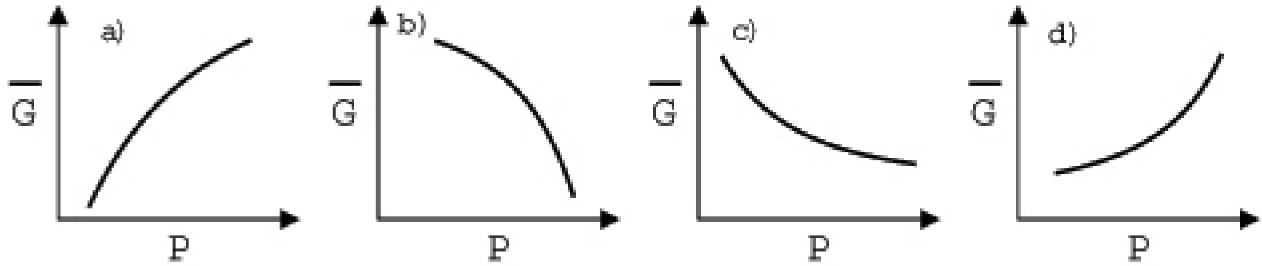
Thermodynamics of Materials 3.00

Example Problems for Week 8

Example Problem 8.1

Select the figure below that illustrates the correct dependence of the molar Gibbs free energy, $\overline{G}$, on pressure, P at constant temperature for a single component solid. Explain your choice.



Solution 8.1

Starting from the differential expression for $\overline{G}$ we can write expressions for the slope and curvature.

$$d\overline{G} = -T\overline{S} + \overline{V}dP$$

$$\frac{\partial\overline{G}}{\partial P} = \overline{V} \quad \text{and} \quad \frac{\partial^2\overline{G}}{\partial P^2} = \frac{\partial\overline{V}}{\partial P} = -\beta_T\overline{V}_0$$

Where the definition of the isothermal compressibility has been used, $\beta_T = -\frac{1}{V_0}\left(\frac{\partial V}{\partial P}\right)_T$ with units 1/Pascal. This definition ensures that $\beta_T > 0$ so the curvature is negative, $\frac{\partial^2\overline{G}}{\partial P^2} < 0$. This excludes curves c and d. The slopes of each curve gives the molar volume which is a positive quantity. This excludes curve b. Therefore curve a gives the correct slope and curvature.

Example Problem 8.2

The Gibbs free energy has natural variable T and P for a single component system. Consider the molar Gibbs free energy at constant temperature $T = 100C^\circ$, $\overline{G}$, for different phases of H_2O. Draw a schematic of $\overline{G}_l(P)$ and $\overline{G}_g(P)$ as a function of pressure about the transformation pressure, P_t. Identify P_t for this transformation and the regions of liquid and gaseous stability. Speculate on the change in the transformation temperature if the temperature is increased.

Solution 8.2

First let's consider the transformation pressure at fixed temperature. At this pressure the molar Gibbs free energies of the liquid and gas are equal, $\overline{G}_l(P_t) = \overline{G}_g(P_t)$. Therefore, the curves intersect at P_t.

We know $\overline{V}_g > \overline{V}_l$. Using this information we can draw and identify both curves. At the transformation pressure the gas and liquid are in equilibrium and can co-exist. If the pressure is lowered the equilibrium phase is gas as it has the lowest molar Gibbs free energy. If the pressure is perturbed upwards from the transformation pressure then the equilibrium phase is liquid.

For H_2O this transformation pressure is $P_t = 1$atm. If the temperature is increased the transformation pressure also increases. Think about boiling water for cooking with no lid on a pan. If you put a lid on the pan you increase the pressure and the water finds a new boiling point. That new boiling point is $T > 100C_\circ$. Because $\overline{G}$ is a state function we know that fixing the pressure and finding the new transformation temperature will give the same result as fixing the temperature and finding the new transformation pressure. Therefore, raising the temperature will increase the transformation pressure.