

NEW PRESSURE DSC CELL AND SOME APPLICATIONS

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Physical properties and chemical reactions can be investigated by pressure DSC. There are 3 possibilities of sample preparation with respect to the contact with the furnace atmosphere which are illustrated by typical applications:

1. Free access of furnace atmosphere
2. Sealed crucible (constant volume)
3. Limited access of furnace atmosphere (self generated atmosphere)

With water as the most important volatile solvent it is shown how evaporation and vaporization can be controlled by different contact between sample and furnace atmosphere.

An appropriate computer simulation helps to understand evaporation and vaporization of volatiles at various conditions.

Keywords: pressure DSC cell

Introduction

Why pressure DSC ? While the temperature is the key parameter for all applications in thermal analysis, pressure is one of the most important remaining properties. Since DSC measurements are usually performed at ambient pressure (0.1 MPa) it is not specially mentioned. However, pressure greatly influences all physical transitions and chemical reactions involving volume changes.

The experiments were run with the DSC 27HP cell (high pressure DSC) of the Mettler TA4000 system. The curves were recorded and evaluated by means of the Mettler software package GraphWare TA72.5.

Measurements with free access to the purge gas of the furnace

Figure 1 shows an example where an open crucible and high pressure are essential: The hydrogenation of an edible oil using 1 MPa of hydrogen. Edible fats and oils are triglycerides of different fatty acids, some being

mono or poly unsaturated. With increasing saturation (hydrogenation) the temperature range of fusion increases and the oils are transformed into fats.

With DSC, two aspects are analyzed: The melting behaviour before (Mettler DSC30) and after hydrogenation and the hydrogenation itself.

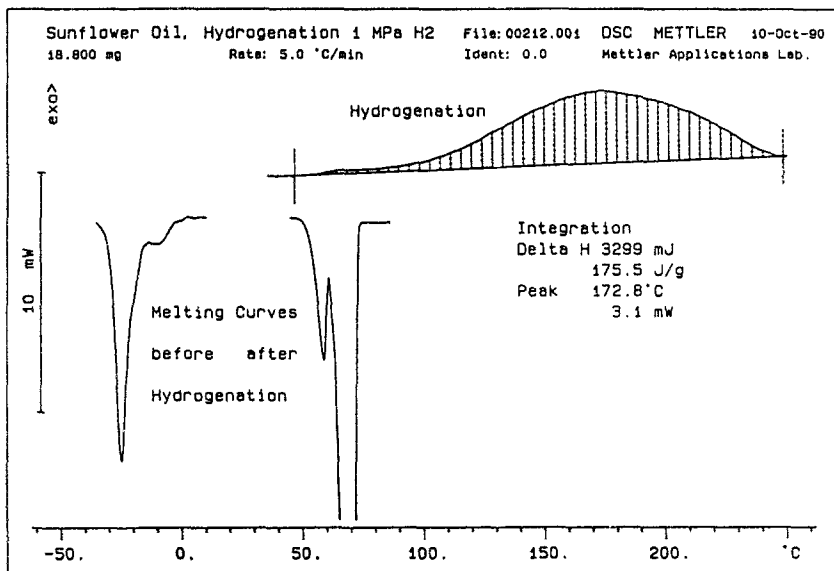


Fig. 1 DSC curves of sunflower oil in an aluminum crucible. Approx. 0.2 mg of ethanol moist Raney nickel act as a catalyst for hydrogenation. Large holes in the lid ensure a good contact with the purge gas of the furnace (hydrogen) while the lid itself protects the cell against products creeping out of the crucible

Another example of the application of open crucibles is the evaporation of a liquid (curve 1 of Fig. 2). The evaporation peak occurs far below the respective equilibrium boiling temperature of the liquid at the current pressure. This is due to the free evaporation below boiling temperature. Curve 3 of Fig. 2 shows that the evaporation below boiling temperature is suppressed by increasing pressure. A similar effect is observed when the size or the number of the holes in the lid is reduced (curve 2). More mass (curve 4) does not influence the shape of the curves but displaces the end point (or peak).

