Relaxation Processes in Glass and Polymers

Lecture 2: Phenomenology of viscoelasticity & glass transition

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Research and Technology Development

SCHOTT AG

In the following, examples from the progress of relaxation research in glass will be shown in order to illustrate what relaxation is about. It is neither a comprehensive picture of the history of relaxation research nor a balanced assessment of the contributions of all individuals involved.

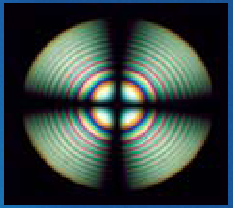
To illustrate glass properties, references will be made to different companies. These references have been picked arbitrarily for educational reasons, copyright issues etc., not to provide a balanced view of the achievements of different companies.

Despite its careful preparation, the manuscript may contain errors.

Dr. Ulrich Fotheringham

Observation 1a (before 1912!):

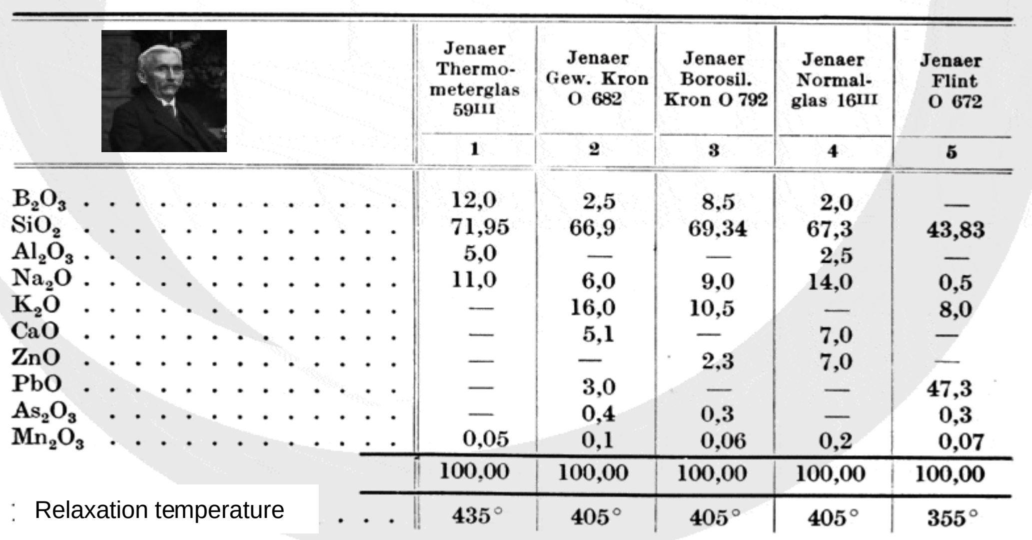
Glass, if heated to high temperatures and cooled down rapidly, shows birefringence like Calcite:



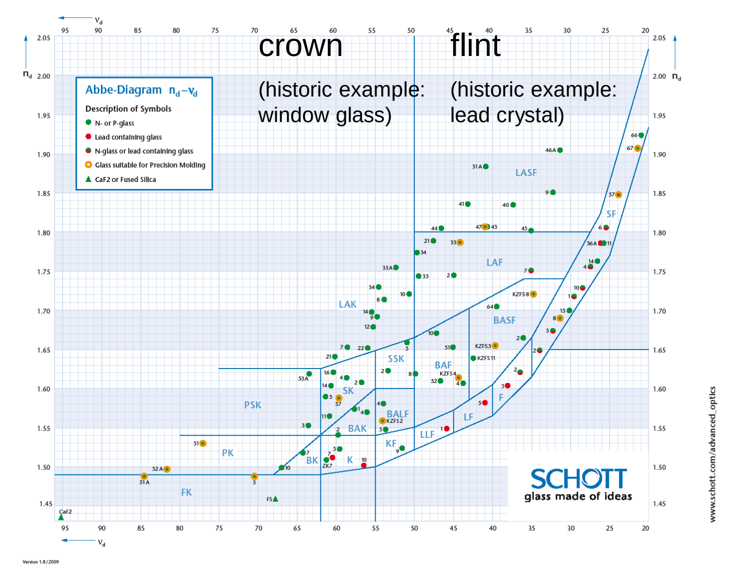
(calcite birefringence picture from Carl Zeiss AG, information on polarisation microscopy)

In contrast to the permanent birefrigence of Calcite, the birefringence in glass is stress-induced.

Otto Schott found that it will relax if the sample is held for 24h at a minimum temperature which depends on the composition:



	Jenaer Thermo-meterglas 59III	Jenaer Gew. Kron O 682	Jenaer Borosil. Kron O 792	Jenaer Normal-glas 16III	Jenaer Flint O 672
	1	2	3	4	5
B_2O_3	12,0	2,5	8,5	2,0	—
SiO_2	71,95	66,9	69,34	67,3	43,83
Al_2O_3	5,0	—	—	2,5	—
Na_2O	11,0	6,0	9,0	14,0	0,5
K_2O	—	16,0	10,5	—	8,0
CaO	—	5,1	—	7,0	—
ZnO	—	—	2,3	7,0	—
PbO	—	3,0	—	—	47,3
As_2O_3	—	0,4	0,3	—	0,3
Mn_2O_3	0,05	0,1	0,06	0,2	0,07
	100,00	100,00	100,00	100,00	100,00
Relaxation temperature	435°	405°	405°	405°	355°



crown

(historic example: window glass)

flint

(historic example: lead crystal)

