

# Chemistry 2710 Spring 2003 Test 1 Solutions

1. (a)

$$v = 0.26 \text{ mol L}^{-1} \text{ min}^{-1} = -\frac{1}{2} \frac{d[\text{NO}_2]}{dt}$$
$$\therefore \frac{d[\text{NO}_2]}{dt} = -2(0.26 \text{ mol L}^{-1} \text{ min}^{-1}) = -0.52 \text{ mol L}^{-1} \text{ min}^{-1}$$

(b) The rate should go up by a factor of  $3 \times 2 = 6$ , i.e. we expect a rate of

$$6(0.26 \text{ mol L}^{-1} \text{ min}^{-1}) = 1.56 \text{ mol L}^{-1} \text{ min}^{-1}$$

2. In experiments, 1, 4 and 5, the concentration of A is constant but the concentration of B changes while the rate remains essentially constant. The partial order with respect to B is therefore 0. In experiments 1 and 2, the concentration of B is constant while  $a$  increases by a factor of 2.3. The rate increases by a factor of 1.35. It's not completely clear what the order is, so we'll have to do a little algebra:

$$v \propto a^n$$
$$\therefore \frac{v_i}{v_j} = \left(\frac{a_i}{a_j}\right)^n$$
$$\therefore n = \frac{\ln(v_i/v_j)}{\ln(a_i/a_j)}$$

From experiments 1 and 2, we get  $n \approx 0.36$  while from experiments 1 and 3, we get  $n \approx 0.33$ . The partial order of reaction with respect to A is therefore about  $\frac{1}{3}$ . The overall order is

$$0 + \frac{1}{3} = \frac{1}{3}$$

The rate law is

$$v = ka^{1/3}$$

We can calculate the rate constant from each of the experiments by  $k = v/a^{1/3}$ . We get the following values:

Experiment	1	2	3	4	5	Average
$k \text{ (mol}^{2/3}\text{L}^{-2/3}\text{s}^{-1}\text{)}$	14851	15149	14794	15724	14851	$1.51 \times 10^4$

(Sample calculation, from experiment 1:

$$k = \frac{17 \times 10^3 \text{ mol L}^{-1} \text{ s}^{-1}}{(1.5 \text{ mol L}^{-1})^{1/3}} = 14851 \text{ mol}^{1-1/3} \text{ L}^{-1-(-1/3)} \text{ s}^{-1} = 14851 \text{ mol}^{2/3} \text{ L}^{-2/3} \text{ s}^{-1}.)$$

The rate constant is therefore  $1.51 \times 10^4 \text{ mol}^{2/3} \text{ L}^{-2/3} \text{ s}^{-1}$ .

3. (a)

$$\begin{aligned}\frac{d(\Delta V)}{dt} &= -\frac{\Delta V}{RC} \\ \therefore \frac{d(\Delta V)}{\Delta V} &= -\frac{dt}{RC} \\ \therefore \int_{\Delta V_0}^{\Delta V} \frac{dx}{x} &= -\frac{1}{RC} \int_0^t dt'.\end{aligned}$$

(Note that I've replaced  $\Delta V$  by  $x$  in the left-hand integral just for clarity. This isn't a necessary step.)

$$\begin{aligned}\therefore \ln x \Big|_{\Delta V_0}^{\Delta V} &= -\frac{1}{RC} t' \Big|_0^t \\ \therefore -\frac{t}{RC} &= \ln(\Delta V) - \ln(\Delta V_0) = \ln\left(\frac{\Delta V}{\Delta V_0}\right).\end{aligned}\tag{1}$$

$$\begin{aligned}\therefore \frac{\Delta V}{\Delta V_0} &= e^{-t/(RC)} \\ \therefore V - V_{\text{eq}} &= \Delta V_0 e^{-t/(RC)} \\ \therefore V &= V_{\text{eq}} + \Delta V_0 e^{-t/(RC)}.\end{aligned}\tag{2}$$

