

## 24. ZADATAK

Piknometrijskom su metodom određene gustoće otopina metanola(1) i vode(2) u cijelom području sastava:

$w_1/\%$	0	20	40	60	80	90	100
$\rho/(\text{g cm}^{-3})$	0,9982	0,9666	0,9345	0,8946	0,8469	0,8202	0,7917

Treba odrediti parcijalni molarni volumen obje komponenata za otopinu sastava  $x_1=0,40$  metodom **odsječka**.

Podaci:

$$M_1=32 \text{ g mol}^{-1}; \quad M_2=18 \text{ g mol}^{-1}$$

## Metoda odsječka

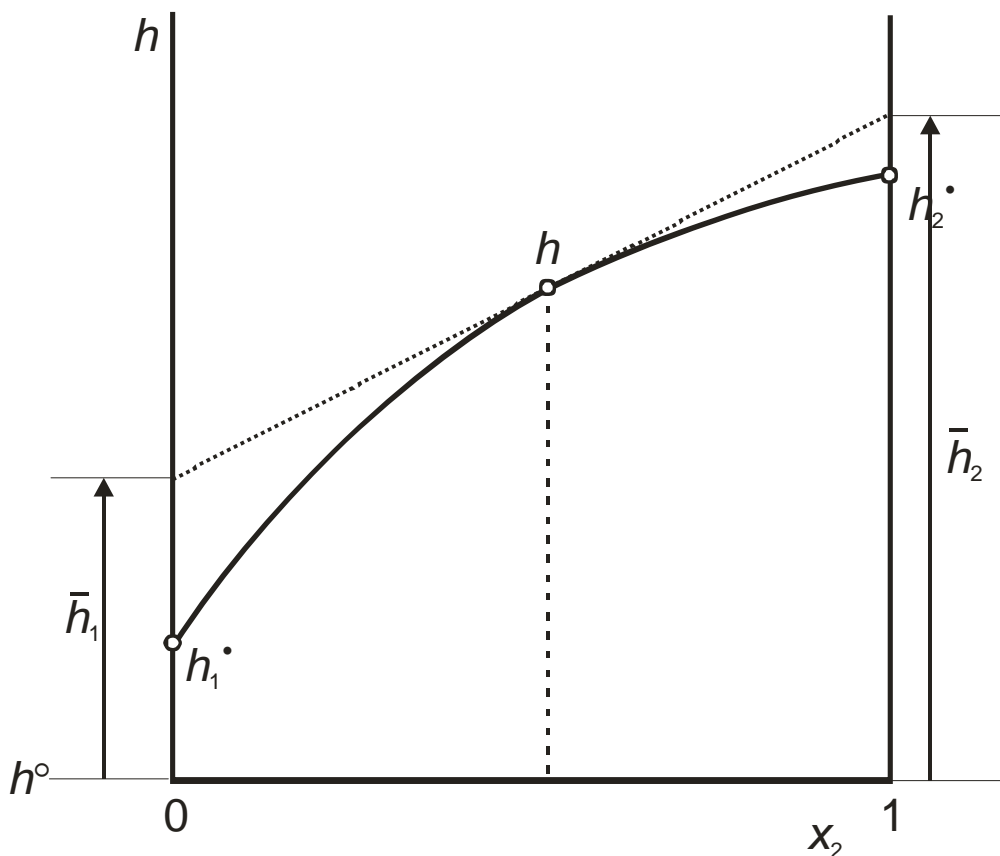
Određivanje parcijalnih molarnih veličina iz ovisnosti intenzivne veličine o sastavu!

$$\bar{y}_i = y - \sum_{k \neq i} x_k \left( \frac{\partial y}{\partial x_k} \right)_{p,T, x_{j \neq i, k}}$$

Za dvokomponentne sustave,  $y=v$

$$\bar{v}_1 = v - x_2 \left( \frac{\partial v}{\partial x_2} \right)_{p,T}$$

$$\bar{v}_2 = v - x_1 \left( \frac{\partial v}{\partial x_1} \right)_{p,T}$$



1. Postavljanje baze proračuna, npr. 100 g otopine

2. Izračunavanje količina komponenata

$$n_1 = \frac{mw_1}{M_1} = \frac{100 \cdot 0,20}{32} = 0,625 \text{ mol}$$

$$n_2 = \frac{m(1-w_1)}{M_2} = \frac{100 \cdot (1-0,20)}{18} = 4,44 \text{ mol}$$

$n_1/\text{mol}$	0	0,625	1,250	1,875	2,50	2,8125	3,125
$n_2/\text{mol}$	5,555	4,444	3,333	2,222	1,111	0,555	0

3. Izračunavanje molarnih udjela

$$x_1 = \frac{n_1}{n_1 + n_2} = \frac{0,625}{0,625 + 4,444} = 0,123 \text{ mol}$$

$$x_2 = \frac{n_2}{n_1 + n_2} = \frac{4,444}{0,625 + 4,444} = 0,877 \text{ mol}$$

