

Set 2, Additional problem

The quantity that is minimized at constant pressure for thermal equilibrium is the Gibbs Free Energy

$$\begin{aligned}G &= H - TS \\ &= U + pV - TS.\end{aligned}$$

At very high pressures, the second term becomes important. Since increases in *pressure* cause the melting, only the second term can be involved.

If raising the pressure, causes melting, that means that raising pressure lowers  $G$ . The only way this can happen is if  $V_{\text{liquid}}$  is less than  $V_{\text{solid}}$ , which means that the liquid is denser than the solid.

This is not true for most materials, but it is true for water and sodium.