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DSC BY THE TGA/SDTA851^e CONSIDERING MASS CHANGES

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Abstract

DSC measurements in open pans are often disturbed by mass losses such as sublimation during melting or release of water during chemical reactions. By simultaneous DSC and TG measurements the DSC signal can be corrected. For this purpose, a temperature dependent calibration function has to be determined by which the SDTA signal from the TGA/SDTA851^e measuring cell can be converted into a heat flow curve (DSC).

By this procedure, accurate heat of melting can be determined despite ongoing sublimation in open pans. This method is illustrated with reference of the melting of anthracene.

Additionally, condensation reactions were investigated and analyzed by DSC/TG even under ambient pressure, knowing the heat of evaporation. Using phenol formaldehyde resins the influence of the presence or the release of volatile reaction products on the reaction rate and kinetic parameters were studied.

In general, the method can be used to correct DSC curves for thermal effects related to mass change.

Keywords: anthracene, calibration, DSC, DTA, evaporation, phenol formaldehyde resin, simultaneous DSC and TG

Introduction

Results of differential scanning calorimetry (DSC) measurements are usually normalized to the initial sample mass. Hereby it is assumed that the sample mass remains constant. However, this is not always true and mass changes can not be neglected [1]:

- if sublimation takes place during melting of a material which lowers the amount of that compound considerably or
- if material evaporates during a chemical reaction.

In such cases the heat flow measured has to be related to the actual mass.

To avoid the problem of mass losses DSC measurements are often performed at constant volume in sealed pressure pans. But, such a condition may not meet the required condition of ambient pressure. Therefore, the DSC curve and mass change have to be determined simultaneously.

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Today, thermogravimetric analyzers (e.g. TGA/SDTA851^e) are equipped with an additional sensor to record the temperature difference between the temperature measured directly at the sample and the model reference temperature [2, 3]. This measuring signal is called SDTA (single DTA) and it indicates for example whether a transition is exothermic or endothermic, analogously to DSC. The SDTA curve can be converted to a heat flow curve (DSC') knowing the temperature dependent calibration function.

This simultaneous recording of TG and DSC curves allows one to normalize the heat flow to the actual mass. Hence, the heat of melting can accurately be determined in spite of a parallel sublimation of the same substance.

The characterization of reactions which produce water is another field of combined TG-DSC studies. In such cases, the exothermic heat of reaction is overlapped by the endothermic heat of evaporation of the water formed. But the evaporation rate may not be the same as the reaction rate. Hence the DSC curve alone gives a wrong picture of the rate of the reaction. Again, with simultaneous TG and DSC measurements the DSC signal can be corrected by the heat of evaporation determined from the rate of mass loss.

Experimental

The measurements in open pans were performed with a METTLER TOLEDO STAR^e System (software version 6 under Windows NT®) and the TGA/SDTA851^e module equipped with the small furnace. Measurements with high pressure pans were performed in the DSC821^e module. Experimental parameters are given together with the results.

Chemicals like sodium chloride, anthracene were of analytical grade.

Curing systems: 1. paper impregnated by phenol formaldehyde resin (prepreg). To prepare the sample, the resin was scratched off the paper; 2. molding compound with approx. 20% of phenol formaldehyde resin in powdery form.

Determination of the calibration curve

Melting point standards were used to adjust temperature scale from the heat of fusion of these materials (Table 1). The same measurements were also used for the heat flow calibration.

To prevent metal samples from forming alloys with the platinum crucibles at higher temperatures, about 15 mg of alumina powder were uniformly distributed in the bottom of the crucible and the metals placed on top. Calibration functions can be determined up to 1600°C using the appropriate furnace.

As an example, Fig. 1 shows the SDTA melting curves of four high purity metals. The calorimetric sensitivity of the SDTA signal is determined by comparing the measured SDTA peak area (F_{peak}) with the theoretical heat of fusion (ΔH_{Lit}) for the sample. The corresponding calibration factor K is calculated as follows:

$$K = \frac{m_0 \Delta H_{\mathrm{Lit}}}{F_{\mathrm{peak}}} \tag{1}$$

where m_0 is the sample mass used for the measurement of F_{peak}.

