

## Lecture # 11 Classroom Examples (Initial Rates).

For the reaction  $J \rightarrow \text{Products}$ , the following initial rates were obtained for the respective initial concentrations of J:

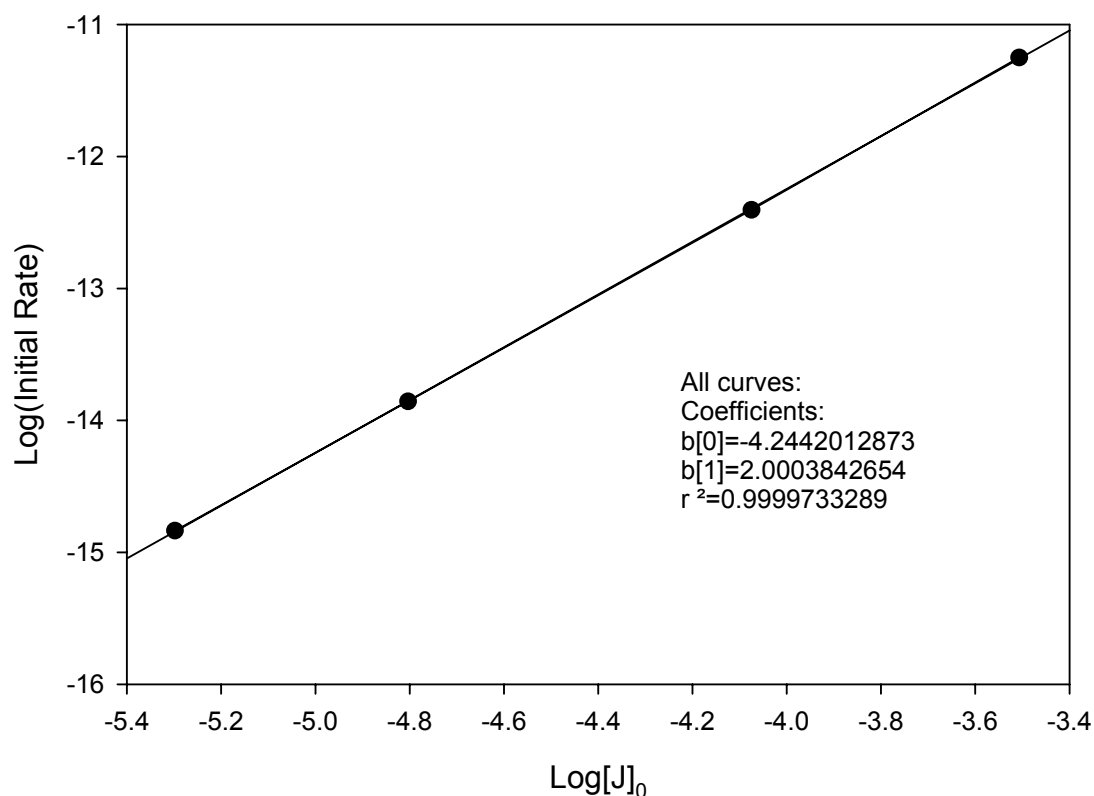
$[J]_0$ (M)	0.005	0.0082	0.017	0.03
$V_0$ (M s <sup>-1</sup> )	3.6E-7	9.6E-7	4.1E-6	1.3E-5

Determine the reaction's order with respect to concentrations of J.

Solution: Create a log-log plot and determine the slope.

$\ln[J]_0$	-5.298	-4.8036	-4.0745	-3.5066
$\ln v_0$	-14.837	-13.856	-12.405	-11.251

Log - Log Plot of initial rate vs initial concentrations



The slope of this log-log plot is exactly 2.00; and so the order of the reaction with respect to J concentrations is 2: Rate =  $v = -d[J]/dt = k[J]^2$

