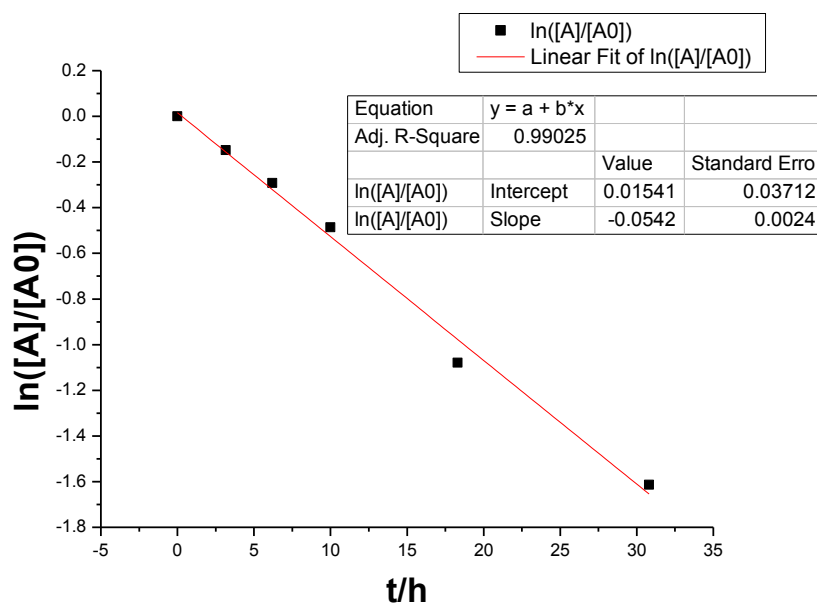


## 21.2 Answers:

Assuming that the reaction is a first-order reaction in terms of  $(\text{CH}_3)_3\text{CBr}$ , we can get the rate equation:

$$\ln \frac{[A]}{[A]_0} = -kt \quad (1)$$

considering the data offered by the question, we can get:



From the figure, the relative coefficient is 0.99. So we the curve is linear. As a result, we know that the assumption is correct, that is, the reaction is a **first-order reaction** in terms of  $(\text{CH}_3)_3\text{CBr}$ . According to the figure above, the rate equation is:

$$\ln \frac{[A]}{[A]_0} = -0.0542t + 0.01541$$

the rate constant  $k$  is 0.0542/h;

if  $t = 43.8\text{h}$ , then we get  $[A] = 0.9824\text{E-}2 \text{ mol/L}$ .

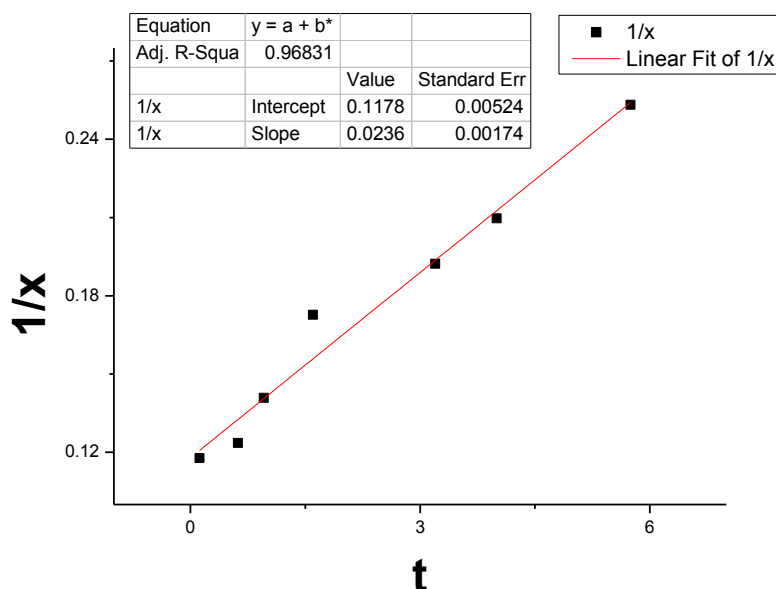
## 21.8 Answers:

It is reasonable that give the assumption of a second-order reaction in terms of ClO,  
so the rate equation is:

$$\frac{1}{x} = kt + \frac{1}{x_0} \quad (2)$$

in which  $x$  means the concentration of ClO.