Table 1 Reference values and measurement data for the substances used (literature values from the STAR^e database). 70 µl platinum crucibles, heating rate 10 K min^{-1}, 40 ml min^{-1} nitrogen gas purge

Substance	Melting point/°C	Heat of fusion, ΔH_{lit}/J g^{-1}	Sample mass/mg	F_{peak}/ s°C	Calibration factor K/ mW °C^{-1}
Indium	156.6	28.5	12.544	65.9	5.42
Zinc	419.5	107.5	5.347	62.0	9.16
Aluminum	660.3	397.0	3.792	97.8	15.40
Gold	1064.2	63.7	11.133	21.6	32.90

Example for aluminum (Table 1):

$$K_{\mathrm{Al}} = 3.792\ \mathrm{mg}\ 397\ \mathrm{J\ g^{-1}}/97.8\ \mathrm{s\ °C^{-1}} = 15.4\ \mathrm{mW\ °C^{-1}} \tag{2}$$

A series of measurements were performed to determine the calibration factors at different temperatures in 70 µl platinum crucibles. Several measurements for each substance were performed. The entire temperature range can be covered by the four metals. For a limited temperature range it is sufficient to measure heat of fusion of e.g. indium and zinc. The temperature dependence of K can be approximated by a

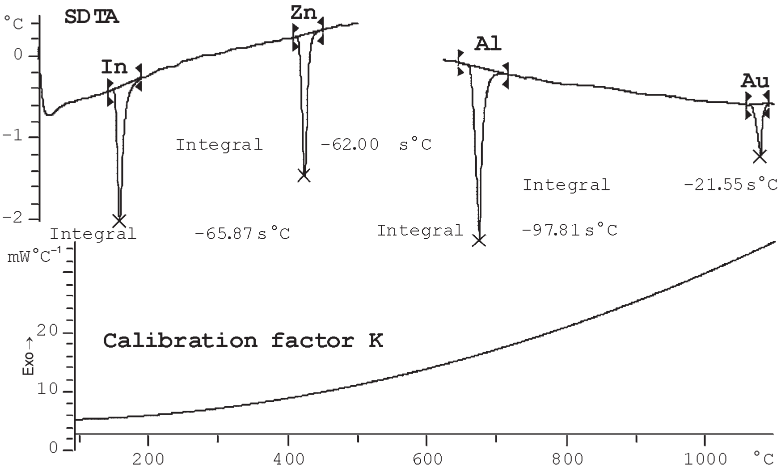

Fig. 1 SDTA melting curves of indium, zinc, aluminum and gold (two metals each in the same platinum crucible, separated by alumina powder). See Table 1 for sample masses. Each peak was integrated with respect to time. The lower curve shows the calibration factor K, which was calculated from these and other measurements. 70 µl platinum pans, heating rate: 15 K min^{-1}

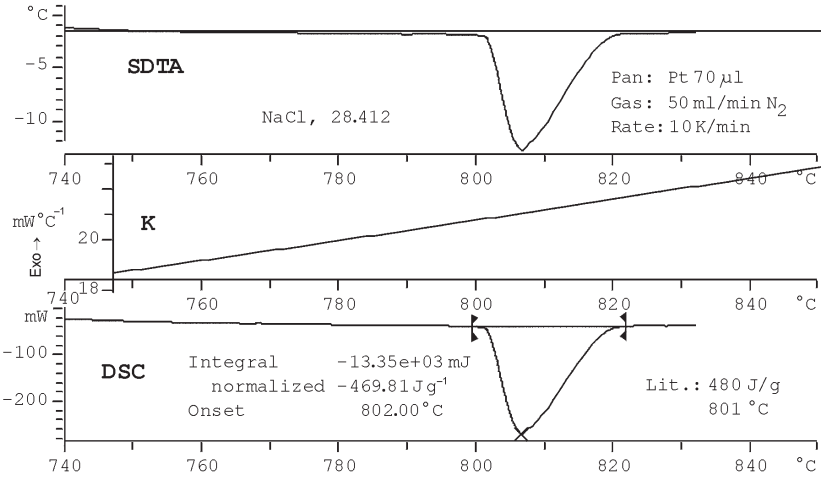

Fig. 2 The determination of the heat of fusion of sodium chloride by a TG/SDTA measurement. The middle curve shows the calibration factor from 740 to 840°C (see also Fig. 1). The lower curve shows the heat flow curve determined, multiplying the SDTA curve by *K*. Theoretical heat of fusion is 480 J g^{-1} [ref: http://www.nlci.com/users/gundlach/]. Sample mass: 28.412 mg; a 70 µl platinum crucible with lid was used to reduce vaporization that begins at this temperature

