A First Course on Kinetics and Reaction Engineering

Example 2.4

Problem Purpose

This problem illustrates how to calculate a heat of reaction using standard heat of formation data, and how to calculate the standard Gibbs free energy change for that reaction at 298 K.

Problem Statement

Methanol can be synthesized in the vapor phase from carbon monoxide and hydrogen according to reaction (1). The heat capacity of a species i, $\hat{C}_{p,i}$, can be calculated using equation (2) where t is equal to the temperature in Kelvin divided by 1000 and A_i through E_i are constants. Values for the constants for species of interest (in the gas phase) are provided in the table below along with values for their standard heats of formation at 298K, $\Delta H_{f,i}^0 (298 \text{ K})$, standard Gibbs free energies of formation, $\Delta G_{f,i}^0 (298 \text{ K})$, and standard entropies, S_i^0 [1]. With the constants given below, the resulting heat capacities will have units of J mol⁻¹ K⁻¹. The heats of formation and the free energies are given in the table in kJ mol⁻¹ and the standard entropies are in units of J mol⁻¹ K⁻¹. Using these data, generate an expression for the standard heat of reaction (1) as a function of temperature and calculate the standard Gibbs free energy change of reaction (1) at 298 K.

$$CO + 2\,H_2 \rightleftarrows CH_3OH \qquad\qquad (1)$$

$$\hat{C}_{p,i} = A_i + B_i t + C_i t^2 + D_i t^3 + \frac{E_i}{t^2} \qquad\qquad (2)$$

i	CO	CO$_2$	H$_2$	CH$_3$OH
A_i	25.567590	24.997350	33.107800	21.138073
B_i	6.096130	55.186960	-11.508000	70.878654
C_i	4.054656	-33.691370	11.609300	25.853554
D_i	-2.671301	7.948387	-2.844400	-28.497905
E_i	0.131021	-0.136638	-0.159665	0.0
$\Delta H_{f,i}^0 (298 \text{ K})$	-110.53	-393.52	0.0	-201.0
$\Delta G_{f,i}^0 (298 \text{ K})$	-137.3689	-394.64777	0.0	-162.6153
S_i^0	197.6482155	213.7689511	130.6656268	239.7234884

Problem Solution

The heat of reaction (in J mol−1) at temperature T is found using equation (3). The resulting value is then used in equation (4) to generate an expression for the standard heat of reaction as a function of temperature, equation (5).

$$\Delta H_j^0(298\text{ K}) = \sum_{i=1}^{N_{species}} \left(v_{i,j} \Delta H_{f,i}^0(298\text{ K}) \right) \tag{3}$$

$$\Delta H_1^0(298\text{ K}) = v_{CO,1}\Delta H_{f,CO}^0(298\text{ K}) + v_{H_2,1}\Delta H_{f,H_2}^0(298\text{ K}) + v_{CH_3OH,1}\Delta H_{f,CH_3OH}^0(298\text{ K})$$

$$\Delta H_1^0(298\text{ K}) = (-1)(-110.53\text{ kJ mol}^{-1}) + (-2)(0\text{ kJ mol}^{-1}) + (+1)(201.0\text{ kJ mol}^{-1})$$

$$\Delta H_1^0(298\text{ K}) = -90.407\text{ kJ mol}^{-1}$$

$$\Delta H_j^0(T) = \Delta H_j^0(298\text{ K}) + \sum_{i=1}^{N_{species}} \left(v_{i,j}\int_{298K}^T \hat{C}_{p,i}\,dT \right) \tag{4}$$

$$\Delta H_1^0(T) = \Delta H_1^0(298\text{ K}) + \left(v_{CO,1}\int_{25}^T \hat{C}_{p,CO}\,dT \right) + \left(v_{H_2,1}\int_{25}^T \hat{C}_{p,H_2}\,dT \right)$$
$$+ \left(v_{CH_3OH,1}\int_{25}^T \hat{C}_{p,CH_3OH}\,dT \right)$$

$$\Delta H_1^0(T) = -90.47\text{ kJ mol}^{-1}$$

$$+(-1)\int_{25}^T \left(\begin{array}{l} 25.56759 + 6.09613\left(\dfrac{T}{1000\text{ K}}\right) \\[2mm] +4.054656\left(\dfrac{T}{1000\text{ K}}\right)^2 - 2.671301\left(\dfrac{T}{1000\text{ K}}\right)^3 + \dfrac{0.131021}{\left(\dfrac{T}{1000\text{ K}}\right)^2} \end{array} \right) dT$$

$$+(-2)\int_{25}^T \left(\begin{array}{l} 33.1078 - 11.508\left(\dfrac{T}{1000\text{ K}}\right) \\[2mm] +11.6093\left(\dfrac{T}{1000\text{ K}}\right)^2 - 2.8444\left(\dfrac{T}{1000\text{ K}}\right)^3 - \dfrac{0.159665}{\left(\dfrac{T}{1000\text{ K}}\right)^2} \end{array} \right) dT$$

$$+(+1)\int_{25}^T \left(\begin{array}{l} 21.138073 + 70.878654\left(\dfrac{T}{1000\text{ K}}\right) \\[2mm] +25.853554\left(\dfrac{T}{1000\text{ K}}\right)^2 - 28.497905\left(\dfrac{T}{1000\text{ K}}\right)^3 \end{array} \right) dT$$

$$\Delta H_1^0(T) = \left(\begin{array}{l} -72632 - \dfrac{1.883\times 10^5}{T} - 70.645T + 0.0439T^2 \\[2mm] -4.732\times 10^{-7}T^3 - 5.034\times 10^{-9}T^4 \end{array} \right) \text{J mol}^{-1} \tag{5}$$

The Gibbs free energy change at 298 K can be found from the Gibbs free energies of formation and the stoichiometric coefficients using equation (6).

$$\Delta G_j^0\left(298\text{ K}\right)=\sum_{i=1}^{N_{species}}\left(v_{i,j}\Delta G_{f,i}^0\left(298\text{ K}\right)\right) \tag{6}$$

$$\Delta G_1^0\left(298\text{ K}\right)=v_{CO,1}\Delta G_{f,CO}^0\left(298\text{ K}\right)+v_{H_2,1}\Delta G_{f,H_2}^0\left(298\text{ K}\right)+v_{CH_3OH,1}\Delta G_{f,CH_3OH}^0\left(298\text{ K}\right)$$

$$\Delta G_{3.4A(298K)}^0=\left(-1\right)\left(-137.3689\text{ kJ mol}^{-1}\right)+\left(-2\right)\left(0\text{ kJ mol}^{-1}\right)+\left(+1\right)\left(162.6153\text{ kJ mol}^{-1}\right)$$

$$\Delta G_{3.4A(298K)}^0=-25.246\text{ kJ mol}^{-1}$$

Reference Cited

1. Chase, M. W., Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald and A. N. Syverud, "JANAF Thermochemical Tables," 3rd ed. American Chemical Society and American Institute of Physics, New York, 1986.