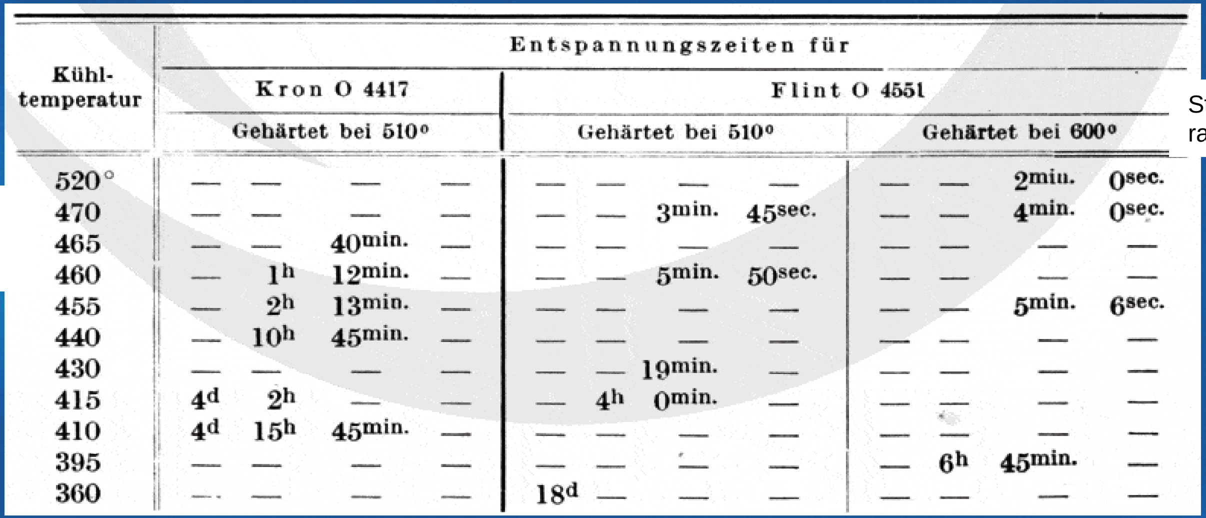
(left: from Zschimmer, Chemische Technologie des Glases, Jena, 1913;
Right: Abbe-Diagram with optical glasses from Schott AG, from Internet)

Observation 1b (before 1912!):

Similarily, Schott´s coworker Zschimmer measured relaxation times of stressed cubes (by a rapid quench from a high temperature) at different temperatures:

Temperature at which relaxation was investigated

Start temperature of rapid quench



Kühl-temperatur	Entspannungszeiten für											
	Kron O 4417				Flint O 4551							
	Gehärtet bei 510°				Gehärtet bei 510°				Gehärtet bei 600°			
520°	—	—	—	—	—	—	—	—	—	—	$2^{miu.}$	$0^{sec.}$
470	—	—	—	—	—	—	$3^{min.}$	$45^{sec.}$	—	—	$4^{min.}$	$0^{sec.}$
465	—	—	$40^{min.}$	—	—	—	—	—	—	—	—	—
460	—	1^{h}	$12^{min.}$	—	—	—	$5^{min.}$	$50^{sec.}$	—	—	—	—
455	—	2^{h}	$13^{min.}$	—	—	—	—	—	—	—	$5^{min.}$	$6^{sec.}$
440	—	10^{h}	$45^{min.}$	—	—	—	—	—	—	—	—	—
430	—	—	—	—	—	—	$19^{min.}$	—	—	—	—	—
415	4^{d}	2^{h}	—	—	—	4^{h}	$0^{min.}$	—	—	—	—	—
410	4^{d}	15^{h}	$45^{min.}$	—	—	—	—	—	—	—	—	—
395	—	—	—	—	—	—	—	—	—	6^{h}	$45^{min.}$	—
360	—	—	—	—	18^{d}	—	—	—	—	—	—	—

The interpretation was: The rapid quench leads to the freezing of deformations ε. This causes stress σ (M elastic modulus):

$$\sigma = M \cdot \varepsilon$$

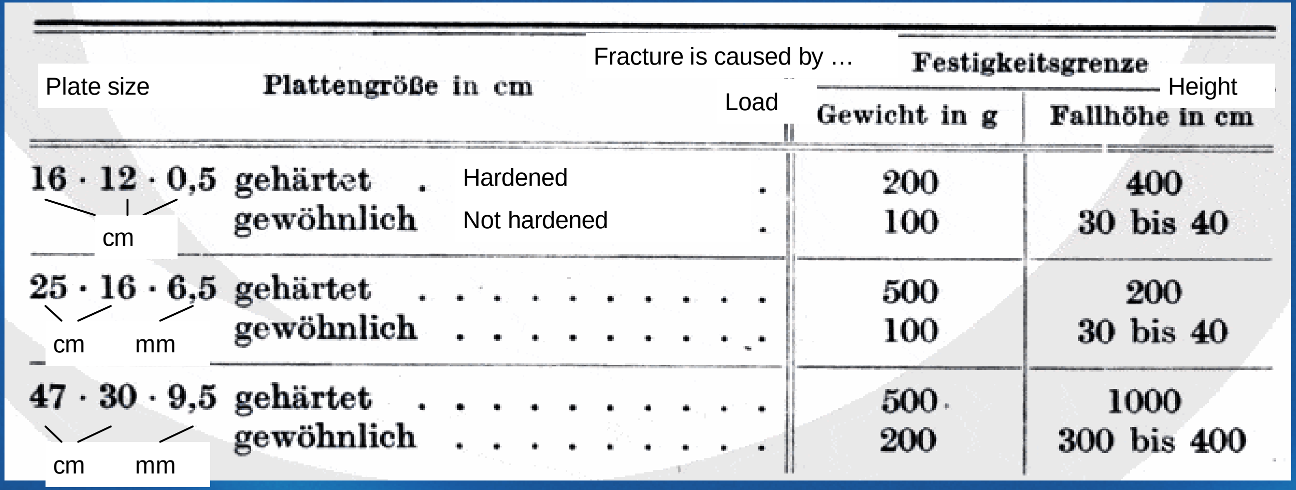
At high temperatures, the stress will relax via viscous flow. If one assumes stress relaxation to be proportional to the remaining stress, one arrives at Maxwell´s relaxation law (τ: relaxation time):

$$\sigma = \sigma_0 \cdot e^{-t/\tau}$$

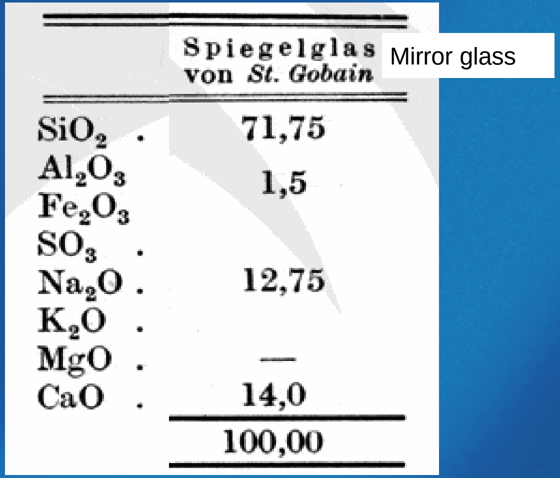
(from Zschimmer, Chemische Technologie des Glases, Jena, 1913)

