

32. ZADATAK

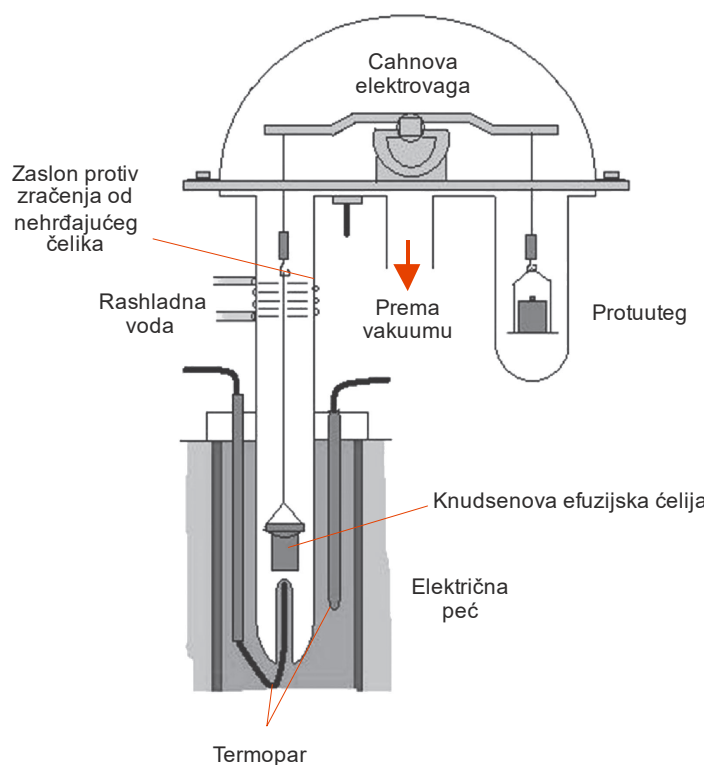
Izračunati aktivitet titanija u sustavu titanij (1) – krom (2) sastava $x_1=0,60$ u skladu s Gibbs-Duhemovom jednačbom na temelju mjernih podataka (tablica) određenih pri temperaturi od 1250 °C:

a) direktno

b) putem koeficijenta aktiviteta

Podaci:

x_2	0,09	0,19	0,27	0,37	0,47	0,67	0,78	0,89
a_2	0,302	0,532	0,660	0,778	0,820	0,863	0,863	0,906



GIBBS-DUHEMOVA JEDNADŽBA

Daje međuovisnost parcijalnih molarnih veličina u višekomponentnim sustavima:

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

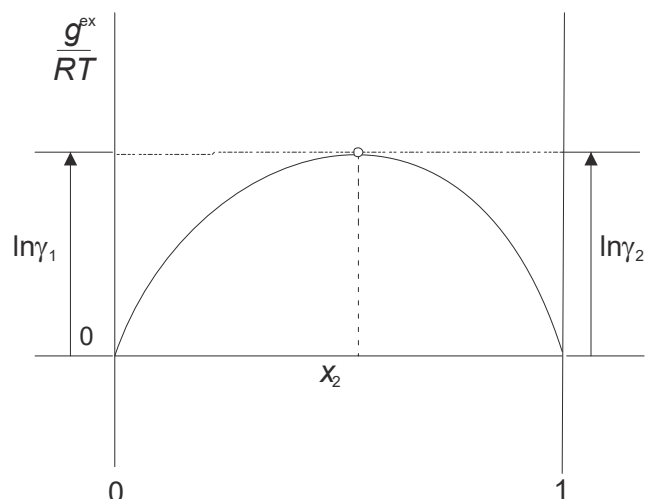
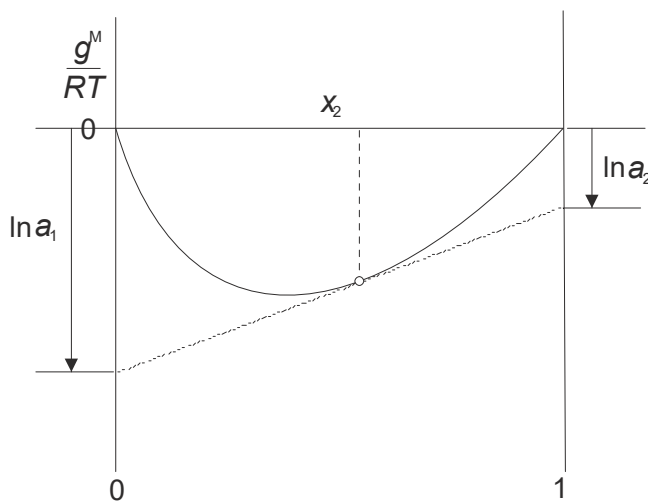
$$\sum x_i d\bar{y}_i = 0$$

