

25.4

a. Beer's Law states that $A = \epsilon b [\text{BPB}]$

where ϵ is the molar absorptivity of BPB, b is the cell path length. The rate of the reaction is:

$$\text{Rate} = -\frac{d[\text{BPB}]}{dt} = -\frac{d\left(\frac{A}{\epsilon b}\right)}{dt} = -\frac{1}{\epsilon b} \frac{dA}{dt}$$

b. Since the reaction is a second order reaction of type II, the integrate. rate equation has the form:

$$\frac{1}{[\text{OH}^-]_0 - [\text{BPB}]_0} \ln \left[\frac{[\text{OH}^-]/[\text{OH}^-]_0}{[\text{BPB}]/[\text{BPB}]_0} \right] = kt \quad \text{--- equation 25.}$$

$$\frac{1}{[\text{OH}^-]_0 - \frac{A_0}{\epsilon b}} \ln \left[\frac{[\text{OH}^-]/[\text{OH}^-]_0}{A/A_0} \right] = kt$$

$$\begin{aligned} \ln\left(\frac{A}{A_0}\right) &= \ln\left[\frac{[\text{OH}^-]}{[\text{OH}^-]_0}\right] - \left\{([\text{OH}^-]_0 - \frac{A_0}{\epsilon b})kt\right\} \\ &= \ln\left[\frac{10^{-(14-\text{pH})}}{[\text{OH}^-]_0}\right] - \left\{([\text{OH}^-]_0 - \frac{A_0}{\epsilon b})kt\right\} \quad (\text{relation with pH}) \end{aligned}$$

c. A plot of $\ln\left(\frac{A}{A_0}\right)$ vs. time is predicted to be linear.

$$\text{slope} = -\left([\text{OH}^-]_0 - \frac{A_0}{\epsilon b}\right)k$$

$$\text{rate constant } k = -\frac{\text{slope}}{[\text{OH}^-]_0 - \frac{A_0}{\epsilon b}}$$

25.13

First-order reaction, rate constant can be found from half-life:

$$k = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{4.5 \times 10^3 \text{ day}} = 1.54 \times 10^{-4} \text{ day}^{-1}$$

$$\ln\left(\frac{[A]}{[A]_0}\right) = -kt$$

$$t = \frac{1}{1.54 \times 10^{-4} \text{ day}^{-1}} \ln(10\%) = 1.495 \times 10^4 \text{ day} \approx 41 \text{ year}$$

Engel 26.2

The differential rate expression for methane:

$$\frac{d[\text{CH}_4]}{dt} = k_2 [\text{CH}_3\cdot] [\text{CH}_3\text{CHO}]$$

Steady-state for intermediates:

$$\frac{d[\text{CH}_2\text{CHO}\cdot]}{dt} = k_2 [\text{CH}_3\cdot] [\text{CH}_3\text{CHO}] - k_3 [\text{CH}_2\text{CHO}\cdot] = 0$$

$$\Rightarrow [\text{CH}_2\text{CHO}\cdot] = \frac{k_2}{k_3} [\text{CH}_3\cdot] [\text{CH}_3\text{CHO}]$$

$$\frac{d[\text{CH}_3\cdot]}{dt} = k_1 [\text{CH}_3\text{CHO}] - k_2 [\text{CH}_3\cdot] [\text{CH}_3\text{CHO}] + k_3 [\text{CH}_2\text{CHO}\cdot] - 2k_4 [\text{CH}_3\cdot]^2$$

$$\Rightarrow k_1 [\text{CH}_3\text{CHO}] - k_2 [\text{CH}_3\cdot] [\text{CH}_3\text{CHO}] + k_2 [\text{CH}_3\cdot] [\text{CH}_3\text{CHO}] - 2k_4 [\text{CH}_3\cdot]^2 = 0$$

$$\Rightarrow k_1 [\text{CH}_3\text{CHO}] = 2k_4 [\text{CH}_3\cdot]^2$$

$$\Rightarrow [\text{CH}_3\cdot] = \sqrt{\frac{k_1}{2k_4}} [\text{CH}_3\text{CHO}]^{1/2}$$

