14.4

Time(s)	Mol A	(a) Mol B	Δ Mol A	(b) Rate (Δ mol A/s)
0	0.100	0.000		
40	0.067	0.033	0.033	8.3×10^{-4}
80	0.045	0.055	-0.022	5.5×10^{-4}
120	0.030	0.070	-0.015	3.8×10^{-4}
160	0.020	0.080	-0.010	2.5×10^{-4}

(c) The volume of the container must be known to report the rate in units of concentration (mol/L) per time.

14.10 (a) rate = $-\Delta[HBr]/2\Delta t = \Delta[H_2]/\Delta t = \Delta[Br_2]/\Delta t$

(b) rate = $-\Delta[SO_2]/2\Delta t = -\Delta[O_2]/\Delta t = \Delta[SO_3]/2\Delta t$

(c) rate = $-\Delta[NO]/2\Delta t = -\Delta[H_2]/2\Delta t = \Delta[N_2]/\Delta t = \Delta[H_2O]/2\Delta t$

14.11 Analyze/Plan. Use Equation 14.4 to calculate [illegible]

P.S. #23

14.12 (a) $-\Delta[C_2H_4]/\Delta t = \Delta[CO_2]/2\Delta t = \Delta[H_2O]/2\Delta t$

$-2\Delta[C_2H_4]/\Delta t = \Delta[CO_2]/\Delta t = \Delta[H_2O]/\Delta t$

C_2H_4 is burning, $-\Delta[C_2H_4]/\Delta t = 0.23$ *M*/s

CO_2 and H_2O are produced, at twice the rate that C_2H_4 is consumed.

$\Delta[CO_2]/\Delta t = \Delta[H_2O]/\Delta t = 2(0.23)$ *M*/s = 0.46 *M*/s

(b) In this reaction, pressure is a measure of concentration.

$-\Delta[N_2H_4]/\Delta t = -\Delta[H_2]/\Delta t = \Delta[NH_3]/2\Delta t$

N_2H_4 is consumed, $-\Delta[N_2H_4]/\Delta t = 45$ torr/hr

H_2 is consumed, $-\Delta[H_2]/\Delta t = 45$ torr/hr

NH_3 is produced at twice the rate that N_2H_4 and H_2 are consumed,

$\Delta[NH_3]/\Delta t = -2\Delta[N_2H_4]/\Delta t = 2(45)$ torr/hr = 90 torr/hr

$\Delta P_T/\Delta t$ = (+90 torr/hr - 45 torr/hr - 45 torr/hr) = 0 torr/hr

14.15 *Analyze/Plan.* Follow the logic in Sample Exercise 14.6. *Solve*:

(a) rate = $k[N_2O_5] = 4.82 \times 10^{-3}\ s^{-1}\ [N_2O_5]$

(b) rate = $4.82 \times 10^{-3}\ s^{-1}$ (0.0240 *M*) = 1.16×10^{-4} *M*/s

(c) rate = $4.82 \times 10^{-3}\ s^{-1}$ (0.0480 *M*) = 2.31×10^{-4} *M*/s

When the concentration of N_2O_5 doubles, the rate of the reaction doubles.

14.21 *Analyze/Plan.* Follow the logic in Sample Exercise 14.6. *Solve*:

(a) From the data given, when $[OCl^-]$ doubles, rate doubles. When $[I^-]$ doubles, rate doubles. The reaction is first order in both $[OCl^-]$ and $[I^-]$. rate = $[OCl^-][I^-]$

(b) Using the first set of data:

$$k = \frac{\text{rate}}{[OCl^-][I^-]} = \frac{1.36 \times 10^{4}\ M/s}{(1.5 \times 10^{-3} M)(1.5 \times 10^{-3} M)} = 6.0444 \times 10^{9} = 6.04 \times 10^{9}\ M^{-1}s^{-1}$$

(c) $$\text{rate} = \frac{6.044 \times 10^{9}}{M \cdot s}(1.0 \times 10^{-3}\ M)(5.0 \times 10^{-4}\ M) = 3.02 \times 10^{3}\ \text{M/s}$$

14.24 (a) Doubling $[NH_3]$ while holding $[BF_3]$ constant doubles the rate (experiments 1 and 2). Doubling $[BF_3]$ while holding $[NH_3]$ constant doubles the rate (experiments 4 and 5). Thus, the reaction is first order in both BF_3 and NH_3; rate = $k[BF_3][NH_3]$.

(b) The reaction is second order overall.

