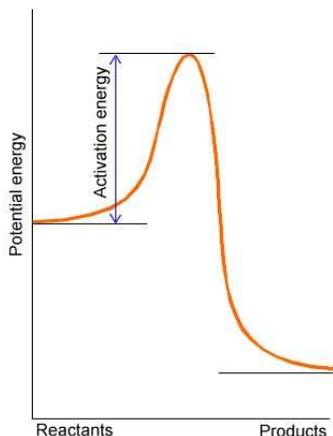


experiments that this situation is described quantitatively by the following formula for the rate constant

$$k = Ae^{-E_a/RT} \quad (20)$$

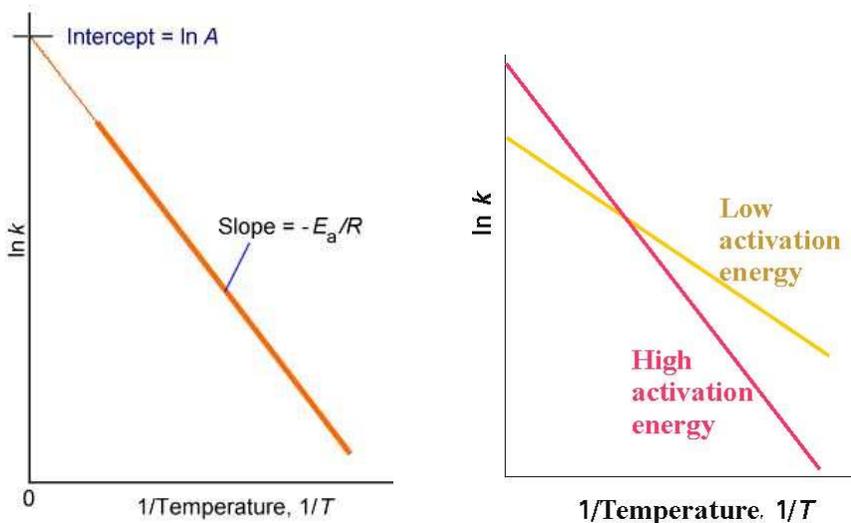
in which E_a and A are called an activation energy and a pre-factor.[‡] R is the gas constant ($= 8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}$).



By taking the natural logarithms (\log_e or \ln) of both sides,

$$\ln k = \ln A - \frac{E_a}{RT} \quad (21)$$

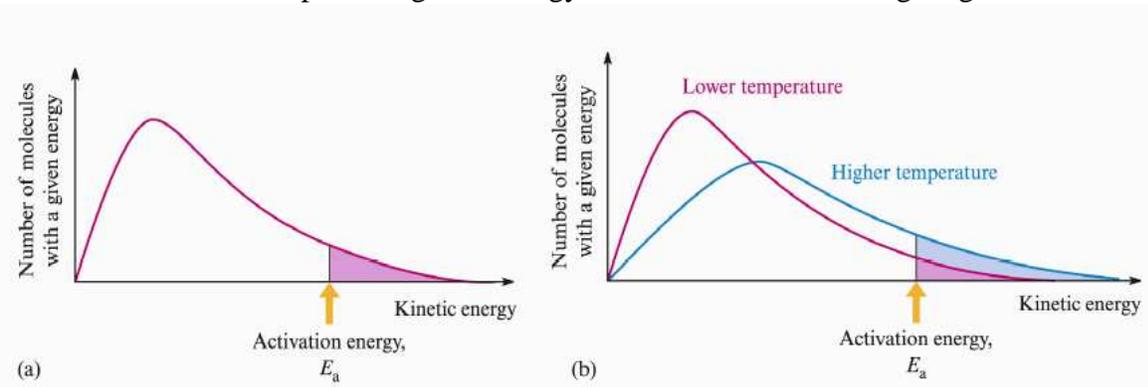
Therefore, by plotting $\ln k$ against $1/T$, we will obtain a straight line as shown in the next diagrams. From the slope and the intercept of the plot we can calculate the activation energy E_a and the pre-factor A .