Veza Gibbsove energije miješanja i aktiviteta:

$$\frac{g^M}{RT} = \sum x_i \ln a_i$$

Veza ekscesne Gibbsove energije i koeficijenta aktiviteta:

$$\frac{g^{ex}}{RT} = \sum x_i \ln \gamma_i$$



Logaritam aktiviteta i logaritam koeficijenta aktiviteta su parcijalne molarne veličine:

Logaritam aktiviteta

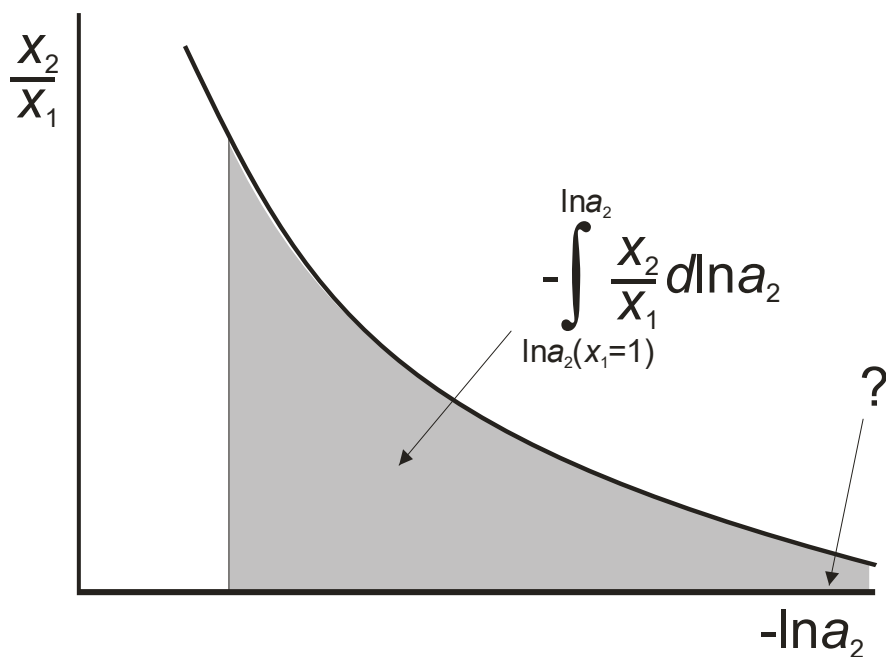
$$\sum x_i d \ln a_i = 0$$

$$x_1 d \ln a_1 + x_2 d \ln a_2 = 0$$

$$d \ln a_1 = -\frac{x_2}{x_1} d \ln a_2,$$

$$\int_{\ln a_1(x_1=1)}^{\ln a_1(x_1)} d \ln a_1 = - \int_{\ln a_2(x_1=1)}^{\ln a_2(x_1)} \frac{x_2}{x_1} d \ln a_2.$$

$$\ln a_1(x_1) - 0 = - \int_{\ln a_2(x_1=1)}^{\ln a_2(x_1)} \frac{x_2}{x_1} d \ln a_2.$$



RJEŠENJE

$$\gamma_1 = ?$$

$$a_1 = ?$$

titaniј (1) – krom (2)

$$x_1 = 0,6000$$

Gibbs-Duhem

$$x_1 = 1 - x_2$$

x_1	0,91	0,81	0,73	0,63
x_2/x_1	0,0989011	0,234568	0,369863	0,587302
$\ln a_2$	-1,19733	-0,631112	-0,415515	-0,251029
x_1	0,53	0,33	0,22	0,11
x_2/x_1	0,886792	2,0303	3,54545	8,09091
$\ln a_2$	-0,198451	-0,147341	-0,147341	-0,098716

