12.35

$$NO_{2(g)} + CO(g) \longrightarrow NO_{(g)} + CO_{2(g)} \quad Rate = k[NO_2]^m$$

See attached sheet $\Rightarrow$ 2^{nd} order

$$\Rightarrow \quad Rate = k[NO_2]^2 \qquad (m = 2)$$

$$Rate = \frac{-d[NO_2]}{dt} = k[NO_2]^2 \Rightarrow \frac{-d[NO_2]}{[NO_2]^2} = k\,dt$$

$$\Rightarrow \int_{[NO_2]_0}^{[NO_2]_t} \frac{-d[NO_2]}{[NO_2]^2} = \int_0^t k\,dt \Rightarrow \frac{1}{[NO_2]_t} = kt + \frac{1}{[NO_2]_0}$$

Based on the plot $k = 2.10 \times 10^{-4}\ M^{-1}s^{-1}$

$[NO_2]$ after 2.70×10^4 s ?

$$\frac{1}{[NO_2]_t} = kt + \frac{1}{[NO_2]_0} \Rightarrow \frac{1}{[NO_2]_{2.70\times10^4}} = (2.10\times10^{-4} \times 2.70\times10^4) + \frac{1}{0.500}$$

$$\Rightarrow \frac{1}{[NO_2]} = 7.67 \Rightarrow [NO_2] \text{ at } 2.70\times10^4\ s = 0.130\ mol/L$$

12.55

$$C_4H_9Br \longrightarrow C_4H_9^+ + Br^- \quad \text{slow}$$

$$C_4H_9^+ + H_2O \longrightarrow C_4H_9OH_2^+ \quad \text{Fast}$$

$$C_4H_9OH_2^+ + H_2O \longrightarrow C_4H_9OH + H_3O^+ \quad \text{Fast}$$

As the first reaction is slow $\Rightarrow$ it's the rate limiting step $\Rightarrow$ Rate $= k[C_4H_9Br]$

The overall balanced equation is

$$C_4H_9Br + 2H_2O \longrightarrow C_4H_9OH + Br^- + H_3O^+$$

The intermediates are : $C_4H_9^+$ and $C_4H_9OH_2^+$

12.61

$$N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2}O_2$$

T (K)	k (s^{-1})	$\frac{1}{T}$	ln k
338	4.9×10^{-3}	2.96×10^{-3}	-5.32
318	5.0×10^{-4}	3.14×10^{-3}	-7.60
298	3.5×10^{-5}	3.36×10^{-3}	-10.26

See attached sheet

$$k = Ae^{\frac{-Ea}{RT}} \Rightarrow \ln k = \frac{-Ea}{R}\frac{1}{T} + \ln A$$

$$\text{Slope} = \frac{-E_a}{R} \Rightarrow -12341 = -\frac{E_a}{8.3145}$$

$$\Rightarrow E_a = 102609 \text{ J} \Rightarrow E_a = 103 \times 10^3 \text{ J}$$

12.65

$$k = A e^{-E_a/RT} \Rightarrow \ln k = \frac{-E_a}{R}\frac{1}{T} + \ln A$$

$$\Rightarrow \ln k_1 - \ln k_2 = \frac{-E_a}{R}\frac{1}{T_1} + \ln A - \left(\frac{-E_a}{R}\frac{1}{T_2} + \ln A\right)$$

$$= -\frac{E_a}{R}\frac{1}{T_1} + \ln A + \frac{E_a}{R}\frac{1}{T_2} - \ln A$$

$$\Rightarrow \ln\frac{k_1}{k_2} = \frac{-E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

if $T_1 = 22°C$ and T_2 (to be found)

$$\frac{k_2}{k_1} = 7.00$$

$$\Rightarrow \ln\frac{1}{7} = -\frac{54 \times 10^3}{8.3145}\left(\frac{1}{295} - \frac{1}{T_2}\right)$$

$$\Rightarrow T_2 = 324 \text{ K} = 51°C$$

12.97

$$NO_{(g)} + O_{3\,(g)} \longrightarrow NO_{2(g)} + O_{2(g)}$$

a. Based on the plots (attached sheet), this reaction is of a first-order with respect to each of the reactants.

b. Rate = $k\,[NO]\,[O_3]$

c. When $[O_3]$ is constant $= 1.0 \times 10^{14}$ molecules / cm^3

Rate = $k'\,[NO]$

from the plot $k' = -$slope $\Rightarrow k' = 1.8 \times 10^{-3}\ ms^{-1} = 1.8\ s^{-1}$

When $[NO]$ is constant $= 2.0 \times 10^{14}$ molecules / cm^3

Rate = $k''\,[O_3]$

from the plot $k'' = -$slope $\Rightarrow k'' = 3.6 \times 10^{-3}\ ms^{-1} = 3.6\ s^{-1}$

