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**SOME APPLICATIONS OF THERMOMECHANICAL
ANALYSIS**

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The purpose of this work was to show some possibilities of Thermomechanical Analysis in material research. It was demonstrated that the intercalation process or physical aging of non-crystalline materials can successfully be studied by this method. The measurement of thermal expansion coefficient of solids or viscosity of highly undercooled glass forming liquids are interesting applications. The results of these measurements yield valuable information which can be of help in material processing.

Introduction

In thermomechanical analysis (TMA), the dimensional change (expansion, contraction) is measured under defined load (static or dynamic) as a function of time or temperature. This requires a high-resolution measurement of the linear displacement and, therefore, a sensitive TMA instrument is needed for a reliable measurement. By using TMA technique the following properties of a material can be measured:

- Thermal expansion coefficient in defined temperature interval (linear

approximation method)

- Temperature dependence of thermal expansion coefficient
- Softening points of amorphous materials and melting of crystalline materials
- Volume relaxation and physical aging of non-crystalline solids
- Changes of viscoelastic properties of materials
- Glass transformation temperature
- Viscosity measurements
- Dimensional changes of crystals during dehydration, intercalation etc.
- Softening of thin films and coatings
- Residual stress in materials

Some of these measurements require, however, high sensitivity and excellent baseline stability of the TMA instrument. Most TMA instruments available on the market, unfortunately, allow no such sensitive measurements as e.g. the volume relaxation process of non-crystalline solids below the glass transition temperature or intercalation process in extremely thin layer crystals. This was the main reason why the new TMA CX03RA/T instrument was developed. In this report we describe some practical applications of this newly developed instrument.

Experimental

Materials

The materials studied were $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ for intercalation studies, arsenic sulfide glass for thermal expansion coefficient and physical aging measurements, and Standard lead silica glass NBS 711 for viscosity measurements. The test samples were approximately 2 mm thick for thermal expansion and viscosity measurement and about 8 mm thick for physical aging studies. All the measurements were carried out in air atmosphere.

Instrumentation

The TMA CX03RA/T instrument was developed to provide a highly sensitive tool for reproducible measurements of subtle dimensional changes even during extremely long isothermal annealing. In conventional TMA instruments the sample is placed on a quartz base and a measuring probe (weight is compensated) measures its dimension. In the case of CX03RA/T instrument the sample is placed on a movable sample tray connected with a displacement sensor which measures dimensional changes of the sample. Schematic outline of the instrument is shown in Fig. 1. This construction design improves

considerably the temperature stability and decreases the sample holder deformation. Basic technical specifications of the CX03RA/T instrument can be summarized as follows:

- Temperature range of furnace: room temperature - 750 °C (up to 1000 °C with thermocouple Pt-PtRh)
- Heating rate: 0.1 - 20 °C/min
- Cooling rate: up to 20 °C/min (depending on furnace temperature)
- Temperature precision: min. ± 2 °C (typically ± 0.2 °C)
- Sample temperature measurement: typically better than ± 2 °C¹⁾
- Number of program steps: 1 - 40
- Max. length of isotherm: 9999 min, i.e. approx. 166 h
- Max. length of the Temp/Force program: min. 266 days
- Max. sample diameter: 6 mm (typically 8mm)
- Max. sample length: 16mm (typically 20mm)²⁾
- Displacement sensor measuring range: 0 - 20 mm
- Max. dimensional change: ± 3 mm
- Resolution: 0.01 μm
- Linearity: better than 0.1% (20 mm scale)
- Noise level: lower than 0.02 μm (without filtering)
- Baseline drift (as a function of room temperature): typically ± 0.05 $\mu\text{m}/^{\circ}\text{C}$
- Baseline drift (as a function of furnace temperature): lower than ± 0.002 $\mu\text{m}/^{\circ}\text{C}$ ³⁾
- Baseline drift (as a function of time): typically lower than ± 0.1 $\mu\text{m}/\text{day}$
- Probe loading: 0 to 1000 mN (step mN)
- Accuracy of load programmed: typically ± 1 % (of programmed force)
- Maximum time of probe loading in dynamic regime: 1 to 9999 min

