CH 2252 Instrumental Methods of Analysis

Unit – III

www.msubbu.in

Differential Scanning Calorimetry

M. Subramanian

Assistant Professor
Department of Chemical Engineering
Sri Sivasubramaniya Nadar College of Engineering
Kalavakkam – 603 110, Kanchipuram (Dist)
Tamil Nadu, India
msubbu.in@gmail.com

Introduction

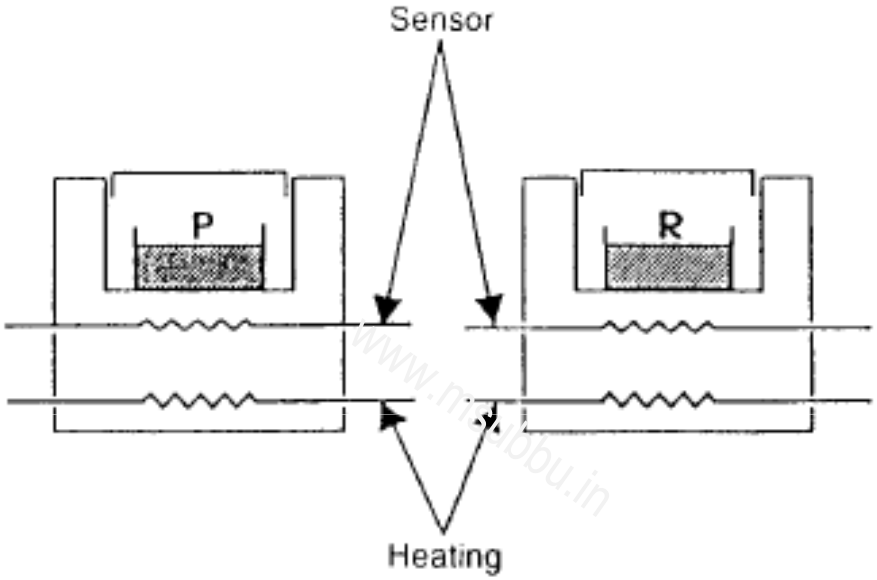
- Differential scanning calorimetry (DSC) is the most widely used of the thermal techniques available to the analyst and provides a fast and easy to use method of obtaining a wealth of information about a material, whatever the end use envisaged

- It has found use in many wide ranging applications including polymers and plastics, foods and pharmaceuticals, glasses and ceramics, proteins and life science materials; in fact virtually any material, allowing the analyst to quickly measure the basic properties of the material

- A DSC analyser measures the energy changes that occur as a sample is heated, cooled or held isothermally, together with the temperature at which these changes occur

Principle of DSC

- In DSC, differences in heat flow into a reference and sample are measured vs. the temperature of the sample.
- The difference in heat flow is a difference in energy; DSC is a calorimetric technique, and results in more accurate measurement of changes in enthalpy and heat capacity than that obtained by DTA.
- There are two main types of DSC instrumentation, heat flux DSC and power compensated DSC.
- The resultant thermal curve is similar in appearance to a DTA thermal curve, but the peak areas are accurate measures of the enthalpy changes.
- Differences in heat capacity can also be accurately measured and are observed as shifts in the baseline before and after an endothermic or exothermic event or as isolated baseline shifts due to a glass transition



Schematic of a power-compensated DSC.