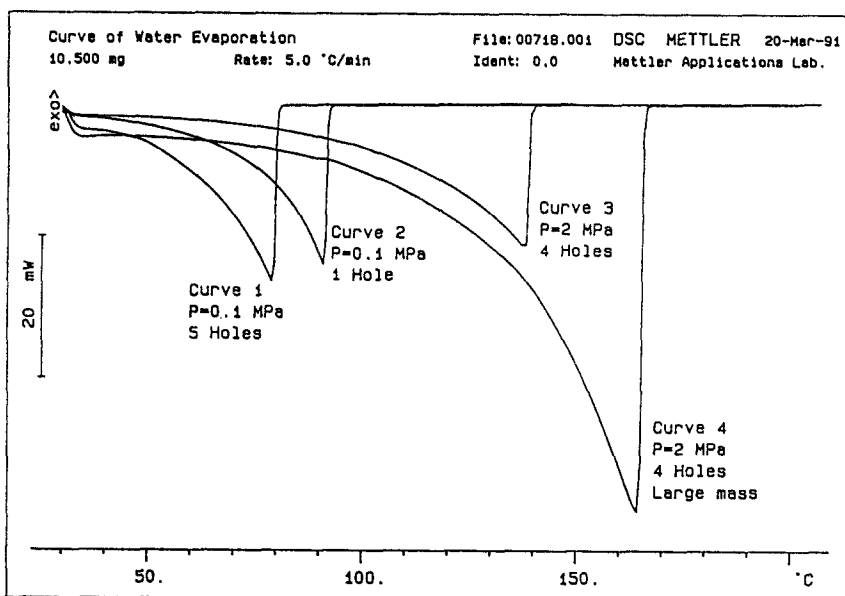


Fig. 2 DSC evaporation curves of water at 0.1 and 2 MPa. The 2 MPa curves are shifted to higher temperatures. The diameter of the hole is approx. 1 mm

Measurements without gas exchange

Most organic solids sublime over a wide range of temperature below the melting point, although the tendency to sublime varies widely from compound to compound. In an open crucible the sublimation/evaporation peak would hide the fusion peak to a certain extent. The evaporation can be suppressed by sealing the crucible. However, the common aluminum crucibles explode at a certain overpressure. To avoid the explosion, pressure is applied in the DSC cell to maintain the shape of the crucible enabling undisturbed measurements of e.g. melting phenomena or chemical reactions at constant volume.

An example of DSC at constant volume is the polycondensation reaction of a phenolic resin (Fig. 3).

The self generated atmosphere

In the determination of boiling points, it is important to prevent the evaporation of the sample. The following technique proved successful: The aluminum crucible lid is placed on a solid support and a hole is made with a

sharp pin. The perforated lid is checked under a microscope. The hole diameter should be 30 to 50 μm . Finally the perforated lid is cold welded on top of the crucible.

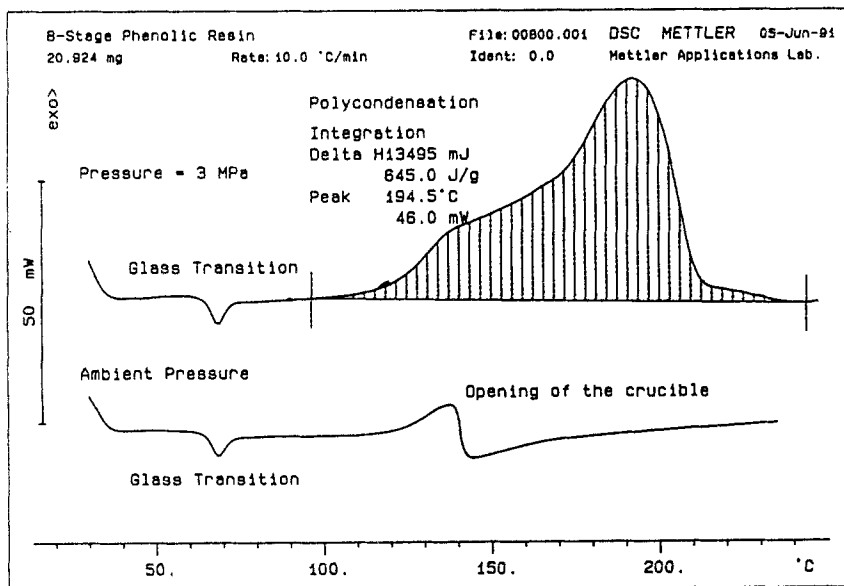


Fig. 3 DSC curves of B-stage phenolic resin. Both curves exhibit the glass transition in the range of 70°C with a small peak due to enthalpy relaxation. The exothermic course of the polycondensation reaction can be measured under an overpressure of 3 MPa without any interferences, while at ambient pressure the condensation is not visible because the sealed aluminum crucible explodes at 145°C due to the vapour pressure of the formed condensation water

Contrary to measurements in open crucible (Fig. 2) the boiling point is now reached, because the sample and most of the formed vapour remains in the crucible (self generated atmosphere) until the respective boiling point is reached. A liquid begins to boil when a temperature increase causes its vapour pressure to be equal to or higher than the surrounding pressure (Fig. 4). During the whole vaporization peak the sample remains at the boiling point.

