Problem 2. Van der Waals equation of state
Solution
Part A. Non-ideal gas equation of state

A1. If $V = b$ is substituted into the equation of state, then the gas pressure turns infinite. It is obvious that this is the moment when all the molecules are tightly packed. Therefore, the parameter b is approximately equal to the volume of all molecules, i.e.

$$b = N_A d^3 \tag{A1.1}$$

A2. In the most general case the van der Waals equation of state can be rewritten as

$$P_c V^3 - (RT_c + bP_c)V^2 + aV - ab = 0 \tag{A2.1}.$$

Since at the critical values of the gas parameters the straight line disappears, then, the solution of (A2.1) must have one real triple root, i.e. it can be rewritten as follows

$$P_c(V - V_c)^3 = 0 \tag{A2.2}.$$

Comparing the coefficients of expression (A2.1) and (A2.2), the following set of equations is obtained

$$\begin{cases} 3P_c V_c = RT_c + bP_c \\ 3P_c V_c^3 = a \\ P_c V_c^3 = ab \end{cases} \tag{A2.3}.$$

Solution to the set (A2.3) is the following formulas for the van der Waals coefficients

$$a = \frac{27R^2 T_c^2}{64P_c} \tag{A2.4},$$

$$b = \frac{RT_c}{8P_c} \tag{A2.5}.$$

Alternative solution

The critical parameters are achieved in the presence of an inflection point in the isotherm, at which the first and second derivatives are both zero. Therefore, they are defined by the following conditions

$$\left(\frac{dP}{dV}\right)_T = 0 \tag{A2.6},$$

and

$$\left(\frac{d^2 P}{dV^2}\right)_T = 0 \tag{A2.7}.$$

Thus, the following set of equations is obtained

$$\begin{cases} -\frac{RT_c}{(V_c-b)^2} + \frac{2a}{V_c^3} = 0 \\ \frac{2RT_c}{(V_c-b)^3} - \frac{6a}{V_c^4} = 0 \\ \left(P_c + \frac{a}{V_c^2}\right)(V_c - b) = RT_c \end{cases} \tag{A2.8},$$

which has the same solution (A2.4) and (A2.5).

A3. Numerical calculations for water produce the following result

$$a_w = 0.56 \frac{\text{m}^6 \cdot \text{Pa}}{\text{mole}^2} \tag{A3.1}.$$

$$b_w = 3.1 \cdot 10^{-5} \frac{\text{m}^3}{\text{mole}} \tag{A3.2}.$$

A4. From equations (A1.4) and (A3.2) it is found that

$$d_w = \sqrt[3]{\frac{b}{N_A}} = 3.7 \cdot 10^{-10} \text{m} \approx 4 \cdot 10^{-10} \text{m} \tag{A4.1}$$

Part B. Properties of gas and liquid

B1. Using the inequality $V_G \gg b$, the van der Waals equation of state can be written as

$$\left(p_0 + \frac{a}{V_G^2}\right)V_G = RT \tag{B1.1},$$

which has the following solutions

$$V_G = \frac{RT}{2p_0}\left(1 \pm \sqrt{1 - \frac{4ap_0}{R^2 T^2}}\right) \tag{B1.2}.$$

Smaller root in (B1.2) gives the volume in an unstable state on the rising branch of the van der Waals isotherm. The volume of gas is given by the larger root, since at $a = 0$ an expression for the volume of an ideal gas should be obtained, i.e.

$$V_G = \frac{RT}{2p_0}\left(1 + \sqrt{1 - \frac{4ap_0}{R^2T^2}}\right) \tag{B1.3}.$$

For given values of the parameters the value $\frac{ap_0}{(RT)^2} = 5.8 \cdot 10^{-3}$. It can therefore be assumed that $\frac{ap_0}{(RT)^2} \ll 1$, then (B1.3) takes the form

$$V_G \approx \frac{RT}{p_0}\left(1 - \frac{ap_0}{R^2T^2}\right) = \frac{RT}{p_0} - \frac{a}{RT} \tag{B1.4}.$$

