Relaxation kinetics of glasses
Isothermal relaxation
Non isothermal relaxation; Equation of Ritland- Bartenev

Structural relaxation is a process of establishing **Equilibrium State**.
The **time scale** of this process is determined by the relaxation time t.
The system that is examined a time much longer than t is seen to be in an equilibrium.
When the observation time is much shorter then the relaxation time we see a snap shot of a frozen in nonequilibrium system.

While every equilibrium system can be determined by a set of intensive thermodynamic parameters like pressure P and temperature T, at least one additional parameter is needed for the complete description of a nonequilibrium system. For that reason Tool introduced the so-called **"*fictive*"** or **"*structural*"** temperature, T_f. Generally, T_f is the temperature at which the fixed structure would be in equilibrium.

Are the structural relaxation and the viscous flow connected with the same process of rearrangement of building units of the system?
The two processes will be controlled by the same activation energy. Moreover, many scientists suppose that the activation energy that controls the viscous flow is equal to the activation energy controlling the crystallization process.
There are some indications that these assumptions are not always correct. The problem is not trivial. It means that the most important part of the structural relaxation is connected with a spatial rearrangement of the building units. For relatively simple systems the building units can be considered as hard spheres so that this assumption is quite OK.
Many oxide glasses build up of continuous network. In such systems the building units are strongly bonded, they are characterized by high viscosity and long relaxation times. It seems that in this case this assumption is again OK.
　　　There are, however, many glass forming melts that consists of relatively long chain macromolecules. This is the case of most of the low melting glassformers like phosphates as well as for almost all organic polymers. There are some entanglements between the macro molecular

chains. For that reason many authors assume that the activation energy of viscous flow is determined by the energy necessary to break these entanglements, while the activation energy of structural relaxation is determined by the difficulties connected with the motion of segments between the entanglements.

Fictive temperature
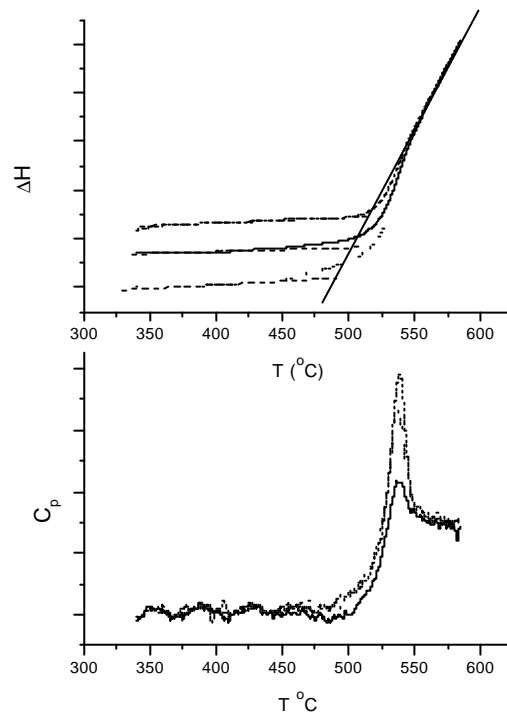
So far the relaxation of viscosity, of refraction indexes, of enthalpy, and of density has been studied as well as the mechanical relaxation, the neutron scattering relaxation etc.

Equation of Ritland – Bartenev

For a given cooling rate, $q^- = dT/dt = \Delta T/\Delta t$, a given structure is fixed.

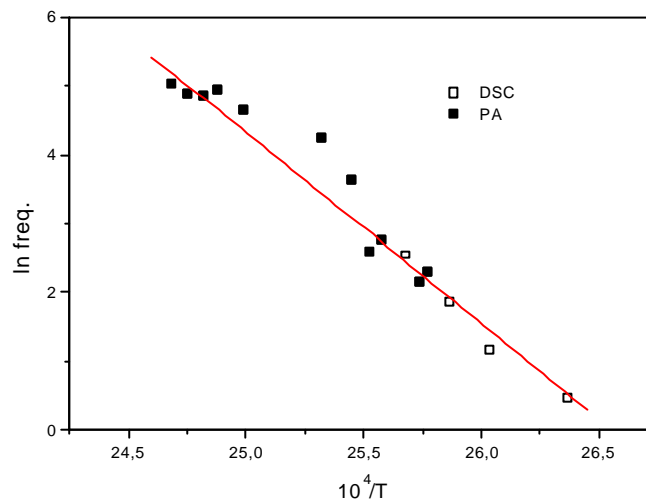**Assumption:** $\dfrac{t(T_f)}{\Delta t} = c$

