

Soluzione preliminare del problema 6

Problema 6) Legami nel dibenzile

Presentiamo due soluzioni, la prima proposta da Luca Zucchini, la seconda da Riccardo Laterza.

1^a soluzione:

Riassumiamo tutti i dati a disposizione:

$$\Delta H^\circ_f \text{CO}_2(\text{g}) = -393.5 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ_f \text{H}_2\text{O}(\text{l}) = -285.8 \text{ kJ mol}^{-1}$$

$$\text{C}_7\text{H}_8(\text{g}) \Rightarrow \text{C}_6\text{H}_5\text{CH}_2^*(\text{g}) + \text{H}^* \quad \Delta H^\circ_d = 378.4 \text{ kJ mol}^{-1}$$

$$\text{C}_7\text{H}_8(\text{l}) + 9 \text{O}_2 \Rightarrow 7 \text{CO}_2 + 4 \text{H}_2\text{O} \quad \Delta H^\circ_c = -3910.2 \text{ kJ mol}^{-1}$$

$$\text{C}_7\text{H}_8(\text{l}) \Rightarrow \text{C}_7\text{H}_8(\text{g}) \quad \Delta H^\circ_{\text{vap}} = 38 \text{ kJ mol}^{-1}$$

$$\text{H}_2 \Rightarrow 2\text{H}^* \quad \Delta H^\circ_{\text{at}} = 436 \text{ kJ mol}^{-1}$$

a.(i) Dall'equazione di combustione abbiamo che:

$$\Delta H^\circ_c = 4 \Delta H^\circ_f \text{H}_2\text{O}(\text{l}) + 7 \Delta H^\circ_f \text{CO}_2(\text{g}) - 9 \Delta H^\circ_f \text{O}_2(\text{g}) - \Delta H^\circ_f \text{C}_7\text{H}_8(\text{l})$$

$$-3910.2 = 4(-285.8) + 7(-393.5) - 9(0) - \Delta H^\circ_f \text{C}_7\text{H}_8(\text{l})$$

$$\text{Da cui } \Delta H^\circ_f \text{C}_7\text{H}_8(\text{l}) = 12.5 \text{ kJ mol}^{-1}$$

a.(ii) Dalla reazione pirolitica abbiamo che

$$\Delta H^\circ_d \text{C}_7\text{H}_8(\text{g}) = \frac{1}{2} \Delta H^\circ_{\text{at}} \text{H}_2 + \Delta H^\circ_f \text{C}_6\text{H}_5\text{CH}_2^*(\text{g}) - \Delta H^\circ_f \text{C}_7\text{H}_8(\text{g})$$

$$378.4 = \frac{1}{2}(436) + \Delta H^\circ_f \text{C}_6\text{H}_5\text{CH}_2^*(\text{g}) - (12.5 + 38)$$

$$\Delta H^\circ_f \text{C}_6\text{H}_5\text{CH}_2^*(\text{g}) = 210.9 \text{ kJ mol}^{-1}$$

b.(i) Sapendo che $\Delta S^\circ_{\text{vap}} \text{toluene} = 99 \text{ J mol}^{-1} \text{ K}^{-1}$

Dalla relazione $\Delta G^\circ_{\text{vap}} = \Delta H^\circ_{\text{vap}} - T\Delta S^\circ_{\text{vap}}$ otteniamo $38 - 298(0,099) = 8,498 \text{ kJ mol}^{-1}$

b.(ii) $\Delta G^\circ_{\text{vap}} = -RT \ln K_{\text{eq}}$ ma K_{eq} per la nostra reazione corrisponde alla pressione del toluene gassoso, e quindi alla sua tensione di vapore.

$\ln K_{\text{eq}} = -\Delta G^\circ_{\text{vap}} / RT$ $K_{\text{eq}} = P = 0.0324 \text{ atm}$. Quindi il toluene a 25°C è un liquido.