B2. For an ideal gas

$$V_{G0} = \frac{RT}{p_0} \tag{B2.1},$$

hence,

$$\left(\frac{\Delta V_G}{V_{G0}}\right) = \frac{V_{G0} - V_G}{V_{G0}} = \frac{1}{2}\left(1 - \sqrt{1 - \frac{4ap_0}{R^2T^2}}\right) \approx \frac{ap_0}{R^2T^2} = 0.58\%. \tag{B2.2}$$

B3. Mechanical stability of a thermodynamic system is in power provided that

$$\left(\frac{dP}{dV}\right)_T < 0. \tag{B3.1}$$

The minimum volume, in which the matter can still exist in the gaseous state, corresponds to a point in which

$$V_{Gmin} \rightarrow \left(\frac{dP}{dV}\right)_T = 0 \tag{B3.2}.$$

Using the van der Waals equation of state (B3.2) is written as

$$\left(\frac{dP}{dV}\right)_T = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3} = 0 \tag{B3.3}.$$

From (B3.2) and (B3.3), and with the help of $V_{Gmin} \gg b$, it is found that

$$V_{Gmin} = \frac{2a}{RT} \tag{B3.4}.$$

Thus,

$$\frac{V_G}{V_{Gmin}} = \frac{R^2T^2}{2ap_0} = 86 \tag{B3.5}.$$

B4. Using the inequality $P \ll a/V^2$, the van der Waals equation of state is written as

$$\frac{a}{V_L^2}(V_L - b) = RT, \tag{B4.1}$$

whose solution is

$$V_L = \frac{a}{2RT}\left(1 \pm \sqrt{1 - \frac{4bRT}{a}}\right) \tag{B4.2}.$$

In this case, the smaller root should be taken, since at $T \rightarrow 0$ the liquid volume $V_L = b$ must be obtained according to (B4.1), i.e.

$$V_L = \frac{a}{2RT}\left(1 - \sqrt{1 - \frac{4bRT}{a}}\right) \approx b\left(1 + \frac{bRT}{a}\right). \tag{B4.3}.$$

B5. Since (B4.3) gives the volume of the one mole of water its mass density is easily found as

$$\rho_L = \frac{\mu}{V_L} = \frac{\mu}{b\left(1 + \frac{bRT}{a}\right)} \approx \frac{\mu}{b} = 5.8 \cdot 10^2 \frac{\text{kg}}{\text{m}^3} \tag{B5.1}.$$

B6. In accordance with (B4.3) the volume thermal expansion coefficient is derived as

$$\alpha = \frac{1}{V_L}\frac{\Delta V_L}{\Delta T} = \frac{bR}{a + bRT} \approx \frac{bR}{a} = 4.6 \cdot 10^{-4}\text{K}^{-1} \tag{B6.1}.$$

B7. The heat, required to convert the liquid to gas, is used to overcome the intermolecular forces that create negative pressure a/V^2, therefore,

$$E = L\mu \approx \int_{V_L}^{V_G} \frac{a}{V^2}dV = a\left(\frac{1}{V_L} - \frac{1}{V_G}\right) \tag{B7.1},$$

and using $V_G \gg V_L$, (B7.1) yields

$$L = \frac{a}{\mu V_L} = \frac{a}{\mu b\left(1 + \frac{bRT}{a}\right)} \approx \frac{a}{\mu b} = 1.0 \cdot 10^6 \frac{\text{J}}{\text{kg}} \tag{B7.2}.$$

B8. Consider some water of volume V. To make a monolayer of thickness d out of it, the following work must be done

$$A = 2\sigma S \tag{B8.1}.$$

Fabrication of the monomolecular layer may be interpreted as the evaporation of an equivalent volume of water which requires the following amount of heat

$$Q = Lm \tag{B8.2},$$

where the mass is given by

$$m = \rho S d \tag{B8.3}.$$

Using (A4.1a), (B5.1) and (B7.2), one finally gets

$$\sigma = \frac{a}{2b^2} d_w = 0.12 \cdot 10^{-2} \, \frac{N}{m} \tag{B8.4}.$$

Part C. Liquid-gas systems

C1. It follows from the Maxwell rule that

$$\int_{V_L}^{V_G} P(V)dV = p_0(V_G - V_L) \tag{C1.1}.$$

Evaluation of the integral leads to the following equation for determining p_0

$$\int_{V_L}^{V_G} \left(\frac{RT}{V-b} - \frac{a}{V^2}\right) dV = RT \ln\left(\frac{V_G - b}{V_L - b}\right) + a\left(\frac{1}{V_G} - \frac{1}{V_L}\right) = p_0(V_G - V_L) \tag{C1.2}.$$