[‡] The pre-factor A is sometimes called a frequency factor.

Equations (20) and (21) are called the **Arrhenius equation** and the plot of $\ln k$ against $1/T$ the **Arrhenius plot**.

The Arrhenius law is closely related to the **Boltzmann's law**. In thermal equilibrium at temperature T , the molecules can take various energies.[§] The distribution of the number of molecules plotted against energy E will look the following diagrams.



As seen, the number of molecules decreases as the energy increases (in the high energy region). According to the picture of the activation energy barrier lying between the reactant and product states, the reaction rate will be proportional to the number of molecules having higher energy than E_a , i.e., in the shaded area of the diagram. By raising the temperature the molecules will receive energy from the surroundings, and then the distribution graph will shift toward the right, i.e., toward the higher energy. This results in an increase of the number of molecules above E_a and hence the increase of the reaction rate. This behaviour is described quantitatively by the Arrhenius equation (20) or (21).

3 Data analysis

Suppose that we have carried out a series of experiments to observe changes along time of the concentrations of the reactants and products as in the diagrams in Section 2.1 From these and other supplementary data, we attempt to determine the rate law, i.e., the orders with respect to the species involved and the rate constant.

3.1 Unimolecular reaction $A \rightarrow P$

We begin with a very simple reaction in which only one specie A is involved in the reactant.



[§]The temperature T is proportional to the **average** kinetic energy of the molecules. The energy of each molecule may deviate from this average.

We do not consider the backward reaction. We also assume that there is no intermediate species or intermediate steps involved in the reaction. That is, (22) is a single step reaction. This is an example of the **elementary** reaction.

In this case, the rate law will contain only the concentration of A,

$$\text{Rate} = k[\text{A}]^n \quad (23)$$

Because the reaction rate is that of the loss of A, $-d[\text{A}]/dt$, the above equation is a simple differential equation

$$-\frac{d[\text{A}]}{dt} = k[\text{A}]^n \quad (24)$$

which can be integrated mathematically.

3.1.1 Zero order reaction

Let us first consider the zero order case, $n = 0$. Because $[\text{A}]^0 = 1$, (24) becomes

$$-\frac{d[\text{A}]}{dt} = k \quad (25)$$

This means that the gradient $d[\text{A}]/dt$ is a constant $-k$. Therefore, [A] decays at a constant rate and the plot of [A] along time will be a straight line.

$$[\text{A}]_t = [\text{A}]_0 - kt \quad (26)$$

Here and hereafter, we denote the concentration of A by $[\text{A}]_t$ when we wish to emphasize its dependence on time. The initial concentration at $t = 0$ is $[\text{A}]_0$.

3.1.2 First order reaction

For $n = 1$, we have

$$\frac{d[\text{A}]}{dt} = -k[\text{A}] \quad (27)$$

The solution[¶] is an exponential function

$$[\text{A}]_t = [\text{A}]_0 e^{-kt} \quad (28)$$

This is equivalent to

$$\ln[\text{A}]_t = \ln[\text{A}]_0 - kt \quad (29)$$

Therefore, the plot of $\ln[\text{A}]_t$ against time t is a straight line.

[¶] For simplicity we write $A(t)$ instead of $[\text{A}]_t$. It follows from (27) that

$$\frac{dA}{dt} = -kA \Rightarrow \int \frac{dA}{A} = -k \int dt \Rightarrow \ln A(t) = -kt + C$$

Putting $t = 0$, we find $C = \ln A(0)$. We thus get (29) which is equivalent to (28).

3.1.3 Second order reaction

For $n = 2$,

$$\frac{d[A]}{dt} = -k[A]^2 \quad (30)$$

The solution is^{||}

$$[A]_t = \frac{[A]_0}{1 + kt[A]_0} \quad (31)$$

Or equivalently,

$$\frac{1}{[A]_t} = \frac{1}{[A]_0} + kt \quad (32)$$

Therefore, the plot of $1/[A]_t$ against time t is a straight line.