(c) From experiment 1: $$k = \frac{0.2130\ M/s}{(0.250\ M)(0.250\ M)} = 3.41\ M^{-1}s^{-1}$$

(Any of the five sets of initial concentrations and rates could be used to calculate the rate constant k. The average of these 5 values is $k_{avg} = 3.41\ M^{-1}s^{-1}$)

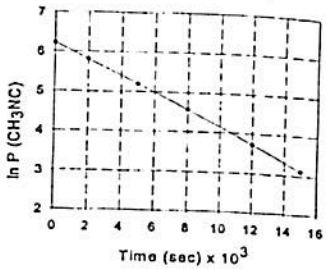
14.30 (a) $t_{1/2} = 0.693/k = 0.693/7.0 \times 10^{-4}\ s^{-1} = 990 = 9.9 \times 10^2\ s$

(b) $k = \dfrac{0.693}{t_{1/2}} = \dfrac{0.693}{56.3\ min} \times \dfrac{1\ min}{60\ s} = 2.052 \times 10^{-4} = 2.05 \times 10^{-4}\ s^{-1}$

14.34

t(s)	P_{CH_3NC}	ln P_{CH_3NC}
0	502	6.219
2000	335	5.814
5000	180	5.193
8000	95.5	4.559
12000	41.7	3.731
15000	22.4	3.109

A graph of ln P vs t is linear with a slope of $-2.08 \times 10^{-4}\ s^{-1}$. The rate constant k = -slope = $2.08 \times 10^{-4}\ s^{-1}$. Half-life = $t_{1/2} = 0.693/k = 3.33 \times 10^3$ s.



14.47 *Analyze/Plan.* Given k_1, at T_1, calculate k_2 at T_2. Change T to Kelvins, then use the Ahrrenius equation [14.21] to calculate k_2. *Solve:*

$T_1 = 20°C + 273 = 293$ K; $T_2 = 60°C + 273 = 333$ K; $k_1 = 2.75 \times 10^{-2} s^{-1}$

(a) $\ln\left(\dfrac{k_1}{k_2}\right) = \dfrac{E_a}{R}\left(\dfrac{1}{333} - \dfrac{1}{293}\right) = \dfrac{75.5 \times 10^3\ J/mol}{8.314\ J/mol}(-4.100 \times 10^{-4})$

$\ln(k_1/k_2) = -3.7229 = -3.72$; $k_1/k_2 = 0.0242 = 0.024$; $k_2 = \dfrac{0.0275\ s^{-1}}{0.0242} = 1.1\ s^{-1}$

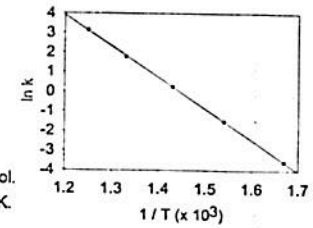
(b) $\ln\left(\dfrac{k_1}{k_2}\right) = \dfrac{105 \times 10^3\ J/mol}{8.314\ J/mol}\left(\dfrac{1}{333} - \dfrac{1}{293}\right) = -5.1776 = -5.18$

$k_1/k_2 = 5.642 \times 10^{-3} = 5.6 \times 10^{-3}$; $k_2 = \dfrac{0.0275\ s^{-1}}{5.642 \times 10^{-3}} = 4.9\ s^{-1}$

P.S. # 23

14.50

k	ln k	T(K)	1/T(× 10^3)
0.028	-3.58	600	1.67
0.22	-1.51	650	1.54
1.3	0.26	700	1.43
6.0	1.79	750	1.33
23	3.14	800	1.25



Using the relationship $\ln k = \ln A - E_a/RT$, the slope, $-15.94 \times 10^3 = -16 \times 10^3$, is $-E_a/R$.
$E_a = 15.94 \times 10^3 \times 8.314$ J/mol = 1.3×10^2 kJ/mol.
To calculate A, we will use the rate data at 700 K.
From the equation given above, 0.262 = $\ln A - 15.94 \times 10^3/700$; $\ln A = 0.262 + 22.771$.
$A = 1.0 \times 10^{10}$.

14.61 *Analyze/Plan.* Given a proposed mechanism and an observed rate law, determine which step is rate determining. *Solve:*

(a) If the first step is slow, the observed rate law is the rate law for this step.
rate = $k[NO][Cl_2]$

(b) Since the observed rate law is second-order in [NO], the second step must be slow relative to the first step; the second step is rate determining.

14.73 *Analyze/Plan.* Let k = the rate constant for the uncatalyzed reaction,
k_c = the rate constant for the catalyzed reaction

According to Equation [14.22], $\ln k = -E_a/RT + \ln A$

Subtracting ln k from ln k_c,

$\ln k_c - \ln k = -\left[\dfrac{55\ kJ/mol}{RT} + \ln A\right] - \left[-\dfrac{95\ kJ/mol}{RT} + \ln A\right]$. *Solve:*

(a) RT = 8.314 J/K•mol × 298 K × 1 kJ/1000 J = 2.478 kJ/mol; ln A is the same for both reactions.

