PS 5 Key

1.

a. $\text{Rate} = -\frac{1}{2}\frac{\Delta[I^-]}{\Delta t} = +\frac{\Delta[I_2]}{\Delta t}$

b. $\text{Rate} = k[I^-]^m[S_2O_8^{2-}]^n$

- As $[I^-]$ doubles (Exp. 2 → Exp. 1), rate doubles.
  → $m = 1$
- As $[S_2O_8^{2-}]$ doubles (Exp. 3 → Exp 1), rate doubles.
  → $n = 1$

$\text{Rate} = k[I^-][S_2O_8^{2-}]$

c. Use data from any one Exp. to find $k = \frac{\text{Rate}}{[I^-][S_2O_8^{2-}]}$

(From Exp. 1) $k = \frac{12.5 \times 10^{-6}\ \frac{M}{s}}{(0.080M)(0.040M)} = \boxed{3.9 \times 10^{-3}\ M^{-1}s^{-1}}$

$(\text{Rate} = 3.9 \times 10^{-3}\ M^{-1}s^{-1}\ [I^-][S_2O_8^{2-}])$

2. Make graphs based on integrated first, second, & zeroth order integrated rate Laws. The one that is (most) linear gives the order in H_2O_2 and allows determination of k.

Zeroth Order: $[A] = -kt + [A]_0$ Plot [A] vs. time
$y = mx + b$ slope $= -k$

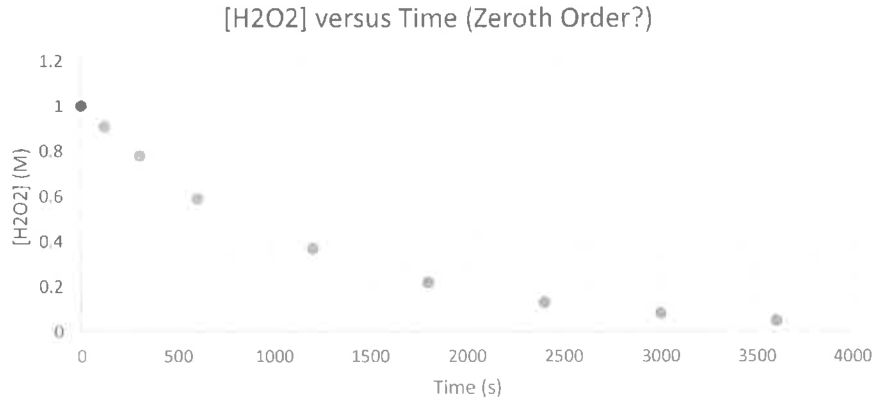
1^{st} Order: $\ln[A] = -kt + \ln[A]_0$ Plot $\ln[A]$ vs. time
slope $= -k$

2^{nd} Order: $\frac{1}{[A]} = kt + \frac{1}{[A]_0}$ Plot $\frac{1}{[A]}$ vs. time
slope $= k$

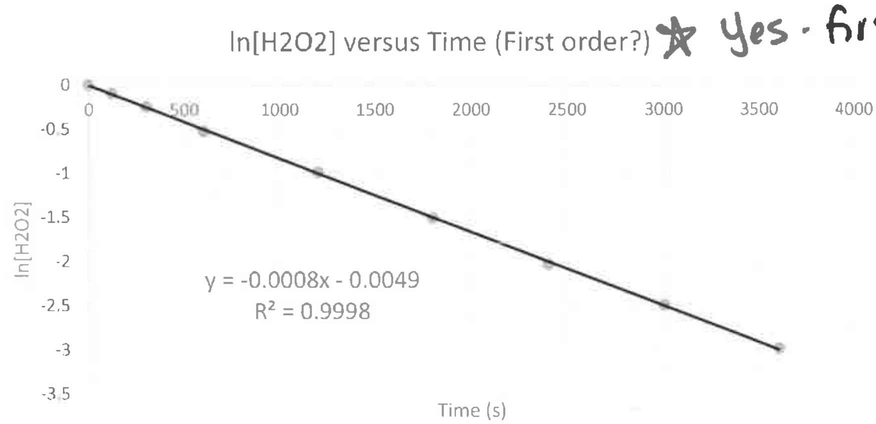
my graphs (next page) show that the reaction is first order in H_2O_2

