Chemistry 2740 Spring 2022 Assignment 2 Solutions

1. The rate of this elementary reaction is, according to the law of mass action,

$$v = k[\mathrm{AuCl_4^-}][\mathrm{H_2O}].$$

Since the reaction occurs in aqueous medium, water is in great excess. Accordingly, its concentration is constant throughout the reaction. We can therefore write

$$v = k_{\mathrm{app}}[\mathrm{AuCl_4^-}]$$

with

$$k_{\mathrm{app}} = k[\mathrm{H_2O}].$$

2. We have $k = k_{\mathrm{app}}/[\mathrm{H_2O}]$. At 10.0 °C, we therefore have

$$\begin{aligned} k &= \frac{0.40 \times 10^{-2}\,\mathrm{s^{-1}}}{55.45\,\mathrm{mol\,L^{-1}}} \\ &= 7.2 \times 10^{-5}\,\mathrm{L\,mol^{-1}s^{-1}} \end{aligned}$$

I repeated this calculation at each temperature in a spreadsheet, using the appropriate mole density each time, and obtained the following elementary rate constants:

T/°C	10.0	15.3	20.0	26.0	34.5
$k/10^{-4}\mathrm{L\,mol^{-1}s^{-1}}$	0.72	1.1	1.8	2.80	5.62

3. The best way to get the enthalpy and entropy of activation is to use an Eyring plot. This is a graph of $\ln(kh/k_BT)$ against T^{-1}. Given that this is a solution-phase reaction, k is in the correct units for an Eyring plot. I carried out all of the calculations in a spreadsheet. My graph is shown in figure 1. The slope and intercept of the line are

$$\begin{aligned} \text{slope} &= -(7.07 \pm 0.16) \times 10^3\,\mathrm{K} \\ \text{intercept} &= -14.0 \pm 0.5 \end{aligned}$$

(I used the Excel `LINEST` function to get the standard errors. You didn't need to do that, but it's interesting to see how many significant figures we end up with in the final answers.) The slope is $-\Delta^\ddagger H^\circ/R$ and the intercept is $\Delta^\ddagger S^\circ/R$. Thus we have

$$\begin{aligned} \Delta^\ddagger H^\circ &= -(8.314\,472\,\mathrm{J\,K^{-1}mol^{-1}})\left[-(7.07 \pm 0.16) \times 10^3\,\mathrm{K}\right] \\ &= 58.8 \pm 1.3\,\mathrm{kJ\,mol^{-1}} \\ \Delta^\ddagger S^\circ &= (8.314\,472\,\mathrm{J\,K^{-1}mol^{-1}})(-14.0 \pm 0.5) \\ &= -116 \pm 4\,\mathrm{J\,K^{-1}mol^{-1}} \end{aligned}$$

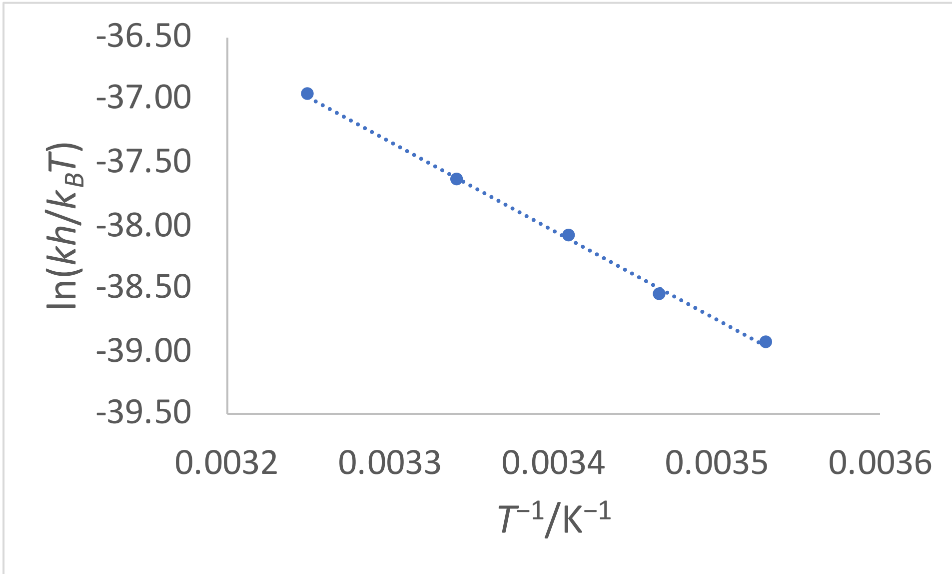

Figure 1: Eyring plot

4. The relatively large negative entropy of activation is consistent with the partial formation of a bond during this process. The following is a reasonable hypothesis for the transition state geometry: