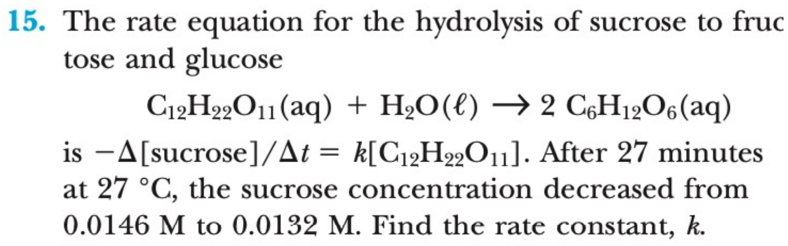


15. The rate equation for the hydrolysis of sucrose to fructose and glucose

$$C_{12}H_{22}O_{11}(aq) + H_2O(\ell) \longrightarrow 2\ C_6H_{12}O_6(aq)$$

is $-\Delta[\text{sucrose}]/\Delta t = k[C_{12}H_{22}O_{11}]$. After 27 minutes at 27 °C, the sucrose concentration decreased from 0.0146 M to 0.0132 M. Find the rate constant, *k*.

Rate = $k[C_{12}H_{22}O_{11}]$ → first order reaction

$$\ln[A] - \ln[A]_0 = -kt \rightarrow$$

$$\ln(0.0132\ M) - \ln(0.0146\ M) = -k(27min)$$

$$k = 3.73 \times 10^{-3}\ \text{min}^{-1}$$

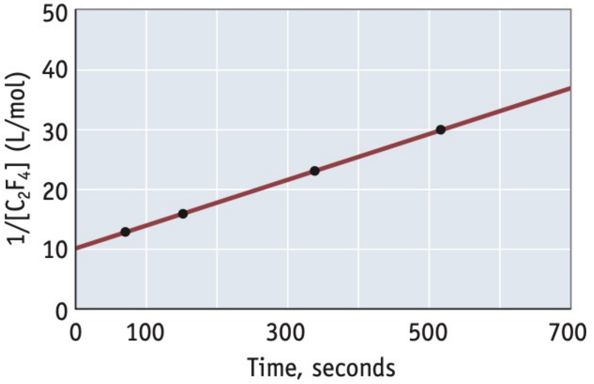
55. When heated, tetrafluoroethylene dimerizes to form octafluorocyclobutane.

$$C_2F_4(g) \rightarrow \tfrac{1}{2}\, C_4F_8(g)$$

To determine the rate of this reaction at 488 K, the data in the table were collected. Analysis was done graphically, as shown below:

$[C_2F_4]$ (M)	Time (s)
0.100	0
0.080	56
0.060	150.
0.040	335
0.030	520.

(a) What is the rate law for this reaction?
(b) What is the value of the rate constant?
(c) What is the concentration of C_2F_4 after 600 s?



$1/[C_2F_4]$ vs. t linear → 2nd order

Rate = $k[C_2F_4]^2$

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

$$k = slope = \frac{\Delta y}{\Delta x}$$

$$= \frac{(0.080\ M)^{-1} - (0.100\ M)^{-1}}{56\ s - 0\ s}$$

$$= 0.045\ M^{-1}s^{-1}$$

$$\frac{1}{[A]} = (0.045\ M^{-1}s^{-1})(600\ s) + \frac{1}{0.100\ M} \rightarrow$$

A = 0.027 M

Sample problem

Sucrose, $C_{12}H_{22}O_{11}$, decomposes to fructose and glucose in acid solution with the rate law

Rate = $k[C_{12}H_{22}O_{11}]$ k = $0.216\ h^{-1}$ at 25 ˚C

1. What is the half-life of $C_{12}H_{22}O_{11}$ at this temperature?
2. What amount of time is required for 87.5% of the initial concentration of $C_{12}H_{22}O_{11}$ to decompose?