quadratic polynomial. This polynomial is saved directly as a calibration curve with the correct units and permits the simple and direct conversion of the SDTA curves into heat flow curves by multiplying the SDTA curve by the calibration curve. As an example, Fig. 2 shows the melting of sodium chloride. The respective SDTA curve is multiplied by the calibration curve in the corresponding temperature range thus delivering the DSC curve. Integration of the melting peak yields the heat of fusion of the substance which is in reasonable agreement with the literature value.

Parameters affecting the calibration factor

A variety of measurements were performed to study other than temperature influences on the calibration factor *K* [4]:

- Type of furnace atmosphere: the change from air or nitrogen to helium resulted in a marked decrease of the calorimetric sensitivity by a factor of 3 (measured at 156°C) due to the better thermal conductivity of helium.
- The type of crucible had only a minor effect on the calibration curve *K*.
- A negligible effect of sample mass was measured using 1 to 30 mg indium. Results from different masses are within the accuracy of the evaluation (position of the baseline for integration).
- Changing the heating rate from 5 to 20 K min^{-1} had no influence on *K*.

- Changes in the nitrogen purge gas flow rate from 10 to 30 ml min^{-1} had no effect on the value of K.

In general, calorimetric effects can be quantitatively determined by SDTA with an error level of less than 10%.

Results

The simultaneous DSC and TG measurements have been used to normalize the heat flow to the correct mass and to compensate evaporation effects, as shown in the following applications.

Heat of melting during sublimation

Anthracene melts at 220°C but begins to sublime below this temperature. Hence, if measured in a pan with pierced lid, the heat of fusion normalized to the initial sample mass is too small (134 J g^{-1}) as compared to the literature value (161 J g^{-1}). With continuous mass correction the true value is measured, as in a sealed pan (Figs 3 and 4). Due to the different way of sample preparation more or less sublimation takes place and up to 50% loss has been measured at the beginning of the melting (Table 2). If the mass loss is getting larger (e.g. 50%) the evaporation in an open pan is so fast, that the compensation by the mass loss is incomplete due to inaccurate determination of the integration baseline on the steep DSC curve.

In Table 2 the numerical results calculated from the curves shown in Figs 3 and 4 are summarized.

Table 2 Mass losses and heat of melting of anthracene

	Sealed pan	Lid with 2 pinholes	Open pan
Sample mass/mg	16.672	14.670	18.164
Loss at 217°C/%	0.1	11.0	52.4
Heat of melting:			
Normalized to initial mass/J g^{-1}	159.45	134.72	44.01
Normalized to actual mass/J g^{-1}	159.77	159.36	143.03

Curing studies of condensation reactions: prepreg of formaldehyde resin

DSC measurements of phenol formaldehyde resins are usually done in pressure pans [5]. Without pressure resistant sealing the vapor pressure of the reaction water opens the standard aluminum pan at elevated temperatures. Consequently, in open pans, evaporation disturbs the DSC curve. Hence, curing studies at ambient pressure are not possible in standard pans.

The combination of simultaneous TG and DSC allows the compensation of the heat of evaporation. As an example, a phenolic resin prepreg was investigated. The

