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2.1 Without experimental data we cannot answer this question. The order of reaction need not match the stoichiometry, and often doesn't

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2.3 Why should the way you write the stoichiometry affect the rate of reaction? The rate expression remains unchanged.

2.5 $$r_R = -2r_A = -\frac{2}{3}r_B \quad \text{or} \quad -r_A = -\frac{1}{3}r_B = \frac{1}{2}r_R$$

2.7 a) We are given $-\frac{dp_A}{dt} = k_p p_A^2$

($-\frac{dp_A}{dt}$: atm/hr; k_p: 3.66; p_A^2: $(atm)^2$)

Balancing dimensions we find $k_p = 3.66\ (atm)^{-1}(hr)^{-1}$ ← a)

b) For an ideal gas $p_A V = n_A RT$ or $p_A = C_A RT$

Thus $-\frac{dp_A}{dt} = 3.66 p_A^2$ ... becomes ... $-\frac{d(C_A RT)}{dt} = 3.66 (C_A RT)^2$

or $$-\frac{dC_A}{dt} = \underbrace{[3.66\ (atm)^{-1} hr^{-1}]RT}_{\text{new rate constant} = k'} C_A^2$$

where $$k' = 3.66 \frac{1}{atm \cdot hr} \cdot \frac{(1 atm)(22.4 l)}{(1 mol)(273^\circ K)} \cdot (400^\circ K) = 120\ (hr)^{-1}(mol/l)^{-1}$$ ← b)

2.9 From Eq. 35 we write

$$\frac{k_{650}}{k_{500}} = e^{-\frac{E}{R}\left(\frac{1}{T_{650}} - \frac{1}{T_{500}}\right)}$$

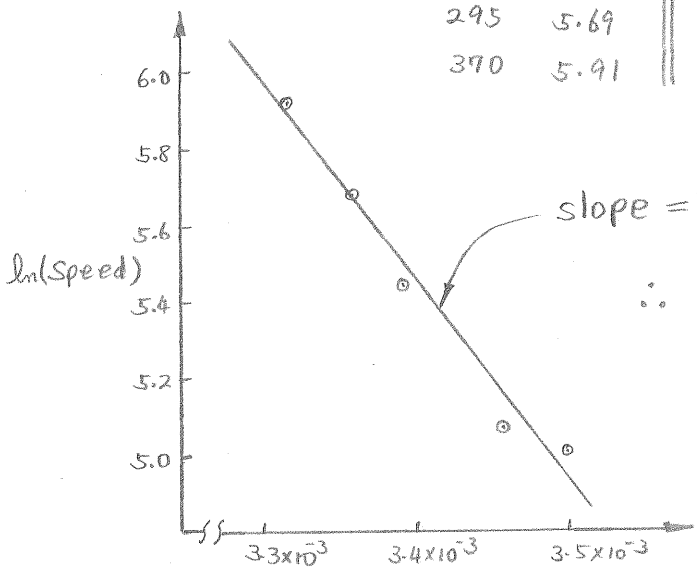
$$= e^{-\frac{300\,000}{8.314}\left(\frac{1}{923} - \frac{1}{773}\right)}$$

$$= 1971$$ ←

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2.11

Speed	ln S	T	$(\frac{1}{T})\times 10^3$
150	5.01	13	3.4965
160	5.07	16	3.4602
230	5.44	22	3.3898
295	5.69	24	3.3670
370	5.91	28	3.3220