The displacement sensor is the most important part of the TMA instrument and considerable effort was focused on its development. A completely new concept of displacement sensor different from classical LVDT (Linear Variable Differential Transformer) ensures linearity (better than 0.1%), high sensitivity (0.01 μm resolution), low noise (typically 0.02 μm without signal filtering), good temperature stability (typically 0.05 $\mu\text{m}/^{\circ}\text{C}$) and small drift (0.1 $\mu\text{m}/\text{day}$). The temperature of the displacement sensor and some electronic parts is precisely controlled, which improves the baseline stability and reproducibility. Because of this design and exceptionally low noise level, extremely sensitive measurements can be performed even on a routine basis. As the measuring range of the displacement sensor is higher than 20 mm, it is

¹⁾ depending on thermocouple location near the sample

²⁾ without special quartz plates

³⁾ in the temperature range 0 - 750 °C

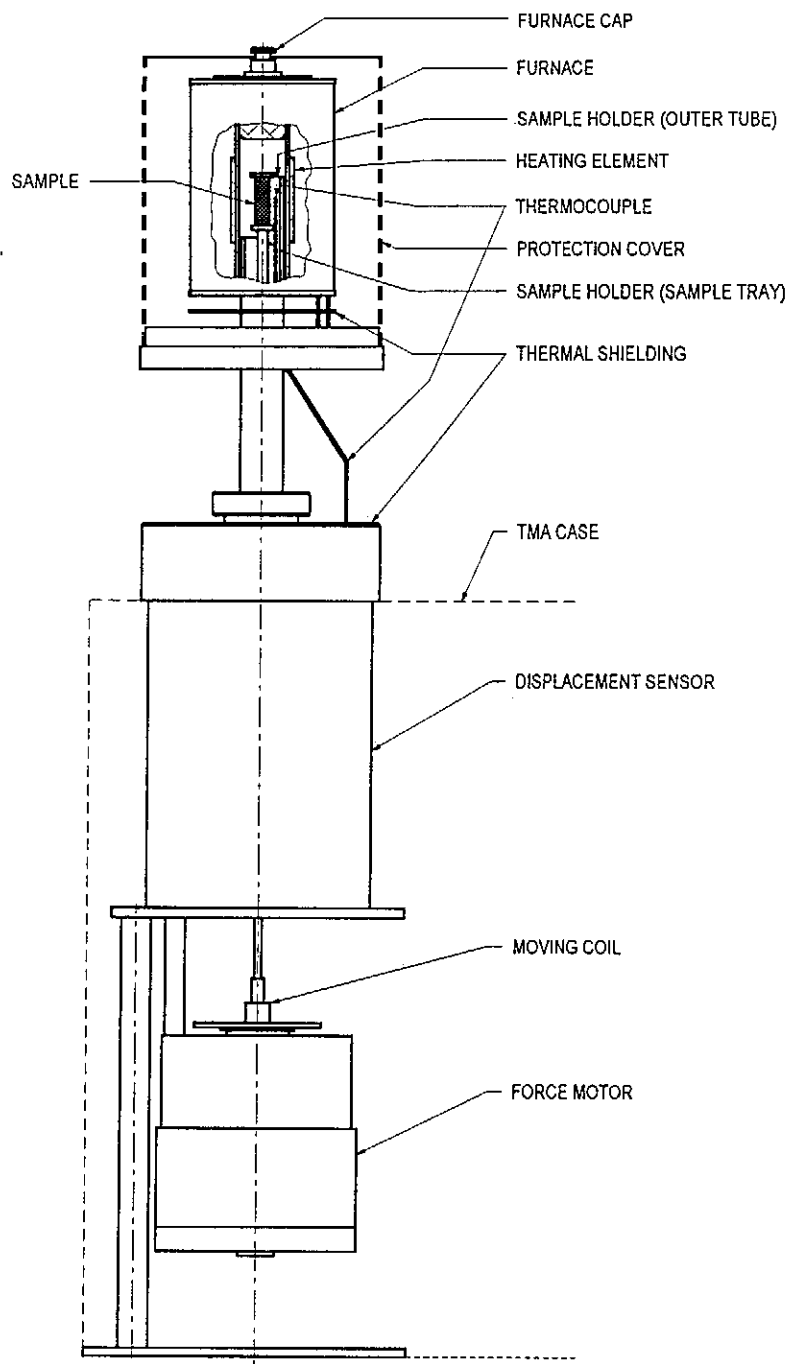


Fig. 1 Schematic outline of the Thermomechanical analyzer CX03RA/T.

possible to measure height directly and, therefore, it is not necessary to adjust mechanically any part of the analyzer. This also improves temperature stability and reliability of the instrument.

A novel electronic system is used to control the load generating linear motor which can be expanded to flexible high-performance dynamic operation. Loading up to 1000 mN (1 mN steps) may be programmed in two modes: constant load and dynamic load where it is possible to change loading during the measurement by means of precise electronic and computer control of the instrument. The furnace heater is designed to give high mechanical resistance and long life even at maximum temperatures. Situated above the TMA instrument, the furnace possesses good homogeneity and temperature stability, major qualities for producing good thermomechanical measurements. The volume of the furnace tube is minimized to allow the inner atmosphere to be replaced rapidly. Various inert gasses (nitrogen, helium etc.) may be utilized. The inert gas is first preheated in the furnace mantle and then introduced into the sample holder.

