# Chemistry 2710 Spring 2003 Test 3 Solutions

1. In transition state theory, we start by decomposing the elementary reaction (R → P) as follows:

$$R \rightleftharpoons TS \rightarrow P.$$

   We treat accession to the steady-state as a pseudo-equilibrium with equilibrium constant $K^{\ddagger}$. Conceptually, this presents some difficulties since the transition state is not an equilibrium structure.

2. The Brønsted-Bjerrum equation is

$$\ln k = \ln k_0 + 2.214 \times 10^{-10} Z_A Z_B \left(\varepsilon T\right)^{-3/2} \sqrt{I}.$$

   Since B is uncharged ($Z_B = 0$), the theory predicts that the rate constant will not depend on the ionic strength, i.e. that $k = 2.9 \times 10^3 \, \mathrm{L\,mol^{-1}s^{-1}}$ at any ionic strength. It seems unlikely that the rate constant doesn't depend at all on the ionic strength. The difficulty is that we don't have a theory to cover non-ionic solutes.

3. (a) We need to do a linear regression of $\ln k$ vs $T^{-1}$.

| $10^3 T^{-1}$ (K$^{-1}$) | 1.4859 | 1.4025 | 1.3280 | 1.2771 |
|---|---|---|---|---|
| $\ln k$ | 10.292 | 10.924 | 11.720 | 12.123 |

   Although a graph isn't required, I always like to see it:
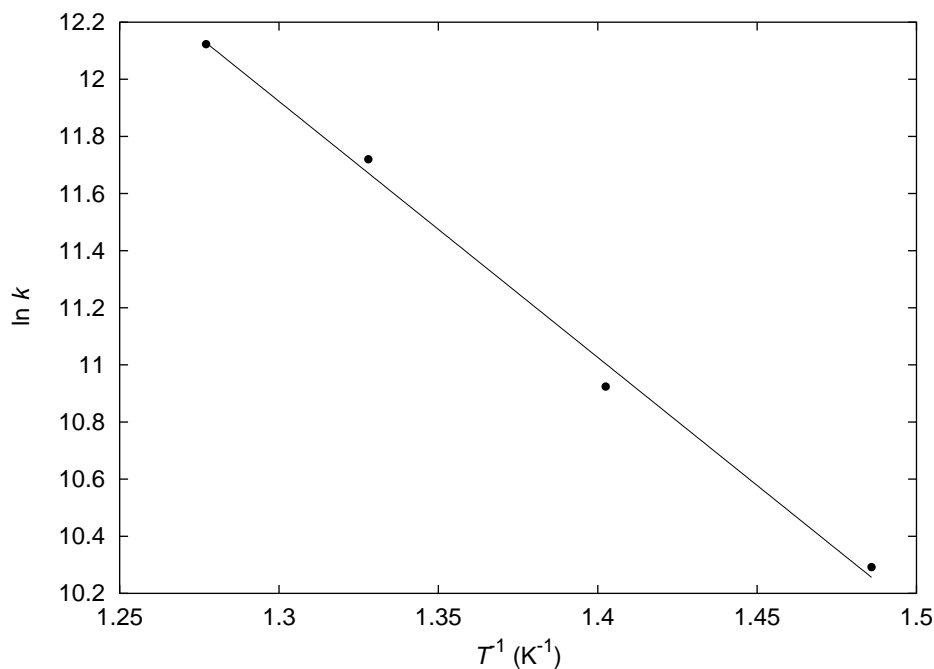
The fit is reasonable. The slope and intercept are, respectively, $-8965\,\mathrm{K}$ and $23.577$. The activation energy and preexponential factor are therefore

$$
\begin{aligned}
\bar{E}_a &= -R(\text{slope}) = -(8.314472\,\mathrm{J\,K^{-1}mol^{-1}})(-8965\,\mathrm{K}) \\
&= 74.5\,\mathrm{kJ/mol}. \\
k_\infty &= e^{\text{intercept}} = e^{23.577} \\
&= 1.74\times10^{10}\,\mathrm{L\,mol^{-1}s^{-1}}.
\end{aligned}
$$

(b) This is a hydrogen abstraction reaction. It seems quite likely that the transition state is something like

$$
\mathrm{HO_2} - - - \mathrm{H} - - - \mathrm{C_5H_9},
$$
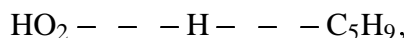
i.e. a weakly bound quasi-molecular species with a bridging H atom. (The bonding in this species would transiently resemble that in diborane, if you know about this compound.) If this is the case, $\Delta \bar{n}^\ddagger = 1 - 2 = -1$. The reaction is in the gas phase, so we also need to convert the preexponential factor to $\mathrm{bar^{-1}s^{-1}}$.