Observation 1c (1875 and 1877!):

Hardening of glass. De Bastie found that by a very rapid quench such as by diving a hot glass plate into water, glass can be hardened.
Having loads fall from rising heights onto glass plates, Luynes found the following significant increase in toughness:



Plattengröße in cm		Festigkeitsgrenze Gewicht in g	 Fallhöhe in cm
16 · 12 · 0,5	gehärtet	200	400
	gewöhnlich	100	30 bis 40
25 · 16 · 6,5	gehärtet	500	200
	gewöhnlich	100	30 bis 40
47 · 30 · 9,5	gehärtet	500	1000
	gewöhnlich	200	300 bis 400



	Spiegelglas von *St. Gobain*
SiO_2	71,75
Al_2O_3	1,5
Fe_2O_3	
SO_3	
Na_2O	12,75
K_2O	
MgO	—
CaO	14,0
	100,00

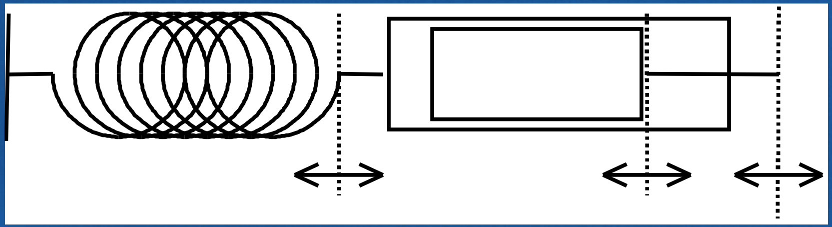
In Zschimmer´s book, this is explained this way: The rapid quench makes the surfaces become rigid quickly which causes intermediary stress between the surfaces and the core. As the core remains soft for some time, these stresses relax. When the core glass stiffens itself, however, it acts like a contracting spring. At the end, there will be permanent compression in the surface and permanent tension in the core.

(from Zschimmer, Chemische Technologie des Glases, Jena, 1913)

Understanding Observations 1a-c, Part 1:

1. Stress relaxation: discovered and made use of > 100 years ago (hardening!).
2. Today we know that there are different stress relaxation mechanisms in glass.
3. Most important mechanism is shear stress relaxation which was discovered investigating fluids by James Clerk Maxwell in 1866.

   Maxwell considers certain materials to be viscoelastic which may be symbolized by combining a spring and a dashpot:

   If the material is sheared, stress will result (elongation of the spring) which may be permanent (hardening) but will relax via viscous flow (dashpot) at high temperatures.
4. Maxwell relaxation time (η: shear viscosity, G: shear modulus):

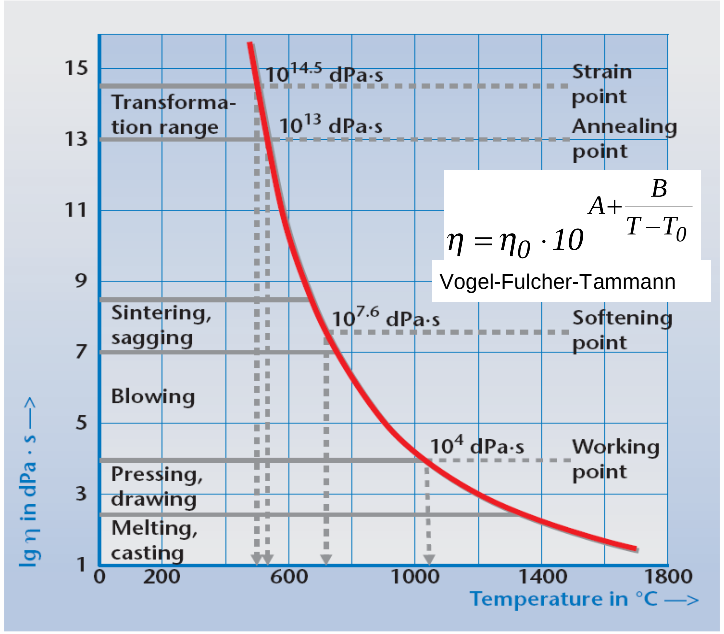
$$\boxed{\tau = \eta / G}$$

Plausibility: τ increases with η: o.k.

τ decreases with G: the higher the modulus, the smaller the deformation for a given stress level and therefore the smaller the path to be covered by viscous

Understanding Observations 1a-c, Part 2:

Viscosity and elastic moduli data.



$$\eta = \eta_0 \cdot 10^{A+\frac{B}{T-T_0}}$$

Vogel-Fulcher-Tammann

Fig. 9. *Typical viscosity-temperature curve; viscosity ranges for important processing techniques and positions of fixed viscosity points*