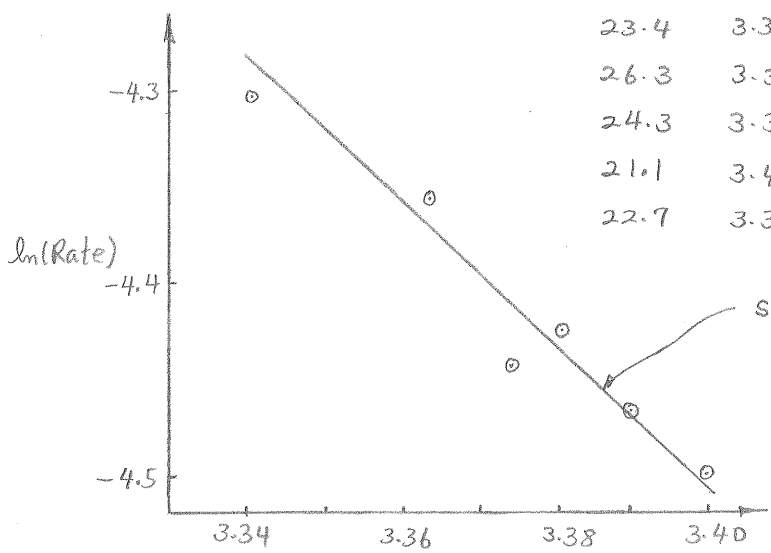
$\text{slope} = \frac{-E}{R} = -5420$

$\therefore E = (5420)(8.314) = 45062\ J$

$\cong 45\ kJ$

2.13

T	$\frac{1}{T}\times 10^{-3}$	Days	ln(Rate) = ln($\frac{1}{\text{days}}$)
22.0	3.390	87	-4.466
23.4	3.374	85	-4.443
26.3	3.341	74	-4.304
24.3	3.364	78	-4.357
21.1	3.400	90	-4.500
22.7	3.382	84	-4.431



$\text{slope} = -\frac{E}{R} = -3392$

$E = (3392)(8.314)$

$= 28201\ J/mol$

$= 28.2\ kJ/mol$

2.15 $-r_A = kC_A^n$ ... $\frac{-r_2}{-r_1} = \frac{k(2C_A)^n}{kC_A^n} = 2^n$ (← 3)

$\therefore n = 1.585$ ←

2.17 Guess that $-r_A = kC_A^a C_B^b$

There are 3 unknowns: k, a and b.
But we have 3 equations

$$50 = k(2)^a(125)^b \quad \text{---(i)}$$
$$32 = k(2)^a(64)^b \quad \text{---(ii)}$$
$$48 = k(3)^a(64)^b \quad \text{---(iii)}$$

C_A	C_B	$-r_A$
2	125	50
2	64	32
3	64	48

Divide (iii) by (ii) gives $a = 1$
Divide (i) by (ii) gives $b = 2/3$
Replace a and b in (i) gives $k = 1$

$\therefore \quad -r_A = C_A C_B^{2/3}$ ←

2.19 a) Consider the mechanism

$$2A \underset{2}{\overset{1}{\rightleftharpoons}} A + A^* \qquad A^* \xrightarrow{3} R + S$$

... and let us find its rate expression.

For reactant A: $-r_A = k_1[A]^2 - k_2[A^*][A]$ ..... (i)

For intermediate: $-r_{A^*} = k_1[A]^2 - k_2[A^*][A] - k_3[A^*] = 0$ ← steady state approximation

from which $[A^*] = k_1[A]^2 / k_2[A] + k_3$ ----- (ii)

Replacing (ii) in (i) so as to eliminate the unmeasurable A^* gives

$$-r_A = \frac{k_1 k_3 [A]^2}{k_2[A] + k_3} \qquad \text{---------- (iii)}$$

And when $k_2[A] \gg k_3$

$$-r_A = \frac{k_1 k_3}{k_2}[A] \quad \text{.... or first order rx} \leftarrow \text{a)}$$

b) Now at low enough C_A we may reach conditions where $k_2[A] \ll k_3$. In such a situation Eq. (iii) will reduce to

$$-r_A = k_1[A]^2 \quad \text{... or } 2^{\text{nd}} \text{ order kinetics}$$

Hence lower C_A more and more. This mechanism predicts that a point will be reached where the reaction order will start rising from one, and will approach and eventually become two. ← b)