All functions (such as tare of the probe, zero load and temperature control) are fully controlled through the computer. The instrument is designed as an independent module which can be connected and controlled by virtually any PC/AT computer by means of two expansion cards (these cards and software for instrument control are supplied). There are several calibration procedures (zero height, temperature setting, linear motor calibration etc.) automatically taking place when the instrument is switched on. Then the measured sample can be placed in and the measurement program entered. The measurement program may contain up to 40 independent steps representing temperature regime (heating, cooling or isothermal holding) and force program (static force 0 - 1000 mN or cyclic switching of two different forces). The maximum time for one program step is 160 hours, i.e. total length of the measurement program may be up to about 266 days. These measurement programs can be saved for future reference and use, which is important e.g. for routine testing in industry.

Another function is monitoring, where the dimensional changes of the sample are measured at room temperature. Loading can be changed during the monitoring regime and the measured data can be saved on hard disk. During TMA measurement experimental data are stored on hard disk. Each program step is saved as an independent ASCII type file (temperature - height - time). During the measurement it is possible to stop the program and skip to another program step or to finish the experiment. A special software for data processing is supplied with the instrument either in MS DOS or Windows version. Advanced software tools for applications such as viscosity measurements and volume relaxation of glasses are available. Both data and graphs can be exported into most graphical and spreadsheet software packages.

Results and Discussion

Observation of the Intercalation and Deintercalation Process

One of interesting application of TMA technique is the study of influence of liquids on some materials such as the study of resistance of rubber or polymers in oils, organic solvents etc. Another similar application in this respect is the study of intercalation process. The changes of thickness of the crystal of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ during heating are shown in the left part of Fig. 2 (Refs^{1,2}). The original thickness of the dihydrate ($l = 0.059$ mm) decreases relatively rapidly to 0.047 mm (monohydrate) and then more slowly to 0.027 mm (dehydrated $\alpha_1 - \text{VOPO}_4$). The right part of Fig. 2 describes the behaviour of the dehydrated sample left at room temperature in the flow of wet air, i.e. intercalation of water into $\alpha_1 - \text{VOPO}_4$. The thickness of the crystal returns to the original value within 1.5 hour. No significant dwell corresponding to a monohydrate formation was observed².

