

# Arrhenius equation

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The **Arrhenius equation** is a simple, but remarkably accurate, formula for the temperature dependence of the reaction rate constant, and therefore, rate of a chemical reaction.<sup>[1]</sup> The equation was first proposed by the Dutch chemist J. H. van 't Hoff in 1884; five years later in 1889, the Swedish chemist Svante Arrhenius provided a physical justification and interpretation for it. Currently, it is best seen as an empirical relationship.<sup>[2]</sup> It can be used to model the temperature-variance of diffusion coefficients, population of crystal vacancies, creep rates, and many other thermally-induced processes/reactions.

A historically useful generalization supported by the Arrhenius equation is that, for many common chemical reactions at room temperature, the reaction rate doubles for every 10 degree Celsius increase in temperature.

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## Overview

In short, the Arrhenius equation gives "the dependence of the rate constant  $k$  of chemical reactions on the temperature  $T$  (in absolute temperature kelvins) and activation energy<sup>[3]</sup>  $E_a$ ", as shown below:<sup>[1]</sup>

$$k = Ae^{-E_a/RT}$$

where  $A$  is the pre-exponential factor or simply the *prefactor* and  $R$  is the Universal gas constant. Alternatively, the equation may be expressed as

$$k = Ae^{-E_a/k_B T}$$

The only difference is the energy units: the former form uses energy/mole, which is common in chemistry, while the latter form uses energy directly, which is common in physics. The different units are accounted for in using either  $R$  = Gas constant or the Boltzmann constant  $k_B$  as the multiplier of temperature  $T$ .

The units of the pre-exponential factor  $A$  are identical to those of the rate constant and will vary depending on the order of the reaction. If the reaction is first order it has the units  $s^{-1}$ , and for that reason it is often called the *frequency factor* or *attempt frequency* of the reaction. Most simply,  $k$  is the number of collisions that result in a

reaction per second,  $A$  is the total number of collisions (leading to a reaction or not) per second and  $e^{-E_a/RT}$  is the probability that any given collision will result in a reaction. When the activation energy is given in molecular units instead of molar units, e.g., joules per molecule instead of joules per mole, the Boltzmann constant is used instead of the gas constant. It can be seen that either increasing the temperature or decreasing the activation energy (for example through the use of catalysts) will result in an increase in rate of reaction.

Given the small temperature range kinetic studies occur in, it is reasonable to approximate the activation energy as being independent of the temperature. Similarly, under a wide range of practical conditions, the weak temperature dependence of the pre-exponential factor is negligible compared to the temperature dependence of the  $\exp(-E_a/RT)$  factor; except in the case of "barrierless" diffusion-limited reactions, in which case the pre-exponential factor is dominant and is directly observable.

Some authors define a **modified Arrhenius equation**,<sup>[4]</sup> that makes explicit the temperature dependence of the pre-exponential factor. If one allows *arbitrary* temperature dependence of the prefactor, the Arrhenius description becomes overcomplete, and the inverse problem (i.e., determining the prefactor and activation energy from experimental data) becomes singular. The modified equation is usually of the form

$$k = A(T/T_0)^n e^{-E_a/RT}$$

where  $T_0$  is a reference temperature and allows  $n$  to be a unitless power. Clearly the original Arrhenius expression above corresponds to  $n = 0$ . Fitted rate constants typically lie in the range  $-1 < n < 1$ . Theoretical analyses yield various predictions for  $n$ . It has been pointed out that *"it is not feasible to establish, on the basis of temperature studies of the rate constant, whether the predicted  $T^{1/2}$  dependence of the pre-exponential factor is observed experimentally."*<sup>[2]</sup> However, if additional evidence is available, from theory and/or from experiment (such as density dependence), there is no obstacle to incisive tests of the Arrhenius law.

Another common modification is the **stretched exponential** form

$$k = A \exp \left[ - \left( \frac{E_a}{RT} \right)^\beta \right]$$

where  $\beta$  is a unitless number of order 1. This is typically regarded as a fudge factor to make the model fit the data, but can have theoretical meaning, for example showing the presence of a range of activation energies or in special cases like the Mott variable range hopping.