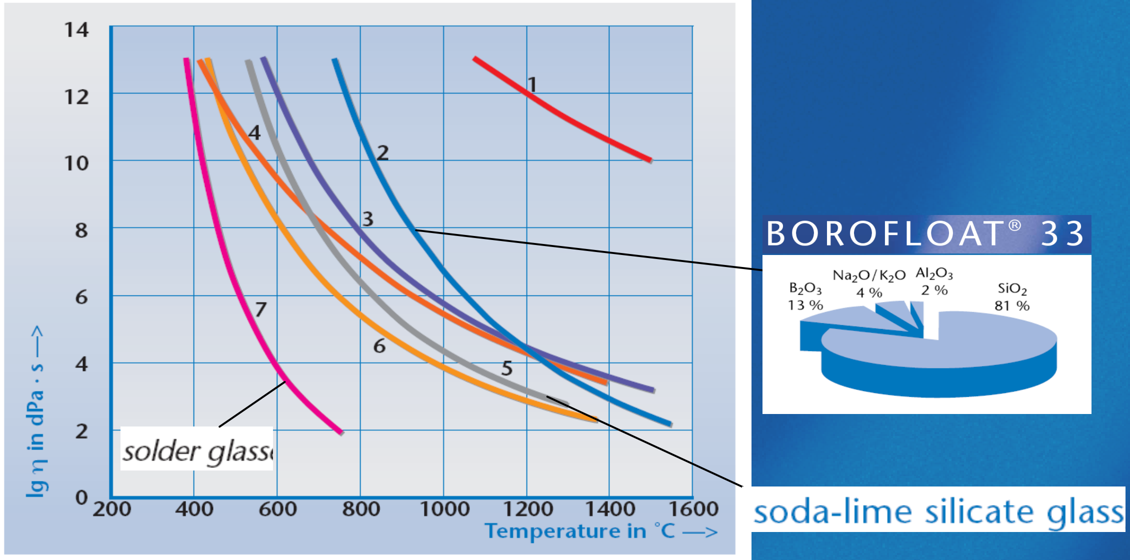


Fig. 10. *Viscosity–temperature curves for some important technical glasses. 1: fused silica, 2: 8409, 3: 8330, 4: 8248, 5: 8350, 6: 8095, 7: 8465. Glasses with steep gradients (7) are called "short" glasses and those with relatively shallow gradients (4) are "long" glasses*

The elastic moduli for most technical glasses is within the range of 50 – 90 GPa. The mean value of 70 GPa is about equal to the Young's modulus of aluminum. The Poisson's ratio of most glasses is in the range 0.21 to 0.25 and is lower than for metals or plastics.

Melting, casting, pressing, drawing, sagging: Maxwell´s relaxation time is extremely short. What is true in the transformation range? Why is it called such and used for stress relaxation? See next slide.

(Left: from Technical Glass Guide, Schott AG; Internet;
Right: from Borofloat® Product Information, Schott AG; Internet)

Some exercises:

1. Assume that the relaxation observed follows Maxwell´s law. Assume that the times given by Zschimmer mean that birefrigence has decreased to 1% of its original value. What are the Maxwell relaxation times at 470°C and at 520°C for the flint glass quenched from 600°C?

2. Consider the solder glass at ca. 380°C. Assume that Young´s modulus E is 48 GPa and that Poisson´s ratio ν is 0.2. Calculate the shear modulus G:

   $$G = \frac{E}{2 \cdot (1+\nu)}$$

   Calculate Maxwell´s relaxation time at 380°C. Go back by 1 slide and guess why the temperature region around 380°C is called transformation range.

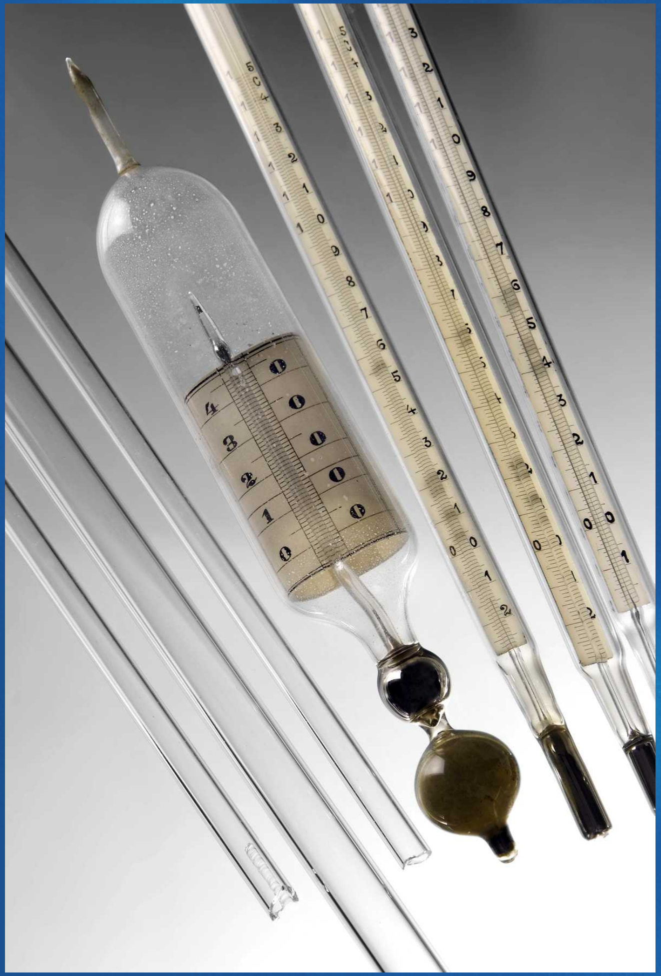
3. (Optional:) Assume that the temperature dependence of a Maxwell relaxation time is of the Arrhenius type, i.e.

   $$\tau = \tau_0 \cdot e^{\frac{H}{R \cdot T}}$$

   with T being the temperature in Kelvin. What is the activation enthalpy H for Zschimmer´s flint glass if R = 8.3145 J/(mol·K) is the gas constant?

Observation 2a (1870-1890!):

Glass dimensions depend on thermal history which means that one and the same piece of glass may have different dimensions at the same temperature, depending on prior thermal treatment. The first systematic study of this effect has been carried out considering glass thermometers.



