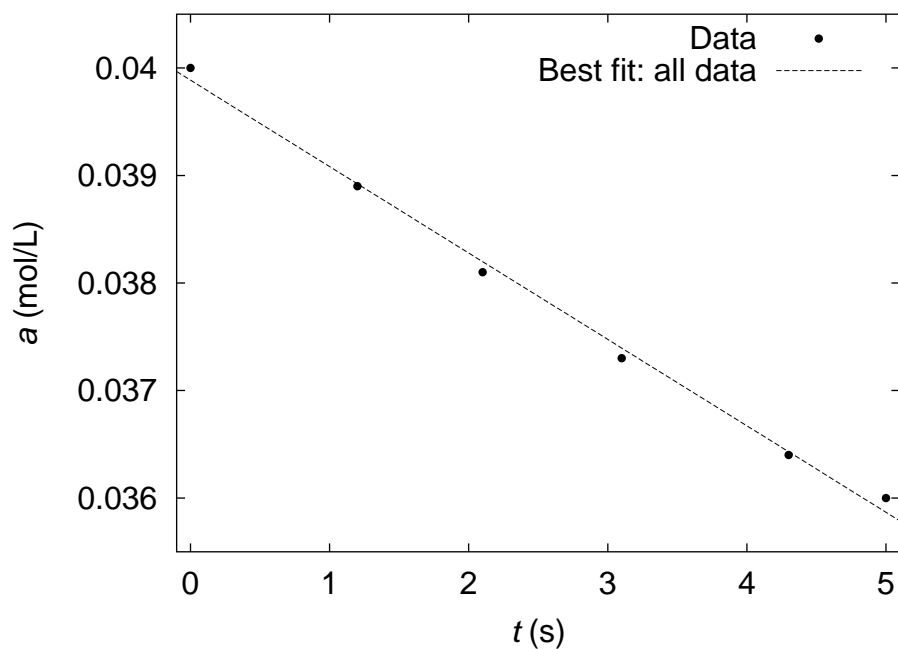# Chemistry 2710 Spring 2001 Assignment 2 Solutions

1. (a) The graph below shows the data along with the line of best fit of all six points:

There is an obvious systematic deviation of the points from the line, so not all points are in the initial rate region. How many of these points define an initial rate is partly a matter of taste. To my eye, there is still some detectable curvature if I take the first four points, but the first three reasonably fit a line:
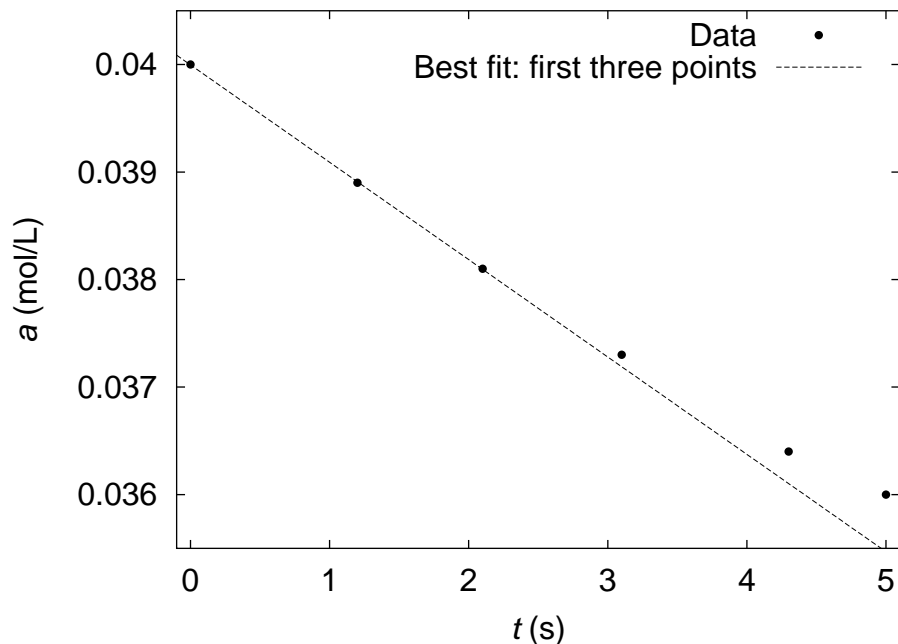
(b) The slope (obtained by linear regression) based on the first three points is $\frac{da}{dt} \approx -9.05 \times 10^{-4}\,\text{mol}\,\text{L}^{-1}\text{s}^{-1}$. The rate of the reaction (by convention) is therefore $v = -\frac{1}{2}\frac{da}{dt} = 4.53 \times 10^{-4}\,\text{mol}\,\text{L}^{-1}\text{s}^{-1}$.