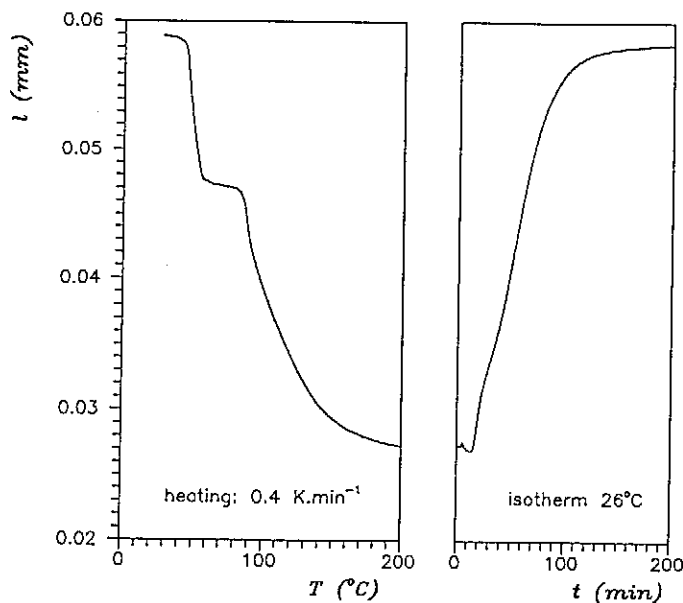


Fig. 2 The changes of the thickness l of the crystal $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ due to deintercalation of water during heating (left part) and intercalation of water at 26 °C (right part)

The thermomechanical analysis has proved to be a useful method for following the dehydration course of layered materials. This method may as well be used for studies of other deintercalation and intercalation processes which are connected with a change of basal spacing². From this point of view it can be considered as an useful complementary diagnostic method to the X-ray

diffraction analysis which is frequently used for intercalation and deintercalation studies.

Thermal Expansion Coefficient

Thermal expansion coefficient is critical to the performance of many composite materials, glasses and polymers. TMA instrument provides accurate and reproducible results of thermal expansion coefficient as illustrated in Fig. 3 for arsenic sulfide glass annealed 20 hours at different temperatures. It is seen that the glass studied exhibits practically constant thermal expansion coefficient ($\alpha_g = 22.3 \pm 0.2$ ppm/K) below the glass transition temperature T_g followed by rapid increase above T_g . The maxima in the $\alpha(T)$ dependence correspond to the structural relaxation caused by physical aging below T_g . This phenomenon is described in the following section.

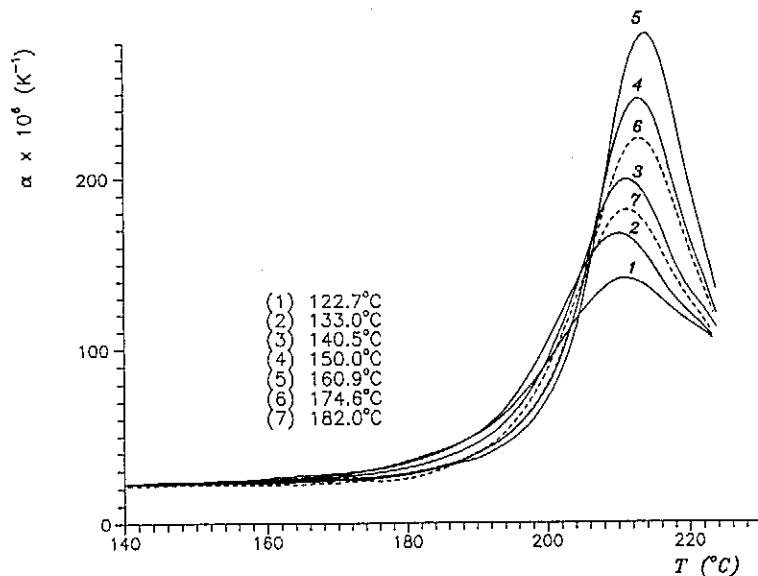


Fig. 3 Temperature dependences of the thermal expansion coefficient of the As_2S_3 glass annealed 20 hours at different temperatures below T_g

