

SAMPLE ANSWERS TO HW SET 3B

First- Please accept my most sincere apologies for taking so long to get these homework sets back to you. I have no excuses that are acceptable.

Like last time, I have copied below some examples of answers to the three problems in this set- don't read anything into why I chose what examples I did. Mostly, I've selected answers that seem straight-forward. The average grade on this set was 91/100

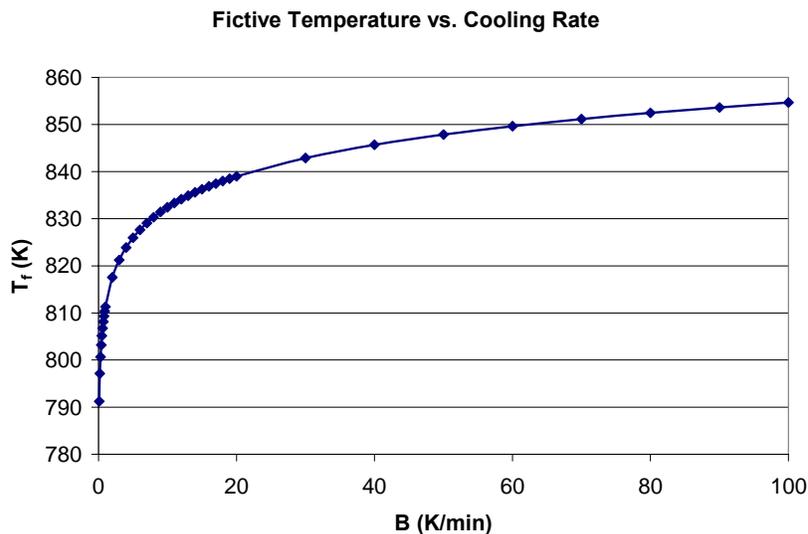
1. Calculate the expected effect of cooling rate on the T_g of a soda-lime glass. Note: use eq. 13.111 in Prof. Varshneya's book as a starting point, and be sure to provide a reference for the activation energy you use to answer this question.

This one is straight-forward once you recognize that you can solve eq. 13.111 by using known/reported values for $T_g (=T_f)$ and B . Here are a couple of examples...

Example 1

In "Estimation of activation energies for structural relaxation and viscous flow from DTA and DSC experiments" in *Thermochimica Acta* 280/281 (1996) 153-162 by C.T. Moynihan, S.-K. Lee, M. Tatsumisago, and T. Minami, the activation energy for shear viscosity in the glass transition region ΔH for NBS 710, a soda lime silica glass, is given as 612 kJ/mol. Additionally, the glass transition temperature at heating rates of 5-20K/min is given as 839K.

Equation 13.111 from Varshneya, $\frac{\partial \ln |B|}{\partial (1/T_f)} = -\frac{\Delta H}{R}$, was used to determine the fictive temperature at different cooling rates. The T_f at a cooling rate of 10K/min was set at 839K.



B (K/min)	ln(B)	T _f (K)	1/T _f
0.1	-2.302585	791	0.001264
0.2	-1.609438	797	0.001254
0.3	-1.203973	801	0.001249
0.4	-0.916291	803	0.001245
0.5	-0.693147	805	0.001242
0.6	-0.510826	807	0.00124
0.7	-0.356675	808	0.001237
0.8	-0.223144	809	0.001236
0.9	-0.105361	810	0.001234
1	0.000000	811	0.001233
2	0.693147	818	0.001223
3	1.098612	821	0.001218
4	1.386294	824	0.001214
5	1.609438	826	0.001211
6	1.791759	828	0.001208
7	1.945910	829	0.001206
8	2.079442	830	0.001204
9	2.197225	831	0.001203
10	2.302585	832	0.001201
11	2.397895	833	0.0012
12	2.484907	834	0.001199
13	2.564949	835	0.001198
14	2.639057	836	0.001197
15	2.708050	836	0.001196
16	2.772589	837	0.001195
17	2.833213	837	0.001194
18	2.890372	838	0.001193
19	2.944439	839	0.001193
20	2.995732	839	0.001192
30	3.401197	843	0.001186
40	3.688879	846	0.001182
50	3.912023	848	0.001179
60	4.094345	850	0.001177
70	4.248495	851	0.001175
80	4.382027	852	0.001173
90	4.499810	854	0.001171
100	4.605170	855	0.00117