3.1.4 Summary

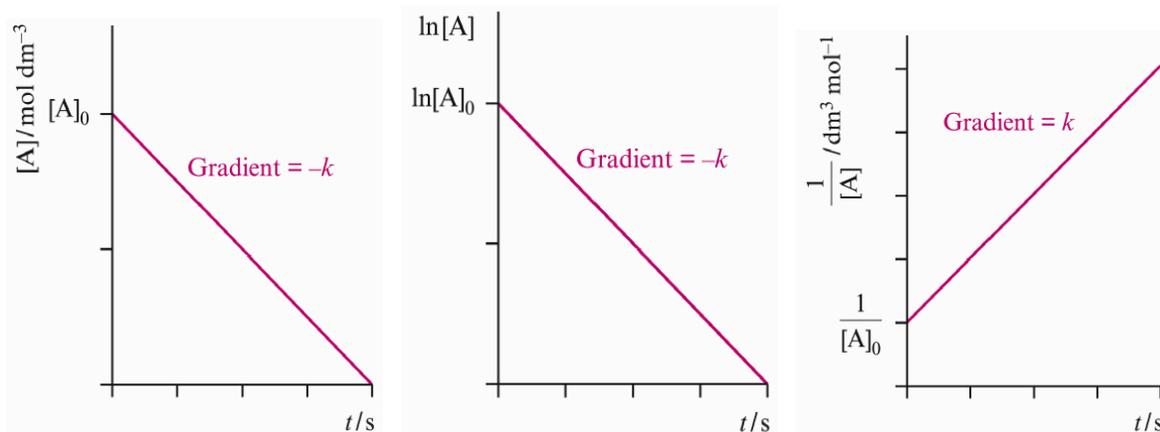
- 0th order: Rate = $-\frac{d[A]}{dt} = k$
 $\Rightarrow [A]_t = [A]_0 - kt$
 \Rightarrow Plot of $[A]_t$ against time t is linear
- 1st order: Rate = $-\frac{d[A]}{dt} = k[A]$
 $\Rightarrow [A]_t = [A]_0 \exp(-kt) \quad \Rightarrow \ln[A]_t = \ln[A]_0 - kt$
 \Rightarrow Plot of $\ln[A]_t$ against time t is linear
- 2nd order: Rate = $-\frac{d[A]}{dt} = k[A]^2$
 $\Rightarrow [A]_t = \frac{[A]_0}{1 + kt[A]_0} \quad \Rightarrow \frac{1}{[A]_t} = \frac{1}{[A]_0} + kt$
 \Rightarrow Plot of $1/[A]_t$ against time t is linear

In this way, the order n and the rate constant k can be determined from the graphs of $[A]$, $\ln[A]$ or $1/[A]$ against time. Suppose we have obtained from experiments the concentration of A as a function of time. We then plot $[A]$, $\ln[A]$ or $1/[A]$ against time. If one of these was found to be a straight line, the order n is 0, 1 or 2, respectively.

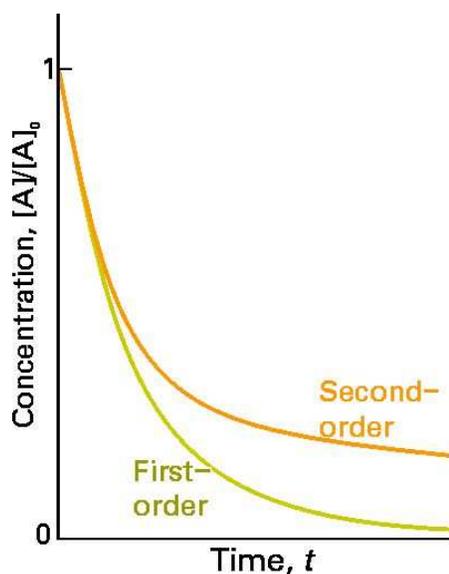
^{||} From (30),

$$\frac{dA}{dt} = -kA^2 \quad \Rightarrow \quad - \int \frac{dA}{A^2} = k \int dt \quad \Rightarrow \quad \frac{1}{A(t)} = kt + C$$

Putting $t = 0$, we find $C = 1/A(0)$. This immediately gives (32) and after rearranging we get (31).