Za želјeni sastav

$$x_1 = 0,6000, \text{ odnosno } x_2 = 0,4000$$

$$x_2/x_1 = 0,666667$$

Linearnom interpolacijom dobije se $\ln a_2$:

$$\ln a_2 = -0,251029 + \frac{-0,198451 - (-0,251029)}{0,886792 - 0,587302} (0,666667 - 0,587302) = -0,237096$$

Za rubni sastav $x_2/x_1 = 0$

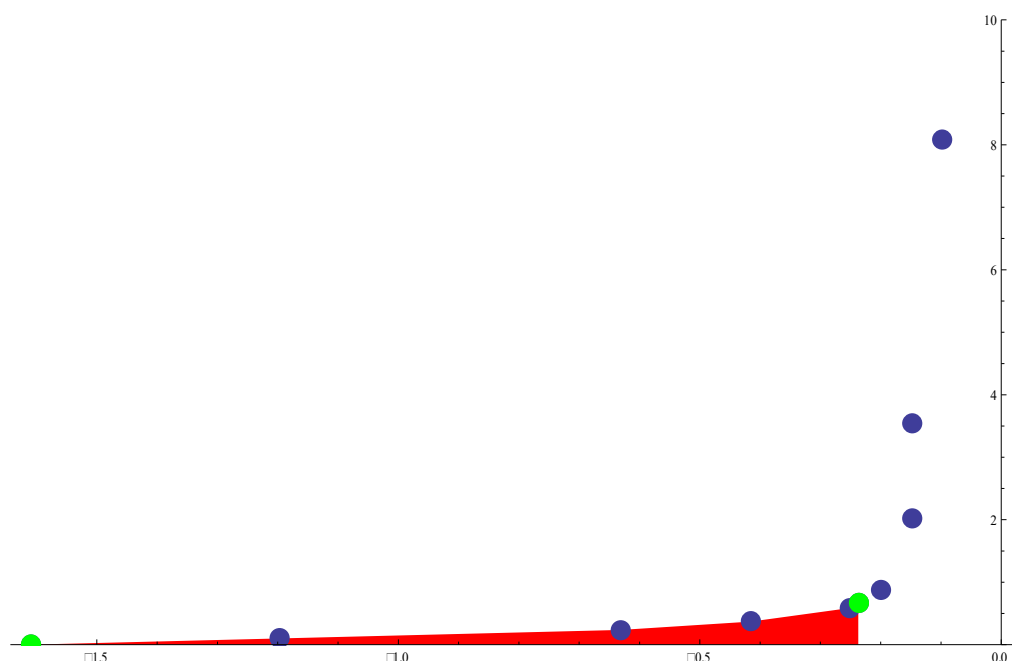
Linearnom ekstrapolacijom dobije se $\ln a_2$:

$$\ln a_2 = -1,19733 + \frac{-0,631112 - (-1,19733)}{0,234568 - 0,0989011} (0 - 0,0989011) = -1,6101$$

Umetanjem rezultata dobije se konačna tablica:

$\ln a_2$	-1,6101	-1,19733	-0,631112	-0,415515	-0,251029
x_2/x_1	0	0,0989011	0,234568	0,369863	0,587302

$\ln a_2$	-0,237096	-0,198451	-0,147341	-0,147341	-0,098716
x_2/x_1	0,666667	0,886792	2,0303	3,54545	8,09091



Površine segmenata izračunate trapeznom formulom:

$$A_1 = 0,0204118$$

$$A_2 = 0,0944078$$

$$A_3 = 0,0651565$$

$$A_4 = 0,0787204$$

$$A_5 = 0,00873585$$

$$A_6 = 0,0300165$$

$$A_7 = 0,0745469$$

$$A_8 = 0$$

$$A_9 = 0,282907$$

Za željeni sastav

$$x_1=0,6000$$

$$\begin{aligned} A &= A_1 + A_2 + A_3 + A_4 + A_5 = \\ &= 0,0204118 + 0,0944078 + 0,0651565 + 0,0787204 + 0,00873585 = \\ &= 0,267432 \end{aligned}$$

