

CRITICAL TEMPERATURE MEASUREMENTS OF LIQUIDS BY MEANS OF DIFFERENTIAL THERMAL ANALYSIS*

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ABSTRACT

When studying crystalline substances and liquids in sealed off glass ampoules by differential thermal analysis the melting ranges but not the heat of evaporation of the liquids and fused substances are found, because inside the glass ampoule, there will always be the vapour pressure equilibrium which corresponds to the temperature. With liquids undergoing decomposition, it is possible to measure the range and heat of decomposition. Given a suitable quantity inside the ampoule the critical temperature, e.g., of water or ethanol can be measured for non-decomposing liquids. The measuring effect is based on the pronounced change of the liquid's specific heat at the critical temperature.

Fundamental studies of the measurement of critical temperatures of liquids were carried out by the turn of the century. One of the methods reported is the meniscus method, an optimal measurement of the critical temperature, which comprises a liquid being filled into a glass tube which is then sealed by melting. The glass tube is heated while observing the meniscus. Its rise means that the critical volume has been exceeded, while a drop means that it has not yet been reached. The conditions are only met when that volume of liquid has been filled into the tube at which the meniscus neither rises nor falls on heating but rather remains, e.g., at mid level of the tube until it disappears. The tube contains the critical volume at the critical density when the critical temperature is reached. The critical pressure is then present. These conditions are obtained when the meniscus disappears and the liquid completely goes over into the vapour phase.

The melting range (and the latent heat of fusion) are found when investigating a crystalline material under normal pressure by differential thermal analysis. Given a suitable arrangement the boiling temperature and, in rough approximation, the heat of evaporation are also found (Fig. 1). The latent heat of fusion is found again when carrying out the same measurement in a closed system (glass tube sealed by melting). The heat of evaporation can no longer be measured since the vapour pressure equilibrium corresponding to the given temperature is present in the glass tube.

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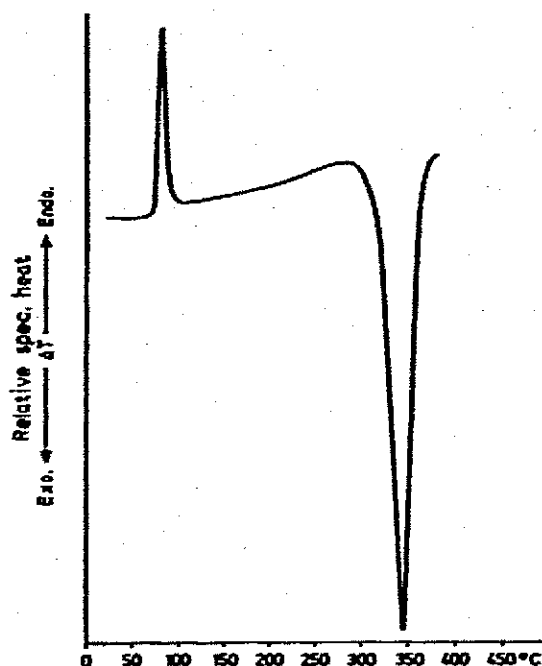
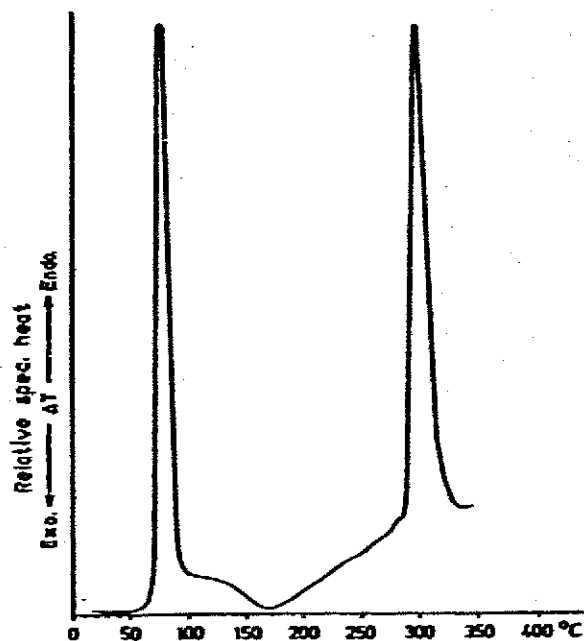


Fig. 1. Organic material (*o*-nitroaniline) with melting and evaporation ranges. 10 mg, 1 bar air; heating rate $20^{\circ}\text{C min}^{-1}$.

Fig. 2. Organic material as in Fig. 1, melting range and strongly exothermic decomposition. 30 mg sealed glass tube; heating rate $5^{\circ}\text{C min}^{-1}$.