According to the data offered by the question, we get the following figure:



the relative coefficient is 0.968, which means we can regard the ClO decay as a  
second-order reaction. Based on the linear fitting, the rate equation is :

$$\frac{1}{x} = 0.0236t + 0.1178$$

So the rate constant of the reaction is  $k = 2.36\text{E}7 \text{ L}/(\text{mol s})$  (considering the unit);

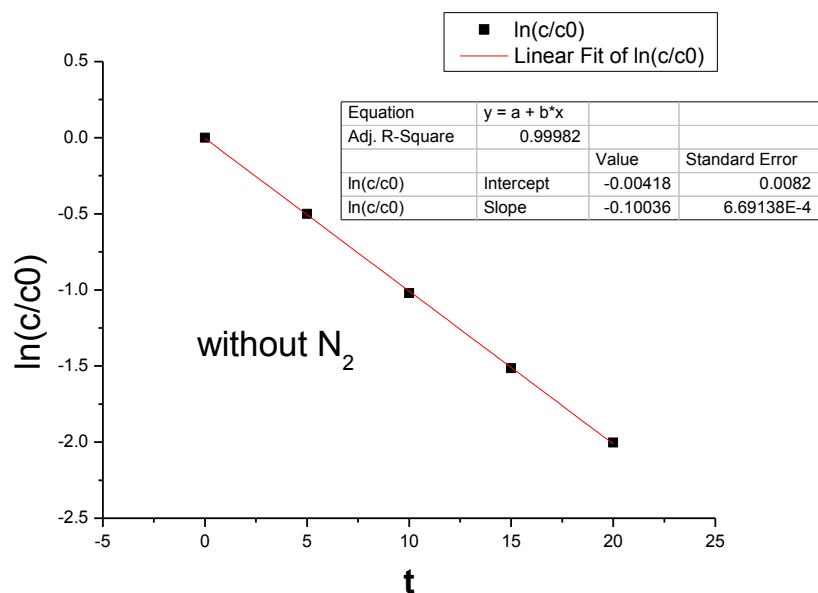
the  $1/x_0 = 0.1178$ , so at half-life,  $1/x = 2/x_0 = 0.2356$ . finally we can get the half-life is:

$$t_{1/2} = 4.991\text{E}-3\text{s}.$$

## 21.20 Answers:

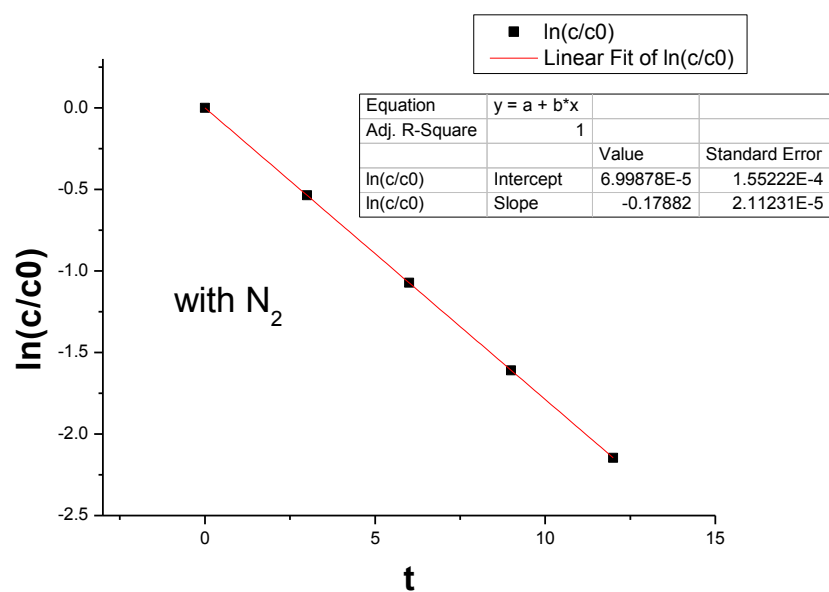
The decay of the relative fluorescence intensity of  $\text{Hg(g)}$  is a first-order reaction.