$$\ln a_1(0,6000) = -0,267432$$

$$a_1(0,6000) = \exp(-0,267432) = 0,765342$$

Logaritam koeficijenta aktiviteta

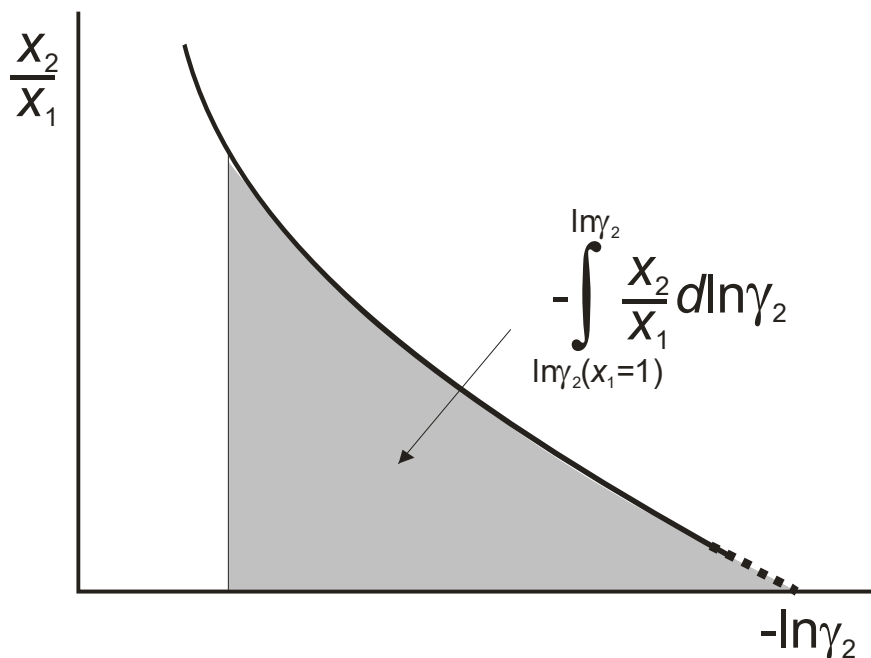
$$\sum x_i d \ln \gamma_i = 0$$

$$x_1 d \ln \gamma_1 + x_2 d \ln \gamma_2 = 0$$

$$d \ln \gamma_1 = -\frac{x_2}{x_1} d \ln \gamma_2 ,$$

$$\int_{\ln \gamma_1(x_1=1)}^{\ln \gamma_1(x_1)} d \ln \gamma_1 = - \int_{\ln \gamma_2(x_1=1)}^{\ln \gamma_2(x_1)} \frac{x_2}{x_1} d \ln \gamma_2 .$$

$$\ln \gamma_1(x_1) - 0 = - \int_{\ln \gamma_2(x_1=1)}^{\ln \gamma_2(x_1)} \frac{x_2}{x_1} d \ln \gamma_2 .$$



RJEŠENJE

$$\gamma_1 = ?$$

$$a_1 = ?$$

titanij (1) – krom (2)

$$x_1 = 0,6000$$

Gibbs-Duhem

$$x_1 = 1 - x_2$$

x_1	0,91	0,81	0,73	0,63
x_2/x_1	0,0989011	0,234568	0,369863	0,587302
γ_2	3,35556	2,8	2,44444	2,1027
$\ln \gamma_2$	1,21062	1,02962	0,893818	0,743224

x_1	0,53	0,33	0,22	0,11
x_2/x_1	0,886792	2,0303	3,54545	8,09091
γ_2	1,74468	1,28806	1,10641	1,01798
$\ln \gamma_2$	0,556572	0,253137	0,101121	0,0178178

Za željeni sastav

$$x_1 = 0,6000, \text{ odnosno } x_2 = 0,4000$$

$$x_2/x_1 = 0,666667$$

Linearnom interpolacijom dobije se $\ln \gamma_2$:

$$\ln \gamma_2 = 0,743224 + \frac{0,556572 - 0,743224}{0,886792 - 0,587302} (0,666667 - 0,587302) = 0,693761$$

