

Reaction Rates¹

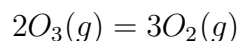
Physical Chemistry, R. A. Alberty, 3rd ed, Ch 18

Alberty 3rd 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 , $A = C$.

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

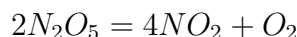
18.2: In studying the decomposition of ozone



in a 2-L reaction vessel, it was found that $\frac{d[O_3]}{dt} = -1.5 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$.

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

18.3: The decomposition of N_2O_5



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

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

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-methylcycloundecane 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 unhydrolyzed 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.

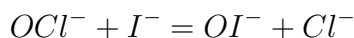
1. Show that this proves that the reaction is second order.
2. What is the value of the rate constant in $Lmol^{-1}s^{-1}$?

18.13: The reaction $A = B$ is n^{th} order (where $n = \frac{1}{2}, \frac{3}{2}, 2, 3, \dots$) 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 25°C:



| $\frac{[OCl^-]}{mol\ L^{-1}}$ | $\frac{[I^-]}{mol\ L^{-1}}$ | $\frac{[OH^-]}{mol\ L^{-1}}$ | $\frac{d[IO^-]/dt}{10^{-4}mol\ L^{-1}s^{-1}}$ |
|-------------------------------|-----------------------------|------------------------------|---|
| 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.