$\ln(k_c/k) = \dfrac{95\ kJ/mol - 55\ kJ/mol}{2.478\ kJ/mol}$; $k_c/k = 1.0 \times 10^7$

The catalyzed reaction is approximately 10,000,000 (ten million) times faster at 25°C.

(b) RT = 8.314 J/K•mol × 398 K × 1 kJ/1000 J = 3.309 kJ/mol

$\ln(k_c/k) = \dfrac{40\ kJ/mol}{3.309\ kJ/mol}$; $k_c/k = 1.8 \times 10^5$

The catalyzed reaction is 180,000 times faster at 125°C.

① To determine rate law, we must 1st determine the rate order for C_4H_6. Since no info is given about the $[C_8H_{12}]$ a graph can be helpful.

by graphing $\ln[C_4H_6]_t$ vs. time

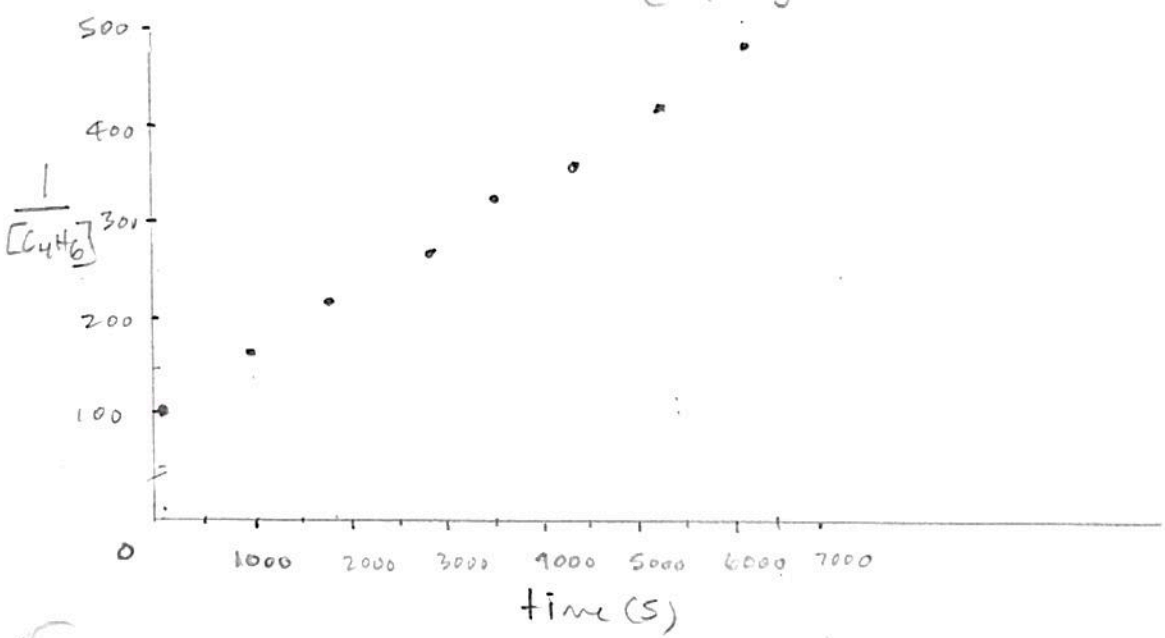
or $1/[C_4H_6]_t$ vs. time

the rate order can be determined. If the $\ln[C_4H_6]$ graph yields a straight line, then it is 1st order, If $\frac{1}{[C_4H_6]}$ is linear then it is second order.

DATA

Time (s)	$[C_4H_6]$ M	$\ln[C_4H_6]$	$1/[C_4H_6]$
0	.01000	-4.61	100
1000	.00625	-5.08	160
1800	.00476	-5.35	210
2800	.00370	-5.60	270
3600	.00313	-5.77	~320
4400	.00270	-5.91	370
5200	.00241	-6.03	415
6200	.00208	-6.21	480

Since it's easier to graph $\frac{1}{[C_4H_6]}$ vs t (I will do that)



(1.) As you can see, this is relatively linear, therefore this reaction is second order

the rate law is rate $= k[C_4H_6]^2$

(B) $\dfrac{\frac{1}{[.00208]} - \frac{1}{[.01000]}}{6200\,s} = K$

$\dfrac{\frac{480.77}{M} - \frac{100}{M}}{6200\,s}$

$\dfrac{380.77}{6200\,s \cdot M} = \boxed{6.14 \times 10^{-2}\ M^{-1} s^{-1} = K}$

From 2nd order rate law (14.14)

$\frac{1}{[A]_t} = Kt + \frac{1}{[A]_0}$

$\dfrac{\frac{1}{[A]_t} - \frac{1}{[A]_0}}{t} = K$

(C) $\frac{1}{2}$ life for 2nd order Rxn $t_{\frac{1}{2}} = \dfrac{1}{K[A]_0} = \dfrac{1}{6.14 \times 10^{-2} M^{-1} s^{-1} (0.01 M)} = \boxed{1.63 \times 10^{3} \text{ Seconds}}$

OR 4.52×10^{-1} hours

OR .45 hours

2) this Rxn rate is doubled as the $[H_2O_2]$ is doubled, therefore it is first ORDER.