-ΔH/R	-73610.78
ΔH (kJ/mol)	816
R (J/Kmol)	8.314

Example 2

This problem can be solved using the following equation as suggested by Moynihan and given by Varsh in Eq. 13.111:

$$\frac{d \ln|B|}{d(1/T_f)} = -\frac{\Delta H}{R},$$

where B is the heating rate (in K/min), T_f is the fictive temperature, ΔH is the activation energy for shear viscosity and R is the universal gas constant. We can make the assumption that $T_f \approx T_g$, since “it is customary to use the term glass transition temperature T_g almost synonymously with T_f to mark the onset of the transition” (from Varsh). (In fact, Moynihan states that the above equation is true and can be used to find T_f when B represents *cooling* rate, where as T_g must be substituted for T_f when B represents *heating* rate.) Making this assumption, rearranging the above equation and integrating yields:

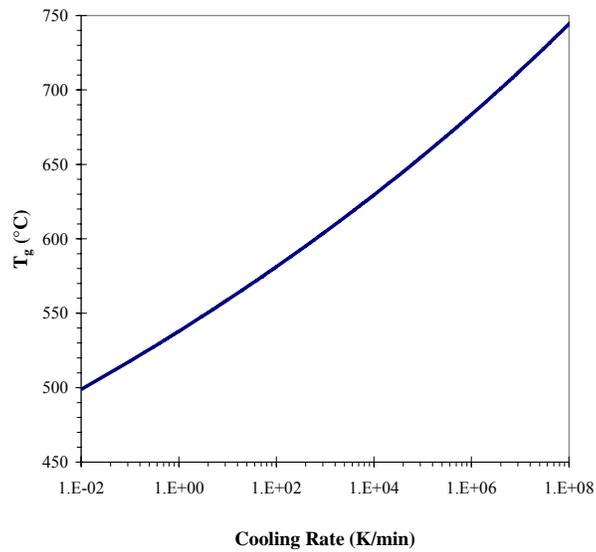
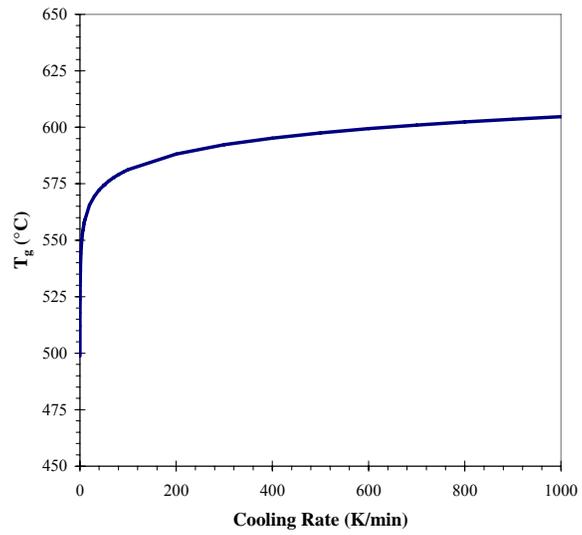
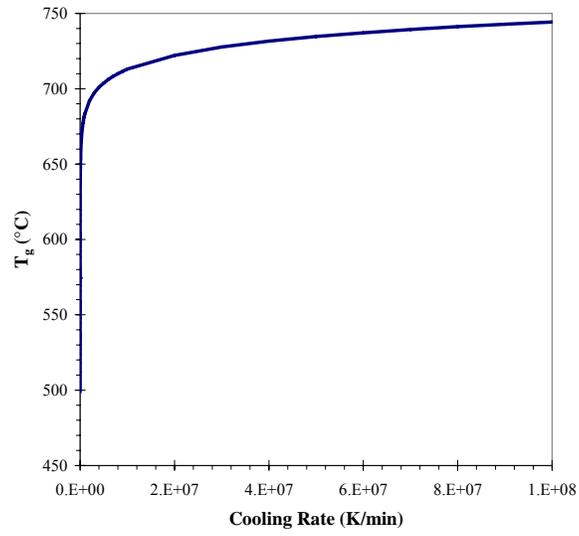
$$d \ln|B| = -\frac{\Delta H}{R} d(1/T_g)$$

$$\int d \ln|B| = -\frac{\Delta H}{R} \int d(1/T_g) \rightarrow \ln|B| = -\frac{\Delta H}{R} \cdot \frac{1}{T_g} + C$$