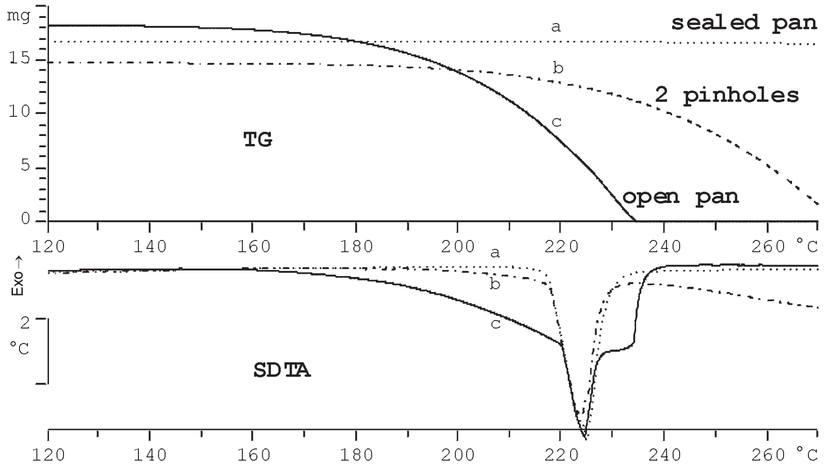

Fig. 3 TG and SDTA curves of anthracene melting/evaporation in sealed and open pans. The melting is shown by SDTA only. Heating rate: 5 K min^{-1}. Aluminum pan 40 µl in three configurations: a – sealed, b – 2 pinholes in the lid, c – without lid. Purge gas: 50 ml min^{-1} nitrogen

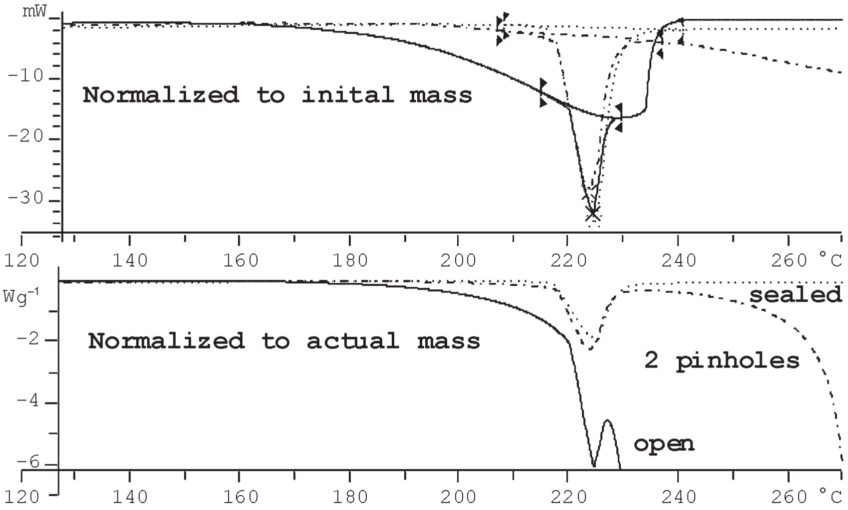

Fig. 4 DSC curves of anthracene melting/evaporation in sealed and open pans as derived from the curves in Fig. 3 with integration of the melting peaks. The upper diagram is not normalized, the lower is normalized to the actual sample mass, as given in Fig. 3

evaluation procedure using the DTG (derivative of TG) and the SDTA curve is shown in Fig. 5.

The TG records the mass loss due to evaporation of water. The DTG curve is multiplied by 2400 J g^{-1} (heat of evaporation of water) delivering the corresponding

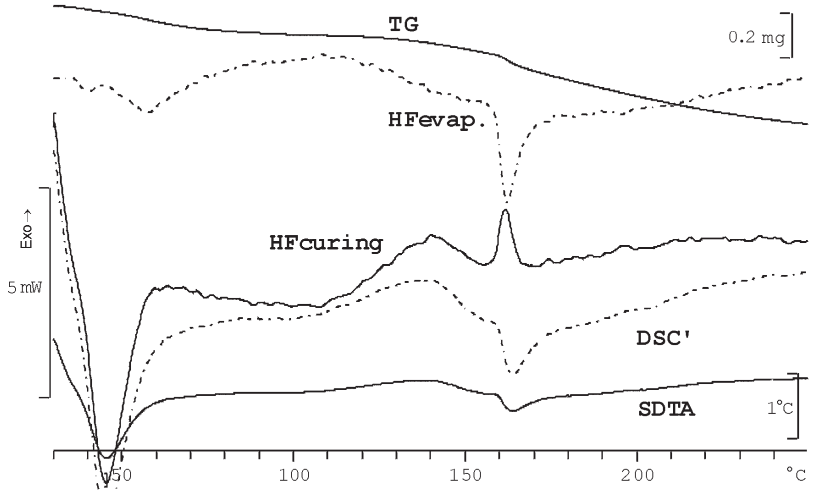

Fig. 5 The curing of phenol formaldehyde resin in open aluminum pan (3.563 mg) is measured by TG (top curve, in mg) and SDTA (bottom curve, in °C). Rate: 10 K min^{-1}, HFevap.=DTG·2400 J g^{-1}, DSC'=SDTA·4.81 mW °C^{-1} HFcuring (in mW) is the heat flow curve of the net reaction, i.e. DSC' – HFevap

