Homework #8
Solutions

1.   (a) formers: SiO_2, P_2O_5, B_2O_3, GeO_2

              modifiers: CaO, MgO, Na_2O ...

   intermediates: Al_2O_3, TiO_2

(b)
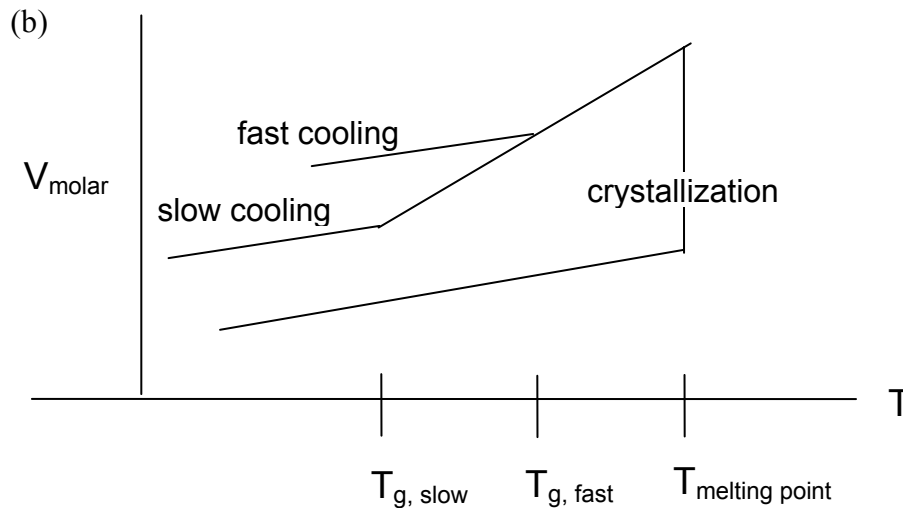
(c)   — change in atomic arrangement required in going from liquid to solid – complexities of both structures

        — cooling rate/viscosity

2.   Al will not form a stable glass because atomic scale (re)ordering into an FCC structure requires only atomic jumps of short distance and thus small amounts of activation energy (available to some extent already at low temperatures). Ordering of Se (transition of Se from glassy to crystalline state) is impeded by the complexity of unit species on lattice sites (Se_8 rings) and by inadvertent chain growth (Se_8 – Se_{20}). These result in steadily increasing viscosity (with decreasing temperature) and, thus, in decreasing probability of stabilizing an ordered atomic structure.

3.   Glasses are brittle because under stress they cannot plastically deform since dislocations, which are necessary for plastic deformation, are absent. Glasses are disordered and thus are inherently incapable of forming dislocations.

4.   (a) The simplest way to differentiate a glass from a crystal is exposure to x-rays. In glass we encounter only scattering; in crystalline material X-rays can give rise to diffraction.

      (b) We can also heat up the substances. Glass will soften gradually; a crystalline material will likely melt at one particular temperature, or a solid and liquid phase will coexist over a temperature range.

(c) Under tensile stress a crystalline material will deform plastically, while the glass will fracture in a brittle mode.

5. T_g is influenced by melt viscosity. At a constant cooling rate, T_g increases with viscosity. The addition of CaO lowers the viscosity of the silicate melt. CaO dissociates to give Ca^{2+} and O^{2-}. The O^{2-} attacks bridging oxygen, $-O-$, and converts it to a terminal oxygen, $-O^-$. Chain scission results in shorter chain lengths which can flow more easily; hence, viscosity decreases. When the temperature drops, the higher fluidity of the melts means there is less chance for trapping excess free volume.

6. (a)
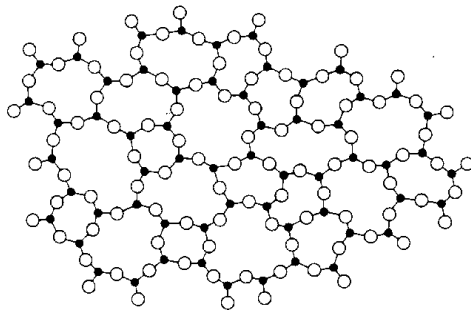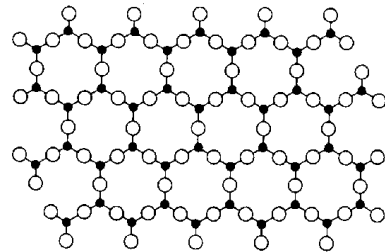
amorphous B_2O_3 crystalline B_2O_3

(b) Na_2O is a modifier. It dissociates to form Na^+ cations and O^{2-} anions. The oxide anions attack the bridging $-O-$ oxygens in the borate network thereby disrupting it. The resulting smaller borate units are able to move more easily than the antecedent larger units. This is manifest in the lower value of viscosity for the modified melt.

(c) Increase. As high cooling rates there is not enough time for the melt constituents to rearrange themselves before the temperature has fallen to the point at which the existing structure is rendered immobile.

(d) 1. Ion exchange. Immerse the glass in a molten salt containing alkali or alkaline-earth cations that are larger than those present in the glass. The concentration gradient in such cations will drive them to diffuse into the glass where they will substitute for smaller ions. This results in the generation of compressive stress in the surface and raises the level of stress needed to break the glass.