Physical Aging

It is well known that non-crystalline solids are not in thermodynamic equilibrium at temperatures below their glass transition T_g , and their properties such as volume, entropy, enthalpy, are subjected to changes with time³. As the

non-equilibrium state appears to be unstable, the material undergoes a process of structural relaxation which attempts to establish a metastable state of equilibrium. This gradual continuation of the glass formation has been called *physical aging*. The description of the influence of physical aging on the mechanical properties of polymers is not only of scientific interest but also of utmost technical importance with respect to the long time application of polymeric materials and glasses.

The process of physical aging is schematically represented in Fig. 4.

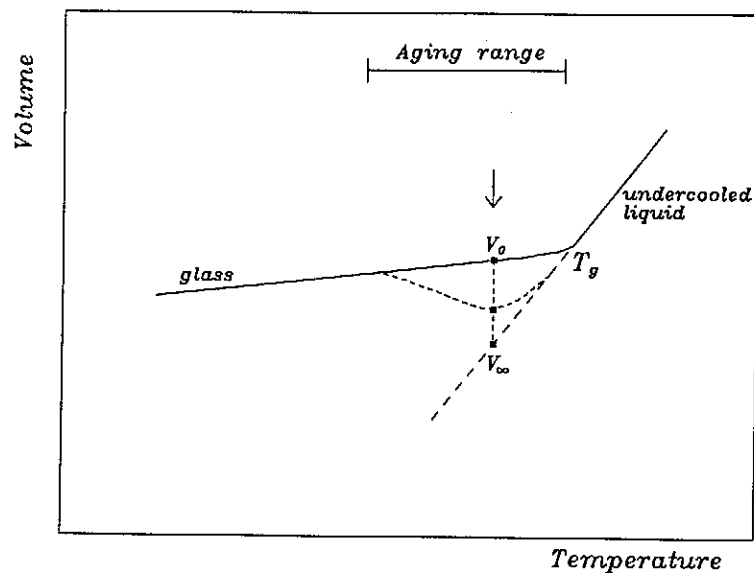


Fig. 4 Schematic diagram of the changes in the specific volume of a glass in the process of isothermal annealing below T_g . Extrapolated equilibrium line of undercooled liquid is shown by broken line. Dotted line shows volume changes corresponding to isothermal annealing of a glass for a given time period

Above T_g the equilibrium line for volume versus temperature is almost straight. This equilibrium line can be extrapolated into the region below T_g . For very low temperatures such an extrapolation brings some problems known as the Kauzmann paradox⁴ but for temperatures say $T_g - 50$ it is plausible. After a quench from the equilibrium above T_g into the non-equilibrium glassy state, the non-crystalline material shows a continuous decrease of the specific volume with time. This macroscopic volume contraction is isotropic and, therefore, it can directly be measured by TMA technique as the sample length change. For practical purposes it is useful to define a new variable^{5,6}

$$\delta = \frac{V - V_{\infty}}{V_{\infty}} \quad (1)$$

Which measures the deviation of the specific volume from its value in equilibrium. The isothermal volume contraction behaviour of the arsenic sulfide glass is shown as the $\delta(\log t)$ function in Fig. 5. This behaviour is due to the decrease of free volume of the material and it is accompanied by a loss of mobility of the molecular clusters in non-crystalline matrix. It is presumed that this change of free volume and mobility is the origin of the variation of physical properties during aging. A deeper insight into the volume relaxation phenomenon of non-crystalline solids should therefore lead to a better understanding of the aging behaviour.