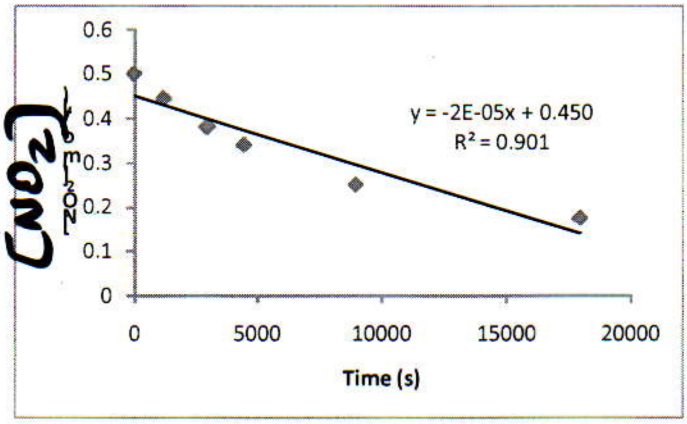
d. $k' = k\,[O_3]$ and $k'' = k\,[NO]$

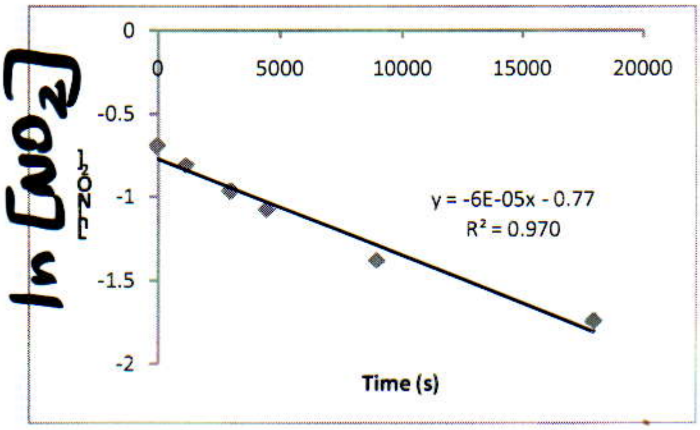
$$\Rightarrow k = \frac{k'}{[O_3]} = \frac{1.8}{1.0 \times 10^{14}} = 1.8 \times 10^{-14}\ cm^3/\text{molecules}.s$$

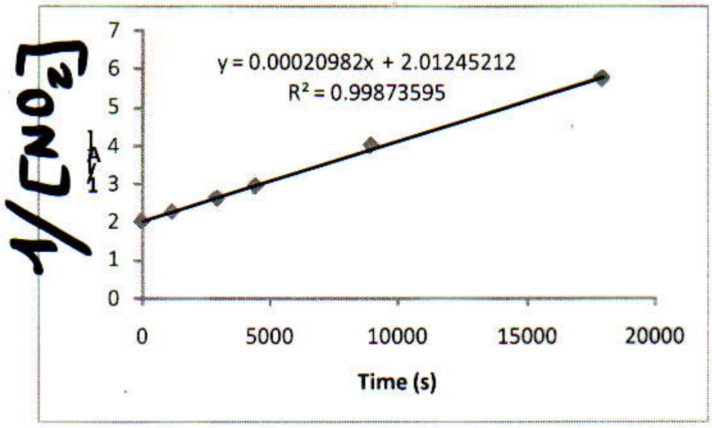
or

$$k = \frac{k''}{[NO]} = \frac{3.6}{2.0 \times 10^{14}} = 1.8 \times 10^{-14}\ cm^3/\text{molecules}.s$$

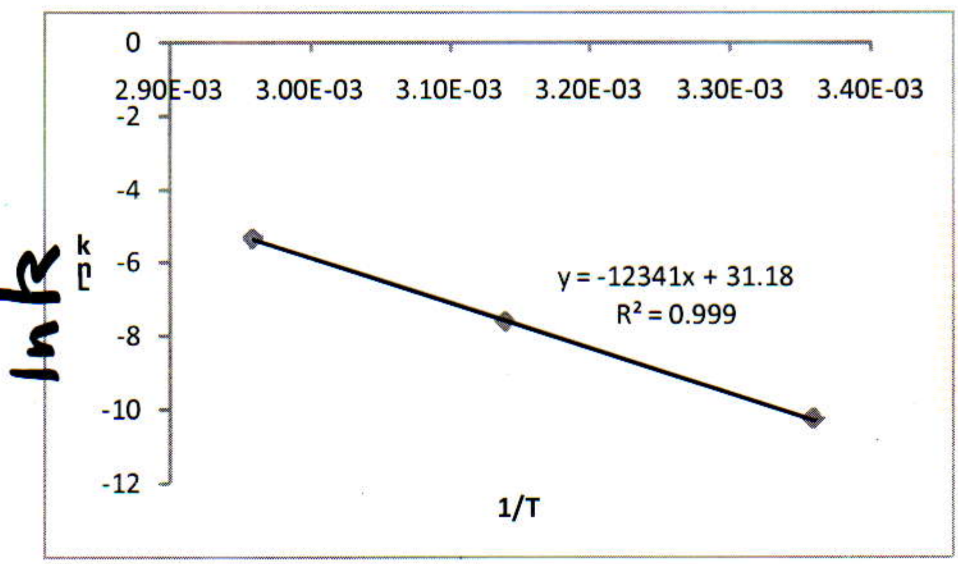
Problem 12.35







Problem 12.61



Problem 12.97