(A) rate $= K[H_2O_2]$

(B) overall order is First order overall, (one reactant @ 1st order)

(C) $K = \dfrac{\text{rate}}{[H_2O_2]}$ I will choose trial 2

$K = \dfrac{3.86 \times 10^{-4}\ M}{0.2000\ M \cdot min} = \boxed{1.93 \times 10^{-3}\ min^{-1}}$

(D) $\frac{1}{2}$ life For 1st order Rxn $= t_{\frac{1}{2}} = \dfrac{0.693}{K}$

$= \dfrac{0.693\ min}{1.93 \times 10^{-3}} = \boxed{331.1 \text{ minutes}}$

use this EQ

(E) $\ln \dfrac{[10.0]}{[30.0]} / -K = t = \dfrac{-1.0986\ min}{-1.93 \times 10^{-3}} = t = \boxed{569 \text{ min.}}$

$\ln \dfrac{[A]_t}{[A]_0} = -Kt$ (14.12)

(3) $2HI_{(g)} \longrightarrow H_{2(g)} + I_{2(s)}$ second order. Given in problem

half life $(t_{\frac{1}{2}})$ = 85 seconds. $[HI]_0 = 0.15\ M$

For 2nd order $t_{\frac{1}{2}} = \frac{1}{k[A_0]}$ (14.16) $= 85\ sec = \frac{1}{k(0.15\ M)}$

(A) $$k = \frac{1}{0.15\ M(85\ sec)} = \boxed{0.0784\ M^{-1}\ sec^{-1}}$$

(B) $\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$ (14.14) $$t = \frac{\frac{1}{[A]_t} - \frac{1}{[A]_0}}{k} = \frac{\frac{1}{.10\ M} - \frac{1}{.30\ M}}{0.0784\ M^{-1}\ sec^{-1}}$$

$$t = \frac{10\ M^{-1} - 3.33\ M^{-1}}{.0784\ M^{-1}\ sec^{-1}} = \boxed{85.1\ seconds}$$

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(4) look @ Rxn as beginning @ $t = 0$ w/ 0.0300 M and t_f = 0.0200 M @ 200 s.

(A) 1st order [14.12] $\ln \frac{[A]_t}{[A]_0} = -kt$ $\ln \frac{[.02]}{[.03]} = -kt$

$$\frac{-0.4055}{-t} = k = \frac{-0.4055}{-200\ Min} = \boxed{k = 2.027 \times 10^{-3}\ min^{-1}}$$

400
−200
200 s

(B) 1st order $\frac{1}{2}$ life $t_{\frac{1}{2}} = \frac{0.693}{k} = \frac{0.693}{2.027 \times 10^{-3}\ min^{-1}} = \boxed{341.9\ min}$

(C) $\frac{\ln [A]_t}{[A]_0} = -kt$ In this case, we want $[A]_0$, we'll use $[A]_t$ at 200 min.

$$\frac{\ln [0.0300]}{[x]} = -2.027 \times 10^{-3}\ min^{-1}\ (200\ min)$$

$$\frac{\ln [0.0300]}{[x]} = -0.4054 \qquad e^{-0.4054} = 0.6667$$

$$\frac{.0300}{x} = .6667$$

$$x = .04499775\ M$$

(5) (A) $[I^-]$ is 1st order because as $[I^-]$ is cut in half, so is the rate.

$[OCl^-]$ is also 1st order because in step (trial 4) $[I^-]$ is doubled (which would double rxn.) while $[OCl^-]$ is halved, the rate is halved (stays the same as trial 1).

1st order

Therefore $\boxed{\text{rate} = k[I^-]^1[OCl^-]^1}$

second order overall $1+1=2$

(B) $$\frac{\text{rate}}{[I^-][OCl^-]} = k \qquad \frac{7.91\times10^{-2}\,M}{(0.12\,M)(0.18\,M)\,\text{min}} = \frac{7.91\times10^{-2}\,M}{0.0216\,M^2\,\text{min}}$$

$$\boxed{k = 3.662\ \frac{}{M\,\text{min}}}$$

rate units are not given (I am assuming $\frac{M}{\text{min}}$?)

(C) initial rate $= k[I^-][OCl^-]$

$$\text{rate}_0 = \frac{3.662}{M\,\text{min}}(.030\,M)(.090\,M) = \boxed{9.887\times10^{-3}\ \frac{M}{\text{min}}}$$