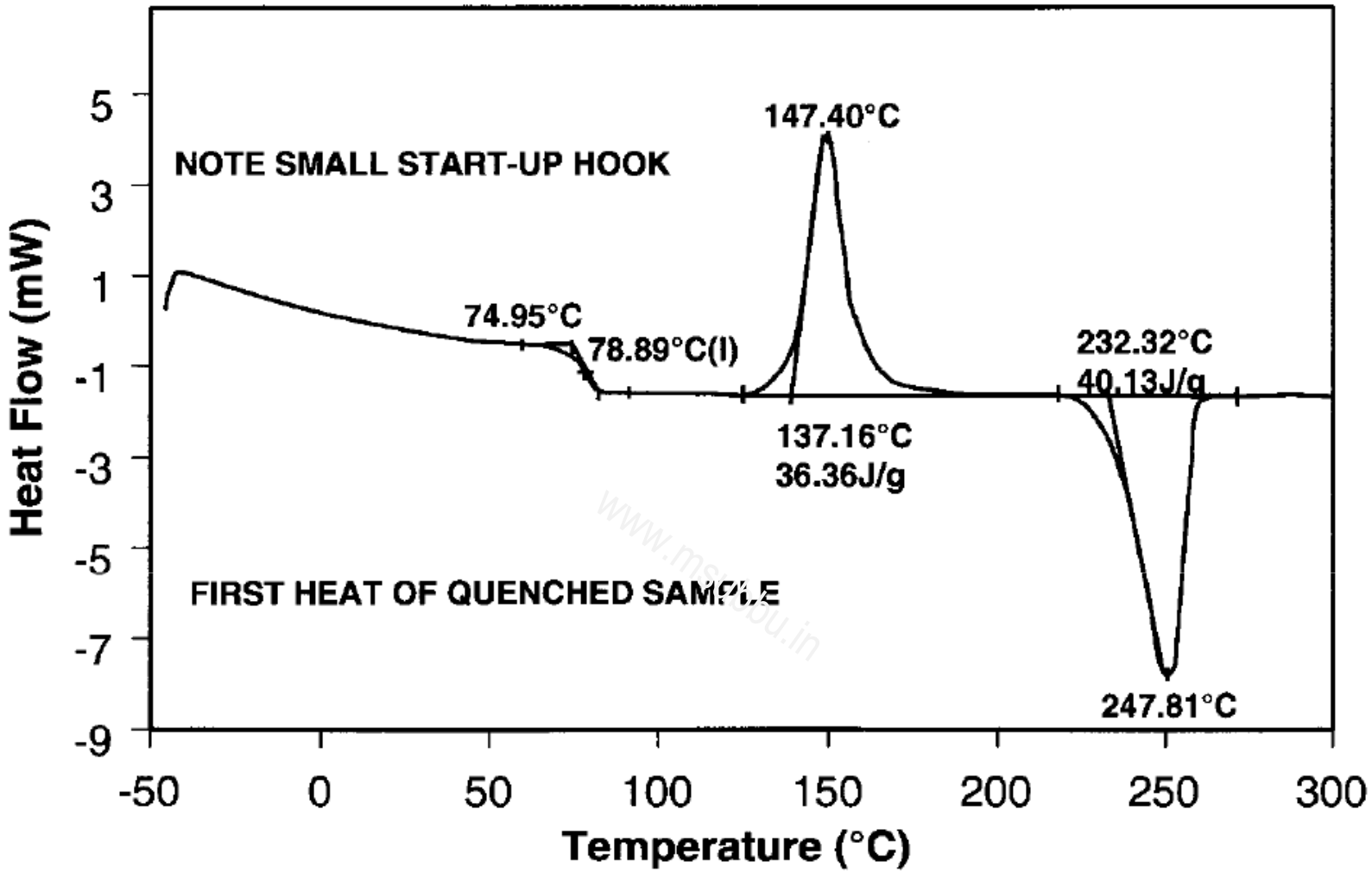


Figure 16.22 DSC thermal curve for a sample of polyethylene terephthalate (PET). T_g is observed at 78.9°C. Crystallization begins at 137°C and the area under the exothermic peak is equivalent to 36.36 J/g PET. Melting begins at about 323°C; the area under the endothermic peak is equivalent to 40.13 J/g PET. (Courtesy of TA Instruments, New Castle, DE, www.tainst.com.)

Robinson et al., Undergraduate Instrumental Analysis, 6th edition, Marcel Dekker, New York

