

Kemijska termodinamika

3. dio

Seminar

31.3.2025.

1. Izračunajte promjenu Gibbsove energije pri 298 K kada se 1 mol vodika:

a) komprimira izotermno s tlaka od 1 atm na tlak od 100 atm,

b) pusti da ekspandira izotermno s volumena $V_1 = 0,5 \text{ dm}^3$ na $V_2 = 1 \text{ dm}^3$. Pretpostavite da se vodik ponaša kao idealan plin.

$$dG = Vdp - SdT$$

$$T = \text{konst.} \rightarrow dG = Vdp$$

Za izotermnu
ekspanziju/kompresiju
idealnog plina

$$\Delta G = nRT \ln \frac{p_2}{p_1} = nRT \ln \frac{V_1}{V_2}$$

a) $\Delta G = nRT \ln(p_2/p_1) = 11\,410 \text{ J} = 11,41 \text{ kJ}$

b) $\Delta G = nRT \ln(V_1/V_2) = - 1,717 \text{ kJ}$

2. Izračunajte promjenu Gibbsove energije 20 g tekućeg metanola, ako mu pri temperaturi od 15 °C tlak poraste s 1 na 20 bara. Gustoća metanola pri toj temperaturi iznosi 0,79 g/mL.

Idealne kondenzirane
faze pri konst. T

$$\Delta G = V \Delta p$$

$$\Delta G = \frac{m(\text{CH}_3\text{OH})}{\rho(\text{CH}_3\text{OH})} (p_2 - p_1) = \frac{20 \text{ g}}{7,9 \cdot 10^5 \text{ g m}^{-3}} \cdot 1,9 \cdot 10^6 \text{ Pa} = 48,1 \text{ J}$$

3. Izračunajte standardnu Gibbsovu energiju stvaranja vode u plinovitom i tekućem stanju pri temperaturi od 298 K. Pri tome koristite sljedeće podatke:

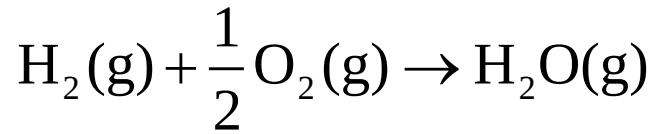
Tablica 1. Standardne entalpije stvaranja i standardne entropije nekih kemijskih vrsta pri 298 K

	$\Delta_f H^\ominus / \text{kJ mol}^{-1}$	$S_m^\ominus / \text{J K}^{-1} \text{mol}^{-1}$
H ₂ O(g)	−241,818	188,825
H ₂ O(l)	−285,830	69,910
H ₂ (g)	0	130,684
O ₂ (g)	0	208,138

$$\Delta_f G^\ominus = \Delta_f H^\ominus - T \cdot \Delta_f S^\ominus$$

$$\Delta_f S^\ominus = \sum_i \nu_i \cdot S_m^\ominus$$

Stvaranje vode u plinovitom stanju

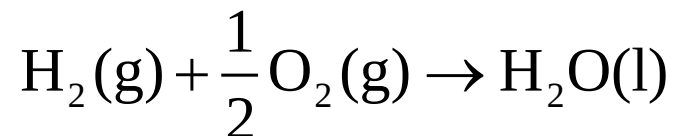


$$\Delta_{\text{f}} G^{\circ}(\text{H}_2\text{O}(\text{g})) = \Delta_{\text{f}} H^{\circ}(\text{H}_2\text{O}(\text{g})) - T \cdot \Delta_{\text{f}} S^{\circ}(\text{H}_2\text{O}(\text{g}))$$

$$\Delta_{\text{f}} S^{\circ}(\text{H}_2\text{O}(\text{g})) = S_{\text{m}}^{\circ}(\text{H}_2\text{O}(\text{g})) - S_{\text{m}}^{\circ}(\text{H}_2(\text{g})) - \frac{1}{2} S_{\text{m}}^{\circ}(\text{O}_2(\text{g})) = -45,93 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta_{\text{f}} G^{\circ}(\text{H}_2\text{O}(\text{g})) = -228,1 \text{ kJ mol}^{-1}$$

Stvaranje vode u tekućem stanju



$$\Delta_{\text{f}} G^{\circ}(\text{H}_2\text{O}(\text{l})) = \Delta_{\text{f}} H^{\circ}(\text{H}_2\text{O}(\text{l})) - T \cdot \Delta_{\text{f}} S^{\circ}(\text{H}_2\text{O}(\text{l}))$$

$$\Delta_{\text{f}} G^{\circ}(\text{H}_2\text{O}(\text{l})) = -236,7 \text{ kJ mol}^{-1}$$

