Exercises on Ch.16 *Interfaces*

16.2 Phase equilibrium at curved interfaces.

Exercise 1

Consider a liquid droplet of pure A with radius *r* floating around in a small container and without any contact with the walls. (This could conceivably be arranged und microgravity in space.) Suppose the only gas in the container comes from the droplet itself. Calculate the pressure in the container if the ordinary vapour pressure of A is ${}^{o}P_A$ at the temperature, which is kept constant.

Hint

Start by (a) calculating the partial pressure of a large amount of A when it is under the pressure *P*. (b) accept that the pressure comes from the vapour of A itself. (c) Finally, add the effect of the surface energy.

Solution

(a) The partial pressure of A is related to its chemical potential. Using Eq. 16.17 we obtain without considering the pressure effect, ${}^{o}\mu_A^L(P=0) = \mu_A^{gas} = K + RT\ln{}^{o}P_A$.
Considering the pressure effect we obtain
$\mu_A^L(P) = \mu_A^L(P=0) + V_m P = K + RT\ln{}^{o}P_A + V_m P = K + RT\ln P_A$ and
$P_A = {}^{o}P_A \cdot \exp(V_m P / RT)$. This relation holds for any P value.
(b) Accept that the only gas is the vapour of A itself, i.e.,
$P_A = {}^{o}P_A \cdot \exp(V_m P_A / RT) \cong {}^{o}P_A \cdot (1 + V_m P_A / RT) = {}^{o}P_A / (1 - V_m\,{}^{o}P_A / RT)$.
(c) For a droplet the pressure is $P = P_A + 2\sigma / r$ and we obtain
$P_A \cong {}^{o}P_A \cdot [1 + V_m (P_A + 2\sigma / r) / RT] = {}^{o}P_A \cdot (1 + 2\sigma V_m / rRT) / (1 - V_m\,{}^{o}P_A / RT)$.