For the first and second order reactions, the raw data of $[A]_t$ will look like

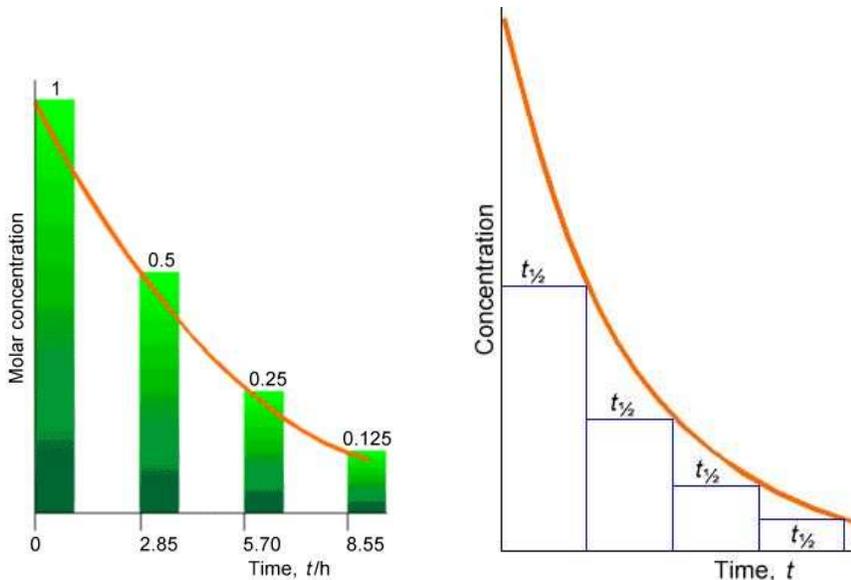


Both curves show smooth decay in which the gradient (= rate) decreases along time as the concentration $[A]$ decreases. This is simply because the rate is proportional to $[A]$ or $[A]^2$. In other words, the chance of the reaction will decrease as we lose the reactant molecules along with the progress of the reaction.

3.1.5 Half-life Method

The **half-life** is the time taken for the concentration of the reactant $[A]$ to halve. It may depend on the starting concentration $[A]$. For example, for zero order reactions where $[A]_t$ is a linear function of t , the half life decreases along time, i.e., as the starting concentration decreases. (Confirm this by drawing a graph.) In contrast, for the first

order reactions the half life is a constant that is independent of the starting concentration. See the diagrams below.



This is a special characteristic of the first order reactions. Let us denote the half life by τ . Then Eq (28) at $t = \tau$ is written as

$$\frac{[A]_0}{2} = [A]_0 \exp(-k\tau) \quad (33)$$

By dividing both sides by $[A]_0$ and taking the natural logarithms, we find

$$\frac{1}{2} = \exp(-k\tau) \Rightarrow \exp(k\tau) = 2 \Rightarrow k\tau = \ln 2 \Rightarrow \tau = \frac{\ln 2}{k} \quad (34)$$

As seen in the previous diagram, the decay profile of the concentration $[A]$ for the second order reaction is quite different from the first order reaction. It is easy to show from Eq (32) that the half life for the second order reaction is proportional to the inverse of the starting concentration, $\tau = 1/k[A]_0$. This means that the half-life increases as the reaction proceeds.

In summary,

- 0th order: half-life = $[A]_0/2k \propto [A]_0$
- 1st order: half-life = $\ln 2/k$ independent of $[A]_0$
- 2nd order: half-life = $1/k[A]_0 \propto 1/[A]_0$

Question: Confirm these behaviours (qualitatively) on graphs. Derive these mathematical formulas of the half-life from Eqs (26) - (32).