Substitute into rate expression for CH₄:

$$\frac{d[\text{CH}_4]}{dt} = k_2 \sqrt{\frac{k_1}{2k_4}} [\text{CH}_3\text{CHO}]^{1/2} [\text{CH}_3\text{CHO}] = k_2 \sqrt{\frac{k_1}{2k_4}} [\text{CH}_3\text{CHO}]^{3/2}$$

$$k_{\text{eff}} = k_2 \sqrt{\frac{k_1}{2k_4}}$$

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Engel 26.5

(a) at time = 0, $[Br_2] = [Br_2]_0$, $[H_2] = [H_2]_0$, $[HBr] = 0$

From question 26.4

$$\frac{d[HBr]}{dt} = \frac{k[H_2][Br_2]^{1/2}}{1 + \frac{m[HBr]}{[Br_2]}}$$

$$\left(\frac{d[HBr]}{dt} \right)_{t=0} = \frac{k[H_2]_0 [Br_2]_0^{1/2}}{1 + \frac{m \times 0}{[Br_2]_0}} = k [Br_2]_0^{1/2} [H_2]_0$$

(b) $k_1 = A_1 e^{-E_{a1}/RT}$ $k_2 = A_2 e^{-E_{a2}/RT}$ $k_5 = A_5 e^{-E_{a5}/RT}$

overall rate constant

$$\begin{aligned} k &= 2k_2 \left(\frac{k_1}{k_5} \right)^{1/2} = 2A_2 e^{-E_{a2}/RT} \left(\frac{A_1 e^{-E_{a1}/RT}}{A_5 e^{-E_{a5}/RT}} \right)^{1/2} \\ &= 2A_2 \left(\frac{A_1}{A_5} \right)^{1/2} e^{(-E_{a2}/RT - E_{a1}/2RT + E_{a5}/2RT)} \\ &= 2A_2 \left(\frac{A_1}{A_5} \right)^{1/2} e^{-\frac{1}{RT} (E_{a2} + \frac{E_{a1}}{2} - \frac{E_{a5}}{2})} \end{aligned}$$

overall activation energy

$$E_a = E_{a2} + \frac{E_{a1}}{2} - \frac{E_{a5}}{2} = 0 + \frac{192}{2} - \frac{74}{2} = \underline{\underline{59 \text{ kJ}\cdot\text{mol}^{-1}}}$$

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$$(c) \quad k_{400K} = A e^{-E_a/RT} = A e^{-E_a/R \cdot 400}$$

$$k_{298K} = A e^{-E_a/R \cdot 298}$$

$$\frac{\text{rate}_{400K}}{\text{rate}_{298K}} = \frac{k_{400K}}{k_{298K}} = \frac{A e^{-E_a/R \cdot 400}}{A e^{-E_a/R \cdot 298}} = e^{-\frac{E_a}{R} \left(\frac{1}{400} - \frac{1}{298} \right)}$$

$$= e^{-\frac{59 \times 10^3 \text{ J} \cdot \text{mol}^{-1}}{8.314} \left(\frac{1}{400} - \frac{1}{298} \right)}$$

$$= 434$$

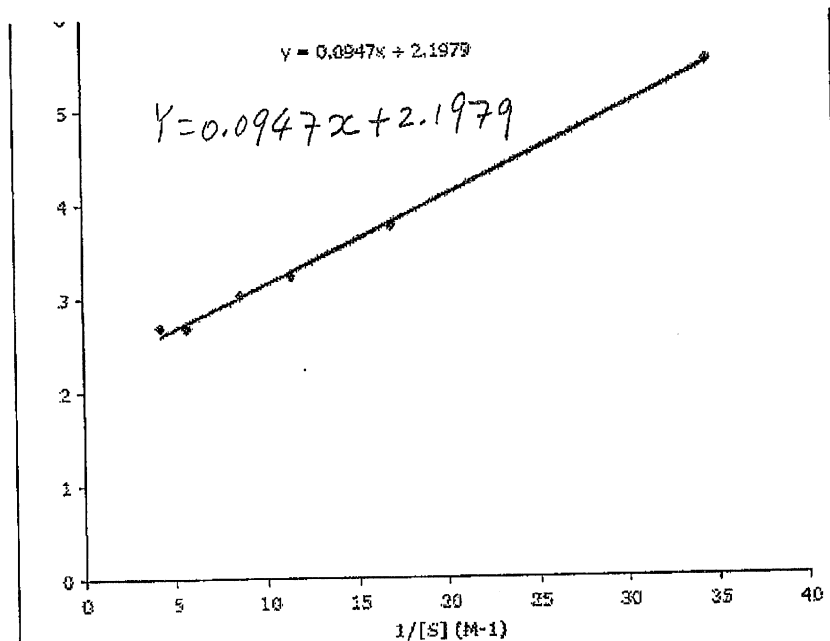
rate will increase to 434 times when temperature is increased from 298K to 400K.