From previous studies conducted by Moynihan, we know that the activation energy for shear viscosity of an alkali lime silicate glass (NBS 710) is ~ 612 kJ/mol, and that the T_g is ~ 832 K when measured by the DSC at a heating rate of 10 K/min (Moynihan et al., *Thermochimica Acta*, 280/281 (1996) 153, and class notes). NBS 710 has a composition of 8.7 Na₂O-7.7K₂O-11.6CaO-70.5SiO₂-1.1Sb₂O₃. Although this composition may vary slightly from that of the most common soda-lime silicate compositions (NBS 710 has higher amounts of potassia), it is assumed that the T_g and viscosity properties for NBS 710 are similar enough for the purpose of this exercise.

Using the aforementioned values for B , ΔH , and T_g , the value of the constant, C , was determined to be 90.777. The effect of cooling rate on T_g can now be determined by rearranging the above equation and plotting the transition temperature as a function of cooling rate, as is shown in the following three figures (expressed in a few different formats and ranges to better describe the behavior).

$$T_g = \frac{\Delta H}{R(C - \ln|B|)}$$



The results indicate that at extremely slow cooling rates (10^{-2} K/min), it is possible to attain T_g values below 500 °C. As the cooling rate increases, the T_g increases sharply at first and then continues to increase at a more gradual rate. At cooling rates equivalent to those achieved through typical air cooling (1-10 K/s), $T_g \sim 575$ -600 °C. At rates achieved by liquid-medium quenching ($\sim 10^3$ K/s), $T_g \sim 650$ °C, and at rates achieved by splat-cooling or melt-spinning (10^5 - 10^8 K/s), $T_g > 700$ °C.

2. Find at least one paper in the literature that compares the enthalpies for structural relaxation and viscous flow (in the transition range) for a glass *other* than those summarized by Moynihan in the table given in slide 24 from the lectures on glass transformation range behavior. Are the viscosity characteristics of the glasses that you select more, or less, fragile than soda-lime silicate glass? Explain your answer.

*This one was pretty easy- *if* you compared the rheological properties of your glasses with those of soda-lime silicates. A couple of examples...*

Example 1

Investigations by Komatsu et al. of structural relaxation and viscous flow enthalpies for alkali and alkaline earth TeO_2 glasses show a large difference in the activation energies of structural relaxation (at temperatures just below T_g) and viscous flow (at temperatures just above T_g). The results for three compositions of TeO_2 glasses are given in the table below:

Composition	ΔH_η (viscous flow, kJ/mol)	ΔH_s (struct. relax., kJ/mol)
20MgO • 80TeO ₂	748	1268
10K ₂ O • 10MgO • 80 TeO ₂	646	977
20 K ₂ O • 80 TeO ₂	540	929

The difference between ΔH_η and ΔH_s is large for the TeO_2 system (compared to a strong glass system like SiO_2), differing by 520 kJ/mol for the glass 20MgO • 80TeO₂, 331 kJ/mol for 10K₂O • 10MgO • 80 TeO₂, and 389 kJ/mol for 20 K₂O • 80 TeO₂. Glasses in the silicate system, as provided in the table from Moynihan, show little or no enthalpy difference between structural relaxation and viscous flow; fragile glasses, like ZBLA, have larger differences in these enthalpies (260 kJ/mol). This means that a larger difference between the enthalpies for relaxation and viscous flow corresponds to a greater change in structure, i.e. an increase in the glass' fragility. The large difference in these enthalpies for the alkali-alkaline earth TeO_2 glasses, in comparison to the alkali-lime silicate glass NBS710, thereby indicates that the TeO_2 glasses are more fragile than soda lime silicate glasses.

