REB, The Course
Class 2, Activity 3 Solution

The vapor phase synthesis of methanol is given in reaction (1). The gas phase heat capacity of reagent i, $\hat{C}_{p,i}$, in J mol^{-1} K^{-1} can be calculated using equation (2) where t is the temperature in K divided by 1000. The constants for use in equation (2), A_i through E_i are given in Table 1, which also includes the standard heat of formation at 298 K, the standard change in Gibbs free energy for formation, and the standard entropy of the reagents in kJ mol^{-1}, kJ mol^{-1}, and J mol^{-1} K^{-1}, respectively. Generate an expression for the heat of reaction (1) as a function of temperature.

$$CO + 2H_2 \rightleftarrows CH_3OH \tag{1}$$

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

i	CO	H_2	CH_3OH
A_i	25.567590	33.107800	21.138073
B_i	6.096130	-11.508000	70.878654
C_i	4.054656	11.609300	25.853554
D_i	-2.671301	-2.844400	-28.497905
E_i	0.131021	-0.159665	0.0
$\Delta H_{f,i}\big\vert_{298K}$	-110.53	0.0	-201.0
$\Delta G_{f,i}\big\vert_{298K}$	-137.3689	0.0	-162.6153
S_i^0	197.6482155	130.6656268	239.7234884

Table 1. Thermodynamic data for Activity 4 from 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.

Calculate the standard heat of reaction at 298 K.

$$\Delta H_j^0\Big|_{T=298K} = \sum_i \left(\nu_{i,j}\Delta H_{f,i}^0\Big|_{T=298K}\right)$$

$$\Delta H^0\Big|_{T=298K} = \left(-\Delta H_{f,CO}^0 - 2\Delta H_{f,H_2}^0 + \Delta H_{f,CH_3OH}^0\right)\Big|_{T=298K}$$

$$\Delta H^0\Big|_{T=298K} = -90.407 \text{ kJ mol}^{-1}$$

Write the expression for the standard heat of reaction at temperature T.

$$\Delta H_j^0 = \Delta H_j^0\Big|_{T=298K} + \sum_i \left(\nu_{i,j}\int_{298\text{ K}}^{T} \hat{C}_{p,i}dT\right)$$

$$\Delta H^0 = \Delta H^0\Big|_{T=298K} + \int_{298K}^{T} \left(-\hat{C}_{p,CO} - 2\hat{C}_{p,H_2} + \hat{C}_{p,CH_3OH}\right) dT$$

Substitute the heat capacities noting that $t = \dfrac{T}{1000}$

$$\begin{aligned}\Delta H^0 = \Delta H^0\Big|_{T=298K} &+ \int_{298K}^{T} \left(-A_{CO} - 2A_{H_2} + A_{CH_3OH}\right) dT \\ &+ \int_{298K}^{T} \left(-B_{CO} - 2B_{H_2} + B_{CH_3OH}\right)\left(\frac{T}{1000}\right) dT \\ &+ \int_{298K}^{T} \left(-C_{CO} - 2C_{H_2} + C_{CH_3OH}\right)\left(\frac{T}{1000}\right)^2 dT \\ &+ \int_{298K}^{T} \left(-D_{CO} - 2D_{H_2} + D_{CH_3OH}\right)\left(\frac{T}{1000}\right)^3 dT \\ &+ \int_{298K}^{T} \left(-E_{CO} - 2E_{H_2} + E_{CH_3OH}\right)\left(\frac{T}{1000}\right)^{-2} dT\end{aligned}$$

$$\Delta H^0 = \begin{pmatrix} -72632 & -\frac{1.883 \times 10^5}{T} & -70.645T \\ +0.0439T^2 & -4.732 \times 10^{-7} T^3 & -5.034 \times 10^{-9} T^4 \end{pmatrix} \text{ J mol}^{-1}$$