



FIGURE 9 Differential thermal analysis and impedance (1000 Hz) of pure glycerol.

again. However, in the course of rewarming it generally undergoes a major structural change known as the *vitreous transformation*. During this process the glass, still in the solid phase, evolves from a solid-like state (with low specific heat and low specific volume) to a liquid-like state with a sharp increase in specific heat and specific volume. This occurs at a well-known temperature, the temperature of vitreous transformation, generally quoted as T_g . A typical example, pure glycerol, is shown in Figure 9. This phenomenon is fully reversible.

In some other cases the glass, when rewarmed, becomes highly unstable, and when the *vitreous transformation* is completed (or sometimes during this transformation itself) it crystallizes out abruptly showing a marked exothermic peak. This, to the contrary, is an irreversible process called *devitrification* (Fig. 10). All of the glass might then disappear or it might devitrify only partially. If the material is then cooled again and rewarmed a second time, the initial vitreous transformation disappears or is substantially reduced (and sometimes shifted to a higher temperature) and the exothermic peak no longer exists. During this cycle, which we called "thermal treatment" in 1960, the metastable system became unstable and has been "annealed." Figure 11 shows this type of evolution in a glycerol-water-Cl Na system. It is worthwhile mentioning that in both cases the vitreous transformation initiates a marked decrease of the electric impedance, though at first sight the system remains a compact solid.

The magnitude and temperature of these events are of course dependent on the system under investigation, as can be seen in Figure 12, which compares D_2O /glycerol and H_2O /glycerol mixtures.

This type of behavior is not uncommon in pharmaceutical preparations. Indeed, it is often required that a thermal treatment be applied to the material to