$$\Delta t = \frac{\Delta T}{q^-}$$

so that

$$q^- t(T_f) = c\Delta T = C$$

$$t(T_f) = t_O\, e^{\frac{E(T_f)}{RT}} \qquad\qquad \pmb{T_f = T}$$

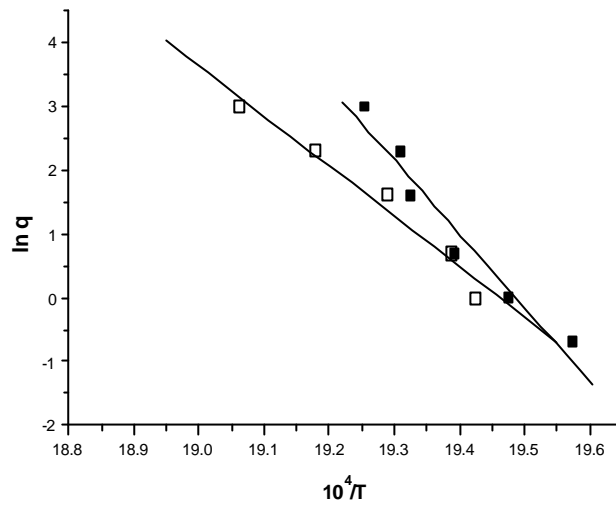$$\ln q^- = \mathrm{Const} - \frac{E(T_f)}{RT_f}$$

HEATING EXPERIMENTS

$$t(T_f, T_g) = t_O\, e^{\frac{E(T_f)}{RT_g}} \qquad\qquad \ln q^+ = \mathrm{Const}_1 - \frac{E(T_f)}{RT_g}$$

$$-L_f = \frac{E(T_f)}{R} + \frac{1}{RT_f}\frac{\partial}{\partial\frac{1}{T_f}}E(T_f) \qquad\qquad -L_o = \frac{E(T_f)}{R}$$

$$E(T_f) = E(T_g) + R\Delta L\left(\frac{T_g}{T} - 1\right)$$

$$E(T_f) = 655 + 300\left(\frac{520}{T_f} - 1\right)\text{kJ/mol}$$

the ratio $\dfrac{\text{L}_g}{\text{L}}$ is about $\dfrac{C_{gl}}{C_p}$

Isothermal relaxation

The aim is to predict the form of the relaxation function

$$\boldsymbol{F} = \frac{T_f - T}{T_{f\,i} - T} \quad,$$

and the temperature dependence of the characteristic time for structural relaxation $\boldsymbol{t}$.

The exponential relaxation law, also known as Maxwell law, follows from the assumption that a given property, x, changes towards its equilibrium value, x_e, as a first order chemical reaction