Komatsu et al., "Decoupling between Enthalpy Relaxation and Viscous Flow in Fragile Oxide Glass-Forming Liquids", *Journal of the American Ceramic Society*, 85 (1), 2002, pp 193-199.

Example 2- same reference, but an interesting analysis...

T. Komatsu et al, Decoupling between enthalpy relaxation and viscous flow and its structural origin in fragile oxide glass-forming liquids, J. Am. Ceram. Soc., 85[1] 193-99(2002).

Table. Values of the Glass-Transition Temperature (T_g), the Activation Energy for Viscous Flow near the Glass-Transition Temperature (E_η), the estimated Degree of Fragility(m), the Heat-Capacity Change in the Glass-Transition Region between the Heat Capacities of Glasses C_{pg} and Supercooled Liquids C_{pe} , ($\Delta C_p = C_{pe} - C_{pg}$) the Ratio C_{pe}/C_{pg} , the Activation Energy for Enthalpy Relaxation (ΔH), and the KAHR parameter for $xK_2O-xMgO-(100 - 2x)TeO_2$ Glasses.

Sample	T_g (K)	E_η (kJ/mol)	m	ΔC_p (J/(mol·K) ⁻¹)	C_{pe}/C_{pg}	ΔH (kJ/mol)	θ (K ⁻¹)
$x = 5$	576	701	64	45.7	1.63	1051	0.38
$x = 7.5$	574	679	62	46.2	1.67	998	0.36
$x = 10$	569	646	59	48.2	1.67	977	0.36
$x = 12.5$	561	658	61	47.2	1.67	950	0.36
$x = 15$	557	577	54	48.7	1.72	919	0.36

A large discrepancy has been found between the activation energies for viscous flow, E_η , and for enthalpy relaxation, ΔH , at and near T_g in TeO_2 -based glasses. For example, for the glass with the composition, $5K_2O-5MgO-90TeO_2$, the activation energy for viscous flow $E_\eta = 701 \text{ kJ mol}^{-1}$, while enthalpy relaxation $\Delta H=1051 \text{ kJ mol}^{-1}$. Therefore, the discrepancy is very significant for this TeO_2 -based glasses. Besides TeO_2 -based glasses, such a discrepancy has also been found in ZrF_4 -based fluoride glasses with a fragile character and in $Ge-Se$ and $Ge-Sb-Se$ glasses. To evaluate the fragility of TeO_2 -based glasses, we take $10K_2O-10MgO-80TeO_2$ as an example, whose viscosity follows the Vogel-Fulcher-Tammann (VFT) equation:

$$\eta = \eta_0 e^{\frac{A}{T - T_0}}$$

for the glass $10K_2O-10MgO-80TeO_2$, $\eta_0 = 10^{-3.4}$, $A = 1356 \text{ K}$, $T_0 = 480 \text{ K}$.