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2.21 Hypothesize:

$$H_3PO_2 + H^+ \underset{k_2}{\overset{k_1}{\rightleftharpoons}} X^* + H^+$$
$$X^* + O_x \underset{k_4}{\overset{k_3}{\rightleftharpoons}} H_3PO_3$$

... where X^* is an unstable intermediate

Then as in the example, pg 19, we write

$$r_{H_3PO_3} = k_3[X^*][O_x] - k_4[H_3PO_3] \quad \text{..... (i)}$$

steady state assumption

$$r_{X^*} = k_1[H_3PO_2][H^+] - k_2[X^*][H^+] - k_3[X^*][O_x] + k_4[H_3PO_3] = 0$$

Thus

$$[X^*] = \frac{k_1[H_3PO_2][H^+] + k_4[H_3PO_3]}{k_2[H^+] + k_3[O_x]} \quad \text{..... (ii)}$$

Assuming $k_4 = 0$ (and we are certainly free to do this since this is our model, our brainchild), replacing (ii) in (i) then gives

$$r_{H_3PO_3} = \frac{k_1 k_3[H_3PO_2][H^+][O_x]}{k_2[H^+] + k_3[O_x]} \quad \text{..... (iii)}$$

Now when $k_3[O_x] \gg k_2[H^+]$ ... i.e. high oxidizer concentration, Eq. (iii) gives

$$r_{H_3PO_3} = k_1[H_3PO_2][H^+] \quad \text{..... (iv)}$$

On the other hand when $k_2[H^+] \gg k_3[O_x]$ .... i.e. low oxidizer concentration Eq. (iii) gives

$$r_{H_3PO_3} = \frac{k_1 k_3}{k_2}[H_3PO_2][O_x] \quad \text{..... (v)}$$

Eqs (iv) & (v) fit the evidence hence the hypothesized model is accepted.

2.23

$$A + E \underset{2}{\overset{1}{\rightleftharpoons}} X \quad \text{.... (1)}$$
$$X \longrightarrow R + E \quad \text{... (2)}$$

with

$$E_0 = E + X \quad \text{... (3)}$$

M-M assume that the reverse reactions of (1) approach equilibrium quickly, or

$$K = \frac{X}{AE} = \frac{k_1}{k_2} \quad \text{... (4)}$$

B-H assume that quickly

$$dX/dt = 0 \quad \text{.. (5)}$$

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2.23 (continued)

For M.M

From (2)

$$r_R = k_3 X \quad \cdots (6)$$

From (5)

$$X = \frac{k_1}{k_2} AE$$

Eliminate E with (3)

$$X = \frac{k_1}{k_2} A(E_0 - X)$$

or

$$X = \frac{\frac{k_1}{k_2} AE_0}{1 + \frac{k_1}{k_2} A} \quad \cdots (7)$$

Eq (7) in (6) gives

$$r_R = \frac{k_3 AE_0}{\frac{k_2}{k_1} + A}$$

For B-H

From (2)

$$r_R = k_3 X \quad \cdots (8)$$

From (5)

$$\frac{dX}{dt} = 0 = k_1 AE - (k_2 + k_3) X$$

Eliminate E with (3)

$$k_1 A(E_0 - X) - (k_2 + k_3) X = 0$$

or

$$X = \frac{k_1 AE_0}{k_1 A + k_2 + k_3} \quad \cdots (9)$$

Eq (9) in (8) gives

$$r_R = \frac{k_3 AE_0}{\frac{k_2 + k_3}{k_1} + A}$$

These equations give essentially the same result

This is called the Michaelis constant, C_M

Note: By careful analysis of careful experiments Chance, in J. Biol. Chem. 151 553 (1943) favors the Briggs–Haldane mechanism. Later evidence reinforces this choice. Thus we end up today with the so called Michaelis–Menten equation which is in fact the B-H modification of the M-M equation

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