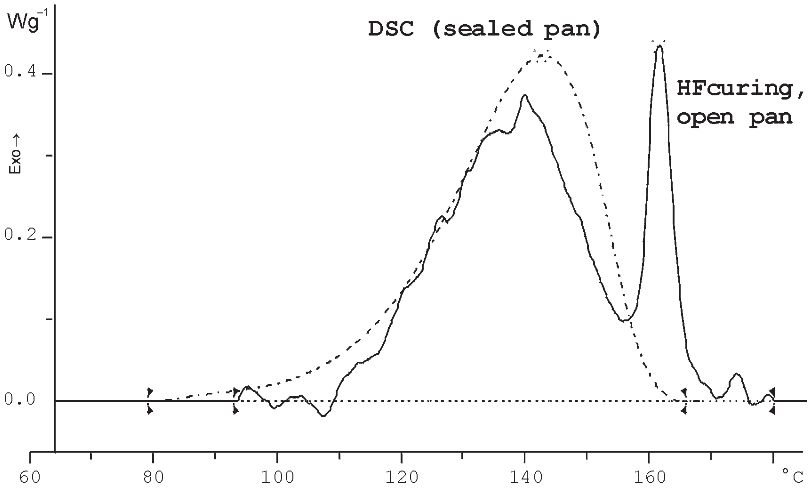

Fig. 6 The net heat flow of the curing reaction in open pan is shown (solid line) and compared to the DSC curve of the same reaction in hermetically sealed high pressure pan (dashed line). Both DSC curves are baseline corrected and normalized to the sample mass

heat flow. For highest accuracy, the temperature dependence of the heat of evaporation should also be considered. The simultaneously measured SDTA records the total heat uptake or release. The respective DSC curve (DSC') is calculated from the SDTA by multiplying with the calibration factor of 4.81 mW °C^{-1}. This factor is appropriate for standard aluminum pans and is approximately constant within the small temperature range considered (c.f. Fig. 1). The net heat output of the curing reaction is the difference between the two curves.

The DSC curve corrected for the evaporation effect is compared to the corresponding measurement in a sealed pan (Fig. 6). In both cases the heat of reaction is virtually the same, despite of the fact, that different final partial pressures of water are reached. The reactions behave similarly up to 140°C. The low partial pressure of water has only a minor effect on the rate. Above this temperature, the different reaction rates may be explained as follows. In the sealed pan, the reaction is in equilibrium with the partial pressure of the produced water. In the open pan a diffusion barrier (film) for the water evaporation is formed at higher degree of cure. The water is not released and slows down the reaction rate. With increasing vapor pressure, the barrier breaks, the water can escape and the reaction can proceed. This is shown by the second peak in the respective DSC curve. This effect is not seen in the pressure pan.

Curing studies of condensation reactions: molding compound

Phenol formaldehyde resin (molding compound) was investigated to detect influences by the water of reaction using the model free kinetics [6]. Similar measurements as described above were performed at different rates in open and sealed pans. TG and the derived DSC curves (DSC’) are shown in upper part of the Fig. 7. The DSC measurements in the high pressure pans are shown in Fig. 8 (left coordinates). The integration of the reaction peaks gives significantly smaller values in open than in the hermetically closed pans. The conversion is reduced if the water evaporates.