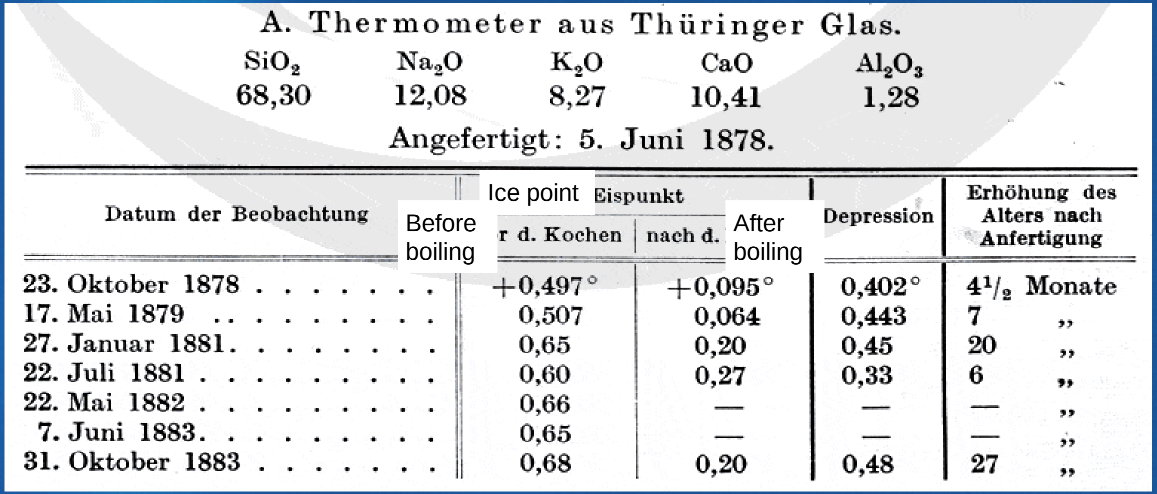
Any increase of the volume of the storage vessel at the bottom will make the fluid (in many cases: mercury) column in the capillary indicate a lower temperature than the actual one (ice point depression) and vice versa (ice point increase).

There are two such effects: one in the transformation range and one in the vicinity of room temperature.

(Picture from Festschrift at the occasion of the 125th anniversary of Schott AG)

Observation 2b (1870-1890!):

Weber compared the depression after boiling which may be observed in ordinary glass and special thermometer glass. He found

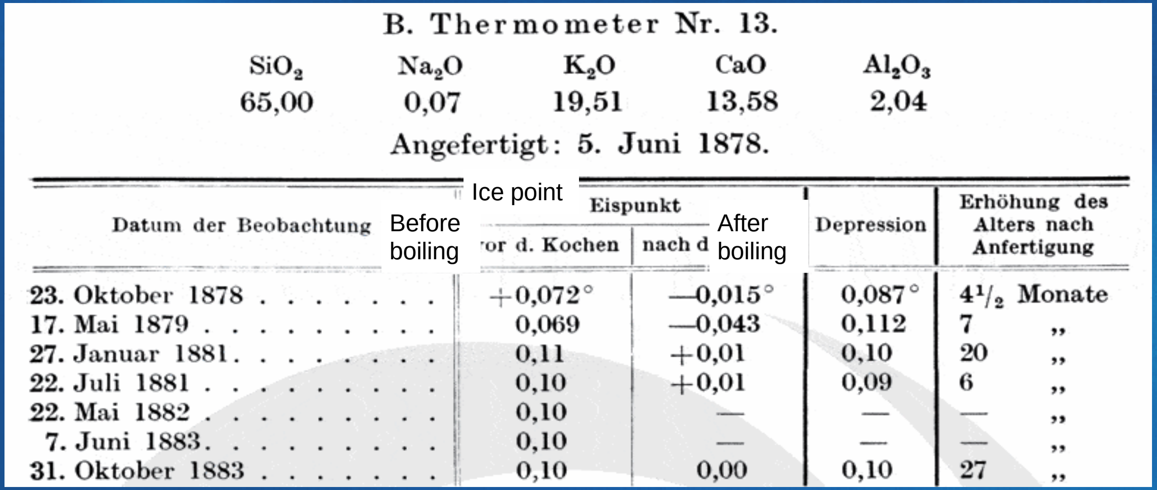


A. Thermometer aus Thüringer Glas.

SiO_2	Na_2O	K_2O	CaO	Al_2O_3
68,30	12,08	8,27	10,41	1,28

Angefertigt: 5. Juni 1878.

Datum der Beobachtung	Ice point Eispunkt		Depression	Erhöhung des Alters nach Anfertigung
	Before boiling r d. Kochen	nach d. After boiling		
23. Oktober 1878	+0,497°	+0,095°	0,402°	$4\,^1/_2$ Monate
17. Mai 1879	0,507	0,064	0,443	7 ,,
27. Januar 1881	0,65	0,20	0,45	20 ,,
22. Juli 1881	0,60	0,27	0,33	6 ,,
22. Mai 1882	0,66	—	—	— ,,
7. Juni 1883	0,65	—	—	— ,,
31. Oktober 1883	0,68	0,20	0,48	27 ,,



B. Thermometer Nr. 13.

SiO_2	Na_2O	K_2O	CaO	Al_2O_3
65,00	0,07	19,51	13,58	2,04

Angefertigt: 5. Juni 1878.

Datum der Beobachtung	Ice point Eispunkt		Depression	Erhöhung des Alters nach Anfertigung
	Before boiling ·or d. Kochen	nach d After boiling		
23. Oktober 1878	+0,072°	—0,015°	0,087°	$4\,^1/_2$ Monate
17. Mai 1879	0,069	—0,043	0,112	7 ,,
27. Januar 1881	0,11	+0,01	0,10	20 ,,
22. Juli 1881	0,10	+0,01	0,09	6 ,,
22. Mai 1882	0,10	—	—	— ,,
7. Juni 1883	0,10	—	—	— ,,
31. Oktober 1883	0,10	0,00	0,10	27 ,,

1. **Boiling increases the specific volume (decreases the density) of glass**
2. **Held at room temperature for several months, the specific volumes decreases again**
3. **The size of the effect is big if there are mixed alkalis in the composition**
4. **The cooperation of Weber and Schott led to the development of essentially single-alkali thermometer glasses.**

