A First Course on Kinetics and Reaction Engineering

Unit 2. Activity 1 Handout

Problem Statement

Suppose a mixture of 3 moles of steam and 1 mole of carbon monoxide is going to react according to reaction (1) to produce a half mole each of hydrogen and carbon dioxide. The reaction will take place at 250 °C and 322 psia. Calculate the standard heat of reaction at 250 °C and 322 psia.

$$CO + H_2O \rightleftarrows CO_2 + H_2 \tag{1}$$

Problem Solution

The standard heats of combustion at 298 K of CO and H_2 were found in a thermodynamics textbook. Carbon dioxide and water don't have heats of combustion, but their heats of formation at 298 K were found in the same book. The values, in cal mol^{-1}, are as follows:

$$\Delta H^0_{f(298K),CO_2} = -94{,}052$$

$$\Delta H^0_{f(298K),H_2O_{(l)}} = -68{,}317$$

$$\Delta H^0_{c(298K),CO} = -67{,}636$$

$$\Delta H^0_{c(298K),H_2} = -68{,}317$$

Equations (2) and (3) were combined and used, with the values above, to compute the standard heat of reaction at 298 K:

$$\Delta H^0_{j(298K)} = \sum_{\substack{i=\text{ all}\\ \text{species}}} \nu_{i,j} \Delta H^0_{f(298K),i} \tag{2}$$

$$\Delta H^0_{j(298K)} = \sum_{\substack{i=\text{ all}\\ \text{species}}} \nu_{i,j} \left(-\Delta H^0_{c(298K),i}\right) \tag{3}$$

$$\begin{aligned}\Delta H^0_{1(298K)} &= \nu_{CO,1}\left(-\Delta H^0_{c(298K),CO}\right) + \nu_{CO_2,1}\Delta H^0_{f(298K),CO_2} + \nu_{H_2O,1}\Delta H^0_{f(298K),H_2O_{(l)}} \\ &\quad + \nu_{H_2,1}\left(-\Delta H^0_{c(298K),H_2}\right) \\ &= (-1)(67{,}636) + (0.5)(-94{,}052) + (-3)(-68{,}317) + (0.5)(68{,}317) \\ &= 124{,}447.5 \text{ cal mol}^{-1}\end{aligned}$$

The heat capacities of liquid water and gaseous CO, H_2 and CO_2 were also found in the same thermodynamics textbook. Their values, in cal mol^{-1} K^{-1}, are as follows: H_2O = 1.0, CO = 6.42, CO_2 =

6.214 and H_2 = 6.947. With these values and the result above, the standard heat of reaction could be found using equation (4).

$$\Delta H^0_{j(T)} = \Delta H^0_{j(298K)} + \sum_{\substack{i=\text{all}\\ \text{species}}} \left(\nu_{i,j} \int_{298K}^{T} \hat{C}_{p,i}\, dT \right) \tag{4}$$

$$\Delta H^0_{j(T)} = \Delta H^0_{j(298K)} + \sum_{\substack{i=\text{all}\\ \text{species}}} \left(\nu_{i,j} \hat{C}_{p,i} \left(T - 298 \right) \right)$$

$$\begin{aligned}\Delta H^0_{1(T)} &= 124{,}447.5 + (-1)(6.42)(543-298) + (0.5)(6.214)(543-298) \\ &\quad + (-3)(1.0)(543-298) + (0.5)(6.947)(543-298)\end{aligned}$$

$$\Delta H^0_{1(543K)} = 123{,}751.82 \text{ cal mol}^{-1}$$