2. Tempering. Subject the glass to surface cooling by air jet. This results in differential cooling rates: the surface region is cooling at a higher rate than the interior. If you look at a plot of V vs T, the final volume of the fast-cooled surface layer will be greater than that of the slow-cooled interior. This results in the generation of compressive stress in the surface and raises the level of stress needed to break the glass.

(e) Covalent bonds. Tightly bound electrons. No dopants that introduce donor or acceptor bands 1 - 3 eV from the valence band or the conduction band.

14-45.   Rate $= k\ [NO]^x[Cl_2]^y$

From the data for the first two reactions, doubling the concentration of NO causes the initial rate of reaction to increase by a factor of 4. The value of x in the reaction equation is 2. From the data for the third and fourth reactions, doubling the concentration of Cl_2 causes the rate of the reaction to also double. The value of y in the reaction equation is 1.

Rate $= k\ (NO)^2(Cl_2)$

14-46.   Rate $= k\ (NO)^2(Cl_2)$ and $k = \dfrac{0.117\ Ms^{-1}}{(0.10\ M)^2\ (0.10\ M)} = 117\ M^{-2}s^{-1}$

so rate $= (117\ M^{-2}s^{-1})\ (0.50\ M)^2\ (0.50\ M) = 15\ Ms^{-1}$

14-47.   Rate $= k\ (NO)^x(O_2)^y$

From the data for the first two reactions we find that $[100/150]^2 = 0.355/0.800$. The reaction is second order in NO (x=2). From the data for the last two reactions $[130/180] = [1.04/1.44]$. The reaction is first order in oxygen. Rate $= k\ (NO)^2(O_2)$.

14-48.   Rate $= k\ (NO)^2(O_2)$ and $k = \dfrac{0.355\ mm\ Hg\,/\,s}{(100\ mm\ Hg)^2\ (100\ mm\ Hg)} = 3.55 \times 10^{-7}\ mm\ Hg^{-2}s^{-1}$

so rate $= \dfrac{3.55 \times 10^{-7}}{mm\ Hg^2 s}$ (250 mm Hg)^2(250 mm Hg) = 5.55 mm Hg s^{-1}

14-62. $ln\,(0.795) = -\,kt$ and $t_{1/2} = \dfrac{-ln(1/2)}{k} = \dfrac{0.693}{k}$ $\therefore\ t = \dfrac{ln(0.795)}{\left(\dfrac{-0.693}{5730\ y}\right)} = 1.90 \times 10^3\ y$

14-95.   The plot of ln k versus 1/T gives a straight line with a slope of -4.02×10^3. The Arrhenius equation can be written,

$ln\ k\ =\ ln\ Z\ -\ \dfrac{E_a}{RT}$ where the slope $= \dfrac{-E_a}{R}$ $\therefore\ ln\ k\ =\ ln\ Z - \dfrac{E_a}{8.314\ \dfrac{J}{mol\ K}\ T}$

$E_a\ =\ 3.34 \times 10^4\ \dfrac{J}{mol}\ =\ 33.4$ kJ/mol rxn

7. (a)   To show that the reaction is first order try fitting the logarithm of concentration versus time. Least-squares analysis gives

$ln\ c\ =\ 0.831\ -\ 7.21 \times 10^{-4}\,t$

with a correlation coefficient of 0.998.

 (b)   The half-life is given by $t_{1/2}\ =\ \dfrac{ln\,2}{k}\ =\ \dfrac{0.693}{7.21 \times 10^{-4}}\ =\ 961\,s$

(c) To decrease the concentration to 25% of initial value would take 2 half-lives, since after $t_{1/2}$ the concentration would be 50% and after 2 $t_{1/2}$ it would be 50% of 50%. So the answer is 2×961 s $= 1922$ s.

8. (a) Radioactive decay is a 1st order reaction which can be modeled as

$$-\frac{dc}{dt} = kc \quad \text{or} \quad c = c_o e^{-kt}$$

With a little algebra we can get an expression for the relationship between time, t, and the instant value of the decay rate:

at any time, t, we can write $\quad -\frac{dc}{dt} = kc = kc_o e^{-kt}$ ❶

and at time zero $\quad -\frac{dc}{dt} = kc_o$ ❷

divide ❶ by ❷ to get $\dfrac{r_t}{r_o} = e^{-kt}$ ❸, where to reduce clutter let $r = \dfrac{dc}{dt}$.

Take the logarithm of both sides of ❸ and substitute $k = \dfrac{\ln 2}{t_{1/2}}$. With rearrangement this gives

$$t = -\frac{t_{1/2}}{\ln 2} \cdot \ln \frac{r_t}{r_o} \quad ❹.$$

So, for the oldest specimen we would measure the minimum instant decay rate of 0.1 ± 0.1 disintegrations per minute per gram. Set this equal to r_t in ❹ and solve for t to get 41585 ± 5730 years.

(b) For the youngest specimen we would measure the maximum instant decay rate of 15.2 ± 0.1 disintegrations per minute per gram. Set this equal to r_t in ❹ and solve for t to get 54 ± 54 years.

Note that although the experimental uncertainty remains constant at 0.1 disintegrations per minute per gram, because this is compared against a measurement that can vary from 15.3 down to undetectable, the derived uncertainty in time varies greatly from 54 years to 54 years, respectively.