Without  $\text{N}_2$ , we can get:



the rate constant for the energy transfer process is equal to 0.1003/us;

with  $\text{N}_2$ , similarly we can get:



and the rate constant is 0.1778/us.

## 21.28 Answers:

In fact: for the  $n$ th-order reaction, the rate equation is :

$$\frac{1}{c_0^{n-1}} - \frac{1}{c^{n-1}} = (1-n)kt \quad (n \neq 1) \quad (3)$$

if  $c = 1/2 c_0$ , then we can get:

$$t_{1/2} = \frac{1 - 2^{n-1}}{(1-n)kc_0^{n-1}};$$

if  $c = 3/4 c_0$ , then we can get:

$$t_{3/4} = \frac{1 - (\frac{4}{3})^{n-1}}{(1-n)kc_0^{n-1}}$$

finally, we can get:

$$t_{1/2} / t_{3/4} = \frac{1 - 2^{n-1}}{1 - (\frac{4}{3})^{n-1}}$$

Obviously, the result is a function of  $n$  alone;

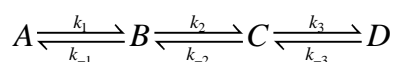
Besides, if  $n = 1$ , we know that the reaction is a first-order reaction, then

$t_{1/2} / t_{3/4} = 1/2$ , which can be regarded as a function of " $n$ ".

So from the  $t_{1/2} / t_{3/4}$ , we can know the order of a reaction.

## 21.29 Answers:

for the consecutive reaction:



for B,  $\frac{dB}{dt} = r_2 = k_1[A] - k_{-1}[B] - k_2[B] + k_{-2}[B]$

for C,  $\frac{dC}{dt} = r_3 = k_2[B] - k_{-2}[C] - k_3[C] + k_{-3}[D]$

Because the product D is removed from the system as soon as it is formed, we can get:

$$r_3 = k_2[B] - k_{-2}[C] - k_3[C]$$

If the system is steady,  $r_2=r_3=0$ . Then we can get:

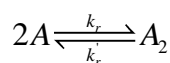
$$[B] = \frac{k_1(k_{-2} + k_3)[A]}{k_{-1}k_{-2} + k_{-1}k_3 + k_2k_3}$$

$$[C] = \frac{k_1k_2[A]}{k_{-1}k_{-2} + k_{-1}k_3 + k_2k_3}$$

finally, we can get:  $\frac{[B]}{[C]} = \frac{k_2}{k_{-2} + k_3}$

## 21.30 Answers:

at the equilibrium for the reaction:



the reaction rate is 0, so

$$k_r[A]_e^2 = k'_r[A_2]_e$$

at the moment, there is a disturbance  $[A_2]_e + \Delta x$ , as a result, we can get:

$$\begin{aligned} \frac{d[A_2]}{dt} &= \frac{d\Delta x}{dt} = k_r([A]_e - 2\Delta x)^2 - k'_r([A_2]_e + \Delta x) \\ &= k_r([A]_e^2 - 2[A]_e\Delta x) - k'_r([A_2]_e + \Delta x) \quad (\text{ingore the } \Delta x^2) \\ &= -(4k_r[A]_e + k'_r)\Delta x \end{aligned}$$

then we can get:

$$\ln \frac{\Delta x}{\Delta x_0} = -(4k_r[A]_e + k'_r)t$$

finally we get:

$$\tau = \frac{1}{4k_r[A]_e + k'_r}$$