

## Session #21: Homework Solutions

### Problem #1

Account for the fact that aluminum (Al) does not form a stable glass while elemental selenium (Se) does.

### Solution

Al will not form a stable glass because atomic scale reordering 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 ( $\text{Se}_8$  rings) and by inadvertent chain growth ( $\text{Se}_8 - \text{Se}_{20}$ ). These result in steadily increasing viscosity (with decreasing temperature) and, thus, in decreasing probability of stabilizing an ordered atomic structure.

### Problem #2

Describe two analytical techniques that allow you to distinguish an amorphous solid from a crystalline solid.

### Solution

- (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.

### Problem #3

Under what conditions will some liquid phases not assume ordered (crystalline) structures upon cooling to below their melting points?

### Solution

The formation of a crystalline (ordered) phase upon cooling to below the melting point of a given system requires the relocation of atoms or molecules from their random, disordered position in the liquid phase to specific positions dictated by the characteristics of the "unit cell" system. This ordering process on atomic dimensions is normally accomplished by "diffusion" which requires mobility of species in the liquid state.

The formation of an ordered (crystalline) state is impeded (1) if the mobility of the species in the liquid state is very limited, such as is the case during the formation of three-dimensional covalent networks of oxides ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{B}_2\text{O}_3$ ,  $\text{P}_2\text{O}_5$ , and others) or (2) if the unit cell involved is complex or, for example, demands the formation of

ring structures in given lattice positions (S, Se, Te). Alternately, the formation of a crystalline phase can also be prevented if the atomic or molecular unit cell structure in two- or multi-component systems demands specific components (elements) in specific unit cell locations and if, upon rapid cooling (quenching), the species involved “prematurely” lose their kinetic energy and thus their mobility. All disordered solids formed are in principle unstable and tend to assume, at largely varying rates, ordered configuration.

#### Problem #4

For silica glass, Pyrex, and soda-lime glass:

- (a) give the respective working and softening temperatures.
- (b) explain the differences in the listed temperatures by comparison with the observed temperatures in silica glass.

#### Solution

(a)	$T_w$ ( $^{\circ}\text{C}$ )	$T_s$ ( $^{\circ}\text{C}$ )
Silica	~1950	1700
Pyrex	~1200	800
Soda-Lime	~900	700

- (b) Both  $T_w$  and  $T_s$  are expected to be highest in silica glass where matrix breakdown is strictly thermal. Replacement of some 15 wt% of  $\text{SiO}_2$  with  $\text{B}_2\text{O}_3$  results in a lowering of the overall bond density since B has 3 covalent bonds while Si has 4. As a consequence, the working temperature, the temperature at which the viscosity assumes a value of  $\sim 10^6$  poise, is reduced from  $\sim 1900^{\circ}\text{C}$  to  $\sim 1200^{\circ}\text{C}$  and the softening temperature ( $T_s$ ) from  $1700^{\circ}\text{C}$  to  $800^{\circ}\text{C}$ . The reduction of both temperatures is even more pronounced when considering the difference between silica glass and soda-lime glass. It can be attributed to the large ionic content which results in the irreversible rupture of covalencies, and thus, in a further decrease of the viscosity at any given temperature.

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