Using the inequalities $b, V_L \ll V_G$ and formulas (B2.1) and (B4.3), this equation is simplified to

$$RT \ln\left(\frac{RT}{p_0} \frac{a}{b^2 RT}\right) - \frac{a}{b} = RT \tag{C1.3}.$$

(C1.3) is simply rearranged as

$$\ln p_0 = \ln \frac{a}{b^2} - \frac{a}{bRT} - 1 \tag{C1.4}.$$

Consequently, expressions for A and B are obtained as follows

$$A = \ln\left(\frac{a}{b^2}\right) - 1 \tag{C1.5},$$

$$B = -\frac{a}{bR} \tag{C1.6}.$$

C2. Collecting formulas (C1.4), (C1.5) and (C1.6), the vapor pressure is found as

$$p_0 = \frac{a}{b^2 \exp\left(\frac{a}{bRT} + 1\right)} = 6.2 \cdot 10^5 \, Pa \tag{C2.1}.$$

C3. At equilibrium, the pressure in the liquid and gas should be equal at all depths. The pressure p in the fluid at the depth h is related to the pressure of saturated vapor above the flat surface by

$$p = p_0 + \rho_L g h \tag{C3.1}.$$

The surface tension creates additional pressure defined by the Laplace formula as

$$\Delta p_L = \frac{2\sigma}{r} \tag{C3.2}.$$

The same pressure p in the fluid at the depth h depends on the vapor pressure p_h over the curved liquid surface and its radius of curvature as

$$p = p_h + \frac{2\sigma}{r} \tag{C3.3}.$$

Furthermore, the vapor pressure at different heights are related by

$$p_h = p_0 + \rho_S g h \tag{C3.4}.$$

Solving (C3.1)-(C3.4), it is found that

$$h = \frac{2\sigma}{(\rho_L - \rho_S)gr} \tag{C3.5}.$$

Hence, the pressure difference sought is obtained as

$$\Delta p_T = p_h - p_0 = \rho_S g h = \frac{2\sigma}{r} \frac{\rho_S}{\rho_L - \rho_S} \approx \frac{2\sigma}{r} \frac{\rho_S}{\rho_L} \tag{C3.6}.$$

Note that the vapor pressure over the convex surface of the liquid is larger than the pressure above the flat surface.

C4. Let P_e be vapor pressure at a temperature T_e, and $P_e - \Delta P_e$ be vapor pressure at a temperature $T_e - \Delta T_e$. In accordance with **B4**, when the ambient temperature falls by an amount of ΔT_e the saturated vapor pressure changes by an amount

$$\Delta P_e = P_e \frac{a}{bRT_e^2} \Delta T_e \tag{C4.1}.$$

In accordance with the Thomson formula obtained in part **C3**, the pressure of saturated vapor above the droplet increases by the amount of Δp_T. While a droplet is small in size, the vapor above its surface remains unsaturated. When a droplet has grown up to a certain minimum size, the vapor above its surface turns saturated.

Since the pressure remains unchanged, the following condition must hold

$$P_e - \Delta P_e + \Delta p_T = P_e \qquad (C4.2).$$

Assuming the vapor is almost ideal gas, its density can be found as

$$\rho_S = \frac{\mu P_e}{RT_e} \ll \rho_L \qquad (C4.3).$$

From equations (C4.1)-(C4.3), (B5.1) and (C3.6) one finds

$$\frac{2\sigma}{r}\frac{\mu P_e}{RT_e} = P_e\frac{a\Delta T_e}{bRT_e^2} \qquad (C4.4).$$

Thus, it is finally obtained that

$$r = \frac{2\sigma b^2 T_e}{a\Delta T_e} = 1.5 \cdot 10^{-8}\text{m} \qquad (C4.5).$$