Integrated Rate Laws Derivations

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as I mentioned in class you are not responsible for these derivations, but they are helpful...

1st Order

$$Rate = k[A]$$

I can write this in the differential form

$$Rate = \frac{-\partial[A]}{\partial t} = k[A]$$

Now we integrate both sides over the interval

$$\int_{[A]_0}^{[A]} \frac{\partial[A]}{\partial[A]} = -k\int_{t_0}^{t} dt$$

initial conc.

From calculus

$$\int \frac{1}{x}\,dx = \ln x \qquad \int dx = x$$

$$\ln[A]\Big|_{[A]_0}^{[A]} = -kt\Big|_{t_0}^{t}$$

$$\ln[A] - \ln[A]_0 = -k(t-t_0)$$

If we assume $t_0 = 0$ then and rearrange:

$$\ln[A] = -k(t) + \ln[A]_0$$

Where did the half life formula come from?

Assume we start w/ 100 A, at the half way point we would have 50.

$$\ln[50] = -kt_{1/2} + \ln[100]$$

$$3.912 = -kt_{1/2} + 4.605$$

$$-0.693 = -kt_{1/2}$$

$$\frac{0.693}{k} = t_{1/2}$$

← half life comes right from integrated rate law.

2nd Order

$$Rate = k[A]^2$$

Follow same process as above...

$$Rate = \frac{-\partial[A]}{\partial t} = k[A]^2$$

$$\int_{[A]_0}^{[A]} \frac{\partial[A]}{\partial[A]^2} = -k\int_{t_0}^{t} dt$$

From calculus:

$$\int x^n dx = x^{n+1} \quad \text{if } n=2 \quad \int x^{-2}dx = x^{-1}(-1)$$

$$-\frac{1}{[A]}\Big|_{[A]_0}^{[A]} = -kt\Big|_{t_0}^{t}$$

$$\frac{1}{[A]_0} - \frac{1}{[A]} = -k(t-t_0)$$

If we assume $t_0 = 0$ then...

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

move around to avoid (-) signs

Let's do half life again... where $A_0 = 100$ & $A = 50$

$$\frac{1}{50} = kt_{1/2} + \frac{1}{100}$$

$$0.02 = kt_{1/2} + 0.01$$

$$0.01 = kt_{1/2}$$

$$\frac{0.01}{k} = t_{1/2}$$

notice $0.01 = \frac{1}{100}$, the initial conc... so we need to take initial conc into account.

$$\frac{1}{[A]_0 k} = t_{1/2}$$

← we do this by substituting in $\frac{1}{[A]_0}$

0th Order

$$Rate = k[A]^0$$

Follow same process...

$$Rate = -\frac{\partial[A]}{\partial t} = k[A]^0 = k$$

$$d[A] = -k\,dt$$

$$\int_{[A]_0}^{[A]} d[A] = -k\int_{t_0}^{t} dt$$

From calculus:

$$\int dx = x$$

$$[A]\Big|_{[A_0]}^{[A]} = -kt\Big|_{t_0}^{t}$$

$$[A] - [A_0] = -k(t-t_0)$$

If we assume $t_0 = 0$ and rearrange...

$$[A] = -kt + [A]_0$$

Let's do half life again with 100 & 50...

$$50 = -kt + 100$$

$$-50 = -kt$$

$$\frac{50}{k} = t$$

← If the conc change, then the values would change so lets write in regards to A_0

$$\frac{[A]_0}{2k} = t$$

← $A_0 = \frac{100}{2}$