4. Standardna entalpija za reakciju



iznosi $-92,2 \text{ kJ mol}^{-1}$, a standardna reakcijska Gibbsova energija $-32,9 \text{ kJ mol}^{-1}$ pri 298 K. Izračunajte standardnu reakcijsku Gibbsovu energiju pri 500 i 1000 K, uz pretpostavku da je standardna reakcijska entalpija konstantna u zadanom temperaturnom intervalu.

$$\begin{aligned} \Delta_{\text{r}} G^{\circ}(T_1) &= \Delta_{\text{r}} H^{\circ} - T_1 \cdot \Delta_{\text{r}} S^{\circ} \\ \Delta_{\text{r}} G^{\circ}(T_2) &= \Delta_{\text{r}} H^{\circ} - T_2 \cdot \Delta_{\text{r}} S^{\circ} \end{aligned} \quad \begin{aligned} &\nearrow \\ &\nwarrow \end{aligned} \quad \Delta_{\text{r}} S^{\circ} = \frac{\Delta_{\text{r}} H^{\circ} - \Delta_{\text{r}} G^{\circ}(T_1)}{T_1}$$

$$\Delta_{\text{r}} G^{\circ}(T_2) = \Delta_{\text{r}} H^{\circ} - \frac{T_2 \left(\Delta_{\text{r}} H^{\circ} - \Delta_{\text{r}} G^{\circ}(T_1) \right)}{T_1}$$

$$\Delta_{\text{r}} G^{\circ}(500 \text{ K}) = 7,3 \text{ kJ mol}^{-1}$$

$$\Delta_{\text{r}} G^{\circ}(1000 \text{ K}) = 106,8 \text{ kJ mol}^{-1}$$

5. Za reakciju $\text{Zn(g)} + \text{H}_2\text{O(g)} \rightarrow \text{ZnO(s)} + \text{H}_2\text{(g)}$ standardna reakcijska entalpija iznosi 224 kJ mol^{-1} , a standardna reakcijska Gibbsova energija iznosi 33 kJ mol^{-1} pri 1280 K . Pretpostavite da je $\Delta_r H^\circ$ neovisna o temperaturi te odredite temperaturu na kojoj pri standardnim uvjetima reakcija postaje spontana.

$\Delta_r G^\circ < 0$ za spontan proces

→ temp. pri kojoj reakcija prelazi iz nespontane u spontanu (T_x) je temp. pri kojoj je $\Delta_r G^\circ = 0$

$$\Delta_r H^\circ = T_x \cdot \Delta_r S^\circ \rightarrow T_x = \frac{\Delta_r H^\circ}{\Delta_r S^\circ} = \frac{\Delta_r H^\circ}{\frac{(\Delta_r H^\circ - \Delta_r G^\circ(1280 \text{ K}))}{1280 \text{ K}}} = 1501 \text{ K}$$

6. Standardna reakcijska Gibbsova energija hidrolize ATPa:



iznosi -31 kJ mol^{-1} pri 37°C . U tipičnim bakterijskim stanicama koncentracije ATP, ADP i fosfata iznose redom: 8 mmol dm^{-3} , 1 mmol dm^{-3} i 8 mmol dm^{-3} . Koliko iznosi reakcijska Gibbsova energija pri navedenim uvjetima?

$$\Delta_r G = \Delta_r G^\ominus + RT \ln \prod_i a_i^{v_i}$$

$$\Delta_{\text{r}} G = \Delta_{\text{r}} G^{\circ} + RT \ln \frac{a(\text{ADP}) \cdot a(\text{P}_{\text{i}})}{a(\text{ATP})}$$

Pri niskim koncentracijama – približno idealne otopine

$$\Delta_{\text{r}} G = \Delta_{\text{r}} G^{\circ} + RT \ln \frac{\frac{c(\text{ADP})}{c^{\circ}} \cdot \frac{c(\text{P}_{\text{i}})}{c^{\circ}}}{\frac{c(\text{ATP})}{c^{\circ}}}; c^{\circ} = 1 \text{ mol dm}^{-3}$$

$$\Delta_{\text{r}} G = -48,8 \text{ kJ mol}^{-1}$$