A First Course on Kinetics and Reaction Engineering

Example 5.4

Problem Purpose

This example illustrates the calculation of a rate coefficient using collision theory.

Problem Statement

The decomposition of HI, equation (1) is elementary. Use collision theory to estimate the forward rate coefficient at 300K assuming the collision cross-section to equal 38.5 Å^2 and the activation energy to be 184.1 kJ mol^{-1}.

$$2\ HI \rightleftarrows H_2 + I_2 \tag{1}$$

Problem Solution

This reaction involves 2 molecules of the same type, so equation (2) is the appropriate rate expression. Noting that for this problem A is HI, the concentration of A can be factored out of the right hand term, and the remaining terms can be lumped together as the rate coefficient, equation (3).

$$r_{AA,f} = N_{Av}\sigma_{AA}C_A^2\sqrt{\frac{2k_BT}{\pi\mu}}\exp\left(\frac{-E_j}{RT}\right) \quad \Rightarrow \quad r_{1,f} = k_{1,f}C_{HI}^2 \tag{2}$$

$$k_{1,f} = N_{Av}\sigma_{HI-HI}\sqrt{\frac{2k_BT}{\pi\mu}}\exp\left(\frac{-E_1}{RT}\right) \tag{3}$$

The quantities appearing in these equations are known universal constants or they can be computed in a consistent set of units.

$$\sigma_{HI-HI} = \left(38.5\ \text{Å}\right)\left(\frac{10^{-8}\ \text{cm}}{\text{Å}}\right)^2 = 3.85\times10^{-15}\ \text{cm}^2$$

$$k_B = 1.3806\times10^{-16}\,\frac{\text{g cm}^2}{\text{s}^2\ \text{K}}$$

T = 300 K

$$\mu = \frac{m_{HI}^2}{2m_{HI}} = \frac{m_{HI}}{2} = \frac{1}{2}\left(128\ \frac{g}{mol}\right)\left(\frac{\text{mol}}{6.0222\times10^{23}}\right) = 1.063\times10^{-22}\ \text{g}$$

E_1 = 184,100 J mol^{-1}

R = 8.3144 J mol^{-1} K^{-1}

Substituting gives $k_{1,f}$ = 3.22 x 10^{-19} cm^3 mol^{-1} s^{-1}.