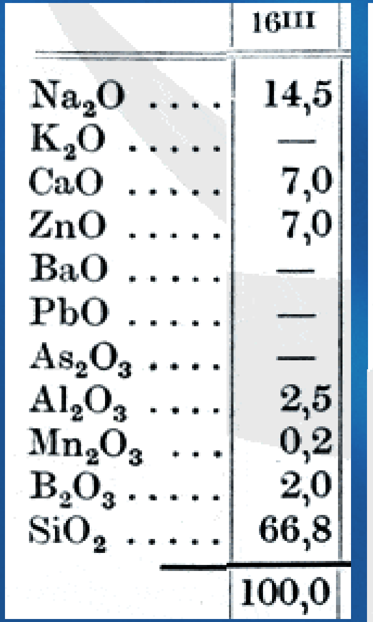
(from Zschimmer, Chemische Technologie des Glases, Jena, 1913)

Observation 2c (1870-1890!):

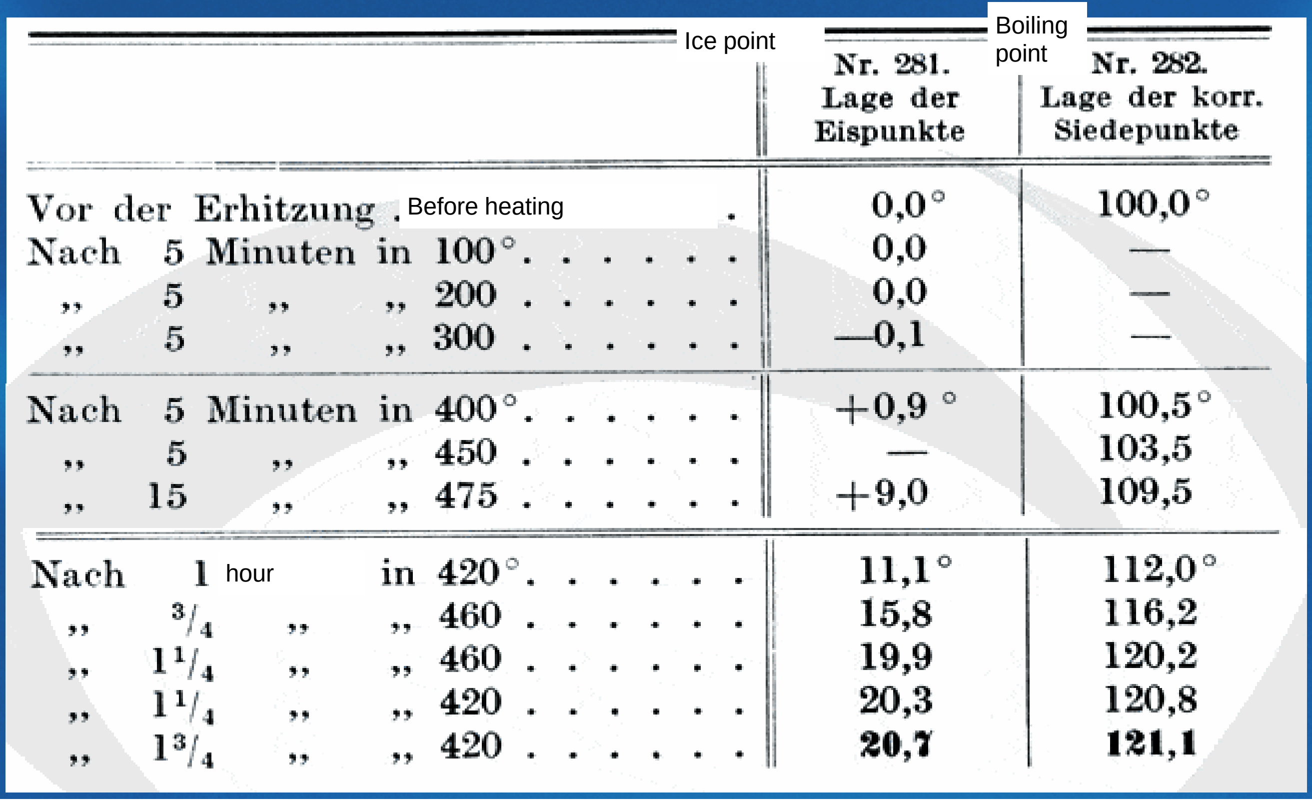
In the 19th century (and still today!), glass thermometers were used up to several hundred degrees Celsius.

So ice point and boiling point positions of a thermometer from thermometer glass 16^{III} were checked after exposure to temperatures around the range (400°C-410°C) for which significant stress relaxation within 24h had been observed.

A significant decrease of the specific volume was found compared to the original state resulting from rapid cooling at the end of the manufacturing process.



	16III
Na_2O	14,5
K_2O	—
CaO	7,0
ZnO	7,0
BaO	—
PbO	—
As_2O_3	—
Al_2O_3	2,5
Mn_2O_3	0,2
B_2O_3	2,0
SiO_2	66,8
	100,0



	Ice point Nr. 281. Lage der Eispunkte	Boiling point Nr. 282. Lage der korr. Siedepunkte
Vor der Erhitzung . Before heating .	0,0°	100,0°
Nach 5 Minuten in 100°	0,0	—
,, 5 ,, ,, 200	0,0	—
,, 5 ,, ,, 300	—0,1	—
Nach 5 Minuten in 400°	+0,9°	100,5°
,, 5 ,, ,, 450	—	103,5
,, 15 ,, ,, 475	+9,0	109,5
Nach 1 hour in 420°	11,1°	112,0°
,, 3/4 ,, ,, 460	15,8	116,2
,, 1 1/4 ,, ,, 460	19,9	120,2
,, 1 1/4 ,, ,, 420	20,3	120,8
,, 1 3/4 ,, ,, 420	20,7	121,1

(from Zschimmer, Chemische Technologie des Glases, Jena, 1913)

Understanding Observations 2a-c, Part 1 (1900-1930):

Arthur Q. Tool, Franz Simon, Gustav Tammann and others investigated the drastic changes of properties like thermal expansion or specific heat in the glass transformation range.