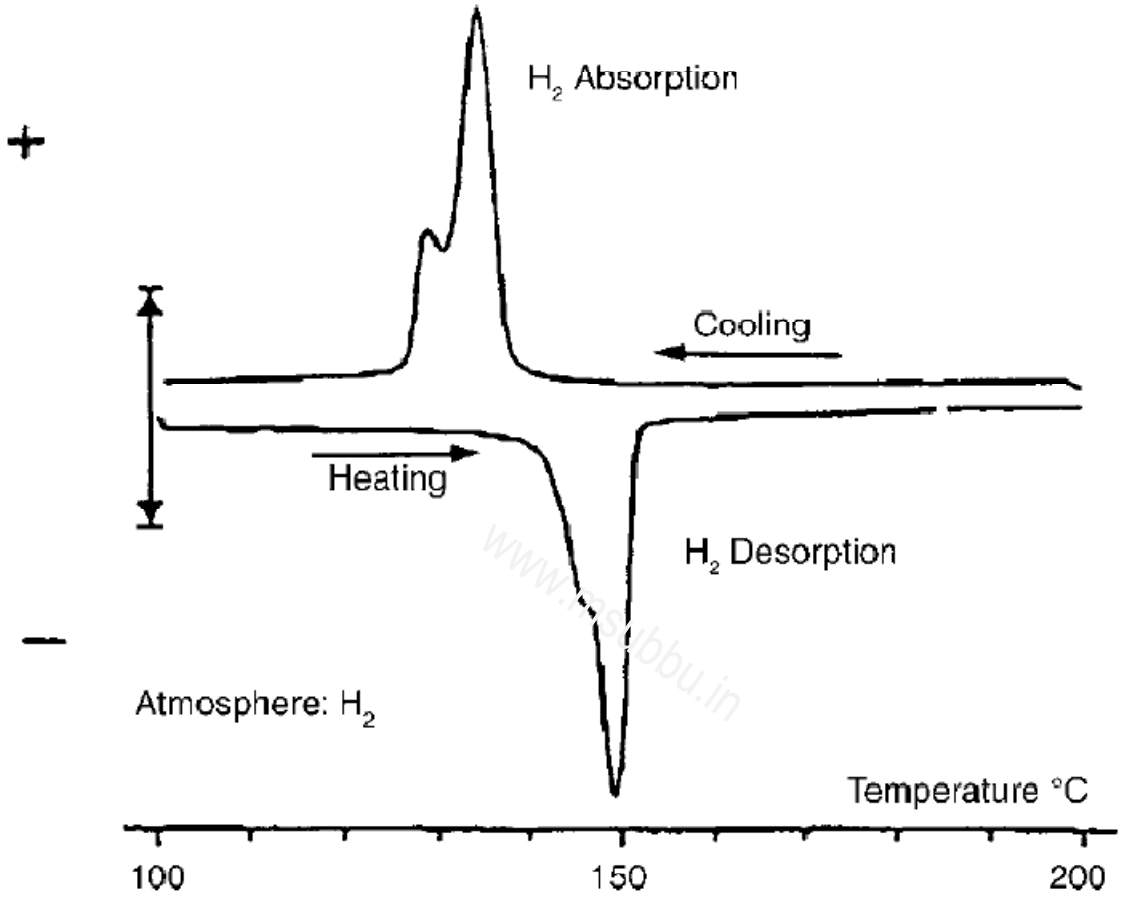


Figure 16.24 DSC thermal curve of adsorption and desorption of hydrogen from a precious metal catalyst under constant pressure.

Robinson et al., Undergraduate Instrumental Analysis, 6th edition, Marcel Dekker, New York

Specific Heat Measurement by DSC

- The specific heat (heat capacity, *C*p) of a material can be determined quantitatively using DSC and is designated C_p since values are obtained at constant pressure.

- Three runs are required to obtain the value of C_p:
  - First run: a baseline with uncrimped empty pans placed in the furnace.
  - Second run: as above but adding a reference (typically sapphire) to the sample pan.
  - Third run: replace the reference with your sample.

- The DSC must be very stable and in practice it is best not to use an instrument at the extremes of its temperature range where stability may be compromised. The standard most often used is sapphire, and the mass used should be similar to the sample