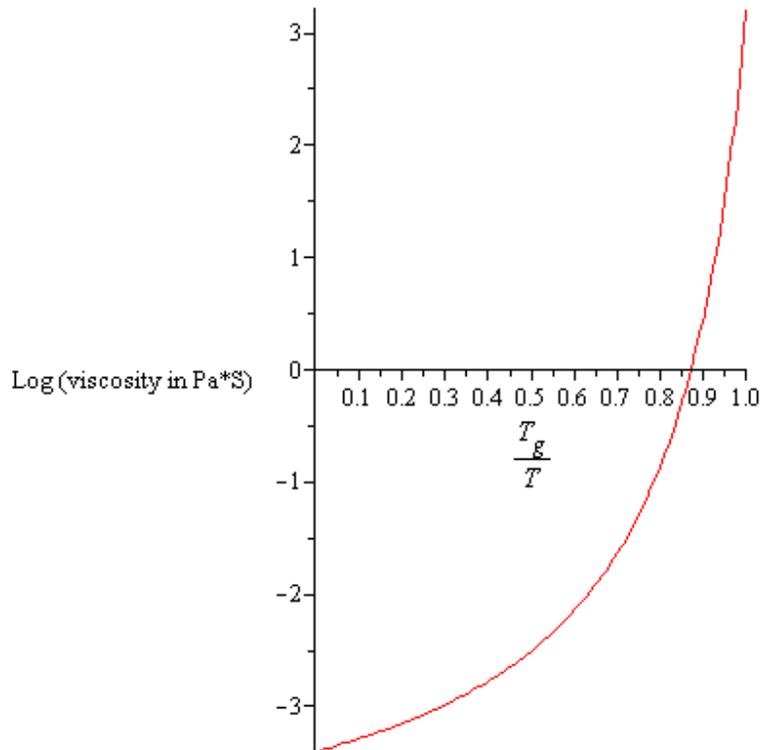
$$\eta_0 := 10^{-3.4}$$

$$A := 1356$$

$$T_0 := 480$$

$$T_g := 569$$

$$\text{plot} \left(\log_{10} \left(10^{-3.4} \cdot e^{\frac{1356}{x} - 480} \right), x = 0.01 \dots 1 \right)$$



From the above plot, it is seen that the viscosity behavior of this glass is highly non-Arrhenius type. As recalled from C.A. Angell's paper on Science, the soda-lime silicate glass is more close to the plot of strong liquid such as SiO₂ and GeO₂, e.g., when T_g/T=0.6, Log(viscosity)≈2; but the plot for this TeO₂-base glass is more close to the fragile liquid, e.g., when T_g/T=0.6, Log(viscosity)≈-2. Therefore, the TeO₂-based glass is more fragile than the soda-lime glass.

3. Based on your careful reading of the article by Scherer (GW Scherer, J. Am. Ceram. Soc., 67[7] 504 (1984) posted at the course website, compare and contrast in detail the use of the Adam-Gibbs model and the Tool-Narayanaswamy model to describe glass transformation range behavior. Please consider the practical applications of the two models as well as the theoretical underpinnings.

This one was also pretty straight-forward- and I graded it quite liberally. Here are two answers that I liked...

Example 1

Narayanaswamy's model of structural relaxation suggests that the relaxation time of a property is dependent upon the activation energy for viscous flow and is partitioned between a temperature-dependent term and a structure-dependent term. The structure-

dependent term is a function of the fictive temperature, T_f , which is defined as the temperature from which the equilibrium liquid must be instantaneously quenched to have the same value for a property as does the glass, and this temperature may be different for different properties. This model assumes that the relaxation of a property is intrinsically nonlinear due to the fictive temperature dependence of viscosity, and also assumes thermorheological simplicity (TRS). TRS suggests that the “functional form of the relaxation does not change with temperature” (from Varsh) and allows for the integration of relaxation occurring at different times. Narayanaswamy’s assumptions allow for the determination of fictive temperature based on the physical temperature and also the structural “memory” due to thermal history. It should also be noted that the Narayanaswamy model for relaxation time reduces to an Arrhenius relationship when $T = T_{fp}$. While the Narayanaswamy model does successfully describe many sets of relaxation data over a large range of temperatures and includes the influence of structure on relaxation times, it is empirically derived and does not have a theoretical basis.

The relaxation time as proposed by Narayanaswamy can be mathematically expressed:

$$\tau_p = \tau_o \exp \left[\frac{x\Delta H}{RT} + \frac{(1-x)\Delta H}{RT_{fp}} \right],$$

where τ_p is the relaxation time for property p, τ_o and x are constants, ΔH is the activation energy for viscous flow, and T_{fp} is the fictive temperature for property p.