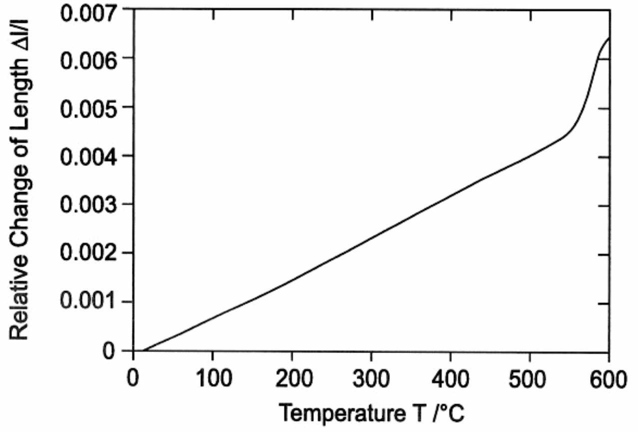


Fig. 5.12. Dilatometric measurement of technically cooled Schott BK 7® glass (heating rate 2 K/min)

This has raised the idea of a glass transition temperature T_G.

Considering dilatometric curves T_G has been defined as the position of the bent between low-temperature and high-temperature branch.

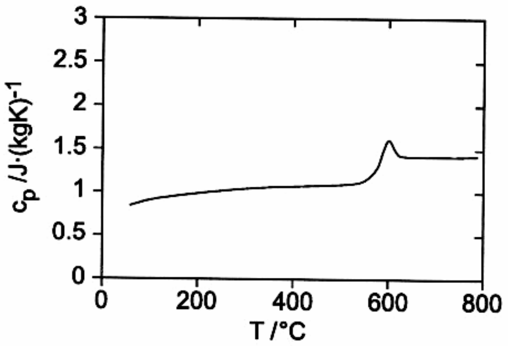


Fig. 5.3. DSC-measured c_p of technically cooled Schott BK 7® glass at a heating rate of 10 °C/min

T_G is seen as transition point between the (high T) supercooled liquid where physical and chemical readjustments happen (with calorimetric & dilatometric fingerprints) and the (low T) glass where they are frozen (not completely, see zero point depression).

(from Properties of Optical Glass, Schott Series on Glass Vol. 3, Springer, Berlin Heidelberg New York, 1998)

Understanding Observations 2a-c, Part 2 (1930-1950):

As the above physical and chemical readjustments are necessary for reaching thermal equilibrium, glass is identified as a non-equilibrium material (with respect to the metastable equilibrium of a supercooled liquid).

Tool introduced fictive temperature T_f to characterize the non-equilibrium state by the temperature where, if exposed to it, the glass would be in equilibrium with its environment without physical or chemical adjustment ("structural relaxation").

Above transformation range:

$T_f \approx T$ (instantaneous structural relaxation)

$\Delta l/l=\alpha_{glass}\cdot\Delta T+\alpha_{structural}\cdot\Delta T_f=(\alpha_{glass}+\alpha_{structural})\cdot\Delta T$

$\Delta h=c_{p,glass}\cdot\Delta T+c_{p,structural}\cdot\Delta T_f=(c_{p,glass}+c_{p,structural})\cdot\Delta T$

Below transformation range:

$T_f \approx$ const. (no structural relxation at all)

$\Delta l/l=\alpha_{glass}\cdot\Delta T$

$\Delta h=c_{p,glass}\cdot\Delta T$

l: length, h: specific enthalpy. If temperature changes above transformation range, there is a 2nd contribution to thermal expansion / specific heat $\propto \Delta T_f$. Below: none.

Questions left:
1. What happens in the transformation range?
2. Remark: room temperature effects (ice point depression) not included.

Understanding Observations 2a-c, Part 3 (1930-1950):

In the transformation range, there is a gradual deviation from equilibrium during cooling and a gradual return to equilibrium during heating. In contrast to a single-point transition at a certain T_G, Tool´s fictive temperature allows for that.

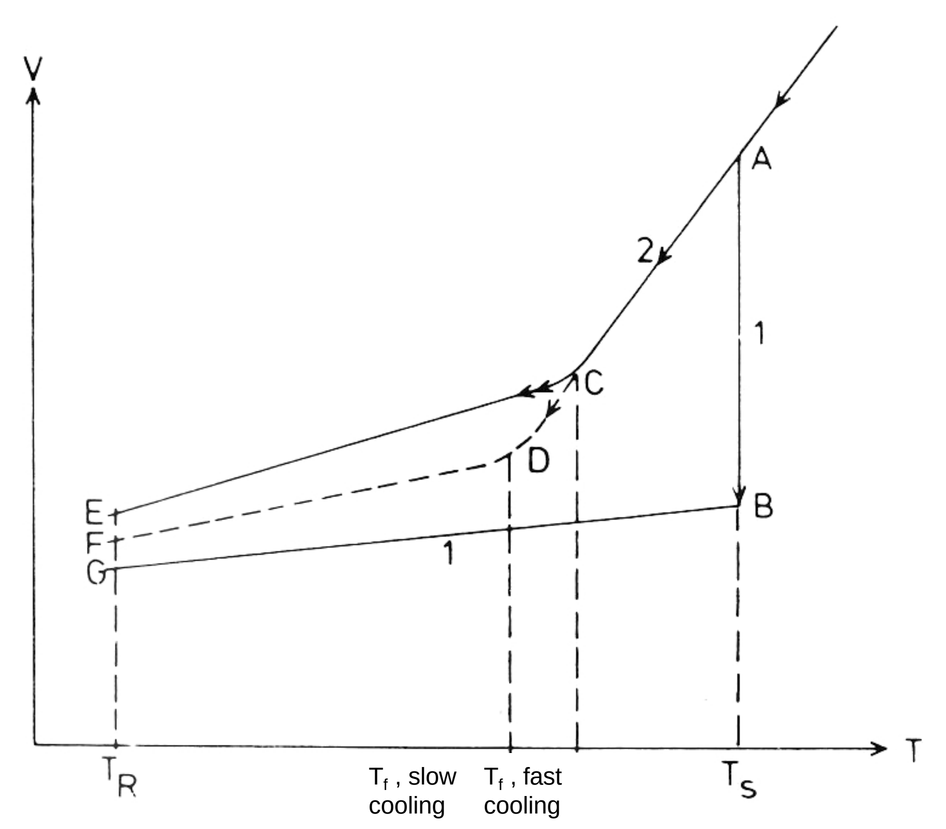


Fig. 2.2 Volume change during the cooling process of a melt forming: (1) a crystal structure; (2) a glass structure.