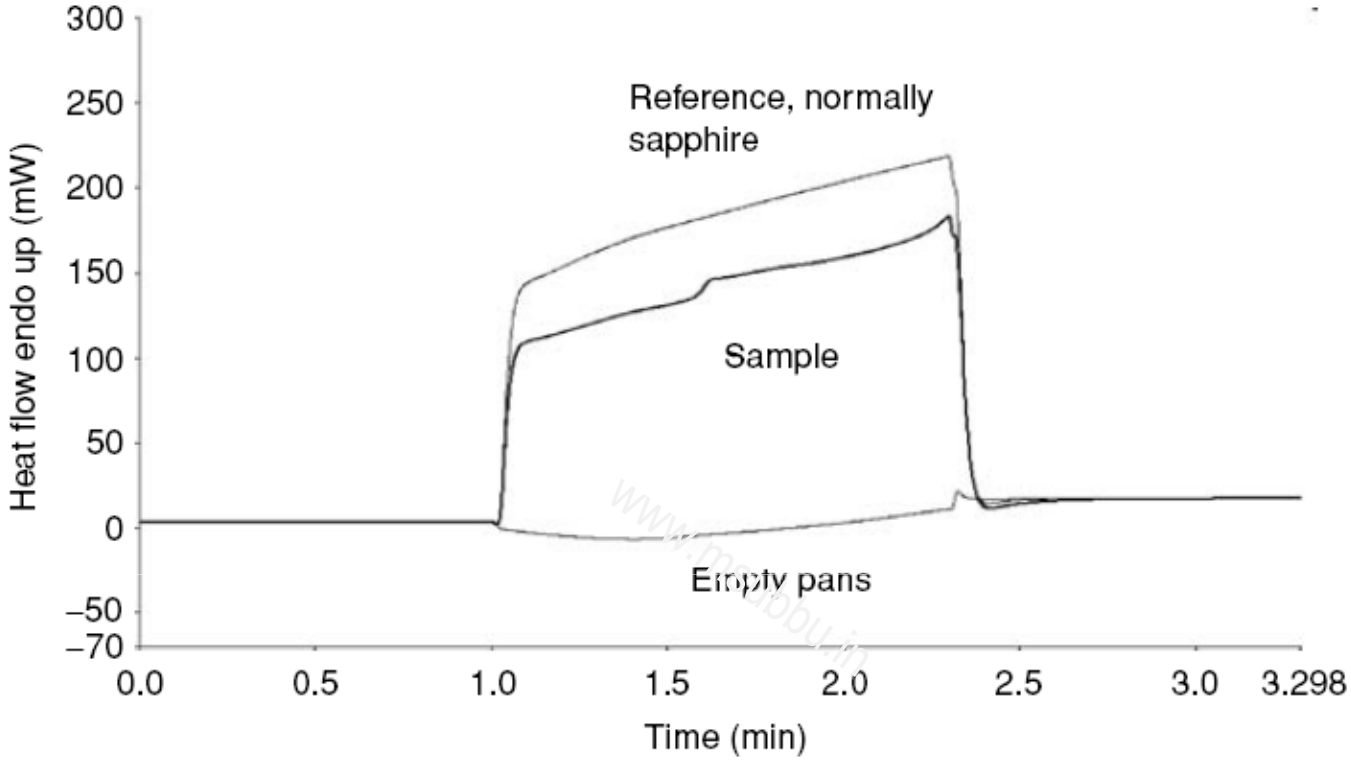


Figure 1.1 Heat capacity of PET obtained using fast scanning techniques showing the three traces required for subtraction. The height of the sample compared to the empty pan is divided by the scan rate and the mass of sample to obtain a value for C_p. This is referenced against a known standard such as sapphire for accuracy.

Paul Gabbott (ed), Principles and Applications of Thermal Analysis, Blackwell Publishing Ltd., Oxford, 2008.

Effect of Scan Rate

- Traditionally, the most common scan rate used by thermal analysts is 10◦C/min, but with commercially available instruments rates can be varied between 0.001 and 500◦C/min, often to significant advantage.

- **Senitivity**: An increased scan rate leads to an increase in sensitivity, so do not use slow rates for small difficult-to-find transitions, unless otherwise unavoidable. The reason for this is that a DSC measures the *flow* of energy and during a fast scan the flow of energy increases, though over a shorter time period.

- ***Resolution****:* Because of thermal gradients across a sample the faster the scan rate the lower the resolution, and the slower the scan rate the sharper the resolution. Thermal gradients can be reduced by reducing sample size and improving thermal contact with the pan by good encapsulation.