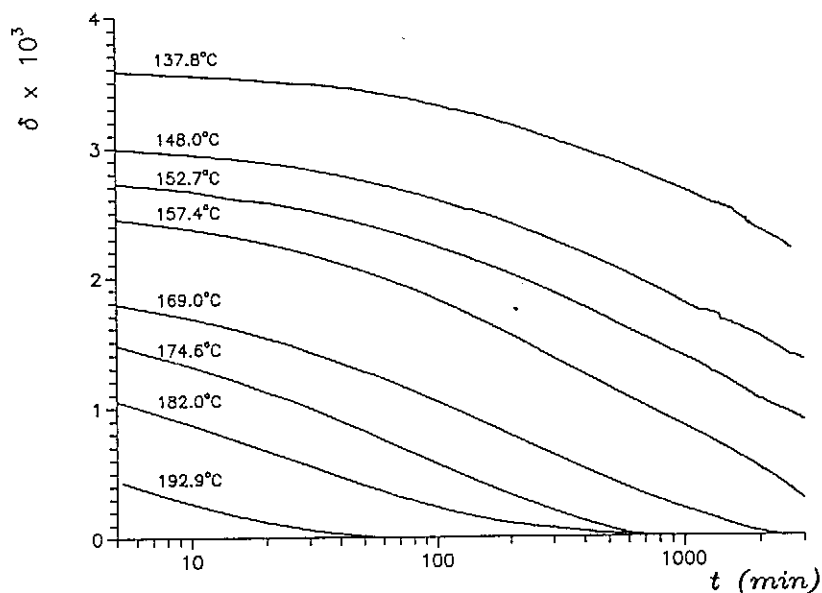


Fig. 5 Time dependence of the relaxation function δ for the As_2S_3 glass at different temperatures below T_g

Volume relaxation of polymers was thoroughly studied by Kovacs^{5,6} using classical mercury filled dilatometers. His excellent papers are frequently cited until now but because of tediousness and complication inherent to classical dilatometry techniques there are only few followers in this direction. In recent years, these dilatometric studies were replaced mainly by Differential Scanning Calorimetry. Unfortunately, this technique cannot provide a direct measurement of the relaxation $\delta(\log t)$ function as shown above. Using a high sensitive TMA CX03RA/T instrument we can study directly volume relaxation even for high T_g inorganic glasses.

Viscosity Measurement

Viscosity in the range of $10^7 - 10^{12}$ Pa s can be measured by a penetration method where a sphere of radius R loaded by a force F penetrates into the sample. The penetration depth l is measured as a function of time t and the viscosity is then determined using equation^{7,8}

$$\eta = \frac{9}{32\sqrt{2R}} \frac{Ft}{l^{2/3}} \quad (2)$$

Therefore, the viscosity may conveniently be determined from the rate of penetration of a hemispherical indenter into the sample. This method is absolute and thus no calibration is needed. The measurement procedure can be outlined as follows:

- Flat specimen of a glass (polished to optical quality) is placed on a quartz plate and a hemispherical quartz indenter is placed over this sample
- Before making any measurement, the specimen and indenter are brought to the desired temperature. Typical scanning parameters: Heating rate 10 K/min, Load 1 mN. Five minutes are then allowed for thermal equilibration.
- The force in the range of $10 < F < 1000$ mN is applied to the hemispherical indenter and the penetration depth is measured as a function of time.
- After one determination is finished, the indenter may be raised and moved over a different part of specimen and a new measurement can be performed.

Viscous flow, like any kinetic process, requires time. In the range above 10^{11} Pa s the viscosity can no longer catch up with any fast cooling rate. Therefore, it should be stressed that the viscosity is dependent on the entire thermal history within the glass transition range. This was documented long ago, for example, by Lilie⁹.

