

25. ZADATAK

U jedan kg H₂O 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:

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

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

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

Podaci:

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

Gibbs-Duhemova jednadžba

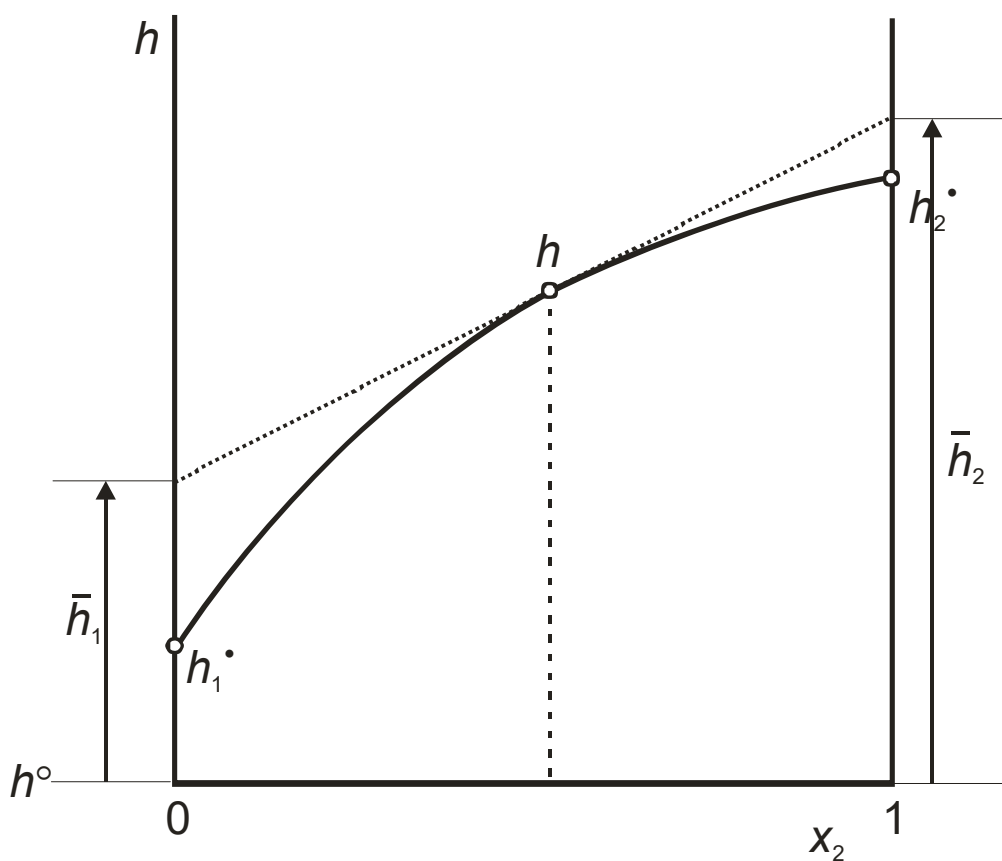
Daje međuovisnost parcijalnih molarnih veličina u višekomponentnim sustavima:

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

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

Za dvokomponentne sustave, $y=v$

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



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

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

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

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

Granice integracije na lijevoj strani!

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

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

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

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

$$\begin{aligned} \bar{v}_2 &= 16,6253 + \frac{3}{2} 1,7738n_2^{1/2} + 2 \cdot 0,1194n_2 = \\ &= 16,6253 + 2,6607n_2^{1/2} + 0,2388n_2 \end{aligned}$$

Diferencijal na desnoj strani – II korak

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

$$\begin{aligned}\frac{\partial \bar{v}_2}{\partial n_2} &= \frac{1}{2} 2,6607n_2^{-1/2} + 0,2388 = \\ &= 1,33035n_2^{-1/2} + 0,2338\end{aligned}$$

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

Uvrštavanje u integral!

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

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

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

Integriranje:

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

Uvrštavanje:

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

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

Parcijalni molarni volumen soli:

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

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