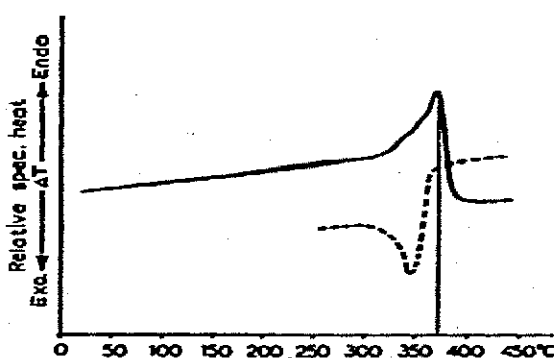
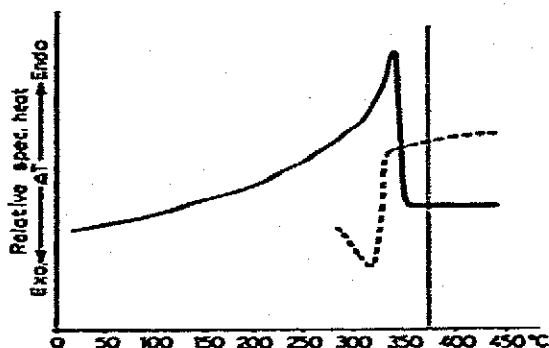


Fig. 3. Critical temperature of water, filled volume 30 mg; $P = 225$ bar; $T = 374.2^{\circ}\text{C}$. Sealed glass tube; heating rate $5^{\circ}\text{C min}^{-1}$. —, Heating; ---, cooling.

Fig. 4. Critical temperature of water, filled volume 120 mg; $P = 225$ bar; $T = 374.2^{\circ}\text{C}$. Sealed glass tube; heating rate $5^{\circ}\text{C min}^{-1}$. —, Heating; ---, cooling.

Temperature and heat of decomposition are measured very conveniently without the related heat of evaporation of the cracked products, (Fig. 2). However, where liquids decomposing only at very high temperatures are concerned, the critical temperature is found. On reaching the critical temperature during heating the liquid goes over into the vapour phase and this is accompanied by a substantial change of

the specific heat in the vicinity of the detecting element. When cooling below the critical temperature the vapour condenses to become a liquid again. This, in turn, is accompanied by a substantial change of the specific heat, (Figs. 3-7). The critical temperature can be adequately measured for a wide variety of purposes provided the proper quantity, i.e., the critical volume, has been filled into the glass tube in line with the conditions outlined above, (Figs. 8 and 9). It is obvious that the glass tubes must be able to withstand the critical pressure (225 kgf cm^{-2} for water). At these pressures and temperatures water attacked the tempered glass which we used for making the sealed tubes, (Fig. 10). This provides an easy method to measure the critical temperature of liquids.

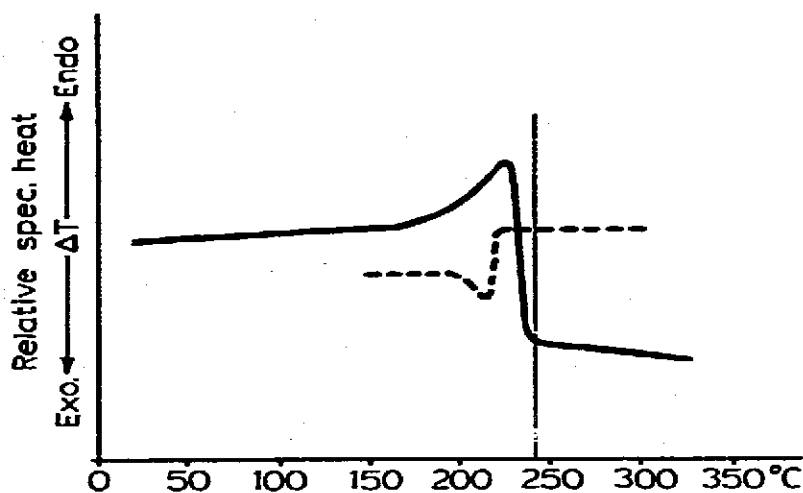


Fig. 5. Critical temperature of ethyl alcohol, filled volume 60 mg; $P = 65 \text{ bar}$; $T = 243^\circ\text{C}$. Sealed glass tube; heating rate 5°C min^{-1} . —, Heating; ---, cooling.

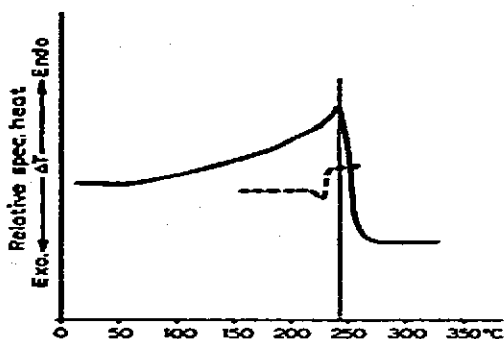


Fig. 6. Critical temperature of ethyl alcohol, filled volume 120 mg; $P = 65 \text{ bar}$; $T = 243^\circ\text{C}$. —, Heating; ---, cooling.

