Reaction Rates[1]

Physical Chemistry, R. A. Alberty, 3^{rd} *ed*, Ch 18

Alberty 3^{rd} edition: 18.2, 18.3, 18.7, 18.10(a), 18.10(b), 18.13, 18.16, 18.19, 18.26,
hint for 18.16 (b): If A and B are at the same concentration, then the rate of decay will be the same as for a reaction which is second-order in A, $A = C$.

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1 atm $= 10^5 Nm^{-2} = 760mm\ Hg$

18.2: In studying the decomposition of ozone

$$2O_3(g) = 3O_2(g)$$

in a 2-L reaction vessel, it was found that $\frac{d[O_3]}{dt} = -1.5\times10^{-2} molL^{-1}s^{-1}$.

1. What is the rate of reaction ($molL^{-1}s^{-1}$). ?
2. What is the rate of conversion $\frac{d\zeta}{dt}$ ($mols^{-1}$).
3. What is the value of $\frac{d[O_2]}{dt}$?

18.3: The decomposition of N_2O_5

$$2N_2O_5 = 4NO_2 + O_2$$

is studied by measuring the concentration of oxygen as a function of time, and it is found that

$$\frac{d[O_2]}{dt} = (1.5 \times 10^{-4} s^{-1})[N_2O_5]$$

at constant temperature and pressure. Under these conditions the reaction goes to completion to the right. What is the half-life of the reaction under these conditions?

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18.7: The hydrolysis of 1-chloro-1-methylcyloundecane in 80% ethanol has been studied at $25\,C$. The extent of hydrolysis was measured by titrating the acid formed after measured intervals of time with a solution of $NaOH$. The data are as follows on the volumes of $NaOH$ required.

t/h	0	1.0	3.0	5.0	9.0	12	∞
V/cm^3	0.035	0.295	0.715	1.055	1.505	1.725	2.197

1. What is the order of the reaction?
2. What is the value of the rate constant?
3. What fraction of the 1-chloro-1-methylcycloundecane will be left unhyrolyzed after $8h$?

18.10(a),(b): The decomposition of HI to $H_2 + I_2$ at $508\,C$ has a half-life of $135\,min$ when the initial pressure of HI is $0.1\ atm$ and $13.5\ min$ when the pressure is $1\ atm$.

1. Show that this proves that the reaction is second order.
2. What is the value of the rate constant in $Lmol^{-1}s^{-1}$?

18.13: The reaction $A = B$ is n^{th} order (where $n = \frac{1}{2}, \frac{3}{2}, 2, 3, \ldots$) and goes to completion to the right. Derive an expression for the half-life in terms of k, n, and $[A]_o$.

18.16: A solution of A is mixed with an equal volume of a solution of B containing the same number of moles, and the reaction $A + B = C$ occurs. At the end of $1h$, A is 75% reacted. How much of A will be left unreacted at the end of $2h$ if the reaction is

1. first order in A and zero in B?
2. first order in both A and B? (see hint above)
3. zero order in both A and B.

18.19: The following table gives kinetic data for the following reaction at $25C$:

$$OCl^- + I^- = OI^- + Cl^-$$

$\frac{[OCl^-]}{mol\ L^{-1}}$	$\frac{[I^-]}{mol\ L^{-1}}$	$\frac{[OH^-]}{mol\ L^{-1}}$	$\frac{d[IO^-]/dt}{10^{-4} mol\ L^{-1} s^{-1}}$
0.0017	0.0017	1.00	1.75
0.0034	0.0017	1.00	3.50
0.0017	0.0034	1.00	3.50
0.0017	0.0017	0.5	3.50

What is the rate law for the reaction, and what is the value of the rate constant?

18.26: The hydrolysis of $(CH_2)_6CClCH_3$ in 80% ethanol follows the first order rate equation. The values of the specific reaction rate constants are as follows:

t/C	0	25	35	45
k/s^{-1}	1.06×10^{-5}	3.19×10^{-4}	9.86×10^{-4}	2.92×10^{-3}

1. Plot $\log k$ against $1/T$.
2. Calculate the activation energy
3. Calculate the pre-exponential factor.