Different glass densities resulting from different cooling rates were explained this way: the slower a glass is cooled, the longer there is time to stay in equilibrium with the environment, the lower the resulting T_f and specific volume are:

$$\Delta T_f \propto \frac{\Delta V}{V} = -\frac{\Delta \rho}{\rho}$$

(from Schott Guide to Glass, Chapman & Hall, London … , 1996)

Understanding Observations 2a-c, Part 4 (1930-1950):

To describe fictive temperature kinetics in a quantitative way, Arthur Q. Tool introduced the following equation:

$$\frac{dT_f}{dt} = \frac{T - T_f}{\tau} = \frac{T - T_f}{\tau_0 \cdot e^{\frac{H}{R \cdot T}}}$$

The Arrhenius-type temperature dependence of the structural relaxation time τ had been inspired by the Arrhenius-type temperature dependence of the viscosity over small temperature ranges (for broader temperature ranges, the VFT equation is used). τ is called structural relaxation time.

For an isothermal hold, T_f becomes:

$$T_f(t) = T + (T_f(0) - T) \cdot e^{\frac{-t}{\tau}}$$

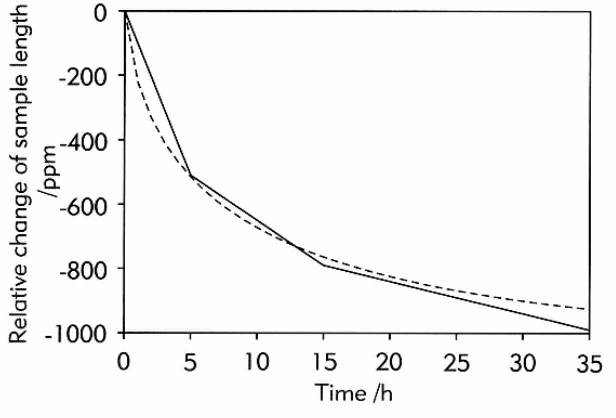


Fig. 4.19. Thermal shrinkage of BK 7 rods during annealing at 510 °C after a 72 h pre-annealing at 540 °C

(from Analysis of the Composition and Structure of Glasses … , Schott Series on Glass Vol. 7, Springer, Berlin Heidelberg New York, 1999)

Further phenomenon (refractive index,1950-1960; optional):

For a linear cooling rate β, one may write:

$$\frac{dT_f}{dt} = \frac{dT_f}{dT}\cdot\frac{dT}{dt} \equiv \frac{dT_f}{dT}\cdot\beta = \frac{T-T_f}{\tau_0\cdot e^{\frac{H}{R\cdot T}}} \Rightarrow \frac{dT_f}{dT} = \frac{T-T_f}{\beta\cdot\tau_0\cdot e^{\frac{H}{R\cdot T}}}$$

So the transition from $T_f \approx T$ (high T) to $T_f \approx$ const. (low T) is expected at a temperature T where $\beta\cdot\tau_0\cdot e^{H/(RT)}$ reaches a certain value. This temperature will be the resulting T_f.

From this, one gets a relation between the resulting T_fs of different coolings:

$$\beta_1\cdot\tau_0\cdot e^{\frac{H}{R\cdot T_{f,resulting,1}}} = \beta_2\cdot\tau_0\cdot e^{\frac{H}{R\cdot T_{f,resulting,2}}} \Rightarrow 1/T_{f,resulting,1} - 1/T_{f,resulting,2} = \ln(\beta_2/\beta_1)$$

Lillie and Ritland concluded for the refractive index n (linearly dependent on T_f):

$$\frac{n_1-n_2}{n_1\cdot n_2} = m\cdot\ln(\beta_2/\beta_1)$$

m is a constant.

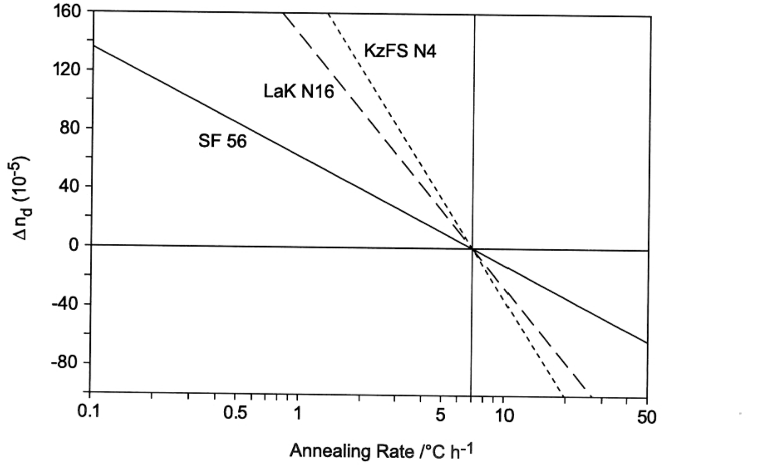


Fig. 2.45. Change of the refractive index n_d (λ_d = 587.56 nm) as a function of the annealing rate v. Reference annealing rate: v_1 = 7 °C/h; data from [2.164]

(from Properties of Optical Glass, Schott Series on Glass Vol. 3, Springer, Berlin Heidelberg New York, 1998)

Some exercises:

1. Make a screen-shot of the slides and mark T_G in the dilatometric measurement on BK7® (Understanding …, Part 1). Make a rough determination of α_{glass} and $\alpha_{structural}$.

2. What is the fictive temperature at the beginning of the isothermal hold of BK7®. (Understanding …, Part 4)? What will be its value when the isothermal hold is long enough?

3. Assume that the isothermal hold has approximately come to an end in the experiment. Can you calculate $\alpha_{structural}$ then? Compare with the value found above. And what is the structural relaxation time in the isothermal hold?

4. (Difficult!) Show where the path of the isothermal hold of BK7® might be in a drawing like the one in “Understanding, …, Part 3”.

5. (Optional:) Calculate “m” for SF56 (Further phenomenon; n(SF56)= ca. 1.8).