The Thermodynamics of Linear Fluids and Fluid Mixtures by Pekař & Samohýl

Exercise 1 to section $4.7.^1$

Calculate the content of carbon dioxide (molar %) on the top of a gasometer of 50 m height. It operates at 25 °C and contains a mixture of carbon dioxide and hydrogen with equimolar composition at its bottom. The gases are ideal and the gravitational acceleration (g) has the value of 9.81 m s⁻².

Try to answer before continuing reading.

Hint: use the Svedberg formula given on page 214, Rem. 23. The formula is:

$$(1/x_1)$$
 grad $x_1 = (M_1/RT)(1 - \rho v_1)$ g

where x_1 is the molar fraction of component 1 (CO₂), M_1 is its molar mass, ρ is the mixture density and v_1 is the specific volume of pure component 1.

The gravitational acceleration has only one non-zero component (of magnitude g) which we locate along the vertical axis (symbol z). Thus, this axis points from top (of the gasometer) down; the gasometer top is located at z = 0 and its bottom at z = 50 m. The Svedberg formula for this case is

$$(1/x_1) (dx_1/dz) = (M_1/RT)(1 - \rho v_1)g.$$
(1)

The density of this two-component mixture is expressed using equations (4.419) and (4.424) from which it follows that:

$$\rho_{\alpha} = (P_{\alpha}M_{\alpha})/RT = (x_{\alpha}PM_{\alpha})/RT, \quad \alpha = 1,2$$
(2)

and $(1=CO_2)$

$$\rho = (P/RT)(x_{\rm CO_2}M_{CO_2} + x_{\rm H_2}M_{H_2}). \tag{3}$$

The product in (1) then is, taking into account also eq. (4.420),

$$\rho v_{\rm CO_2} = x_{\rm CO_2} + x_{\rm H_2} (M_{H_2}/M_{CO_2}) \tag{4}$$

or

$$\rho v_{\rm CO_2} = x_{\rm CO_2} \left(1 - \frac{M_{H_2}}{M_{CO_2}} \right) + \frac{M_{H_2}}{M_{CO_2}}.$$
 (5)

Expression (5) is substituted into the Svedberg formula (1) and after a minor modification we have

$$\frac{dx_{\rm CO_2}}{x_{\rm CO_2} \left[-x_{\rm CO_2} \left(1 - \frac{M_{H_2}}{M_{CO_2}} \right) + 1 - \frac{M_{H_2}}{M_{CO_2}} \right]} = \frac{g M_{CO_2}}{RT} dz.$$
(6)

¹Based on I. Samohýl: Irreversible Thermodynamics. Prague: University of Chemical Technology, 1998 (*in Czech*).

Eq. (6) is integrated using the limits on the left hand side from 0.5 to x (to be calculated), on the right hand side from 50 to 0 (meters), and $M_{CO_2} = 0.044$, $M_{H_2} = 0.002$ (kg/mol). The result is an equation for x the solution of which is x = 0.4979. Thus the carbon dioxide content at the bottom is 49.79% (molar).