- First-order kinetics: $t_{½} = \frac{ln2}{k} = \frac{ln2}{0.216\ h^{-1}} = \mathbf{3.21\ h}$
- 87.5% of $[C_{12}H_{22}O_{11}]$ decomposes → $[C_{12}H_{22}O_{11}] = 0.125\ [C_{12}H_{22}O_{11}]_0$
- $ln\frac{[C_{12}H_{22}O_{11}]}{[C_{12}H_{22}O_{11}]_0} = -kt \rightarrow ln\frac{0.125[C_{12}H_{22}O_{11}]_0}{[C_{12}H_{22}O_{11}]_0} = -(0.216\ h^{-1})t \rightarrow \boldsymbol{t = 9.63\ h}$

Sample problem

Radioactive decay is a first-order process. Radioactive radon-222 gas (^{222}Rn) occurs naturally as a product of uranium decay. The half-life of ^{222}Rn is 3.8 days. Suppose a flask originally contained 4.0×10^{13} atoms of ^{222}Rn. How many atoms of ^{222}Rn will remain after one month (30. days)?

- First-order kinetics: $t_{½} = \frac{ln2}{k} \rightarrow k = \frac{ln2}{3.8\ days} = 0.18\ days^{-1}$
- $\ln[^{222}Rn]_0 - \ln[^{222}Rn] = kt$ →
- $\ln(4.0 \times 10^{13}$ atoms/flask$) - \ln[^{222}Rn] = (0.18\ days^{-1})(30.\ days)$ →
- **$[^{222}Rn] = 1.8 \times 10^{11}$ atoms/flask**

Sample problem

A certain reaction has an activation energy of 54.0 kJ/mol. As the temperature is increased from 22 ˚C to a higher temperature, the rate constant increases by a factor of 7.00. Calculate the higher temperature.

- Let $k_1 = x \rightarrow k_2 = 7x$
- $ln\frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \rightarrow ln7 = -\frac{54000\ Jmol^{-1}}{8.314JK^{-1}mol^{-1}}\left(\frac{1}{T_2} - \frac{1}{295\ K}\right)$
- $\frac{1}{T_2} = 3.00\times10^{-4}K^{-1} + \frac{1}{295\ K} = 0.00309\ K^{-1}$
- **T_2 = 324 K (51 ˚C)**

Sample problem

One of the earliest kinetic studies involved the gas phase reaction of hydrogen gas with iodine gas to make hydrogen iodide:

H_2 (g) + I_2 (g) → 2 HI (g). A proposed mechanism for this process is

- Step 1: $I_2 \Leftrightarrow 2\ I$ (fast, equilibrium)
- Step 2: $I + H_2 \Leftrightarrow H_2I$ (fast, equilibrium)
- Step 3: $H_2I + I \rightarrow 2\ HI$ (slow)

Write the rate law expected for this mechanism.

Sample problem

  - Step 1: $I_2 \Leftrightarrow 2\ I$ (fast, equilibrium)
  - Step 2: $I + H_2 \Leftrightarrow H_2I$ (fast, equilibrium)
  - Step 3: $H_2I + I \rightarrow 2\ HI$ (slow)
- Slow step = RDS
- Rate = $k[H_2I][I]$
- Both H_2I and I are intermediates and can't be in the rate law
- Step 2 equilibrium: $\text{rate}_{\text{forward}} = \text{rate}_{\text{reverse}} \rightarrow k_2[I][H_2] = k_{-2}[H_2I] \rightarrow [H_2I] = k_2'[I][H_2]$
- Substitute $[H_2I]$ in step 3: rate = $k_3'[I][H_2][I] = k_3'[I]^2[H_2]$
- Step 1 equilibrium: $k_1[I_2] = k_{-1}[I]^2 \rightarrow [I]^2 = k_1'[I_2]$
- Substitute $[I]^2$ in step 3: **rate = $k_3''[H_2][I_2]$**