The goal of the following computer simulation is to correlate the experimental curves with a theoretical model which can explain the phenomenon of self generated atmosphere.

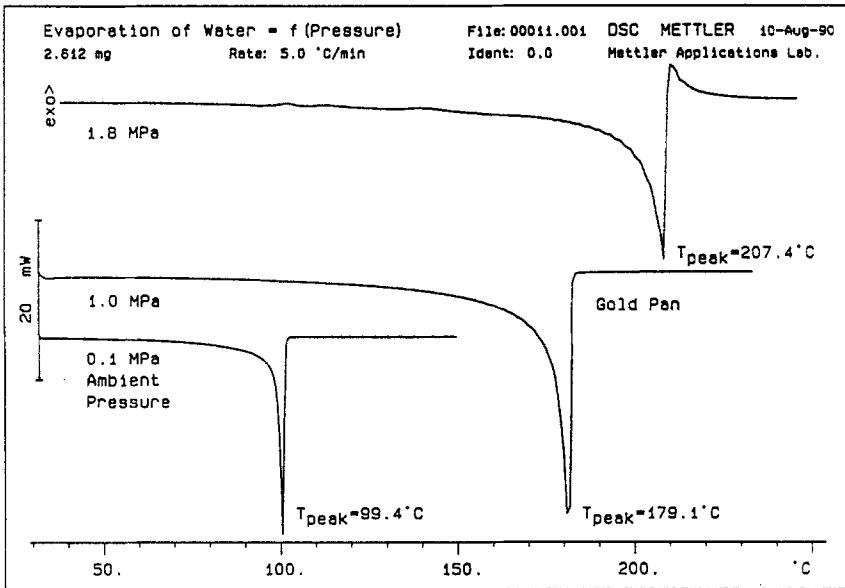


Fig. 4 DSC vaporization curves between 0.1 and 1.8 MPa in self generated atmosphere. The top curve shows an exothermal peak right after the boiling peak. It is assumed to be due to a chemical reaction between water vapour and aluminum. Therefore, this effect disappears when a gold crucible is applied

Simulation model

The selected model for the vapour diffusion through a stagnant gas film [1] is valid up to the boiling point where the partial pressure of water is equal to the total pressure. After having reached the boiling point, the rate of vaporization is limited by the heat transfer between furnace and crucible.

A liquid A is evaporating into a non moving gas B (Fig. 5).

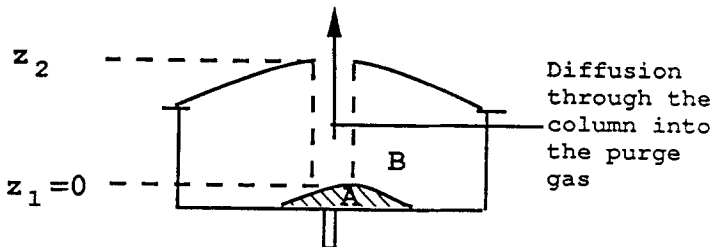


Fig. 5 Schematic cross section through a DSC crucible with pierced lid. z is the height of the column. The liquid level is assumed to be at $z_1=0$

In the case of small holes only the height (thickness) of the lid is taken as the height of the column since diffusion through the hole is far slower than through the atmosphere in the crucible. The following equation gives the concentration profiles in the gas phase.

$$\frac{1-x_A}{1-x_{A1}} = \left(\frac{1-x_{A2}}{1-x_{A1}} \right)^{\left(\frac{z-z_1}{z_2-z_1} \right)} \quad (1)$$

x_A = mole fraction of water in the column at the height z .

The mole fraction of water x_{A2} in the purge gas is assumed to be zero at z_2 . The mole fraction of water at the surface of the liquid phase (z_1) is modelled as $x_{A1} = p_{H_2O}^0 / p_{tot}$

$p_{H_2O}^0$ represents the vapour pressure of water at a given temperature and p_{tot} the total pressure.

With these assumptions Eq. (1) is solved for x_A :

$$x_A = 1 - \left(1 - \frac{p_{H_2O}^0}{p_{tot}} \right)^{\left(1 - \frac{z}{z_2} \right)} \quad (2)$$

The rate of vaporization or mass transfer N_A at the liquid-gas interface is obtained through an equation based on Fick's law:

$$N_A \Big|_{(z_1=0)} = - \frac{C D_{AB}}{1-x_{A1}} \frac{dx_A}{dz} \Big|_{(z=z_1)} \quad (3)$$

x_A is given by Eq. (2) and inserting in Eq. (3), we obtain

$$N_A = \frac{C D_{AB}}{z_2} \ln \left(1 - \frac{p_{H_2O}^0}{p_{tot}} \right) \quad (4)$$

N_A : rate of mass transfer by diffusion [$\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$].