(b) All we really have to do is to plug the appropriate values into equation 1 and solve for  $t$ :

$$\begin{aligned}\Delta V_0 &= 0 - 100 \text{ mV} = -100 \text{ mV} \\ \Delta V &= 99 - 100 \text{ mV} = -1 \text{ mV} \\ \therefore t &= -(10 \times 10^6 \Omega)(15 \times 10^{-12} \text{ F}) \ln\left(\frac{-1 \text{ mV}}{-100 \text{ mV}}\right) = 691 \mu\text{s}.\end{aligned}$$

4. By stoichiometry, the pressure increases by one unit for every unit of acetaldehyde consumed. Accordingly,  $\Delta P$  represents the amount of acetaldehyde consumed, and we have

$$P_{\text{CH}_3\text{CHO}} = P_0 - \Delta P.$$

(If you like a more algebraic way of getting this equation, here it is: The pressure at any time  $t$  is

$$P = P_{\text{CH}_3\text{CHO}} + P_{\text{CH}_4} + P_{\text{CO}}.$$

By stoichiometry,  $P_{\text{CH}_4} = P_{\text{CO}}$  so we have

$$P = P_{\text{CH}_3\text{CHO}} + 2P_{\text{CH}_4}.$$

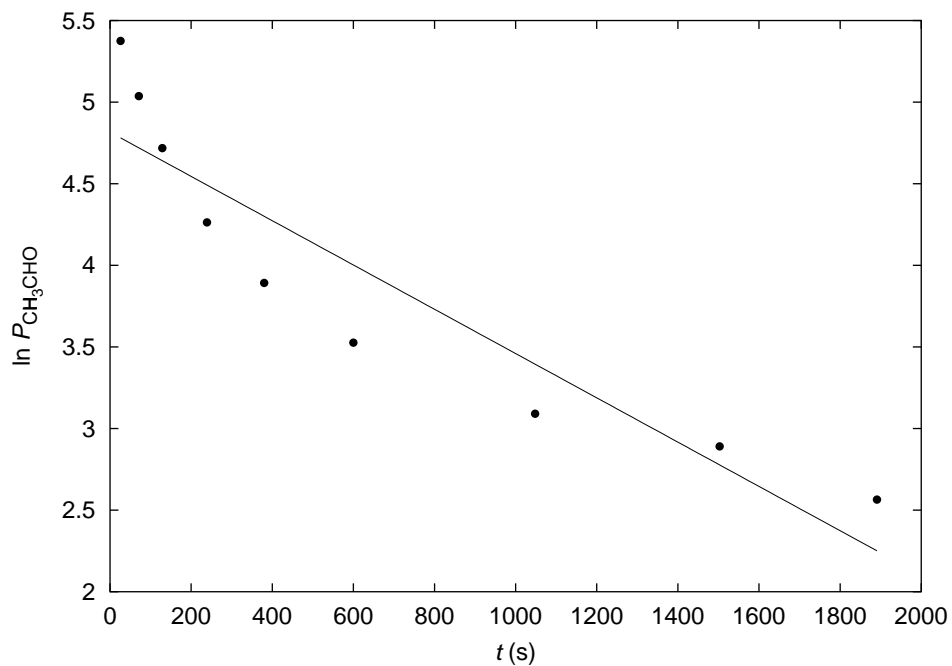
The amount of acetaldehyde consumed is equal to the amount of methane produced, so

$$\begin{aligned}
 P_{\text{CH}_4} &= P_0 - P_{\text{CH}_3\text{CHO}} \\
 \therefore P &= P_{\text{CH}_3\text{CHO}} + 2(P_0 - P_{\text{CH}_3\text{CHO}}) \\
 &= 2P_0 - P_{\text{CH}_3\text{CHO}} \\
 \therefore P_{\text{CH}_3\text{CHO}} &= 2P_0 - P = P_0 - (P - P_0) \\
 \text{But } \Delta P &= P - P_0 \\
 \therefore P_{\text{CH}_3\text{CHO}} &= P_0 - \Delta P
 \end{aligned}$$