b.(iii) Alla T_{eb} avviene il passaggio di stato, liquido e vapore sono in equilibrio ($\Delta G^\circ_{\text{vap}} = 0$)

$$\Delta G^\circ_{\text{vap}} = \Delta H^\circ_{\text{vap}} - T_{\text{eb}} \Delta S^\circ_{\text{vap}} = 0 \quad T_{\text{eb}} \Delta S^\circ_{\text{vap}} = \Delta H^\circ_{\text{vap}} \quad T_{\text{eb}} = \Delta H^\circ_{\text{vap}} / \Delta S^\circ_{\text{vap}}$$

$$T_{\text{eb}} = 38 / 0,099 = 383,8 \text{ K} \quad T_{\text{eb}} = 384 \text{ K} = 111^\circ \text{C}$$

c) Data la reazione $(\text{C}_6\text{H}_5\text{CH}_2)_2(\text{g}) \Rightarrow 2 \text{C}_6\text{H}_5\text{CH}_2^*(\text{g})$

$$\Delta H^\circ_d \text{dibenzile}(\text{g}) = 2 \Delta H^\circ_f \text{C}_6\text{H}_5\text{CH}_2^*(\text{g}) - \Delta H^\circ_f \text{dibenzile}(\text{g})$$

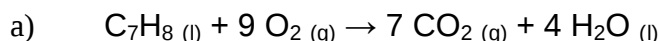
$$\Delta H^\circ_d \text{dibenzile}(\text{g}) = 2(210.9) - 143.9 = 277.9 \text{ kJ mol}^{-1}$$

Soluzione proposta da

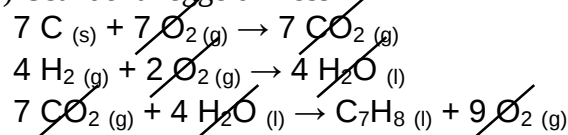
Luca Zucchini

medaglia di bronzo alle olimpiadi IChO 2008

2^ soluzione



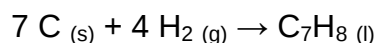
i) Usando la legge di Hess



$$\Delta H^\circ = 7 \Delta_f H^\circ = -2754.5 \text{ kJ}$$

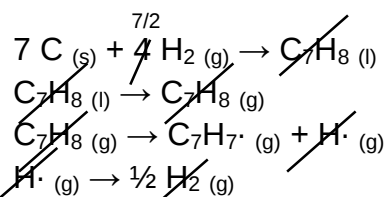
$$\Delta H^\circ = 2 \Delta_f H^\circ = -1143.2 \text{ kJ}$$

$$\Delta H^\circ = -\Delta_c H^\circ = 3910.2 \text{ kJ}$$



$$\Delta_f H^\circ = 12.5 \text{ kJ mol}^{-1}$$

ii) Usando la legge di Hess

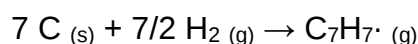


$$\Delta H^\circ = \Delta_f H^\circ = 12.5 \text{ kJ}$$

$$\Delta H^\circ = \Delta_{\text{vap}} H^\circ = 38.0 \text{ kJ}$$

$$\Delta H^\circ = \Delta_{\text{b. d.}} H^\circ = 378.4 \text{ kJ}$$

$$\Delta H^\circ = -1/2 \Delta_{\text{at}} H^\circ = -218.0 \text{ kJ}$$



$$\Delta_f H^\circ = 210.9 \text{ kJ mol}^{-1}$$

b) i) $\Delta_{\text{vap}} G^\circ = \Delta_{\text{vap}} H^\circ - T \cdot \Delta_{\text{vap}} S^\circ = 3.80 \cdot 10^4 \text{ J mol}^{-1} - 298 \text{ K} \cdot 99.0 \text{ J K}^{-1} \text{ mol}^{-1} = 8498 \text{ J}$

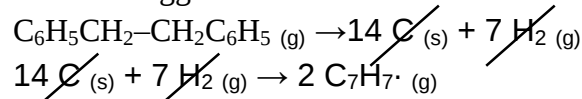
ii) liquido in condizioni standard

iii) durante il passaggio di stato $\Delta G^\circ = 0$

$$\text{per cui } 0 = \Delta_{\text{vap}} H^\circ - T_{\text{eb}} \cdot \Delta_{\text{vap}} S^\circ$$

$$\text{e quindi } T_{\text{eb}} = \Delta_{\text{vap}} H^\circ / \Delta_{\text{vap}} S^\circ = 3.80 \cdot 10^4 \text{ J mol}^{-1} / 99.0 \text{ J K}^{-1} \text{ mol}^{-1} = 384 \text{ K} = 111^\circ \text{C}$$

c) Usando la legge di Hess



$$\Delta H^\circ = -\Delta_f H^\circ = -143.9 \text{ kJ}$$

$$\Delta H^\circ = 2 \Delta_f H^\circ = 421.8 \text{ kJ}$$



$$\Delta_{\text{b. d.}} H^\circ = 277.9 \text{ kJ mol}^{-1}$$

Soluzione proposta da

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