Kinetics Problems

A reaction has a rate constant of 4.58×10^{3} s^{-1}.

- Calculate the half-life (λ) of the reaction.
- How many seconds are required for the concentration of the reactant to decrease by 15.4%.

$$\lambda = \frac{\ln 2}{k} = \frac{\ln 2}{4.58\times10^{3}\ \mathrm{s}^{-1}} = 1.51\times10^{-4}\ \mathrm{s}$$

$$\ln[A]_t = -kt + \ln[A]_0$$

$$[A]_t = 0.846[A]_0$$

$$\ln\left(0.846[A]_0\right) = -kt + \ln[A]_0$$

$$\frac{\ln 0.846}{-k} = t = \frac{\ln 0.846}{-4.58\times10^{3}\ \mathrm{s}^{-1}} = 3.65\times10^{-5}\ \mathrm{s}$$

A reaction (A + 2B C) has the following rate data:

$[A]_0$/M	$[B]_0$/M	$Rate_0$/M s^{-1}
0.1523	0.0115	1.45
0.3051	0.0115	3.00
0.3051	0.0232	5.99

- Calculate the rate law for this reaction.
- Find the rate constant with the units.
- What is the rate of this reaction if [A] = 0.1000 M and [B] = 0.0150 M?

A doubles between 1 and 2 and so does the rate so the reaction is first order in A. B doubles between 2 and 3 and so does the rate so the reaction is first order in B. Rate law: rate = k[A][B]

$$rate = k[A][B]$$

$$k = \frac{rate}{[A][B]} = \frac{1.45\ \mathrm{M\ s}^{-1}}{[0.1523\ \mathrm{M}][0.0115\ \mathrm{M}]} = 828\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$$

$$rate = k[A][B] = \left(828\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}\right)\left(0.1000\ \mathrm{M}\right)\left(0.0150\ \mathrm{M}\right) = 1.24\ \mathrm{M\ s}^{-1}$$

The reaction ($CO + NO_2$ $CO_2 + NO$) has the following proposed mechanism:

$NO_2 + NO_2$ $NO_3 + NO$ (slow)
$CO + NO_3$ $CO_2 + NO_2$ (fast)

What is the predicted rate law for this reaction?

The first step is slow so the rate law is determined from this step.
$Rate = k_1[NO_2]^2$.

The reaction ($2\ NO + Cl_2$ $2\ NOCl_2$) has the following proposed mechanism:

$NO(g) + Cl_2(g)$ ¾ $NOCl_2(g)$ (fast: k_1, k_{-1})
$NOCl_2(g) + NO$ $2NOCl$ (slow: k_2)

Find the predicted mechanism for this reaction.

The second step is slow and gives a rate law of:

$$rate = k_2[NOCl_2][NO]$$

The intermediate must be eliminated from the rate law. This is done with the fast equilibrium in the first step.

$$k_1[NO][Cl_2] = k_{-1}[NOCl_2]$$

$$[NOCl_2] = \frac{k_1}{k_{-1}}[NO][Cl_2]$$

$$rate = k_2\left(\frac{k_1}{k_{-1}}[NO][Cl_2]\right)[NO] = k[NO]^2[Cl_2]$$

A reaction has a rate constant of 4.53×10^{-2} M^{-1} s^{-1} at 22.5 C and 6.89×10^{-2} M^{-1} s^{-1} at 28.9 C. What is the rate constant at 25.0 C?

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

$$E_a=\frac{R\ln\frac{k_2}{k_1}}{\left(\frac{1}{T_1}-\frac{1}{T_2}\right)}=\frac{\left(8.314\times10^{-3}\text{ kJ mol}^{-1}\text{ K}^{-1}\right)\ln\frac{6.89\times10^{-2}\text{ M}^{-1}\text{ s}^{-1}}{4.53\times10^{-2}\text{ M}^{-1}\text{ s}^{-1}}}{\left(\frac{1}{295.7\text{ K}}-\frac{1}{302.1\text{ K}}\right)}=48.6\text{ kJ mol}^{-1}$$

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

$$\ln k_2=\frac{E_a}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)+\ln k_1=\frac{48.6\text{ kJ mol}^{-1}}{\left(8.314\times10^{-3}\text{ kJ mol}\right)}\left(\frac{1}{295.7\text{ K}}-\frac{1}{298.2\text{ K}}\right)+\ln 4.53\times10^{-2}$$

$$=-2.9287$$

$$k_2=e^{-2.9287}=5.35\times10^{-2}\text{ M}^{-1}\text{ s}^{-1}$$