$$
\begin{aligned}
\frac{n}{V} &= \frac{P}{RT} = \frac{100000\,\mathrm{Pa}}{(8.314472\,\mathrm{J\,K^{-1}mol^{-1}})(298\,\mathrm{K})} \\
&= 40.36\,\mathrm{mol/m^3} \equiv 0.04036\,\mathrm{mol/L}. \\
\therefore k_\infty &= (1.74\times10^{10}\,\mathrm{L\,mol^{-1}s^{-1}})(0.04036\,\mathrm{mol\,L^{-1}bar^{-1}}) \\
&= 7.00\times10^8\,\mathrm{bar^{-1}s^{-1}}. \\
\therefore \Delta\bar{S}^\ddagger &= R\left[\ln\left(\frac{hk_\infty}{k_BT}\right) - 1 + \Delta\bar{n}^\ddagger\right] \\
&= (8.314472\,\mathrm{J\,K^{-1}mol^{-1}}) \\
&\quad \times \left[\ln\left(\frac{(6.6260688\times10^{-34}\,\mathrm{J/Hz})(7.00\times10^8\,\mathrm{bar^{-1}s^{-1}})}{(1.3806503\times10^{-23}\,\mathrm{J/K})(298\,\mathrm{K})}\right) - 1 - 1\right] \\
&= -92.2\,\mathrm{J\,K^{-1}mol^{-1}}.
\end{aligned}
$$

The very negative value tells us that our initial guess was probably right, i.e. that the hydrogen atom bridges both molecules in the transition state.

4. (a) If the data obey Michaelis-Menten kinetics, a plot of $v$ vs $v/[\text{phenol}]$ should be linear.

| $10^3 v/[\text{phenol}]$ $(\mathrm{h^{-1}})$ | 3.07 | 2.40 | 1.89 | 1.51 | 1.35 |
|---|---|---|---|---|---|
| $v\,(\mu\mathrm{mol\,L^{-1}h^{-1}})$ | 3.1 | 6.4 | 10 | 12 | 14 |

Here is the plot:
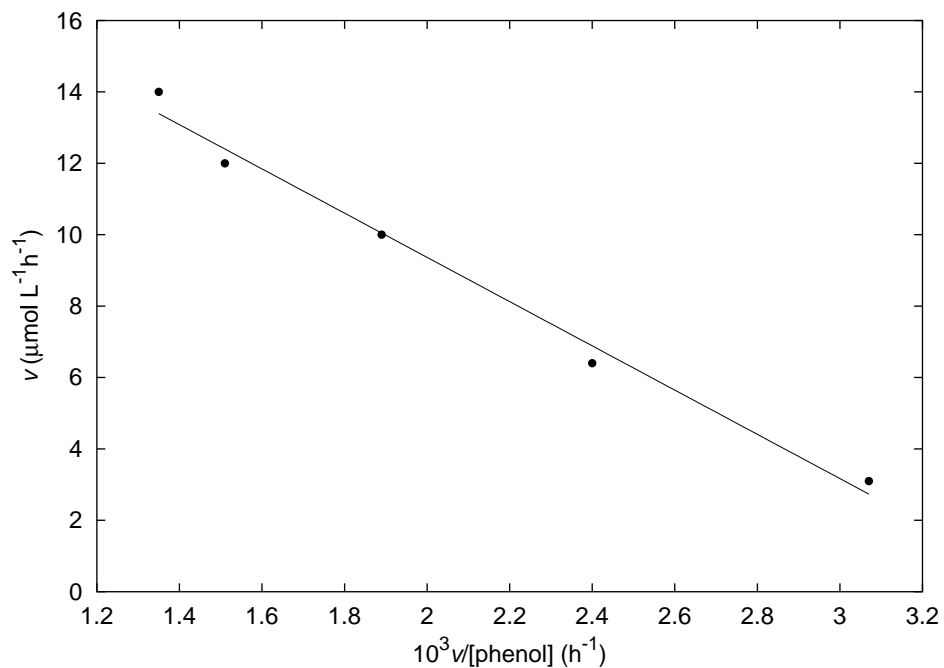
There's a bit of scatter, but it doesn't look like there is significant curvature. Accordingly, I would conclude that these data do follow Michaelis-Menten kinetics.

(b) The slope of the plot is $-6.20 \times 10^{-3}\,\text{mol/L}$, so $K_M = 6.20\,\text{mmol/L}$. The intercept is $v_{\text{max}} = 2.18 \times 10^{-5}\,\text{mol}\,\text{L}^{-1}\text{h}^{-1}$ or $21.8\,\mu\text{mol}\,\text{L}^{-1}\text{h}^{-1}$.