

Formation of black phosphorous

There are three allotropes of phosphorous, white, violet and black, which have densities of 1.88, 2.36 and 2.69 gm/cm³, respectively. At ambient pressure white phosphorous is stable. Given that the free energy for formation of black phosphorous from white phosphorous is 2.7 kJ/mol, what pressure is required to convert white phosphorous to black phosphorous?



NOTE: For any density calculations treat the phosphorous in both species as atomic phosphorous with a mass of 31 a.m.u. Furthermore, for this problem assume that $Q = 1$, which means that the pressure you calculate will be sufficient to begin to convert white phosphorous to black phosphorous.

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Solution:

$$\Delta G = \Delta G^{\circ} + RT \ln Q$$

However, since $Q = 0$, $\Delta G = \Delta G^{\circ}$. In order to force the reaction to occur against a positive ΔG° we use pressure according to

$$\Delta G = \Delta V_m \Delta P$$

Therefore, $\Delta G = -2.7 \text{ kJ/mol}$.

$$\Delta V_m = \frac{M_m}{\rho_{aq}} - \frac{M_m}{\rho_s}$$

$$\Delta V_m = \frac{0.031 \text{ kg/mol}}{2690 \text{ kg/m}^3} - \frac{0.031 \text{ kg/mol}}{1880 \text{ kg/m}^3}$$

$$\Delta V_m = -5.1 \times 10^{-6} \text{ m}^3/\text{mol}$$

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The pressure required to force the formation of black phosphorous to occur is

$$P = 10^5 Pa + \frac{\Delta G}{\Delta V_m}$$

$$P = 10^5 Pa + \frac{-2,700 J/mol}{-5.1 \times 10^{-6} m^3/mol}$$

$$P = 5.27 \times 10^8 Pa = 5270 bars$$