25. ZADATAK

U jedan kg H_2O postupno se, pri stalnom tlaku i temperaturi, dodaje sol S i mjeri se promjena volumena otopine. Rezultati mjerenja prikazani su empirijskom ovisnošću o molalitetu, odnosno količini dodane soli, izrazima:

$$V/\mathrm{cm}^3 = 1001,38 + 16,6253\left[m/\left(\mathrm{mol\,kg^{-1}}\right)\right] + \\ +1,7738\left[m/\left(\mathrm{mol\,kg^{-1}}\right)\right]^{3/2} + \\ +0,1194\left[m/\left(\mathrm{mol\,kg^{-1}}\right)\right]^{2}$$

$$V/\mathrm{cm}^3 = 1001,38 + 16,6253\left[n_2/\mathrm{mol}\right] + \\ +1,7738\left[n_2/\mathrm{mol}\right]^{3/2} + \\ +0,1194\left[n_2/\mathrm{mol}\right]^{2}$$

Treba odrediti parcijalni molarni volumen obiju komponenata za otopinu molaliteta m=0,5 mol kg^{-1}.

Podaci:

$v_1^{\bullet}$=18,08 cm^3mol^{-1}; M_1=18 g mol^{-1}

Gibbs-Duhemova jednadžba

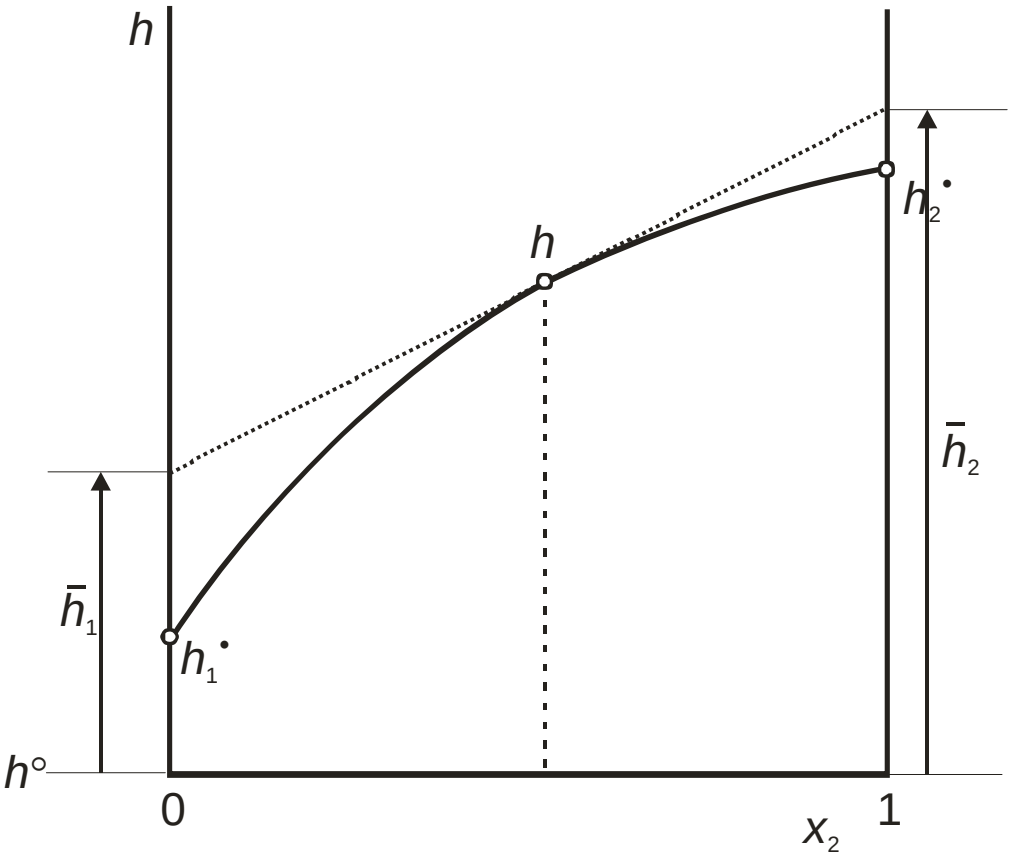
Daje međuovisnost parcijalnih molarnih veličina u višekomponentnim sustavima:

$$\sum n_i d\overline{y}_i = 0$$

$$\sum x_i d\overline{y}_i = 0$$

Za dvokomponentne sustave, $y=v$

$$n_1 d\overline{v}_1 + n_2 d\overline{v}_2 = 0$$



Za dvokomponentne sustave, *y=v*

$$n_1 d\overline{v}_1 + n_2 d\overline{v}_2 = 0$$

$$n_1 d\overline{v}_1 = -n_2 d\overline{v}_2$$

$$d\overline{v}_1 = -\frac{n_2}{n_1} d\overline{v}_2$$

$$\int_0^{n_2/n_1} d\overline{v}_1 = -\int_0^{n_2/n_1} \frac{n_2}{n_1} d\overline{v}_2$$

Granice integracije na lijevoj strani!

$$\overline{v}_1 - v_1^{\bullet} = -\int_0^{n_2/n_1} \frac{n_2}{n_1} d\overline{v}_2$$

Količina vode kao otapala je stalna!

$$n_1 = \frac{m_1}{M_1} = \frac{1}{0,018} = 55,56 \text{ mol}$$

Diferencijal na desnoj strani – I korak

$$\overline{v}_2 = \left(\frac{\partial V}{\partial n_2} \right)_{n_1, p, T}$$

$$\overline{v}_2 = \frac{1}{\partial n_2} \partial \left(1001,38 + 16,6253 n_2 + 1,7738 n_2^{3/2} + 0,1194 n_2^2 \right)$$

$$\overline{v}_2 = 16,6253 + \frac{3}{2} 1,7738 n_2^{1/2} + 2 \cdot 0,1194 n_2 =$$

$$= 16,6253 + 2,6607 n_2^{1/2} + 0,2388 n_2$$

Diferencijal na desnoj strani – II korak

$$\frac{\partial \overline{v}_2}{\partial n_2} = \frac{1}{\partial n_2}\partial\left(16,6253 + 2,6607 n_2^{1/2} + 0,2388 n_2\right)$$

$$\frac{\partial \overline{v}_2}{\partial n_2} = \frac{1}{2} 2,6607 n_2^{-1/2} + 0,2388 =$$

$$= 1,33035 n_2^{-1/2} + 0,2338$$

$$d\overline{v}_2 = \left(1,33035 n_2^{-1/2} + 0,2338\right) dn_2$$

Uvrštavanje u integral!

$$\overline{v}_1 - v_1^{\bullet} = -\int_0^{n_2/n_1} \frac{n_2}{n_1} d\overline{v}_2$$

$$\overline{v}_1 - v_1^{\bullet} = -\int_0^{n_2/n_1} \frac{n_2}{n_1}\left(1,33035 n_2^{-1/2} + 0,2338\right) dn_2$$

$$\overline{v}_1 = v_1^{\bullet} - \frac{1}{n_1}\int_0^{n_2/n_1} \left(1,33035 n_2^{1/2} + 0,2338 n_2\right) dn_2$$

Integriranje:

$$\overline{v}_1 = v_1^{\bullet} - \frac{1}{n_1}\left(1,33035 \cdot \frac{2}{3} n_2^{3/2} + 0,2338 \cdot \frac{1}{2} n_2^2\right)$$

Uvrštavanje:

$$\overline{v}_1 = 18,08 - \frac{1}{55,56}\left(1,33035 \cdot \frac{2}{3} \cdot 0,5^{3/2} + 0,2338 \cdot \frac{1}{2} \cdot 0,5^2\right)$$

$$\overline{v}_1 = 18,078\ \mathrm{cm^3 mol^{-1}}$$

Parcijalni molarni volumen soli:

$$\overline{v}_2 = 16,6253 + 2,6607 \cdot 0,5^{1/2} + 0,2388 \cdot 0,5$$

$$\overline{v}_2 = 18,6261\ \mathrm{cm^3 mol^{-1}}$$