The Adams-Gibbs model for structural relaxation assumes a kinetically controlled glass transition and is based on entropy-dependent viscosity, providing a strong theoretical basis for the model. Enthalpy fluctuations cause regions within the glass system to cooperatively rearrange until all subsystems act as one region and the configurational entropy becomes zero, at which time the structure is “frozen” in place. This model assumes that the rearranging regions are independent of their environment and separates the configurational and vibrational contributions of the partition function. The relaxation time is a function of the configurational entropy, the potential barrier limiting rearrangement, and the number of configurations available to the smallest group of molecules that can undergo rearrangement. Similar to the Narayanaswamy model, this model is also dependent on a fictive temperature, since the configurational entropy will be a function of the existing structure. Another similarity lies in the assumption that different properties will have different fictive temperatures, since “the relaxation of a property is controlled by those cooperative rearrangements involving structural units to which it is most sensitive” (from Scherer). In addition, the Adams-Gibbs model suggests Arrhenius behavior for isostructural flow, but differs from the Narayanaswamy model in that it also suggests that the activation energy will decrease as the fictive temperature increases.

The Adams-Gibbs model is useful in understanding the behavior of fragile and strong liquids. Strong melts will not undergo much structural rearrangement during the glass transition region, and therefore the configurational entropy is not very temperature

dependent. Fragile melts, however, will exhibit significant structural changes upon cooling through the glass transition region and therefore have configurational entropies which are highly temperature dependent. The Adams-Gibbs model has been successfully used to predict viscous flow and structural relaxation in equilibrium and non-equilibrium conditions, and has been applied to studies using many different measures of relaxation, including refractive index and heat capacity. The application of this model may be especially useful in studies where extremely fast quenching rates are used, as Scherer suggests that the Arrhenius equation may not predict property changes as accurately as the Adams-Gibbs model in such cases.

The relaxation time as proposed by Adams-Gibbs can be mathematically expressed:

$$\tau_p = \tau_o \exp \left[\frac{(Q/RT)}{\ln(T_{fp}/T_2) + C(T_{fp} - T_2)} \right],$$

where τ_p is the relaxation time for property p, τ_o is a constant, T_{fp} is the fictive temperature for property p, T_2 is the temperature at which the configuration entropy equals 0, and $Q = AR/C_o$ and $C = C_1/C_o$, where C_i are constants defined by the change in heat capacity near the transition range ($\Delta C_p = C_o + C_1T$) and A is a constant defined by $A = \Delta\mu \cdot \ln W^*$, where $\Delta\mu$ is the potential barrier hindering rearrangement and W^* is the number of configurations available to the smallest group of molecules that can undergo rearrangement.

Example 2

Problem 3

The Tool-Narayanaswamy model for structural relaxation of properties within the glass transition temperature range. The model is phenomenological & has been successful in describing relaxation behavior, however the classical equation used to calculate relaxation time τ using this model is the Arrhenius Equation has no theoretical proof of use in this context. T-N model generically describes the change in property P as a function of time & temperature as

$$P(T, t) = P(T_0, \infty) + \alpha_p [1 - \exp(-\alpha_p \int_0^t M_p(\xi - \xi') \frac{dT}{d\xi'} d\xi')]$$

Use of $\tau_p = \tau_0 \exp\left[\frac{x\Delta H}{RT} + \frac{(1-x)\Delta H}{RT_g}\right]$ for relaxation yields good results in the Arrhenius depend range, however an assumed activation energy partitioning lacks theoretical foundation.

Other equations have been proposed for τ , however this paper & this HW problem refer to the use of the Adam-Gibbs equation in concurrence with the TN model. The AG equation falls out of the assumption of a modeling of structural relaxation which pictures relaxation processes as "cooperative rearrangements of increasingly large numbers of molecules as temperature decreases." Considering this system model allows relaxation time to be theoretically based upon potential barriers & resulting configurational entropy.

$$\tau = \tau_0 \exp\left[\frac{A}{TS_c}\right]$$

where S_c is the overall configurational entropy and A is a constant including potential barrier and entropy of the smallest rearranging group.

Further development of the mathematical form produces

$$\tau_p = \tau_0 \exp\left[\frac{Q/RT}{\ln(T_g/T_2) + C(T_g - T_2)}\right]$$

although this equation does not account well for anharmonic contributions it still models τ very well for viscosity and structural relaxation in equilibrium & non-equilibrium cases. Uncertainty remains as to whether the AG eq. is superior to the T-N model in describing very rapid cooling, however the AG eq. models well normal ranges and has superior theoretical basis.