Figure 6 shows a typical time dependence of viscosity for NBS711 glass measured using the procedure described above. It is evident that in this case it takes about 2 hours to get an equilibrated value of the viscosity. A comparison between our experimental results and data published for NBS 711 glass^{10,11} is shown in Fig. 7.

Conclusion

The results of the studies of intercalation and deintercalation processes of water in vanadyl phosphate and physical aging study of glassy arsenic sulfide clearly demonstrated the usefulness of the Thermomechanical analysis for material

research. Other valuable pieces of information such as temperature dependences of thermal expansion coefficient or viscosity, which can aid in materials selection, optimization of processing and quality control can easily be obtained.

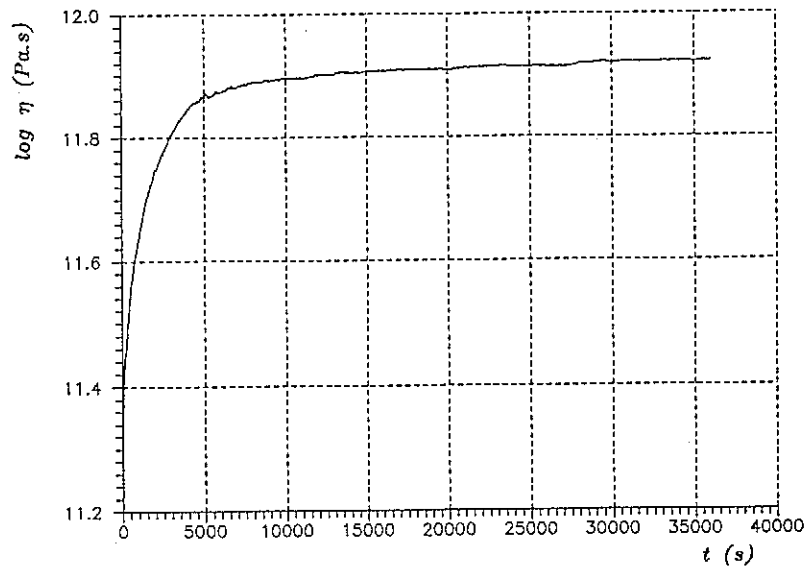


Fig. 6 Time dependence of viscosity of the NBS 711 lead silica glass measured by penetration method at the temperature of $443.1 \pm 0.2 \text{ }^\circ\text{C}$

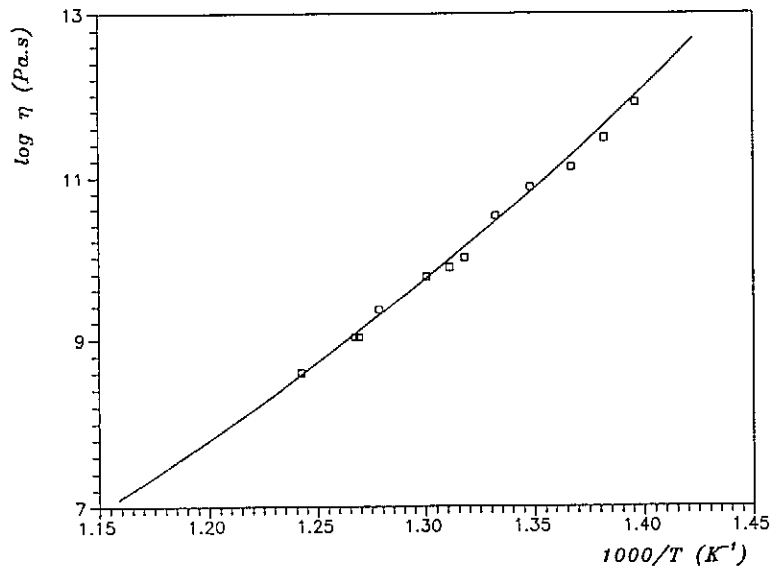


Fig.7 The comparison of measured viscosity (points) of the NBS 711 standard and literature data¹¹ (full line)

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