$x_1$	0	0,1233	0,2727	0,4577	0,6923	0,8352	1
$x_2$	1	0,8767	0,7273	0,5423	0,3077	0,1648	0

4. Izračunavanje srednje molarne mase

$$\bar{M} = x_1 M_1 + x_2 M_2 = 0,877 \cdot 18 + 0,123 \cdot 32 = 19,74 \text{ g mol}^{-1}$$

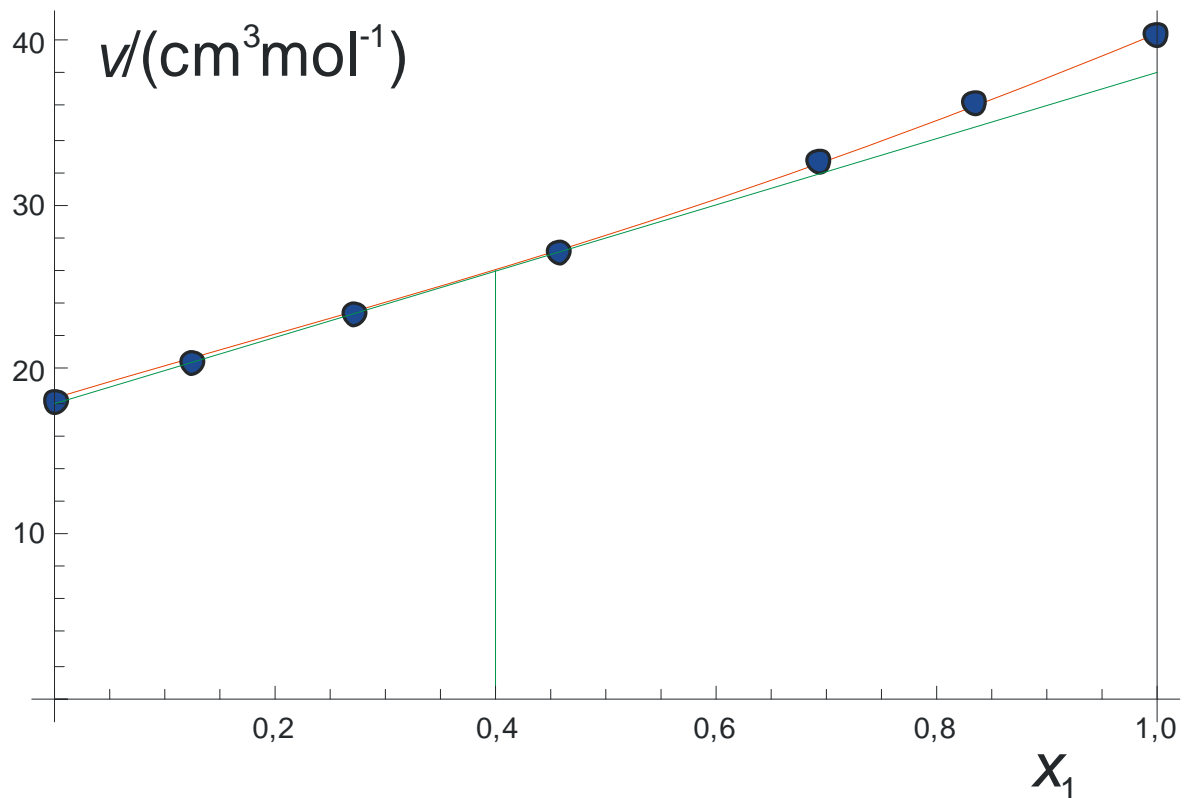
$\bar{M}/(\text{g mol}^{-1})$	18	19,72	21,82	24,41	27,69	29,69	32
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### 5. Izračunavanje molarnog volumena

$$v = \frac{\bar{M}}{\rho} = \frac{19,72}{0,9666} = 20,40 \text{ cm}^3 \text{ mol}^{-1}$$

$v/(\text{cm}^3 \text{ mol}^{-1})$	18,03	20,40	23,35	27,26	32,70	36,20	40,42
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Podaci  $v=f(x_1)$  omogućuju primjenu metode odsječka za određivanje parcijalnog molarnog volumena komponenata:



$$\bar{v}_1 \approx 38 \text{ cm}^3 \text{ g}^{-1}$$

$$\bar{v}_2 \approx 18 \text{ cm}^3 \text{ g}^{-1}$$

Bolje je prirediti ovisnost eksces volumena o sastavu!

