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 NUMERICAL ANSWERS TO ASSIGNED TUTORIAL PROBLEM SETS FOR CHEM206  
 FROM KOTZ & TREICHEL'S CHEMISTRY & CHEMICAL REACTIVITY, 6<sup>th</sup> Ed.
 

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**NOTE: these answers have NOT been verified. Please report any errors.**

Ch.	Q#	Ans.	Units	SFs	Comments
15	4	$3.0 \times 10^{-4} \text{ mol/(L}\cdot\text{min)}$		2	rate of appearance of ammonia
15	10a				Rate = $k[\text{NO}]^2[\text{Br}_2]$
	10b				if $[\text{Br}_2]$ is tripled, rate will triple
	10c				if $[\text{NO}]$ decreases by 1/2, rate will decrease by $\times 1/4$
15	12a				In first 2 data sets: $[\text{H}_2]$ is constant; $[\text{NO}]$ is $\times 1/2$ rate decreases by factor of 4 $\Rightarrow$ rxn = 2 <sup>nd</sup> order in NO In 2 <sup>nd</sup> & 3 <sup>rd</sup> data sets: $[\text{NO}]$ constant; $[\text{H}_2]$ doubled rate also doubles $\Rightarrow$ rxn is 1 <sup>st</sup> order in $\text{H}_2$
	12b				Rate = $k[\text{NO}]^2[\text{H}_2]$
	12c	0.136	mol/(L·s)	3	= rate of formation of $\text{N}_2$
		6.32	$\text{L}^2/(\text{mol}^2\cdot\text{s})$	3	= rate constant, k
	12d	0.159	mol/(L·s)	3	= initial rate of reaction calculated using rate law
15	14a				1 <sup>st</sup> 2 data sets: $[\text{CO}]$ constant; $[\text{NO}_2]$ halved rate also goes down by factor of 2 $\Rightarrow$ 1 <sup>st</sup> order in $\text{NO}_2$ Sets 1 & 3: $[\text{NO}_2]$ constant; $[\text{CO}]$ doubles rate doubles $\Rightarrow$ rxn is 1 <sup>st</sup> order in $\text{NO}_2$ Rate = $k[\text{CO}][\text{NO}_2]$
	14b	1.9	L/(mol·h)	2	= rate constant, k
	14c	$2.0 \times 10^{-7}$	mol/(L·h)	2	= initial rxn rate calculated using rate law
15	16a				rate = $k[\text{H}_2\text{PO}_4^-][\text{OH}^-]^2$
15	16b	$4.2 \times 10^6$	$\text{L}^2/(\text{mol}^2\cdot\text{min})$	2	= k, calculated using initial concentrations & rate
15	16c	0.0044	mol/L	2	= initial conc. $\text{H}_2\text{PO}_4^-$ required for rate = 0.0020 M/min
15	18	0.00557	$\text{min}^{-1}$	3	= k, calculated using integrated 1st order rate law
15	22	0.0490	min	3	= time required to drop $[\text{NO}_2]$ from 2.00 to 1.50 mol/L
15	24	580	s	2	= time required to decompose 3/4 of sample; 1/4 remains
15	28	150	min	2	= time required for 7.50mg $\rightarrow$ 0.25mg; using $k = 0.023 \text{ min}^{-1}$
15	30	4.3	mg	2	remaining after 1.0 day; using $k = 0.26 \text{ d}^{-1}$
15	38	0.025	$\text{min}^{-1}$	2	= k, = -slope of linear graph: $\ln[\text{HOF}]$ vs time (1 <sup>st</sup> order)
15	42	85	kJ/mol	2	= $E_a$ ... rxn 3 $\times$ faster at 310K vs 300K; use Arrhenius' eqn
15	44	270	kJ/mol	2	= $E_a$ calculated using Arrhenius' eqns for 2 T's (2 k's)
15	46a				endothermic
	46b				yes, rxn occurs in two steps

