

Arrhenius Equation

The rate constant “k” for a reaction is related to the absolute temperature T by the equation: -

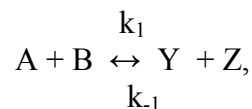
$k = Ae^{-B/T}$ A and B are constants and this equation can be also as $k = Ae^{-E/RT}$
R is gas constant and is equal to $8.3145 \text{ JK}^{-1} \text{ mol}^{-1}$ and E is the activation energy for the reaction. This equation was arrived at by Van’f Hoff and it is often referred to as the Arrhenius equation.

Van’t Hoff argued as follows:

The temperature dependence of a standard equilibrium constant k_c° is given by

$$d \ln k_c^\circ / dT = \Delta U^\circ / RT^2 \dots\dots\dots 1$$

where, ΔU° is the standard internal energy change in the reaction. For the reaction such as



the equilibrium constant k_c is equal to the ratio of the rate constant k_1 and k_{-1} ,

$$k_c = k_1 / k_{-1} \dots\dots\dots 2$$

Substituting for k_c in equation 1 gives,

$$d \ln k_1 / dT - d \ln k_{-1} / dT = \Delta U / RT^2 \dots\dots\dots 3$$

Equation 3 can be split into two equations

$$d \ln k_1 / dT = \text{constant} + E_1 / RT^2 \dots\dots\dots 4$$

and

$$d \ln k_{-1} / dT = \text{constant} + E_{-1} / RT^2 \dots\dots\dots 5$$

In this case, $E_1 - E_{-1}$ is equal to ΔU° . Experimentally, it is found that the constants in equations 4 and 5 can be set to zero and on integrating each of these equations give

$$k_1 = A_1 e^{-E_1 / RT} \dots\dots\dots 6$$

$$k_{-1} = A_{-1} e^{-E_{-1} / RT} \dots\dots\dots 7$$

The quantities A_1 and A_{-1} are known as preexponential factors of the reactions and E_1 and E_{-1} are known as activation energies.

Arrhenius pointed out that the fraction of molecules colliding with sufficient energy to react is small, and according to Boltzmann principle, “the fraction of collisions in which the energy is in excess of a particular E is $e^{-E/RT}$ ”. This fraction is larger the higher the temperature T and the lower the energy E. The rate constant $k \propto e^{-E/RT}$.

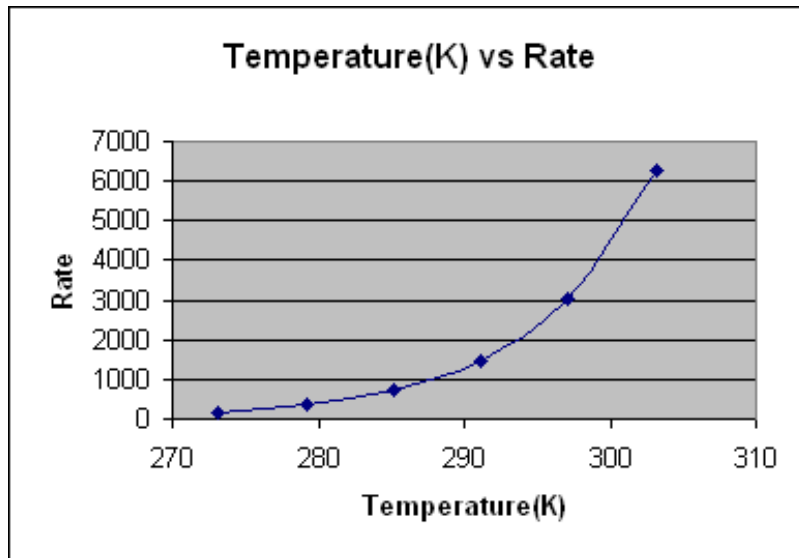
To test Arrhenius equation, take natural logs on both sides

$$\ln k = \ln A - E/RT \dots\dots\dots 8$$

The data below is for the experiment done in 1889 by Hecht and Conrad on ethoxide and methyl iodide

A graph of rate against absolute temperature is exponential as shown below.

Temp. (°C)	Temp.T (K)	Rate k
0	273.15	168
6	279.15	354
12	285.15	735
18	291.15	1463
24	297.15	3010
30	303.15	6250



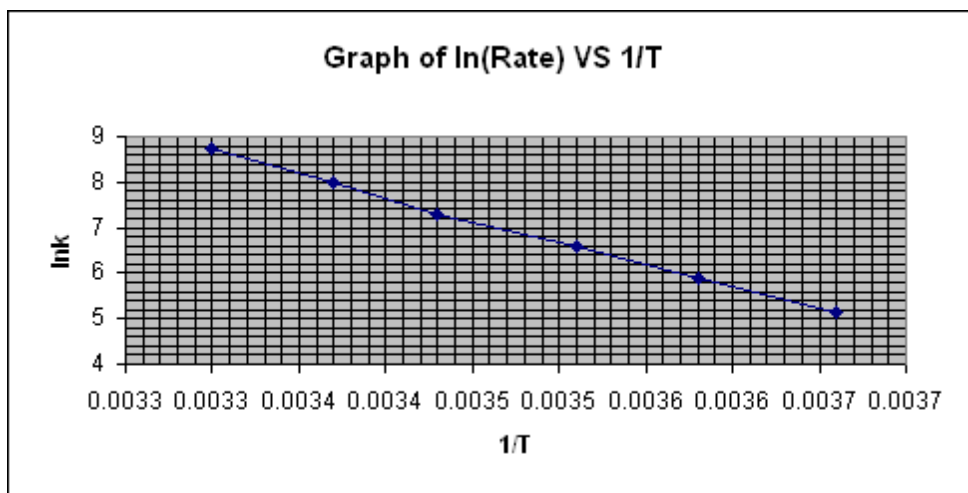
To test Arrhenius equation, take logs on both sides of the equation

$k_1 = A_1 e^{-E_1/RT}$
gives the equation below

$$\ln k = \ln A - E/RT$$

If the law applies, a plot of $\ln k$ against $1/T$ will be a straight line. The slope will be $-E/R$.

Temp.T (K)	Rate	1/T	ln(Rate) k
273.15	168	0.00366	5.124
279.15	354	0.00358	5.869
285.15	735	0.00351	6.6
291.15	1463	0.00343	7.288
297.15	3010	0.00337	8.01
303.15	6250	0.0033	8.74



(Source: <http://webserver.lemoyne.edu/faculty/giunta>)

The slope (which has the units of K) will be $-E/R$. Alternatively, taking common logarithms,

$$\log_{10} k = \log_{10} A - E/2.303RT$$

From the equation, a plot of $\log_{10} k$ against $1/T$ will give a straight line.

The slope of this plot of $\log_{10} k$ against $1/T$ will be $-E/2.303R$. Proving Arrhenius equation. The Arrhenius equation is applicable to various reaction systems. Once activation energy for a reaction is known; it is easy to predict the value for the rate constant k at a different temperature T_1 from its value k at another temperature T . Equation 8 becomes:-

$$\ln(k_1/k) = E_a/R * (1/T - 1/T_1) \text{ for a reaction taking place at } T \text{ and } T_1, \text{ temperatures.}$$

References:

1. P. Atkins; The Elements of Physical Chemistry *with Applications in Biology*, 3rd edition, Freeman new york, pp229-236
2. Laidler, Meiser and, Sanctuary; Physical Chemistry, 4th Edition, Houghton Mifflin, 2003; pp380-385