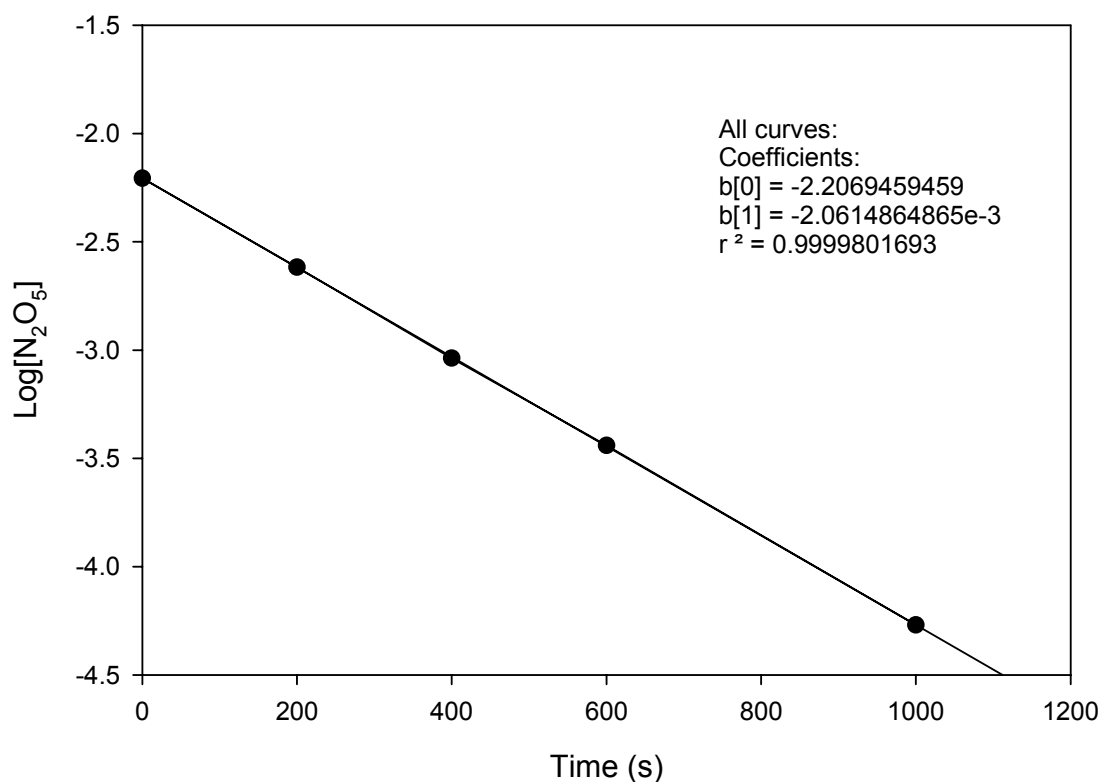
Experimental data are rarely this clean; and in general experimentally determined reaction orders rarely deliver whole integers. One generally rounds off to the nearest integer.

## First Order Kinetics (semi-log plots).

For the reaction:  $\text{N}_2\text{O}_5(\text{aq}) + \text{Br}_2(\text{l}) \rightarrow \text{Products}$ ; the following data are obtained when dinitrogen pentoxide concentrations are followed with respect to time:

Time (s)	0	200	400	600	1000
$[\text{N}_2\text{O}_5]$ (M)	0.110	0.073	0.048	0.032	0.014
$\ln[\text{N}_2\text{O}_5]$	-2.207	-2.617	-3.037	-3.440	-4.269

Semi-Log First Order Plot



The slope of the plot is  $-0.00206$  which equals  $-k$ .  
The rate constant for this reaction is  $0.00206 \text{ s}^{-1}$

The half-life for the reaction is  $0.693/k = 336 \text{ s}$ .

**Apparently, this reaction does not depend on  $\text{Br}_2(\text{l})$  conc<sup>ns</sup>.**

## Homework example on initial rates.

The initial rate for the reaction  $2\text{Fe}^{2+} + \text{Br}_2(\text{l}) \rightarrow 2\text{Fe}^{3+} + 2\text{Br}^-(\text{l})$  was monitored at constant  $[\text{Br}_2(\text{l})]_0$  while varying  $[\text{Fe}^{2+}]_0$ . The following initial rate data was obtained:

$[\text{Fe}^{2+}]_0$	0.030	0.040	0.050	0.060	0.080
Initial Rate, $\text{M s}^{-1}$	0.0122	0.0161	0.0211	0.0240	0.0315

Evaluate reaction order with respect to ferrous ion concentrations.

To start on this problem, assume Initial Rate,  $r_0 = k_0[\text{Fe}^{2+}]_0^x[\text{Br}_2]_0^y$

Then  $\log r_0 = \log k_0 + x \log [\text{Fe}^{2+}]_0 + y \log [\text{Br}_2]_0$

Next, if one is told that  $y = 1$ ; evaluate  $k_0$ . What are the units of  $k_0$ ?

**Another Method is to GUESS the order with respect to  $[\text{Fe}^{2+}]_0$ . Yes, it works!!!!**

**If, say the order (in this case,  $x$ ) is 1.00; then there is a linear relationship between initial rate and initial ferrous ion concentrations, and a plot of Initial rate vs  $[\text{Fe}^{2+}]_0^1$  will give a straight line.**

**If, on the other hand,  $x = 2$  (second order in  $[\text{Fe}^{2+}]_0$ 's; then a plot of Initial rate vs  $[\text{Fe}^{2+}]_0^2$  will give a straight line.**