Za rubni sastav $x_2/x_1=0$

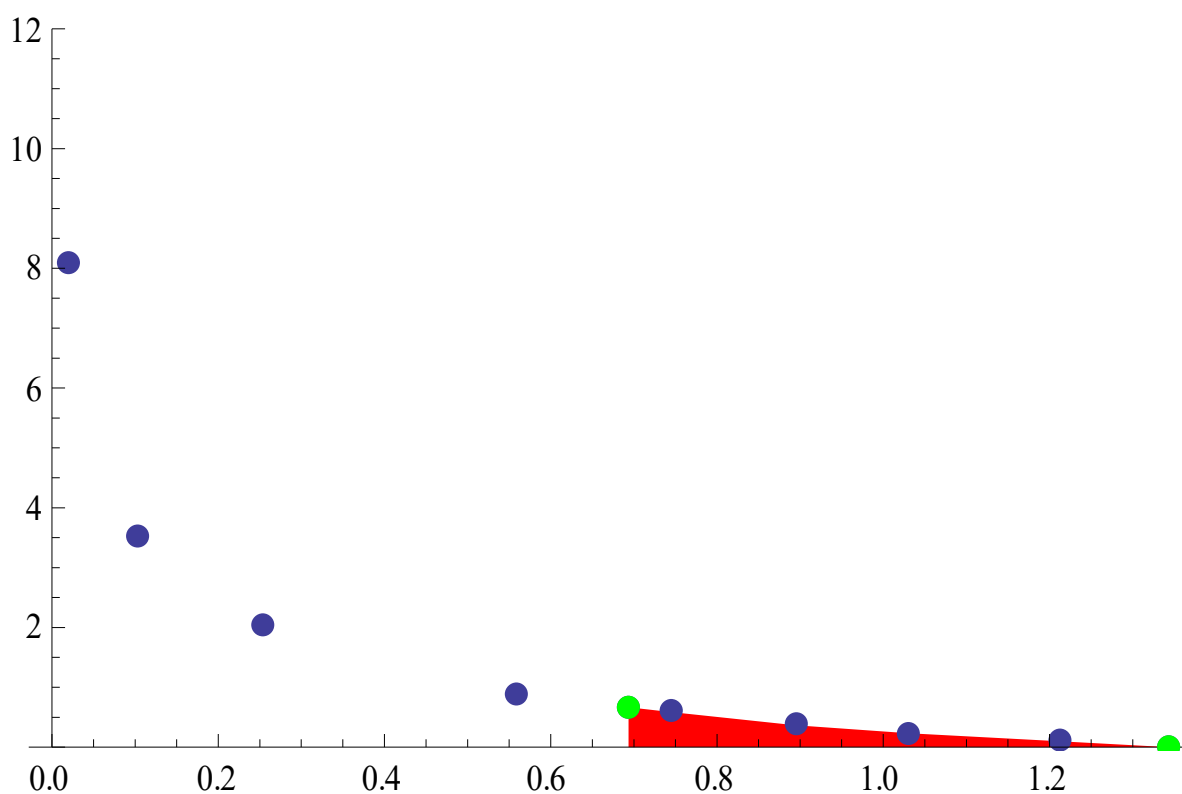
Linearnom ekstrapolacijom dobije se $\ln \gamma_2$:

$$\ln \gamma_2 = 1,21062 + \frac{1,02962 - 1,21062}{0,234568 - 0,0989011}(0 - 0,0989011) = 1,34256$$

Umetanjem rezultata dobije se konačna tablica:

$\ln a_2$	1,34256	1,21062	1,02962	0,893818	0,743224
x_2/x_1	0	0,0989011	0,234568	0,369863	0,587302

$\ln a_2$	0,693761	0,556572	0,253137	0,101121	0,0178178
x_2/x_1	0,666667	0,886792	2,0303	3,54545	8,09091



Površine segmenata izračunate trapeznom formulom:

$$A_1 = -0,00652488$$

$$A_2 = -0,0301786$$

$$A_3 = -0,0410413$$

$$A_4 = -0,0720718$$

$$A_5 = -0,0310124$$

$$A_6 = -0,106559$$

$$A_7 = -0,442574$$

$$A_8 = -0,423803$$

$$A_9 = -0,484672$$

Za željeni sastav

$$x_1 = 0,6000$$

$$\begin{aligned} A &= A_1 + A_2 + A_3 + A_4 + A_5 = \\ &= -0,00652488 - 0,0301786 - 0,0410413 - 0,0720718 - 0,0310124 = \\ &= -0,149817 \end{aligned}$$

$$\ln \gamma_1(0,6000) = 0,149817$$

$$\gamma_1(0,6000) = \exp(0,149817) = 1,16162$$

$$a_1 = x_1 \gamma_1 = 1,16162 \cdot 0,6000 = 0,696973$$