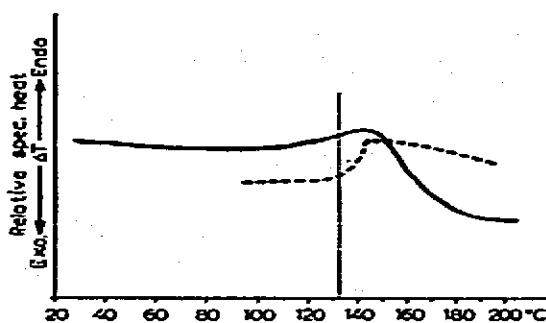


Fig. 7. Critical temperature of ammonia, filled volume 60 mg; $P = 115 \text{ bar}$; $T = 132.4^\circ\text{C}$. —, Heating; ---, cooling.

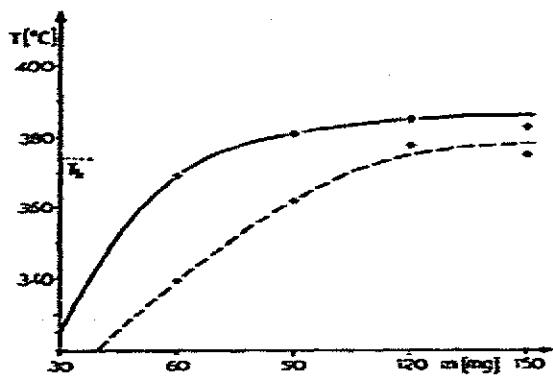


Fig. 8. Critical temperature of water as function of filled volume. $P = 225$ bar; $T = 374.2^\circ\text{C}$.
—, Heating; ---, cooling.

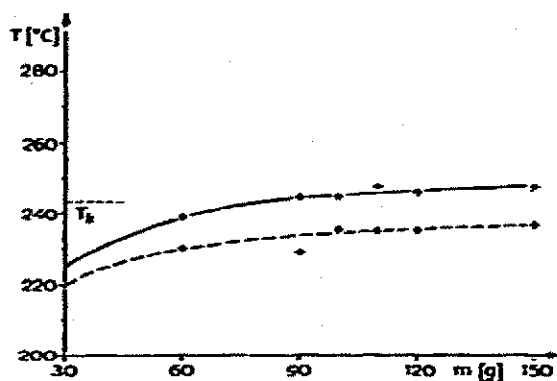


Fig. 9. Critical temperature of ethylalcohol as function of filled volume. $P = 65$ bar; $T = 243^\circ\text{C}$.
—, Heating; ---, cooling.

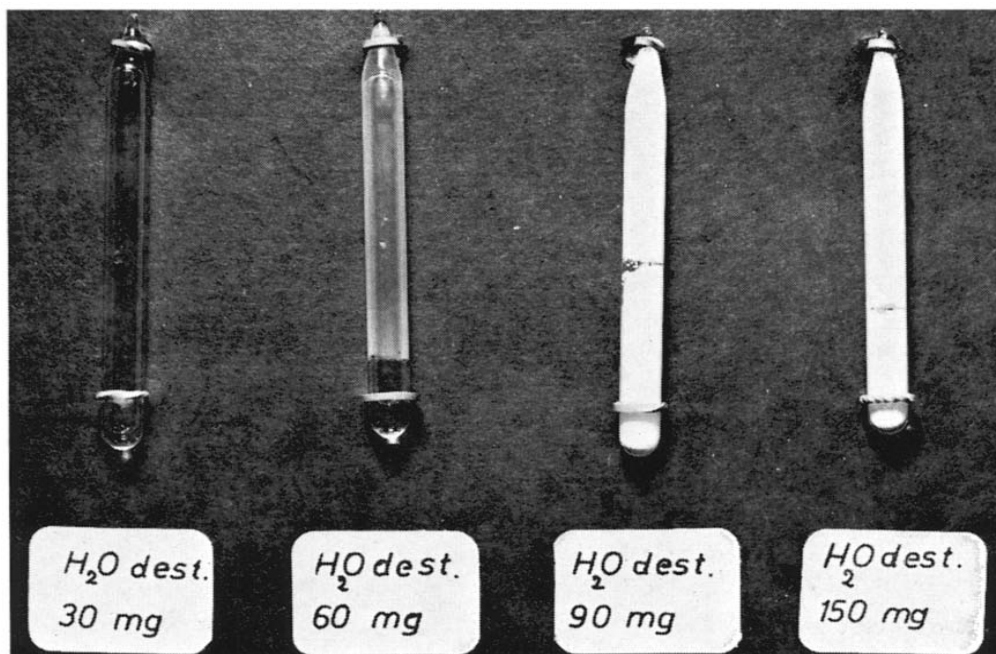


Fig. 10. Sealed glass tubes (1:1) attacked by water to an extent increasing in proportion to filled volume during measurement of the critical temperature.