Taking the natural logarithm of the Arrhenius equation yields:

$$\ln(k) = \frac{-E_a}{R} \frac{1}{T} + \ln(A)$$

So, when a reaction has a rate constant that obeys the Arrhenius equation, a plot of  $\ln(k)$  versus  $T^{-1}$  gives a straight line, whose gradient and intercept can be used to determine  $E_a$  and  $A$ . This procedure has become so common in experimental chemical kinetics that practitioners have taken to using it to *define* the activation energy for a reaction. That is the activation energy is defined to be  $(-R)$  times the slope of a plot of  $\ln(k)$ : vs.  $(1/T)$ :

$$E_a \equiv -R \left[ \frac{\partial \ln k}{\partial (1/T)} \right]_P$$

# Kinetic theory's interpretation of Arrhenius equation

Arrhenius argued that for reactants to transform into products, they must first acquire a minimum amount of energy, called the activation energy  $E_a$ . At an absolute temperature  $T$ , the fraction of molecules that have a kinetic energy greater than  $E_a$  can be calculated from the Maxwell-Boltzmann distribution of statistical mechanics, and turns out to be proportional to  $e^{-\frac{E_a}{RT}}$ . The concept of *activation energy* explains the exponential nature of the relationship, and in one way or another, it is present in all kinetic theories.

## Collision theory

*Main article: Collision theory*

One example comes from the "collision theory" of chemical reactions, developed by Max Trautz and William Lewis in the years 1916-18. In this theory, molecules are supposed to react if they collide with a relative kinetic energy along their lines-of-center that exceeds  $E_a$ . This leads to an expression very similar to the Arrhenius equation.

## Transition state theory

Another Arrhenius-like expression appears in the "transition state theory" of chemical reactions, formulated by Wigner, Eyring, Polanyi and Evans in the 1930s. This takes various forms, but one of the most common is

$$k = \frac{k_B T}{h} e^{-\frac{\Delta G^\ddagger}{RT}}$$

where  $\Delta G^\ddagger$  is the Gibbs free energy of activation,  $k_B$  is Boltzmann's constant, and  $h$  is Planck's constant.

At first sight this looks like an exponential multiplied by a factor that is *linear* in temperature. However, one must remember that free energy is itself a temperature dependent quantity. The free energy of activation is the difference of an enthalpy term and an entropy term multiplied by the absolute temperature. When all of the details are worked out one ends up with an expression that again takes the form of an Arrhenius exponential multiplied by a slowly varying function of  $T$ . The precise form of the temperature dependence depends upon the reaction, and can be calculated using formulas from statistical mechanics involving the partition functions of the reactants and of the activated complex.

## Limitations of the idea of Arrhenius activation energy

Both the Arrhenius activation energy and the rate constant  $k$  are experimentally determined, and represent macroscopic reaction-specific parameters that are not simply related to threshold energies and the success of individual collisions at the molecular level. Consider a particular collision (an elementary reaction) between molecules A and B. The collision angle, the relative translational energy, the internal (particularly vibrational) energy will all determine the chance that the collision will produce a product molecule AB. Macroscopic measurements of  $E$  and  $k$  are the result of many individual collisions with differing collision parameters. To probe reaction rates at molecular level, experiments have to be conducted under near-collisional conditions and this subject is often called molecular reaction dynamics (see Levine).

## See also

- Accelerated aging
- Arrhenius plot
- Eyring equation
- Q10 (temperature coefficient)
- Van 't Hoff equation

## Notes and references

- <sup>a</sup> <sup>b</sup> Arrhenius equation (<http://www.iupac.org/goldbook/A00446.pdf>) - IUPAC Goldbook definition
- <sup>a</sup> <sup>b</sup> Kenneth Connors, *Chemical Kinetics*, 1990, VCH Publishers
- <sup>a</sup> Arrhenius activation energy (<http://www.iupac.org/goldbook/A00102.pdf>) - IUPAC Goldbook definition
- <sup>a</sup> IUPAC Goldbook definition of modified Arrhenius equation (<http://www.iupac.org/goldbook/M03963.pdf>)
  - Laidler, K. J. (1997) *Chemical Kinetics*, Third Edition, Benjamin-Cummings
  - Laidler, K. J. (1993) *The World of Physical Chemistry*, Oxford University Press
  - Levine, R.D. (2005) *Molecular Reaction Dynamics*, Cambridge University Press

## External links

- Carbon Dioxide solubility in Polyethylene (<http://www.composite-agency.com/messages/3945.html>) - Using Arrhenius equation for calculating species solubility in polymers

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