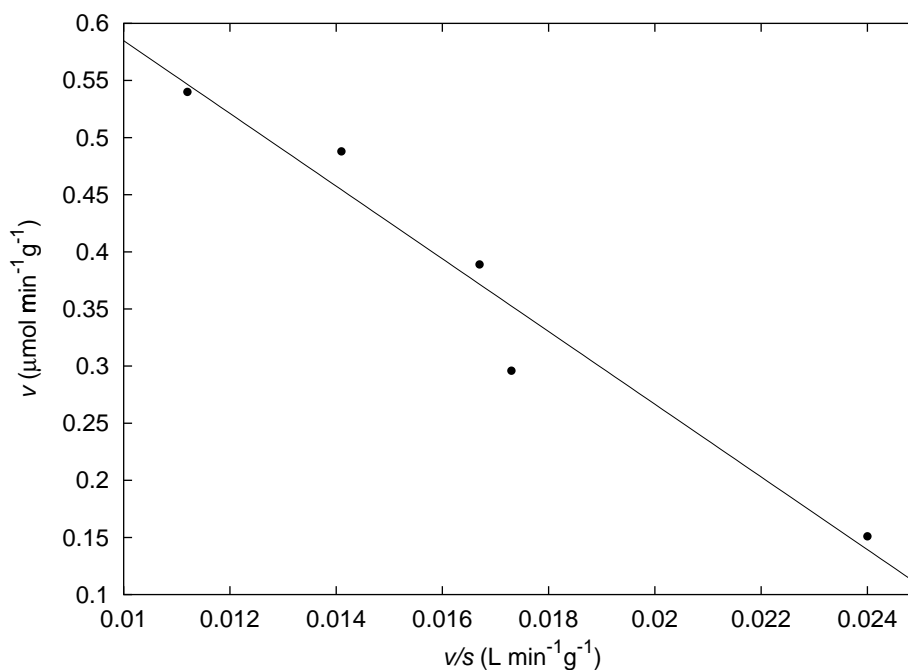


# Chemistry 2710 Spring 2002 Test 3 Solutions

1. (a) To decide whether a reaction obeys Michaelis-Menten kinetics or not, we can generate an Eadie-Hofstee plot:

$v/[sucrose] \text{ (L min}^{-1}\text{g}^{-1})$	0.0240	0.0173	0.0167	0.0141	0.0112
$v \text{ (}\mu\text{mol min}^{-1}\text{g}^{-1})$	0.151	0.296	0.389	0.488	0.540

The graph has the following appearance:



There is significant scatter around the line of best fit, but there is no obvious curvature. Accordingly, we may conclude that the data are consistent with Michaelis-Menten kinetics.

- (b) By linear regression, we find

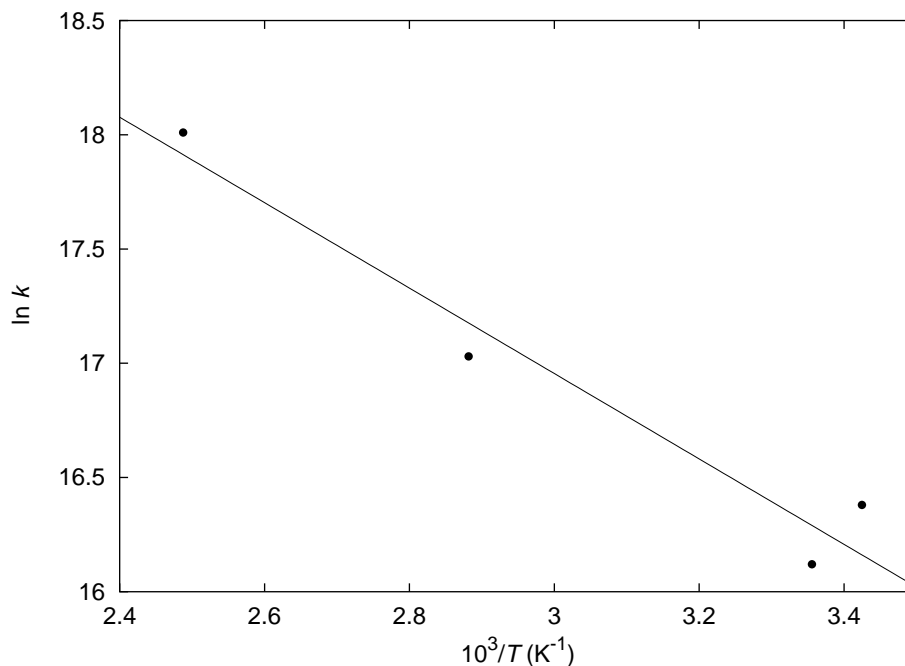
$$v_{\max} = \text{intercept} = 0.903 \mu\text{mol min}^{-1}\text{g}^{-1},$$

$$K_M = -(\text{slope}) = 31.8 \mu\text{mol/L}.$$

2. (a) To get the Arrhenius parameters, we must plot  $\ln k$  vs  $1/T$ :

$10^3/T \text{ (K}^{-1})$	3.4247	3.3557	2.8818	2.4876
$\ln k$	16.38	16.12	17.03	18.01

The Arrhenius plot (which wasn't required) has the following appearance:



The slope and intercept are as follows:

$$\begin{aligned} \text{slope} &= -\frac{\bar{E}_a}{R} = -1869 \text{ K.} \\ \text{intercept} &= \ln k = 22.5633. \\ \therefore \bar{E}_a &= (1869 \text{ K})(8.314472 \text{ JK}^{-1}\text{mol}^{-1}) = 15.5 \text{ kJ/mol.} \\ k_\infty &= e^{22.5633} = 6.30 \times 10^9 \text{ L mol}^{-1}\text{s}^{-1}. \end{aligned}$$

- (b) This is a gas-phase reaction, so the preexponential factor should be expressed in  $\text{bar}^{-1}\text{s}^{-1}$  to calculate the entropy of activation:

$$\begin{aligned} \frac{n}{V} &= \frac{P}{RT} = \frac{100000 \text{ Pa}}{(8.314472 \text{ JK}^{-1}\text{mol}^{-1})(298 \text{ K})} \\ &= 40.36 \text{ mol/m}^3 \\ &\equiv 0.04036 \text{ mol/L.} \\ \therefore k_\infty &= (6.30 \times 10^9 \text{ L mol}^{-1}\text{s}^{-1})(0.04036 \text{ mol L}^{-1}\text{bar}^{-1}) = 2.54 \times 10^8 \text{ bar}^{-1}\text{s}^{-1}. \end{aligned}$$

We also need  $\Delta\bar{n}^\ddagger$ . In this case, the two reactants have to come together to form a product so it seems reasonable to guess that  $\Delta\bar{n}^\ddagger = 1 - 2 = -1$ . Thus we have

$$\begin{aligned}
\Delta\bar{S}^\ddagger &= R \left[ \ln \left( \frac{hk_\infty}{k_B T} \right) - 1 + \Delta\bar{n}^\ddagger \right] \\
&= (8.314472 \text{ J K}^{-1} \text{ mol}^{-1}) \left[ \ln \left( \frac{(6.6260688 \times 10^{-34} \text{ J/Hz})(2.54 \times 10^8 \text{ bar}^{-1} \text{ s}^{-1})}{(1.38065 \times 10^{-23} \text{ J/K})(298 \text{ K})} \right) \right. \\
&\quad \left. - 1 - 1 \right] \\
&= -101 \text{ J K}^{-1} \text{ mol}^{-1}.
\end{aligned}$$

The value is large and negative, which suggests that our guess about  $\Delta\bar{n}^\ddagger$  was right: The transition state is a tightly bound complex of the two reactants.

3. The total amount of enzyme is constant:

$$\begin{aligned}
e + c_1 + c_2 &= e_0. \\
\therefore e &= e_0 - c_1 - c_2.
\end{aligned}$$

There are two intermediate complexes. We apply the SSA to both:

$$\begin{aligned}
\frac{dc_1}{dt} &= k_1 e s - k_{-1} c_1 - k_2 c_1 + k_{-2} c_2 \\
&= k_1 s (e_0 - c_1 - c_2) - c_1 (k_{-1} + k_2) + k_{-2} c_2 \approx 0. \tag{1}
\end{aligned}$$

$$\frac{dc_2}{dt} = k_2 c_1 - k_{-2} c_2 - k_3 c_2 \approx 0. \tag{2}$$

The rate is  $v = k_3 c_2$ . It is therefore best to solve for  $c_1$  first. We can easily solve equation 2 for  $c_1$ :

$$c_1 = \frac{k_{-2} + k_3}{k_2} c_2.$$

Let

$$\alpha = \frac{k_{-2} + k_3}{k_2}.$$

Then  $c_1 = \alpha c_2$ . Substitute this expression into equation 1:

$$\begin{aligned}
0 &= k_1 s (e_0 - \alpha c_2 - c_2) - \alpha c_2 (k_{-1} + k_2) + k_{-2} c_2. \\
\therefore k_1 e_0 s &= c_2 [k_1 s (\alpha + 1) + \alpha (k_{-1} + k_2) - k_{-2}] \\
&= c_2 [k_1 s (\alpha + 1) + k_{-1} \alpha + k_{-2} + k_3 - k_{-2}] \\
&= c_2 [k_1 s (\alpha + 1) + k_{-1} \alpha + k_3]. \\
\therefore c_2 &= \frac{k_1 e_0 s}{k_1 s (\alpha + 1) + k_{-1} \alpha + k_3}. \\
\therefore v &= \frac{k_1 k_3 e_0 s}{k_1 s (\alpha + 1) + k_{-1} \alpha + k_3} \\
&= \frac{\frac{k_3 e_0}{\alpha + 1} s}{s + \frac{k_{-1} \alpha + k_3}{k_1 (\alpha + 1)}}.
\end{aligned}$$

Let

$$\begin{aligned}v_{\max} &= \frac{k_3 e_0}{\alpha + 1} \\ \text{and } K_M &= \frac{k_{-1}\alpha + k_3}{k_1(\alpha + 1)}. \\ \therefore v &= \frac{v_{\max} s}{s + K_M}.\end{aligned}$$

As shown above, the rate law is of the Michaelis-Menten form, with  $v_{\max}$  and  $K_M$  defined as shown above.