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15	48a 48b 48c				rate = $k[\text{Cl}][\text{ICl}]$ rate = $k[\text{O}][\text{O}_3]$ rate = $k[\text{NO}_2]^2$
15	50a 50b 50c 50d				add up 2 rxns & cancel species occurring on both sides... gives overall rxn: $\text{NO}_2 + \text{CO} \rightarrow \text{NO} + \text{CO}_2$ both steps are bimolecular rate = $k[\text{NO}_2]^2$ $\text{NO}_3$ is an intermediate
15	54a 54b 54c				$(\text{CH}_3)_3\text{CBr} + \text{H}_2\text{O} \rightarrow (\text{CH}_3)_3\text{COH} + \text{HBr}$ step 1, the slow step, is rate-limiting (rate-determining) rate = $k[(\text{CH}_3)_3\text{CBr}]$
15	62a 62b 62c 62d	$2 \times 10^{-4}$ $3 \times 10^3$	$\text{s}^{-1}$ s	1 1	1 <sup>st</sup> order in $\text{CH}_3\text{NC}$ : rate = $k[\text{CH}_3\text{NC}]$ $\ln[\text{CH}_3\text{NC}]_t = \ln[\text{CH}_3\text{NC}]_0 - kt$ $k = -\text{slope}$ (slope estimated from graph) = [ ] remaining after 10000s, starting with 0.0166 mol/L initial [ ] from y-intercept of graph: [ ] <sub>0</sub> = $e^{\text{intercept}}$
15	66a 66b	0.59 75	mg h	2 2	using $k = 0.18 \text{ h}^{-1}$ (from $t_{1/2}$ ) & integrated 1 <sup>st</sup> order rate law using integrated 1 <sup>st</sup> order rate law
15	70	103	kJ/mol	3	= $E_a = -\text{slope of graph of } \ln k \text{ vs. } 1/T$
15	72a 72b	75.8 0.33	s unitless	3 2	when 3/4 of $\text{PH}_3$ gone, 1/4 remains; 2 half-lives passed. NOTE: 2SF if treat as <u>exactly</u> 1 min; otherwise: 1SF... $k = 0.0183 \text{ s}^{-1}$ ; use 1 <sup>st</sup> order integrated rate law to calculate $[\text{PH}_3]_t/[\text{PH}_3]_0$
15 15 15	73 73a 73b	also see solutions manual...			$2\text{NO}(\text{g}) + \text{Br}_2(\text{g}) \rightarrow 2\text{BrNO}(\text{g})$ 1: termolecular 2: step1=bimolecular, step2=bimolecular 3: step1=bimolecular, step2=bimolecular
15	73c				mechanism 2: intermediate = $\text{Br}_2\text{NO}(\text{g})$ mechanism 3: intermediate = $\text{N}_2\text{O}_2(\text{g})$
15	73d				Assuming step1 = RLS for each mechanism, all predicted rate equations (rate laws) are different. Mechanism 1: 2 <sup>nd</sup> order in NO, 1 <sup>st</sup> order in $\text{Br}_2$ Mechanism 2: 1 <sup>st</sup> order in both NO & $\text{Br}_2$ Mechanism 3: 2 <sup>nd</sup> order in NO, zero order in $\text{Br}_2$ If assume 2 <sup>nd</sup> step is slow, will get different results....
15	76				slowest rxn has smallest k: rxn (d) fastest rxn has largest k: rxn (c)
15 15	79 79	also see solutions manual... 4.76	min	3SF	must recognize that: $t_{90\text{C}}/t_{100\text{C}} = k_{100\text{C}}/k_{90\text{C}}$ <i>i.e.</i> , shorter rxn time implies faster rate constant and time required to complete a rxn is inversely proportional to k (...from thinking about form of integrated rate law...) Then: Arrhenius' eqns for both T's, combine to solve for $E_a$

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15	82				<p>After 1 <math>t_{1/2}</math>: <math>P_{\text{SO}_2\text{Cl}_2} = 12.5 \text{ mmHg} = P_{\text{SO}_2} = P_{\text{Cl}_2}</math> (by stoich.)            So <math>P_{\text{tot}} = 12.5 + 12.5 + 12.5 = 38 \text{ mmHg}</math> (to 2SF)            To find Ps at 720min: 1<sup>st</sup> use <math>t_{1/2}</math> to find <math>k \dots = 0.00283 \text{ min}^{-1}</math>            Using 1<sup>st</sup> order integrated rate law, <math>k</math> &amp; <math>P_{\text{SO}_2\text{Cl}_2}</math>, solve for  <math>P_{\text{SO}_2\text{Cl}_2}</math> after 720 min = 3.3 mmHg            By stoich.: <math>P_{\text{SO}_2} = P_{\text{Cl}_2} = P_{\text{SO}_2\text{Cl}_2 \text{ consumed}} = 22 \text{ mmHg}</math>            So, <math>P_{\text{tot}}</math> after 720 min = 3.3 + 22 + 22 = 47 mmHg</p>
15	84a				Chemists use initial rates because the presence of products can affect the mechanism of the reaction, and also because the reverse reaction can begin to re-produce reactants (which would make it look like the forward reaction is slowing down more than it is...).
	84b	$3.6 \times 10^{-4}$	mol/L·min	2SF	= rate
15	88				add up steps to get overall: $2\text{O}_3 \rightarrow 3\text{O}_2$ . Cl atoms regenerated ( $\therefore$ catalyst). ClO = intermediate.
15	90a				Incorrect. Reactions are faster at a higher temperature because the fraction of molecules with higher energies increases.
	90b				Correct.
	90c				Correct.
	90d				Incorrect. A catalyst provides a different pathway with a lower activation energy for the rxn.
15	94				Graphs: same net E change for rxns; DIFFERENT $E_a$ 's; catalyzed rxn has LOWER activation E
15	98a				The stoichiometric coefficient of a reactant in an elementary step is the order of the reaction for that reactant in that step.
	98b				Rate = $k[\text{NO}_3^-][\text{CO}]$
	98c				No. Only in the two-step mechanism is there oxygen-atom exchange between $\text{NO}_2$ molecules. If CO reacts directly with $\text{NO}_2$ , the $\text{CO}_2$ can have either $^{16}\text{O}$ or $^{18}\text{O}$ , and the product NO molecules will be either $\text{N}^{16}\text{O}$ or $\text{N}^{18}\text{O}$ .