$$\frac{dx}{dt} = -\frac{x}{\boldsymbol{t}},$$

$$x = \frac{T_f - T}{T} \quad \text{is a small parameter !}$$

Solution gives the response function Φ of a conventional Maxwell relaxation process (1)
It is characterized by a single relaxation time τ and by a deviation of a given property from its equilibrium value.
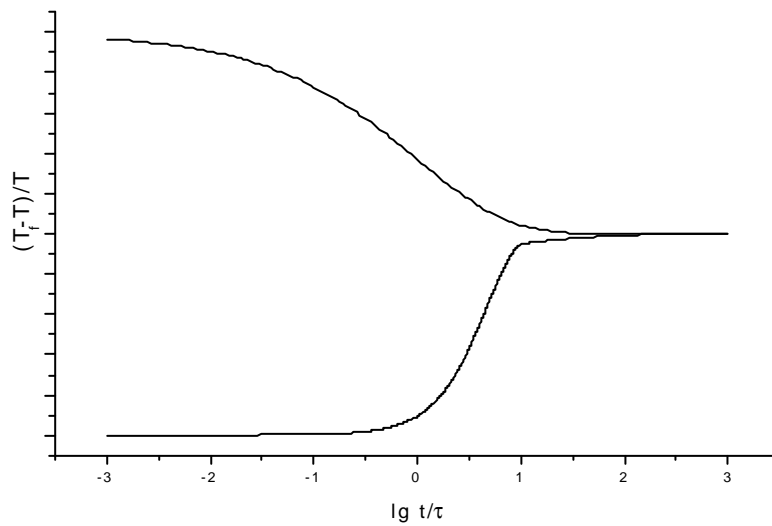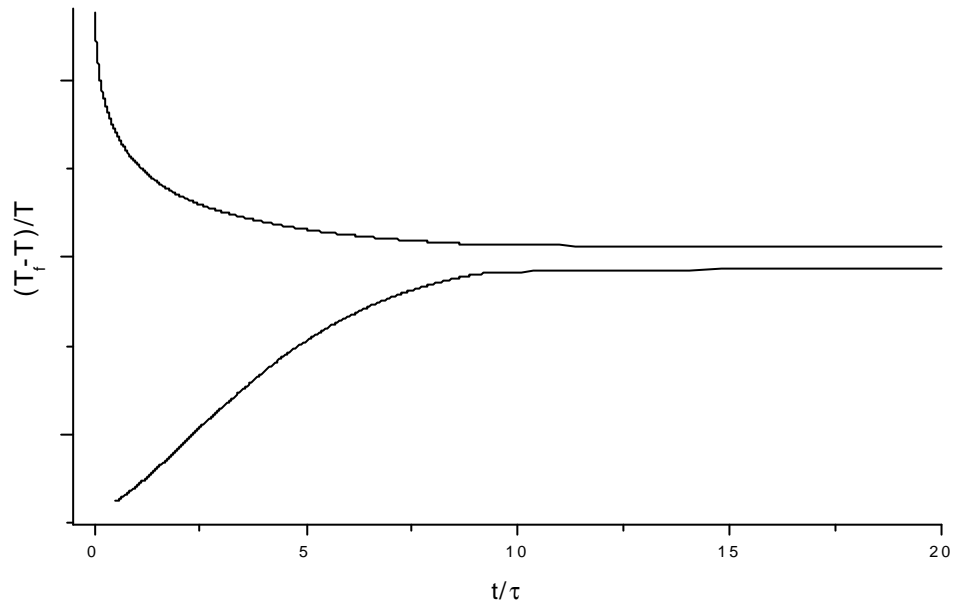
However, kinetics of relaxation of glasses cannot be described quantitatively by Maxwell's equation. Moreover, system with a given structure could manifest different values of T_f when different properties are investigated.

For that reason Kohlrausch assumed that in complex systems the response function is a stretched exponent

$$\Phi(t) = \exp\left[-\left(t/t_K\right)^b\right] \qquad 0<\beta<1$$

This result can be obtained, with some approximation, within the framework of a model based on a fundamental postulate that structural recovery involves a spectrum of relaxation times.

$$\frac{dx}{dt} = -\frac{x}{t}$$

$$t = \frac{t_K^b t^{1-b}}{b} \qquad\qquad \text{or} \qquad\qquad F(x) = -\frac{x}{t_K\, a \left|\ln\dfrac{x}{x_{in}}\right|^{a-1}} \qquad, \; a = \frac{1}{b}$$

$$\frac{\partial\Phi}{\partial \ln t} = \frac{\partial}{\partial y} e^{-\left(\frac{e^y}{t_K}\right)^b} = -b\left(\frac{e^y}{t_K}\right)^b e^{-\left(\frac{e^y}{t_K}\right)^b}$$

$$\frac{\partial^2\Phi}{\partial(\ln t)^2} = \left(-1+\left(\frac{e^y}{t_K}\right)^b\right) b\left(\frac{e^y}{t_K}\right)^b e^{-\left(\frac{e^y}{t_K}\right)^b}$$

extremum at $\quad t = t_K$

The slope is $F'(t = t_K) = -\dfrac{b}{e}$ $\qquad P \quad t_2 - t_1 = e/b$

If a series of isothermal relaxation experiments are performed at a fixed temperature a $\mathbf{F}$ - *time* plot should give (for fixed $\mathbf{b}$ and $\mathbf{t}_K$ values of the *KWW* model) a master curve. However, this is in contradiction with available experimental evidence. It is well known that there is an asymmetry in the relaxation response following positive and negative departures from equilibrium This is an indication that the two adjustable parameters ($\mathbf{b}$ and $\mathbf{t}_K$) in Eq.(23) depend in fact on the initial condition of the system.

Solving isothermal relaxation

$$x = \frac{T_f - T}{T}$$

$$\left(\frac{\partial x}{\partial t} \right)_{T=const} = F(x,t)$$

$$F(x)= \sum_{n=1}^{\infty} \frac{F_{x=0}^{(n)} x^n}{n!}$$

$$F_{x=0}^{(1)} \equiv \frac{\partial F}{\partial x}\bigg|_{x=0} = -1/\mathbf{t}_e$$

$$\mathbf{t} = \mathbf{t}_o . exp\left[\frac{E(x,T)}{RT}\right]$$

$$E(x,T)= E(0,T)+\left(\frac{\partial E(T)}{\partial x}\right)_{x=0} x + ... \qquad (10)$$