C : total concentration of vapour in $\text{mol} \cdot \text{m}^{-3}$ in the gas phase.

D_{AB} : Coefficient of diffusion [$\text{m}^2 \cdot \text{s}^{-1}$]

The concentration C is derived from the ideal gas law:

$$pV = nRT; \quad c = n/V = p/RT$$

The vapour pressure of water, $p_{H_2O}^0$, is calculated with a regression of fifth order based on the data of the Handbook [2]. Over the whole temperature range the difference between the data and the regression model is smaller than 1%.

For a binary gas mixture at low pressure the diffusion coefficient D_{AB} is inversely proportional to the pressure, increases with increasing temperature, and is almost independent of composition for a given gas pair [1]. Equation 16.3-1 in [1] allows to calculate D_{AB} .

Since N_A depends on temperature (via D_{AB} and C), and the temperature is increasing linearly in DSC, the temperature profile is divided into very small intervals of constant temperature. For each temperature level this leads to the mass evaporated (Δm) from the crucible.

$$\Delta m = N_A A \Delta t M_A \tag{5}$$

A : surface of the hole [m^2]

Δt : duration of a temperature step [s], $\Delta t = \Delta T/\beta$

β : heating rate [$K \cdot s^{-1}$]

M_A : molar mass of water [$g \cdot mol^{-1}$]

From the mass evaporated, the remaining mass, $m(t)$, is given by

$$m_t = m_o - \sum_o^t \Delta m \tag{6}$$

Finally, since the temperature steps are of equal size the heat flow H is given by

$$H = C_p m_t \beta + \Delta H_v \frac{\Delta m}{\Delta t} \tag{7}$$

H : heat flow [W]

C_p : specific heat of water [$J \cdot g^{-1} \cdot K^{-1}$]

ΔH_v : Enthalpy of vaporization [$J \cdot g^{-1}$]

The term on the right represents the power for the evaporation during one temperature step.

Equation (7) was assumed to be valid until $p_{H_2O}^o$ is equal to p_{tot} which occurs at the boiling point. Afterwards, the rate of evaporation is limited by the heat transfer from the furnace to the crucible. As the thermal resistance, R_{th} , is known, the evaporated mass Δm for one temperature step is given by

$$\Delta m = \frac{T_r - T_v}{R_{th}} \frac{1}{\Delta H_v} \Delta t \tag{8}$$

Δm : mass loss for each step [g]

The thermal resistance of the sensor of the DSC27HP is taken to be $0.025 \text{ K} \cdot \text{mW}^{-1}$.

T_r = temperature of the reference crucible

T_v = boiling temperature

Results

This simulation has been compared to experimental DSC boiling curves of water for different pressures and different sizes of holes in the lid. The experimental curves originally obtained by GraphWare had to be converted for the use in the MacIntosh computer in order to be plotted together with the simulated ones. Figure 6 shows an experiment at a pressure of 0.1 MPa with 5 large holes in the lid. To show the influence of the model parameters

- mass of the sample (m)
- pressure (p)
- height of the column (z)
- hole diameter (d)

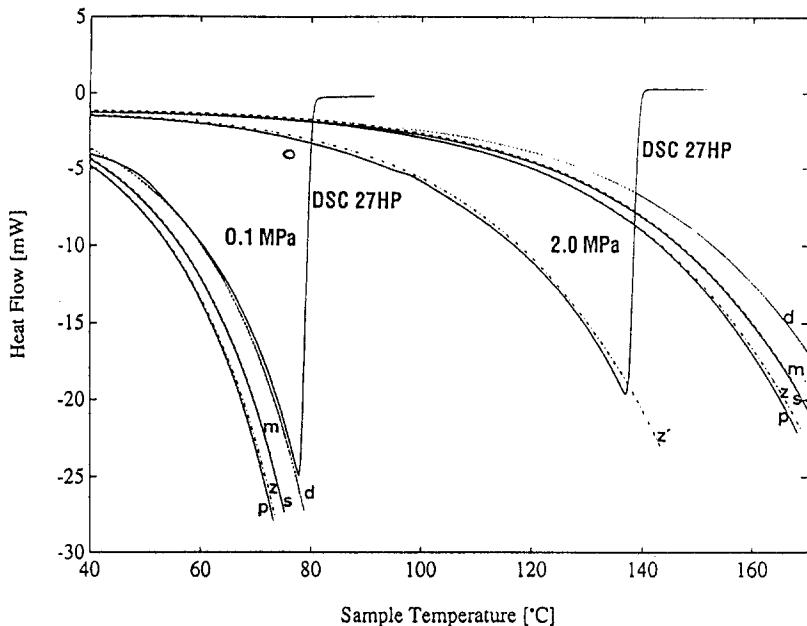


Fig. 6 Evaporation curves of water at 5 deg/min. Lid with 5 holes of 1 mm. The experimental curves (DSC27HP) are drawn until the baseline is attained. Curve s is the simulated curve obtained using the experimental parameters. The other curves visualize the influence of a 10% change of each model parameter. The simulation z' is based on the concept of the effective height