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Engel 26.12

Use these data to determine the Michaelis constant .. plot

Lineweaver-Burke $\frac{1}{\text{Rate}}$ vs. $\frac{1}{[\text{Sucrose}]_0}$



Best fit data to a straight line =

$$\frac{1}{\text{rate}_0} = (0.0947 \text{ s}) \times \frac{1}{[\text{S}]_0} + (2.1979 \text{ M}^{-1} \text{ s})$$

$$R_{\text{max}} = \frac{1}{2.1979 \text{ M}^{-1} \text{ s}} = 0.455 \text{ M s}^{-1}$$

$$K_m = \text{slope} \times R_m = 0.0947 \text{ s} \times 0.455 \text{ M s}^{-1} = 0.0431 \text{ M}$$

Tinoco 732

$$(a) \quad \tau = \frac{1}{4k_1[\bar{P}] + k_{-1}}$$

$$\tau^{-2} = (4k_1[\bar{P}] + k_{-1})^2$$

$$= 16k_1^2[\bar{P}]^2 + 8k_1k_{-1}[\bar{P}] + k_{-1}^2$$

$$\therefore \frac{k_1}{k_{-1}} = \frac{[P_2]}{[\bar{P}]^2} \Rightarrow [\bar{P}]^2 = \frac{k_{-1}}{k_1}[P_2] \text{ plug into } \tau^{-2}$$

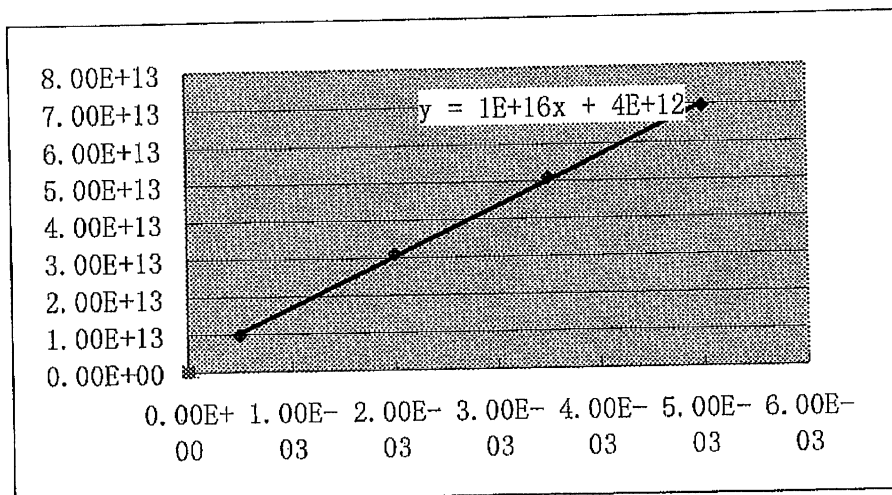
$$\tau^{-2} = 16k_1^2 \frac{k_{-1}}{k_1}[\bar{P}] + 8k_1k_{-1}[\bar{P}] + k_{-1}^2$$

$$= 8k_1k_{-1}(2[\bar{P}] + [\bar{P}]) + k_{-1}^2$$

$$= k_{-1}^2 + 8k_1k_{-1}[P]t$$

(b) Plot τ^{-2} vs $[P]t$

τ	τ^{-2}	$[P]t$
3.20E-07	9.77E+12	5.00E-04
1.80E-07	3.09E+13	2.00E-03
1.40E-07	5.10E+13	3.50E-03
1.20E-07	6.94E+13	5.00E-03



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$$\text{slope} = 8k_1k_{-1} = 1 \times 10^{16} \text{ M}^{-1}\text{S}^{-2}$$

$$\text{intercept} = k_{-1}^2 = 4 \times 10^{12} \text{ S}^{-2}$$

$$k_{-1} = 2 \times 10^6 \text{ S}^{-1}$$

$$k_1 = \frac{1 \times 10^{16} \text{ M}^{-1}\text{S}^{-2}}{8 \times 2 \times 10^6 \text{ S}^{-1}} = 6.25 \times 10^8 \text{ M}^{-1}\text{S}^{-1}$$

$$(c) \Delta G^\circ = -RT \ln K$$

$$= -RT \ln \frac{k_1}{k_{-1}}$$

$$= -8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K} \times \ln \frac{6.25 \times 10^8 \text{ M}^{-1}\text{S}^{-1}}{2.0 \times 10^6 \text{ S}^{-1}}$$

$$= -14.23 \text{ kJ mol}^{-1}$$

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