3/\text{min}$ over both sample and reference was used.

The sensitivity measurement of the difference of temperature, ΔT , between the sample holders is given on the plots of the DTA curves.

Results and discussion

The thermal decompositions of CaCO_3 and $\text{Ni}(\text{COOH})_2$ were studied by DTA:



The stoichiometry of the nickel formate decomposition was established by analysis of the gaseous and solid products by gas chromatography and X-ray diffraction, respectively. The mechanism of this reaction was studied previously [4] under a N_2 atmosphere in order to avoid oxidation of nickel. The kinetic data were not affected at all by variation of the pressure at which the experiments were performed. Analogous conclusions have been drawn for the thermal decompositions of other transition metal formates [4–6].

In contrast, it is well known [7] that the thermal decomposition of CaCO_3 is greatly influenced by the pressure of the surrounding atmosphere.

DTA curves obtained in a static atmosphere of air for CaCO_3 samples (undiluted or diluted with 95 wt % Al_2O_3) are included in Fig. 1, together with those obtained using helium and nitrogen flows of $60 \text{ cm}^3/\text{min}$ over undiluted samples.

This figure shows the marked influence of dilution on the DTA peak temperature of CaCO_3 , that moves from 935 to 830° .

Sample dilution exerts a considerably greater influence than elution with a nitrogen flow. However, with helium as flowing gas, the DTA peak is shifted to a considerably lower temperature, as shown in the same figure.

Figure 2 presents the DTA curves for $\text{Ni}(\text{COOH})_2$ in a N_2 static atmosphere, and under flowing N_2 and He at $60 \text{ cm}^3/\text{min}$. It can be seen that the DTA peak temperature does not change, in spite of the different experimental conditions employed. Dilution of the sample does not influence the peak temperature in this case [8].

The previous results for the irreversible thermal decomposition of $\text{Ni}(\text{COOH})_2$ and for the reversible decomposition of CaCO_3 suggest that sample dilution, the nature of the flowing gas, and the static or dynamic conditions of this, do not change the temperature at which the DTA peak appears in the case of irreversible reactions, though this is not true in the case of reversible reactions such as CaCO_3 decomposition.

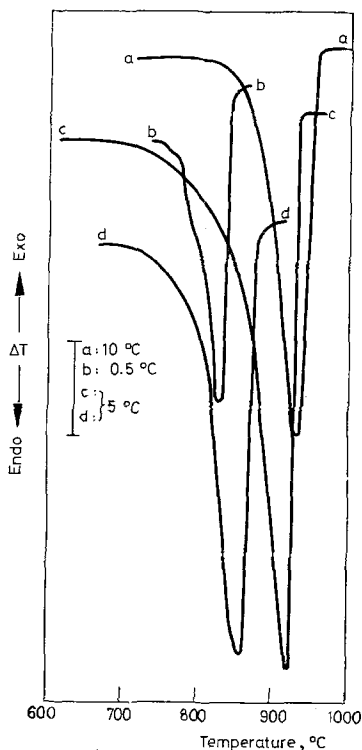


Fig. 1. DTA curves ($16^\circ/\text{min}$) for CaCO_3 , undiluted (*a, c, d*) and diluted with 95 wt % Al_2O_3 (*b*). Surrounding atmosphere: *a*, and *b*, static air; *c*, flowing N_2 at $60 \text{ cm}^3/\text{min}$; *d*, flowing He at $60 \text{ cm}^3/\text{min}$

The shifting of the CaCO_3 DTA curves could be explained by considering that the temperature range at which they appear decreases when the effectivity of the experimental conditions is increased by removal of the CO_2 generated during the salt decomposition.

If such an interpretation were correct, nitrogen would be a much poorer carrier gas than helium. This behavior could easily be explained, bearing in mind that the diffusivity of a gas increases with decreasing molecular weight. Homogeneous

He-CO₂ mixtures could therefore be obtained more quickly than N₂-CO₂ ones, and thus CO₂ would be more effectively removed by helium.

An alternative explanation for the shifting of the CaCO₃ DTA peak would take into account the much higher thermal conductivity of helium compared with

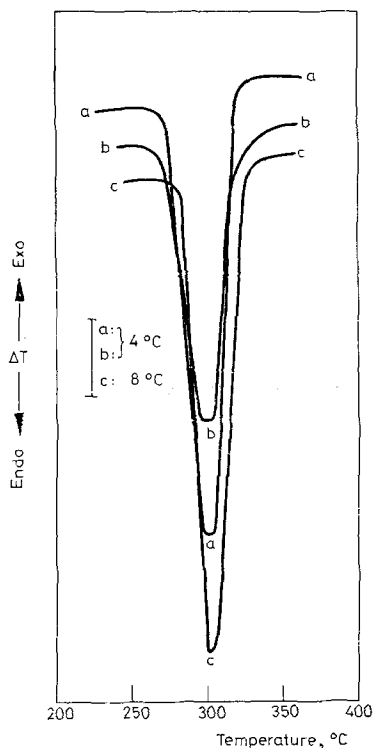


Fig. 2. DTA curves (16°/min) for undiluted Ni(COOH)₂ under different surrounding atmospheres: *a*, flowing He at 60 cm³/min; *b*, static N₂; *c*, flowing N₂ at 60 cm³/min

that of nitrogen. However, this interpretation can be ruled out by the unchanged temperatures of the DTA peaks for Ni(COOH)₂ in Fig. 2, which seem to indicate that the nature of the flowing gas does not influence this process.

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RÉSUMÉ — On a étudié l'influence de la dilution de l'échantillon, de la nature de l'atmosphère ainsi que le fait que celle-ci soit statique ou dynamique, sur les courbes ATD résultant de la décomposition thermique des corps solides. Les résultats obtenus indiquent que de tels facteurs n'influencent de façon sérieuse que les réactions réversibles de décomposition.

ZUSAMMENFASSUNG — Es wurde der Einfluß der Verdünnung der Probe, der Beschaffenheit der Gasatmosphäre und seiner statischen oder Strömungsbedingungen auf die DTA-Kurven der thermischen Zersetzung von Festkörpern untersucht. Die Ergebnisse deuten darauf hin, daß nur die reversiblen Reaktionen der thermischen Zersetzung von Festkörpern durch solche Faktoren stärker beeinflußt werden.

Резюме — Проведено изучение влияния разбавления образца в зависимости от природы газовой атмосферы, а также ее статические свойства и условия ее статические свойства и условия ее течения на кривые ДТА термического разложения твердых тел. Полученные результаты, со всей очевидностью, указывают на то, что только обратимые реакции термического разложения твердых тел в значительной степени затрагиваются такими факторами.