2. (a) The rate does not depend on $[\text{I}_2]$ (experiments 1 and 2). When the concentration of ketone increases by a factor of 2.5, the rate increases by a factor of $2.43 \approx 2.5$ (experiments 1 and 3). Thus, it seems likely that the reaction is of the first order with respect to ketone. Finally, when the hydrogen ion concentration increases by a factor of 3.2, the rate increases by a similar factor (experiments 3 and 4). The rate law is therefore

$$v = k[\text{ketone}][\text{H}^+].$$

(b) $k = v/([\text{ketone}][\text{H}^+])$. Because the data are not perfect (the ratio of rates 1 and 3 isn't exactly the same as the ratio of the ketone concentrations) I calculated the rate constant from each of the four experiments:

Experiment	1	2	3	4
k ($\text{L}\,\text{mol}^{-1}\text{s}^{-1}$)	0.035	0.035	0.034	0.034

In each case, we get a value of about $0.035\,\text{L}\,\text{mol}^{-1}\text{s}^{-1}$.

3. Because there are many points, our best alternative is to use van't Hoff's method. We therefore plot $\ln v$ vs $\ln a$:
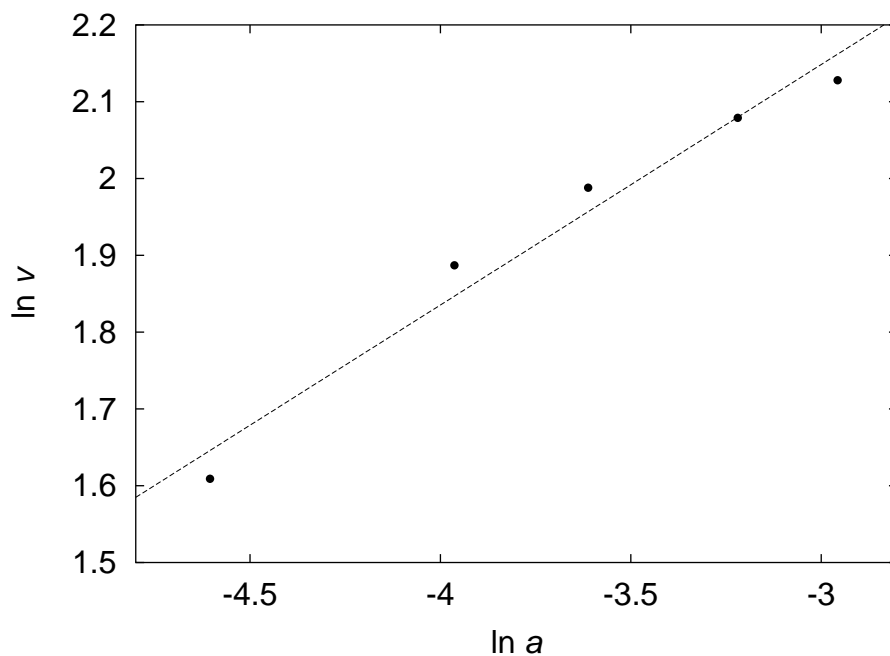
The plot shows obvious curvature, so the data do not fit a simple rate law.

4. (a) $3A \rightarrow 2C$

   (b)

$$\frac{da}{dt} = -k_1 a + k_{-1} b^2 - k_2 ab + k_{-2} c$$

$$\frac{db}{dt} = 2k_1 a - 2k_{-1} b^2 - k_2 ab + k_{-2} c$$

$$\frac{dc}{dt} = k_2 ab - k_{-2} c$$

   (c) Using the principle of detailed balance, we can obtain equilibrium constants for each of the two steps:

$$k_1 a = k_{-1} b^2 \quad \text{and } k_2 ab = k_{-2} c.$$

$$\therefore \quad K_1 = \frac{b^2}{a} = \frac{k_1}{k_{-1}} \text{ and } K_2 = \frac{c}{ab} = \frac{k_2}{k_{-2}}.$$

The overall equilibrium constant $K = c^2/a^3$. Note that

$$K_1 K_2^2 = \left(\frac{b^2}{a}\right)\left(\frac{c^2}{a^2 b^2}\right) = \frac{c^2}{a^3} = K.$$

$$\therefore K = \frac{k_1 k_2^2}{k_{-1} k_{-2}^2}.$$

(d) This question is perhaps slightly harder than first appears. The first step is rate determining with rate $k_1 a$. This step produces two units of B so that two equivalents of C are formed for every A consumed in the first step. In other words,

$$\frac{dc}{dt} \approx 2k_1 a.$$

However, the rate of the reaction is $v = \frac{1}{2}\frac{dc}{dt}$ (from the stoichiometry of the overall reaction) so that $v = k_1 a$.

5.

$$k_1[\text{H}][\text{Br}_2] = k_{-1}[\text{HBr}][\text{Br}].$$

$$\therefore K = \frac{[\text{HBr}][\text{Br}]}{[\text{H}][\text{Br}_2]} = \frac{k_1}{k_{-1}}.$$

$$\therefore k_{-1} = \frac{k_1}{K} = \frac{2.09 \times 10^8 \,\text{L}\,\text{mol}^{-1}\text{s}^{-1}}{1.5 \times 10^{28}}$$

$$= 1.4 \times 10^{-20} \,\text{L}\,\text{mol}^{-1}\text{s}^{-1}.$$