$\text{Rate} = k[H_2O_2]^1$ with $k = 8.35 \times 10^{-4}\ M/s$

Time (s)	[H2O2] (M)
0	1
120	0.91
300	0.78
600	0.59
1200	0.37
1800	0.22
2400	0.13
3000	0.082
3600	0.05



Time (s)	ln [H2O2]
0	0
120	-0.09431
300	-0.24846
600	-0.52763
1200	-0.99425
1800	-1.51413
2400	-2.04022
3000	-2.50104
3600	-2.99573



★ Yes - first order

Slope:

=INDEX(LINEST(known_y's,known_x's),1)

Slope
-0.000834979

Slope = -k

Time (s)	1/[H2O2]
0	1
120	1.098901
300	1.282051
600	1.694915
1200	2.702703
1800	4.545455
2400	7.692308
3000	12.19512
3600	20

3.

First-order kinetics with $t_{\frac{1}{2}} = 6.0\,hrs$

$$t_{\frac{1}{2}} = \frac{0.693}{k} \qquad k = \frac{0.693}{t_{\frac{1}{2}}} = \frac{0.693}{6.0\,hr} = 0.1155\,hr^{-1}$$

$$\ln\frac{[^{99m}Tc]}{[^{99m}Tc]_0} = -kt \qquad \frac{[^{99m}Tc]}{[^{99m}Tc]_0} = 0.010$$

Solve for t.

$$\ln(0.010) = -(0.1155\,hr^{-1})t$$

$$-4.6052 = -0.1155\,hr^{-1}\,t$$

$$\frac{-4.6052}{-0.1155\,hr^{-1}} = t = 39.87\,hr = 4.0\times10^{1}\ hours$$

4. a. $PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$ $\quad K_{sp} = 8.5\times10^{-9}$

$$K_{sp} = [Pb^{2+}][I^-]^2$$

b. $\Delta G^\circ = -RT\ln K$

$$= -(8.31451\,J/mol\cdot K)(298.15K)\ln(8.5\times10^{-9})$$

$$\Delta G^\circ = -4.6067\ J/mol\left(\frac{1\,kJ}{1000\,J}\right) = -46\,kJ/mol$$

ΔG° is negative $\rightarrow$ Spontaneous toward products

c.

	$PbI_2(s)$	$\rightleftharpoons$	$Pb^{2+}(aq)$	+	$2I^-(aq)$
$[\ ]_{init}$			0		0
$\Delta[\ ]$			$+x$		$+2x$
$[\ ]_{\rightleftharpoons}$			x		$2x$

$$x(2x)^2 = 8.5\times10^{-9}$$

$$4x^3 = 8.5\times10^{-9}$$

$$x^3 = 2.125\times10^{-9}$$

$$x = 1.29\times10^{-3}M$$

$$[Pb^{2+}]_{\rightleftharpoons} = x = 1.3\times10^{-3}M$$

$$[I^-]_{\rightleftharpoons} = 2x = 2.6\times10^{-3}M$$

5.

(atm)	$H_2(g)$ +	$I_2(g)$ $\rightleftharpoons$	$2\,HI(g)$
P_{init}	0.90	0.90	5.25
ΔP	$-x$	$-x$	$+2x$
$P_{\rightleftharpoons}$	$0.90-x$	$0.90-x$	$5.25+2x$

$$K_p = \frac{(P_{HI})^2}{(P_{H_2})(P_{I_2})} = 85$$

$$Q_p = \frac{(5.25)^2}{(0.90)^2} = 34$$

$Q < K$ Not at $\rightleftharpoons$

Proceeds $\longrightarrow$

$$K_p = \frac{(5.25+2x)^2}{(0.90-x)^2} = \left(\frac{5.25+2x}{0.90-x}\right)^2 = 85$$

$$\frac{5.25+2x}{0.90-x} = \sqrt{85} = 9.220$$

$$5.25+2x = 9.220(0.90-x)$$

$$5.25+2x = 8.298 - 9.220x$$

$$11.220x = 3.048$$

$$x = 0.272 \text{ atm}$$

Equilibrium Pressures

$$P_{H_2} = P_{I_2} = 0.90-x = 0.63 \text{ atm}$$

$$P_{HI} = 5.25+2x = 5.8 \text{ atm}$$