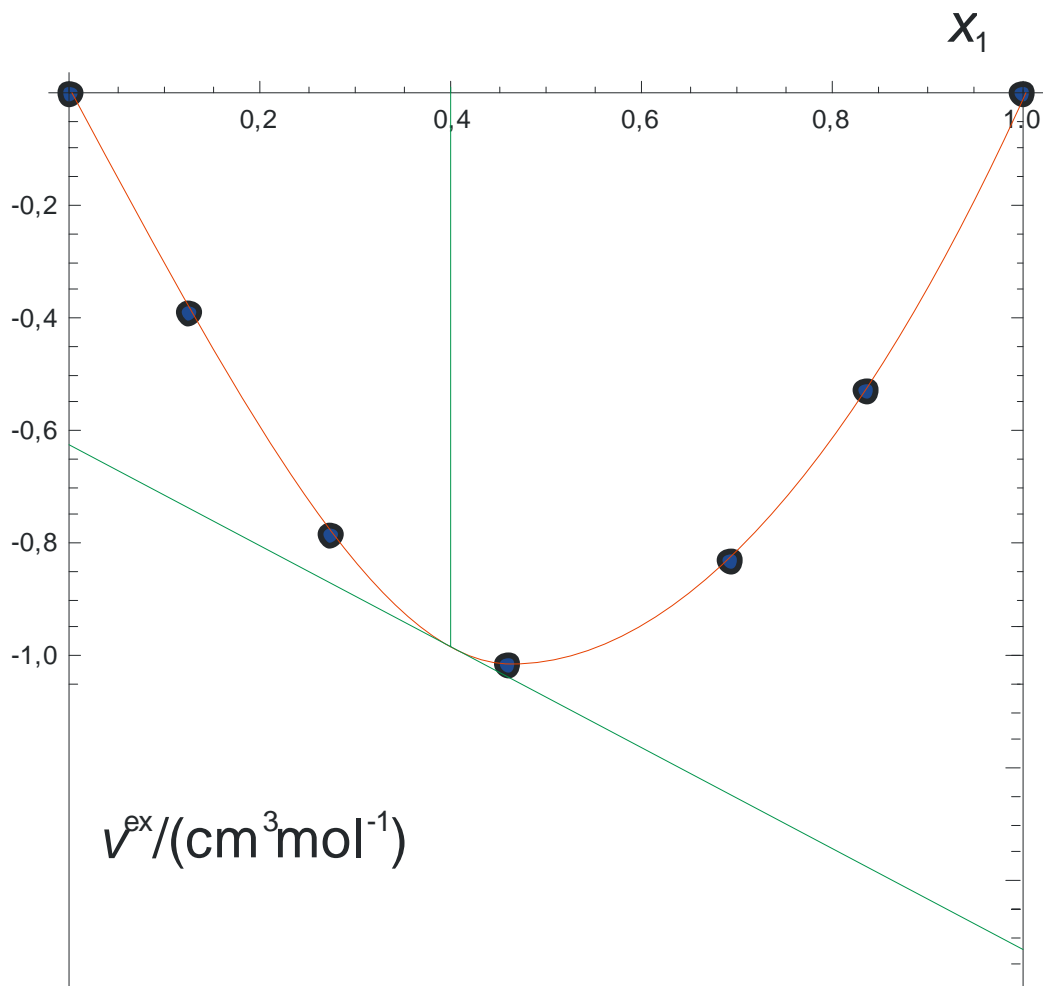
$$v^{\text{id}} = x_1 v_1^{\bullet} + x_2 v_2^{\bullet} = 0,1233 \cdot 40,42 + 0,8767 \cdot 18,03 = 20,7907 \text{ cm}^3 \text{ mol}^{-1}$$

$v^{\text{id}}/(\text{cm}^3 \text{ mol}^{-1})$	18,03	20,7907	24,1358	28,2779	33,5306	36,7301	40,42
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$$v^{\text{ex}} = v - v^{\text{id}} = 20,40 - 20,7907 = -0,390687 \text{ cm}^3 \text{ mol}^{-1}$$

$v^{\text{ex}}/(\text{cm}^3 \text{ mol}^{-1})$	0	-0,390687	-0,785753	-1,0179	-0,830597	-0,530128	0
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Podaci  $v^{\text{ex}}=f(x_1)$  omogućuju primjenu metode odsječka za određivanje parcijalnog eksces molarnog volumena komponenata:



$$\bar{v}_1^{\text{ex}} \approx -1,46 \text{ cm}^3 \text{ g}^{-1}$$

$$\bar{v}_2^{\text{ex}} \approx -0,612 \text{ cm}^3 \text{ g}^{-1}$$

Parcijalni molarni volumeni:

$$\bar{v}_1 = v_1^\bullet + \bar{v}_1^{\text{ex}} = 40,42 - 1,46 = 38,96 \text{ cm}^3 \text{ mol}^{-1}$$

$$\bar{v}_2 = v_2^\bullet + \bar{v}_2^{\text{ex}} = 18,03 - 0,612 = 17,418 \text{ cm}^3 \text{ mol}^{-1}$$