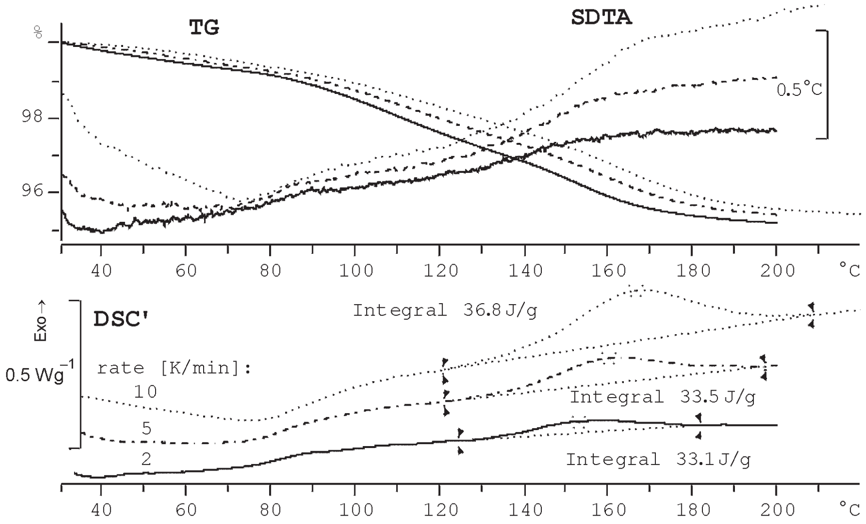

Fig. 7 TG/SDTA measurements of molding compound with 20% of phenol formaldehyde resin in open pans (100 µl aluminum pan without lid, 50 ml min^{-1} nitrogen purge). Rates: 2, 5 and 10 K min^{-1}. DSC’ is the net heat flow of the reactions derived according to the procedure explained in Fig. 5

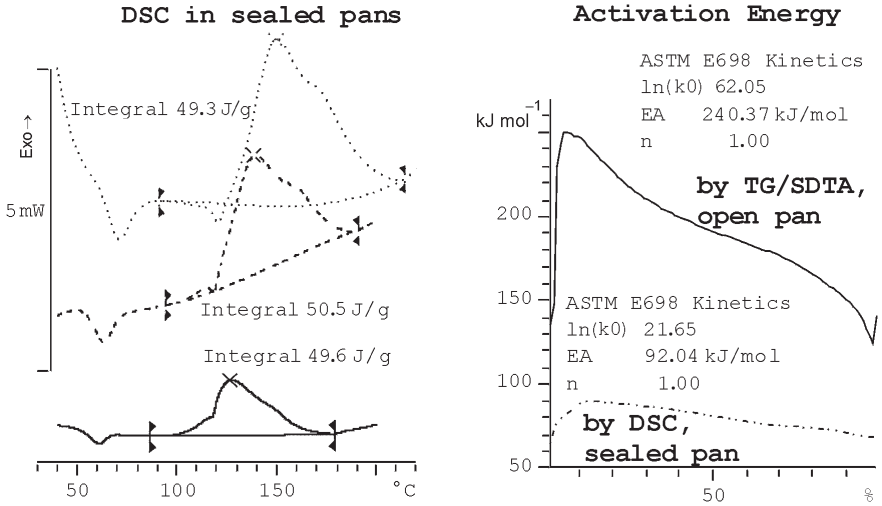

Fig. 8 DSC measurements of molding compound with 20% of phenol formaldehyde resin at rates of 2, 5 and 10 K min^{-1} in sealed pans (50 μl gold plated high pressure pan), left diagram. Right diagram: activation energy curves in function of the conversion calculated from the DSC curves in Figs 7 and 8 respectively. The kinetic parameters evaluated by the ASTM procedure using the respective DSC peak temperatures are listed in the same diagram

Also, the activation energies differ by a factor of 2.5 (ASTM E698 standard procedure and model free kinetics evaluation). It seems, that the curing is accelerated by the produced water (see the steeper DSC peaks by the sealed pans). Using the activation energy curves, the isothermal reaction time can be predicted: for the reaction in open pans the times are approximately three times longer than in sealed pans (e.g. time to 75% at 150°C: open pan: 16.9 min; sealed pan: 5.6 min). Such differences may have a marked influence in the production processes.

Conclusions

The TGA/SDTA851^e module allows quantitative heat flow and simultaneous TG-DSC measurements. Hence, open systems can be analyzed by DSC despite the disturbing evaporations.

Hence, accurate heat of melting can be determined despite of ongoing sublimation in open pans and condensation reactions can be analyzed by DSC even under ambient pressure.

The influence of the presence or the release of volatile reaction products on the reaction rate and kinetic parameters can be studied. The curing behavior of two phenol formaldehyde resin systems has been used to investigate the influence of the water produced by the reaction.

In general, the method can be used to correct DSC curves for thermal effects related to mass change.

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