

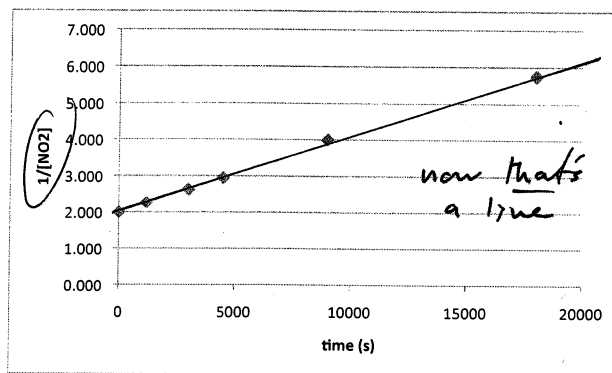
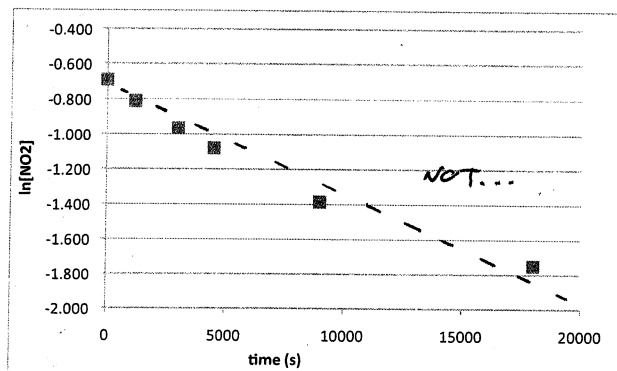
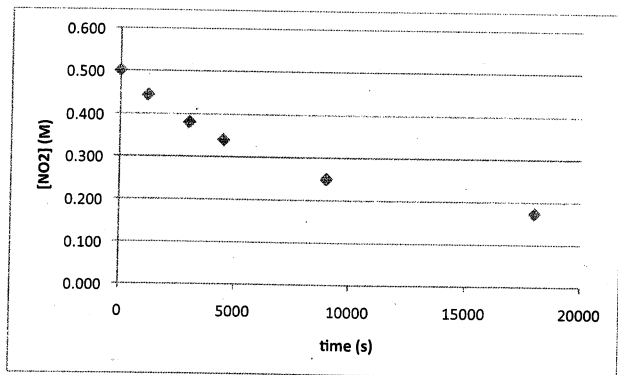
cu 15, 13. H_2 is lost at 3x the rate at which N_2 is lost; NH_3 is formed twice as fast as N_2 is lost; H_2 is lost $\frac{3}{2}$ as fast as NH_3 is formed - i.e. $-\frac{d[H_2]}{dt} = \frac{3}{2} \frac{d[NH_3]}{dt}$
 or $\frac{d[NH_3]}{dt} = -\frac{2}{3} \frac{d[H_2]}{dt}$

17. a. with $[NO]$ constant, doubling $[Cl_2]$ doubles rxn rate;
 with $[Cl_2]$ const, doubling $[NO]$ quadruples rxn rate
 so rate = $k[Cl_2][NO]^2$

b. $k = \frac{\text{rate}}{[Cl_2][NO]^2}$ using each set of data,
 $k = 180, 180, 181 \dots$ let's say $180 \text{ M}^{-2} \text{ min}^{-1}$
 standard unit of time is seconds,
 so $180 \text{ M}^{-2} \text{ min}^{-1} \times \frac{1 \text{ min}}{60 \text{ sec}} = 3.0 \text{ M}^{-2} \text{ s}^{-1}$

33.

time (sec)	[NO ₂] (M)	ln[NO ₂]	1/[NO ₂]
0	0.500	-0.693	2.000
1200	0.444	-0.812	2.252
3000	0.381	-0.965	2.625
4500	0.340	-1.079	2.941
9000	0.250	-1.386	4.000
18000	0.174	-1.749	5.747



cont'd

33. (cont'd)

$$\text{rate} = -\frac{d[\text{NO}_2]}{dt} = k[\text{NO}_2]^2 \quad \text{since the rxn}$$

follows the integrated rate law $\frac{1}{[\text{NO}_2]} = kt + \frac{1}{[\text{NO}_2]_0}$
 (i.e. $\frac{1}{[\text{NO}_2]}$ vs t plot is linear)

$$\text{slope} = k = 2.08 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$$

(using just the 1st + last points)

when $t = 2.70 \times 10^4 \text{ s}$, $\frac{1}{[\text{NO}_2]} = 7.62$, so $[\text{NO}_2] = 0.131 \text{ M}$

39.

$$-\frac{d[\text{PH}_3]}{dt} = k[\text{PH}_3]$$

$$\Downarrow \ln\left(\frac{[\text{PH}_3]_0}{[\text{PH}_3]}\right) = kt$$

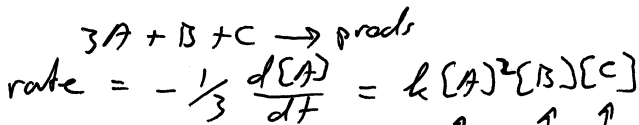
$t = 170 \text{ s}$ for $[\text{PH}_3] = [\text{PH}_3]_0/4$ (2 half-lives)
 so $k = 0.0116 \text{ s}^{-1}$

for $2.00 \text{ M} \rightarrow 0.350 \text{ M}$,

$$\ln\left(\frac{2.00}{0.350}\right) = (0.0116 \text{ s}^{-1}) t$$

$$t = 150 \text{ s}$$

47.



$\begin{matrix} \uparrow & \uparrow & \uparrow \\ 0.1 \text{ M} & 1 \text{ M} & 1 \text{ M} \\ (1.0 \times 10^{-4} \text{ M}) & \text{large!} & \text{large!} \end{matrix}$
 so these are \sim constant

— this is a pseudo-2nd-order rxn.

a. at $t = 180 \text{ s}$, $[A] = 3.26 \times 10^{-5} \text{ M}$

$$-\frac{d[A]}{dt} = \frac{3k[B][C]}{k'} [A]^2 \Rightarrow \frac{1}{[A]} = \frac{1}{[A]_0} + k' t$$

plug in $[A]$, $[A]_0$, $t \Rightarrow k' = 115 \text{ M}^{-1} \text{ s}^{-1}$

so $k = 38.3 \text{ M}^{-3} \text{ s}^{-1}$

b. "t_{1/2}" not meaningful for a 2nd-order rxn.

c. Plug 'n' chug - $[A] = 1.27 \times 10^{-5} \text{ M}$; $[B] \sim$ unchanged!