Linear approximation for the activation energy

As soon as x is a small parameter we truncate Eq.(10) to the linear term so that the structure dependence of the activation energy at a given temperature, $E(x,T)/kT$ is expressed as:

$$\frac{E(x,T)}{kT} = \frac{E (T)}{kT} - bx = \frac{E (T)}{kT}(1 - fx)$$

Here b and f stand for:

$$b = -\frac{1}{kT}\left(\frac{\partial E(T)}{\partial x}\right)_{x=0} ; \quad f = -\frac{1}{E(T)}\left(\frac{\partial E(T)}{\partial x}\right)_{x=0}$$

$$F^{(1)} = -\frac{1}{\mathbf{t}_e} exp(bx)$$

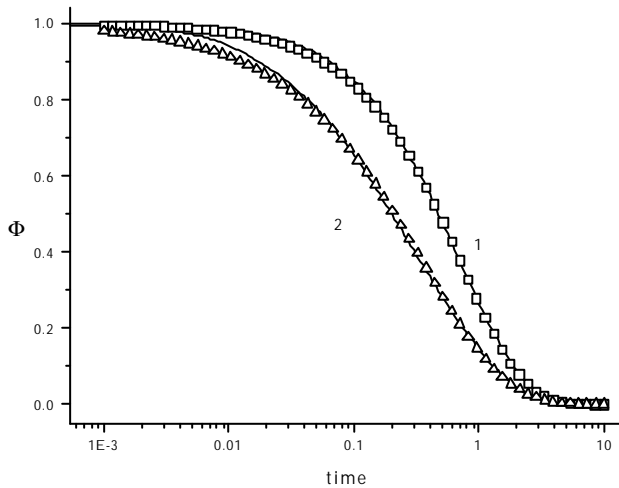The integration of $F^{(1)}$ together with the mentioned equilibrium condition $F(0)=0$ gives:

$$F(x)=-\frac{1}{t_e}\int e^{bx}dx=-\frac{1}{bt_e}\left[e^{bx}-1\right]$$

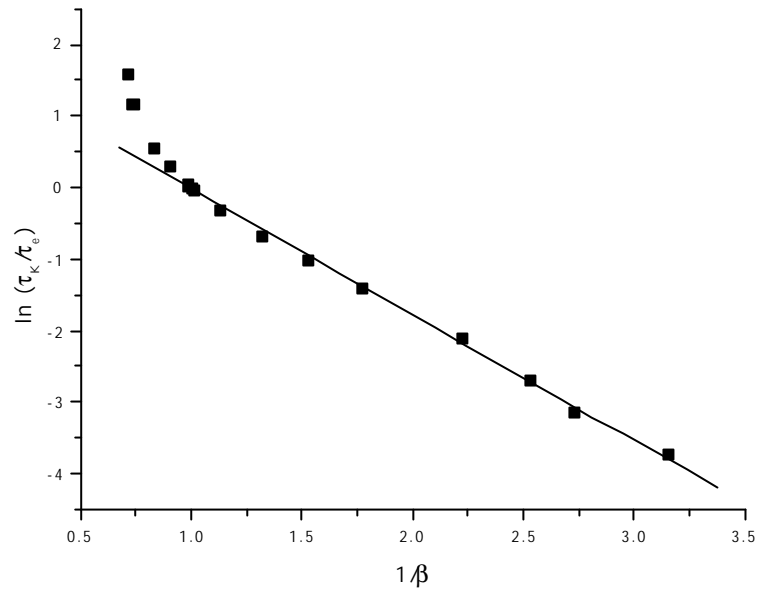$$x=-\frac{\ln\left[1-\left(1-e^{-bx_{in}}\right)e^{-\frac{t}{t_e}}\right]}{b}$$

where x_{in} is x at $t=0$.

$$\frac{E(x,T)}{RT}=\frac{h}{T\Delta S}\qquad\qquad f=\frac{1}{\ln\dfrac{T_f}{T_o}}\approx 3.4\qquad\qquad f=a\frac{DC_p}{R}$$

Comparison of the Eq.(35) with the KWW formula. Curve 1: Solid line with $t_e=1$ and B=1. Curve 2: solid line with $t_e=1$ and B=3. With   - is given the best fit to curve 1 according to the KWW function   with $t_k=0.83$ and $b=0.88$; in analogy Δ- indicates the best fit with $b=0.65$, $t_K=0.36$

$$\boldsymbol{t}_K = 6\boldsymbol{t}_e\, exp\left(-\frac{1.8}{\boldsymbol{b}}\right)$$