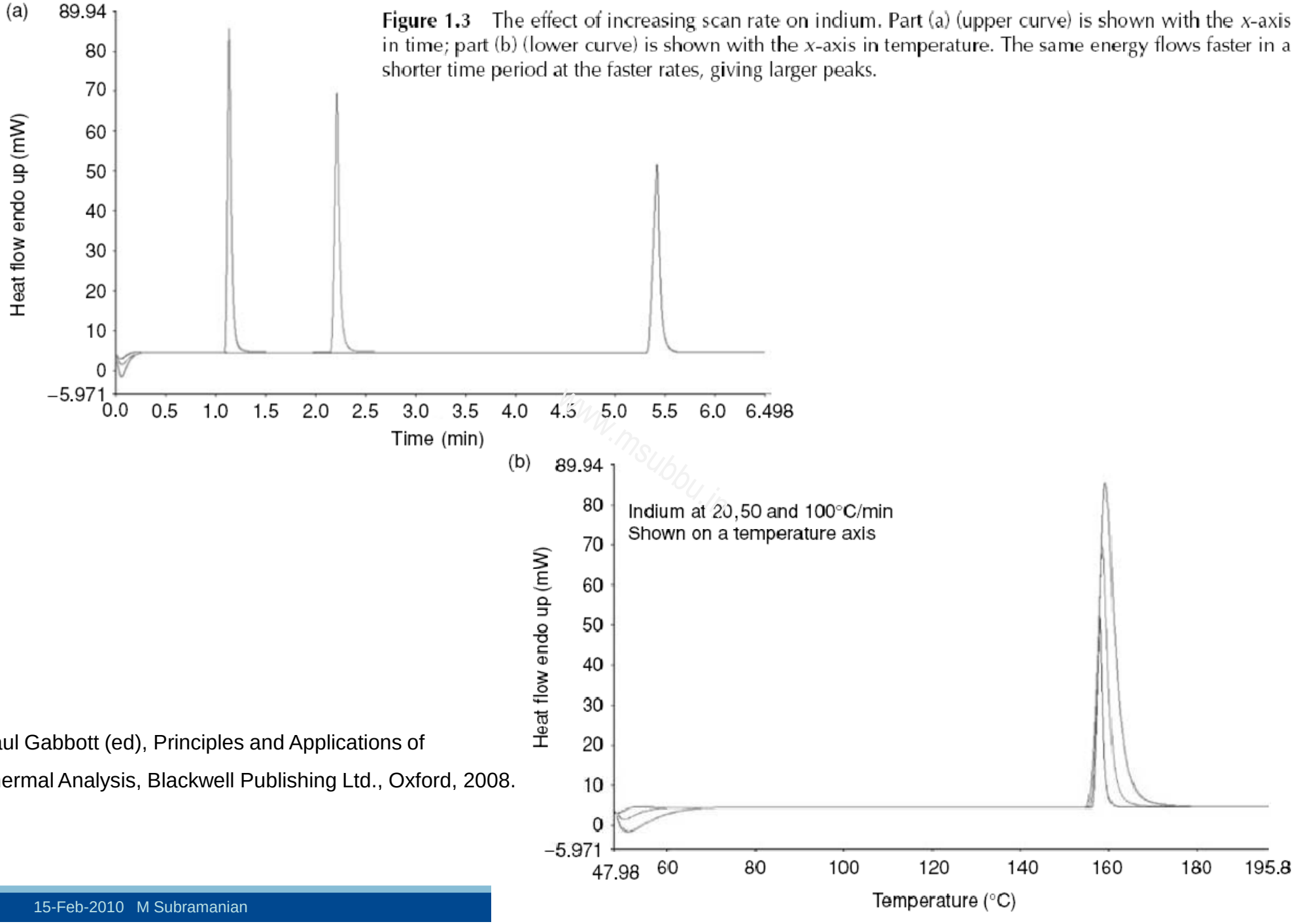


Figure 1.3 The effect of increasing scan rate on indium. Part (a) (upper curve) is shown with the *x*-axis in time; part (b) (lower curve) is shown with the *x*-axis in temperature. The same energy flows faster in a shorter time period at the faster rates, giving larger peaks.

Paul Gabbott (ed), Principles and Applications of Thermal Analysis, Blackwell Publishing Ltd., Oxford, 2008.