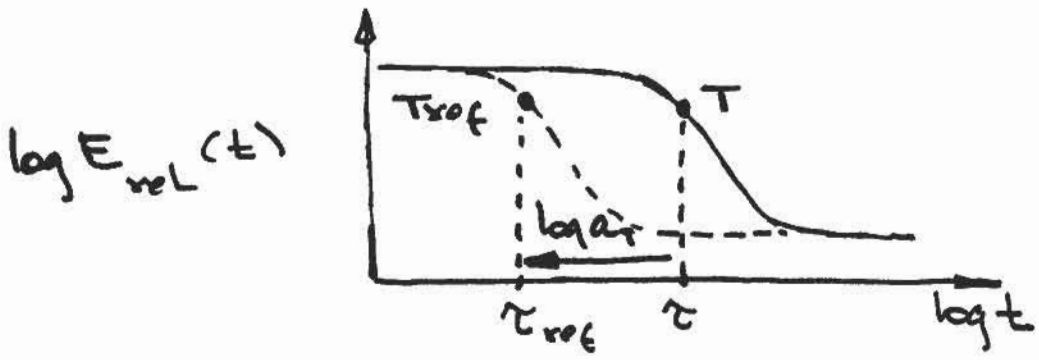
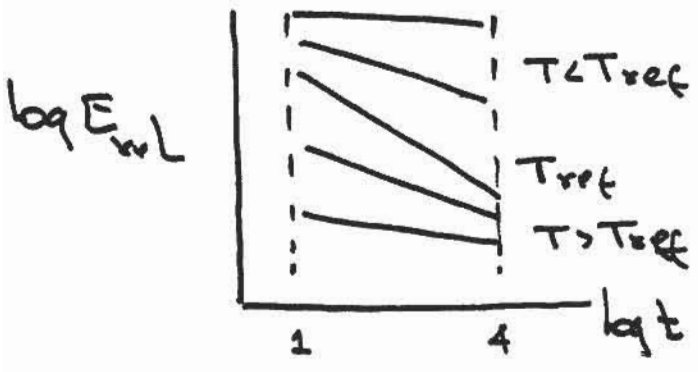
Time - Temperature Superposition



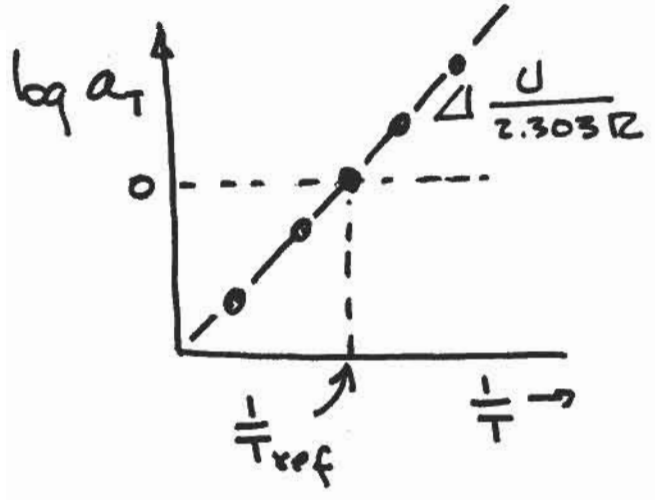
$$\tau = \tau_0 \exp \frac{U^*}{RT} \rightarrow \log \tau = \log \tau_0 + \frac{U^*}{2.303RT}$$

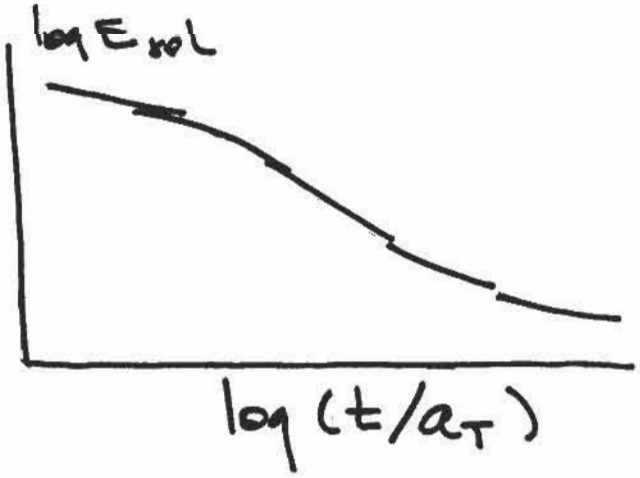
$$\log \tau_{ref} = \log \tau_0 + \frac{U}{2.303R\,T_{ref}}$$

$$\log \tau - \log \tau_{ref} \equiv \log a_T = \frac{U}{2.303R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)$$



T	log a_T
–	–
–	–
T_{ref}	0
–	–
–	–





The WLF Equation

- $$\log a_T = \frac{-17.44\,(T-T_g)}{51.6\,(T-T_g)}$$

- Free-volume interpretation
  - thermal expansion

$$f = f_g + \alpha\,(T-T_g)$$

  - Doolittle equation

$$\tau = \tau_0 \exp\left(\frac{\beta}{f}\right)$$

$$\rightarrow \ln a_T = \ln\tau - \ln\tau_g$$

$$= \beta\left[\frac{1}{f_g+\alpha(T-T_g)} - \frac{1}{f_g}\right]$$

$$= \frac{-(\beta/f_g)(T-T_g)}{(f_g/\alpha) + (T-T_g)}$$

$\alpha \sim 5\times10^{-4}/^\circ C \rightarrow f_g \approx 0.025$

"Effective" time

$$t'(T_{ref}) = \sum_j \frac{t_j(T_j)}{a_T(T_j)} \rightarrow \int_0^t \frac{d\xi}{a_T(\xi)}$$

Example

$$E_{rel}(t) = k_e + k_1 e^{-t/\tau} \qquad t \leftarrow t'$$

$$a_T = 10^{\log a_T}, \quad \log a_T = \frac{-17.44\,(T-T_g)}{51.6\,(T-T_g)} -$$

$$\text{offset} = \frac{-17.44\,(T_{ref}-T_g)}{51.6\,(T_{ref}-T_g)}$$

$$T(t) = T_{avg} + \Delta T \cdot \cos(2\pi t)$$

t ← days

Example

```
> log_aT:=-17.44*(T-Tg)/(51.6+(T-Tg));
```

$$log\_aT := -17.44\,\frac{T - Tg}{51.6 + T - Tg}$$

```
> Digits:=4:Tg:=0:offset:=evalf(subs(T=20,log_aT));
> log_aT:=log_aT-offset;
```

$$log\_aT := -17.44\,\frac{T}{51.6 + T} + 4.871$$

```
> T:=20+5*cos(2*Pi*t);
> aT:=10^log_aT;
> aT:=subs(t=xi,aT);
> t_prime:=int(1/aT,xi=0..t);
> Erel:=ke+k1*exp(-t_prime/tau);
```

$$Erel := ke + k1\,\mathbf{e}^{\left(-\frac{\int_0^t \frac{1}{10^{\left(-17.44\frac{20+5\cos(2\pi\xi)}{71.6+5\cos(2\pi\xi)}+4.871\right)}}\,d\xi}{\tau}\right)}$$

```
> ke:=10:k1:=90:tau:=10:
> plot(Erel,t=0..10,labels=[`t (days)`,`E_rel(t) `]);
```