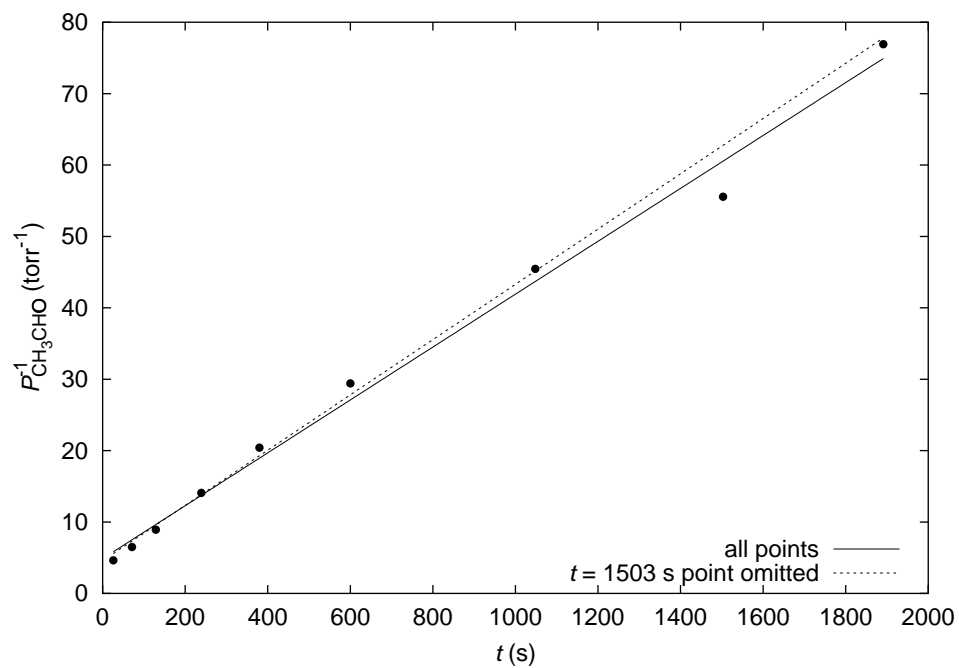
The initial pressure is 240 torr, so we can calculate the pressure of acetaldehyde as a function of time. Since we're going to be testing the hypotheses that we have a first- or a second-order reaction, I also calculate  $\ln P_{\text{CH}_3\text{CHO}}$  and  $1/P_{\text{CH}_3\text{CHO}}$ :

$t$ (s)	$P_{\text{CH}_3\text{CHO}}$ (torr)	$\ln P_{\text{CH}_3\text{CHO}}$	$1000/P_{\text{CH}_3\text{CHO}}$ (torr <sup>-1</sup> )
26	216	5.375	4.629
71	154	5.037	6.494
129	112	4.718	8.929
239	71	4.263	14.085
380	49	3.892	20.408
600	34	3.526	29.412
1048	22	3.091	45.455
1503	18	2.890	55.556
1891	13	2.565	76.923

The first-order plot is definitely curved:



Here's the second-order plot:



If we fit all the points, there isn't any obvious curvature, so we would conclude that this is a second-order reaction with a rate constant  $k = \text{slope} = 3.70 \times 10^{-5} \text{ torr}^{-1} \text{ s}^{-1}$ . However, the

points at  $t = 1530$  s is clearly bad. If we refit the data omitting this point, there does appear to be some curvature, although it's subtle. Frankly, I think you could argue both sides with this one. I would tend to say that it's not a true second-order reaction, but it wouldn't be unreasonable to conclude the opposite on the basis that the very slight curvature might be an experimental artifact. Incidentally, the slope we get if we leave the  $t = 1503$  s point out of the data set is  $3.87 \times 10^{-5} \text{ torr}^{-1} \text{ s}^{-1}$ .