Example 03.07 Enthalpy of Reaction and Equilibrium Composition for n-Butane - Isobutene Isomerization

problem:

Estimate the enthalpy of reaction and the equilibrium concentration y_1 of the theoretically possible isomerization reaction in the gas phase

$$n\text{-butane} \rightleftharpoons \text{isobutane}$$

at $\vartheta = 25\ ^\circ\text{C}$ and $P = 1.01325$ bar. The standard enthalpies of formation and the standard Gibbs energies of formation are

	Δh_f^0 (J/mol)	Δg_f^0 (J/mol)
Isobutane (1)	−134510	−20878
n-Butane (2)	−126150	−17154

As well, calculate the range of possible results if each of these given quantities has an error of ±1%.

general constants and definitions:

$kPa := 1000Pa \qquad R_{gas} := 8.31433 \frac{J}{K \cdot mol} \qquad bar := 100kPa \qquad dm := 0.1m$

input data

$T := 298.15K \qquad P := 1.01325bar$

$$\Delta h^\circ_f := \begin{pmatrix} -134510 \\ -126150 \end{pmatrix} \frac{J}{mol} \qquad \Delta g^\circ_f := \begin{pmatrix} -20878 \\ -17154 \end{pmatrix} \frac{J}{mol}$$

Solution

In the first step the enthalpy and Gibbs energy of reaction are calculated. Isobutane is chosen as the product.

$$\Delta h^\circ_R := \Delta h^\circ_{f_1} - \Delta h^\circ_{f_2} \qquad \Delta h^\circ_R = -8360 \frac{J}{mol}$$

$$\Delta g^\circ_R := \Delta g^\circ_{f_1} - \Delta g^\circ_{f_2} \qquad \Delta g^\circ_R = -3724 \frac{J}{mol}$$

The equilibrium constant is thus: $K_{equil} := \exp\left(\frac{-\Delta g^\circ_R}{R_{gas} \cdot T}\right) \qquad K_{equil} = 4.4919$

Asuming ideal gas behavior, it holds that: $K_{equil} = \frac{p_{isobutane}}{P_{n_butane}}$

and

$$p_{isobutane} + P_{n_butane} = P$$

This leads to:

$$K_{equil} = \frac{p_{isobutane}}{P - p_{isobutane}}$$

and, rearranged, to:

$$p_{isobutane} := K_{equil} \cdot \frac{P}{(K_{equil} + 1)}$$

$$p_{isobutane} = 0.829\,bar$$

The equilibrium composition is thus:

$$y_{isobutane} := \frac{p_{isobutane}}{P} \quad \text{or} \quad y_{isobutane} := \frac{K_{equil}}{(K_{equil} + 1)}$$

$$y_{isobutane} = 0.8179$$

Assuming a relative error of 1% in the opposite direction for both components leads to:

$$\Delta h°_{R1} := 1.01 \cdot \Delta h°_{f_1} - 0.99 \cdot \Delta h°_{f_2} \qquad \Delta h°_{R1} = -10967 \frac{J}{mol} \qquad \frac{\Delta h°_{R1}}{\Delta h°_{R}} \cdot 100 = 131.179$$

The enthalpy of reaction is then more than 30% higher.

$$\Delta h°_{R2} := 0.99 \cdot \Delta h°_{f_1} - 1.01 \cdot \Delta h°_{f_2} \qquad \Delta h°_{R2} = -5753 \frac{J}{mol} \qquad \frac{\Delta h°_{R2}}{\Delta h°_{R}} \cdot 100 = 68.821$$

The enthalpy of reaction is then only about 69%.

The effect on the equilibrium condition can be calculated as:

$$\Delta g°_{R1} := 1.01 \cdot \Delta g°_{f_1} - 0.99 \cdot \Delta g°_{f_2} \qquad K_{equil} := \exp\left(\frac{-\Delta g°_{R1}}{R_{gas} \cdot T}\right) \qquad \frac{K_{equil}}{(K_{equil} + 1)} = 0.8397$$

$$\Delta g°_{R1} = -4.104 \times 10^3 \frac{J}{mol}$$

$$\Delta g°_{R2} := 0.99 \cdot \Delta g°_{f_1} - 1.01 \cdot \Delta g°_{f_2} \qquad K_{equil} := \exp\left(\frac{-\Delta g°_{R2}}{R_{gas} \cdot T}\right) \qquad \frac{K_{equil}}{(K_{equil} + 1)} = 0.7939$$

$$\Delta g°_{R2} = -3.344 \times 10^3 \frac{J}{mol}$$