they were varied around their nominal value by -10% . The resulting bunch of curves shows that a variation in the mass (curve m) has no significant effect on the shape of the curve. Variations of -10% on the height and pressure (curves z and p , respectively) slightly shift the curve to the left. Finally a change of -10% of the hole diameter (curve d) shifts the curve towards the experimental curve. Thus, the model seems to fit the experimental data quite well, considering the error margins in the different parameters.

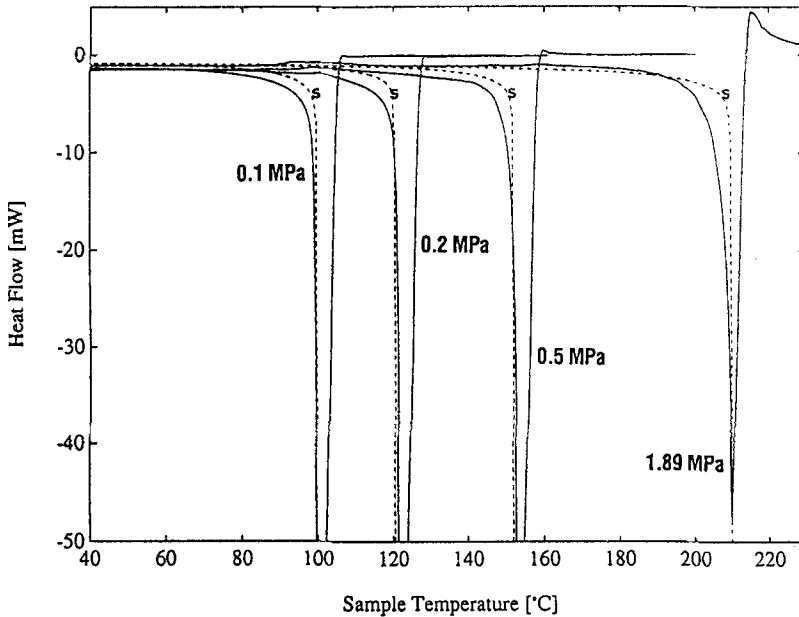


Fig. 7 Vaporization curves of water at 5 deg/min in self generated atmosphere at various pressure. Simulated curves s (dotted lines), experimental curves (solid lines)

The same work was performed with the experimental curve at 2 MPa. In this case the model (curve s) is significantly different from the experimental data. The curves obtained with 10% changes in the model parameters show that measurement errors cannot explain the observed differences. The assumption that the diffusion takes place through all the gas column seems to be no longer valid. Therefore we propose the concept of a so-called effective height. Curve z' shows that by adjusting the height of the crucible to $0.36 z$ the measured values can be modelled very well.

Figure 7 gives the DSC curves in self generated atmosphere (hole diameter $50 \mu\text{m}$). In each case the respective boiling points are reached due to the suppressed evaporation. In the transient area just before reaching the

boiling point the simulated curves differ slightly from the experimental ones, because the purely diffusive model does not apply exactly any more.

Conclusion

Pressure DSC enables the study of the pressure function of thermal effects. In addition, interferences caused by volatile components can be suppressed by appropriate sample preparation.

References

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Zusammenfassung — Mittels Druck-DSC können physikalische Eigenschaften und chemische Reaktionen untersucht werden. Hinsichtlich des Kontaktes mit der Ofenatmosphäre gibt es drei Möglichkeiten zur Probenvorbereitung:

1. Freier Zutritt der Ofenatmosphäre
2. Verschlossener Tiegel (konstantes Volumen)
3. Begrenzter Zugang der Ofenatmosphäre (eigengenerierte Atmosphäre)

Mit Wasser als wichtigstem flüchtigen Lösungsmittel wird gezeigt, wie Verdampfen und Verdunsten durch den verschiedenen Kontakt zwischen Probe und Ofenatmosphäre kontrolliert werden kann.

Eine entsprechende Computersimulation hilft, Verdampfen und Verdunsten von flüchtigen Substanzen bei verschiedenen Bedingungen besser zu verstehen.