The Origin and Status of the Arrhenius Equation

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The purpose of this article is to trace the origins of the Arrhenius equation and, in the light of the extensive data on the temperature dependence of reaction rates, assembled in just over a century of experimental endeavor, to assess in what ways its status has changed over the period since it was first proposed.

The systematic study of the kinetics of chemical reactions commenced (1) mid-way through the nineteenth century. From the beginning it was realized that reaction rates showed an appreciable dependence on temperature, but for the next few decades, kinetic studies were directed more toward quantifying the effect of reactant concentrations (2) rather than that of temperature. Several sets of data on the latter effect were obtained in the eighteen-eighties, and in 1889, Svante Arrhenius showed that in each case temperature and rate constant could be correlated by one simple equation (3). It still bears his name and is widely regarded as one of the most important equations in physical chemistry.

Svante August Arrhenius, born in 1859, was initially a student at Uppsala in Sweden. In Stockholm, he began in 1882 the series of measurements which led to his doctoral thesis, *"Recherches sur la conductibilité galvanique des électrolytes,"* in which he proposed his theory of the dissociation of electrolytes in solution. The conclusions of this young researcher were not highly regarded by his examiners and in 1884 the thesis was awarded only a grading of *"non sine laude approbatur,"* though his defense of it was graded *"cum laude approbatur"* (4). As a consequence he strongly felt a need to vindicate his theory, and for some years his researches were devoted to this end, until eventually it gained general acceptance.

Thus, Arrhenius was primarily an electrochemist. His participation in rate measurements was derived from his desire to gain recognition for his theory of electrolytic dissociation and followed the production by Wilhelm Ostwald of kinetic evidence which supported it (5). The kinetic studies of Arrhenius were mostly of systems involving electrolytes and included measurements of the effects of neutral salts. However, even if he were not specially interested in reaction kinetics *per se*, in one paper (6) he put in a plea for the adoption of the term, "specific reaction rate," rather than "rate constant," on the grounds that this parameter was not invariant. Had his view prevailed it would have obviated the use of the apparently self-contradictory term, "time-dependent rate constant," which arises (7) in connection with the behavior of pairs of reactive entities produced in close proximity in solution.

Over the period 1886–88, a travelling scholarship took Arrhenius to the laboratories of the leading physical chemists in Europe, including Ostwald and van't Hoff. The classic paper (3) which is the main focus of attention here, appeared in 1889 under the title, *"Über die Reaktionsgeschwindigkeit bei der Inversion von Rohrzucker durch Saüren."* In the first section, Arrhenius considered eight sets of published data on the effect of temperature on reaction rates and showed (using more currently conventional symbols) that in each case he could choose a value of the constant C such that $k(T_1)$, the rate constant at a temperature T_1, was represented adequately by the equation,

$$k(T_1) = k(T_0) \exp\{C(T_1 - T_0)/T_1 T_0\} \qquad (1)$$

where T_1 and T_0 are the temperature in Kelvin. This was tantamount to showing that the rate constant could be represented as an explicit function of temperature, namely:

$$k(T) = A \exp\{-C/T\} \qquad (2)$$

where $A = k(T_0) \exp(C/T_0)$ and both A and C are constants for the particular reaction.

The reactions which provided these eight sets of data are listed in the table, along with the respective equations put forward by each author to inter-relate rate constant and temperature, where T refers to the Kelvin and θ to the Celsius scale and a, b, and c are constants. In one instance, the equation originally proposed is identical to that of Arrhenius, which inevitably raises the question as to whether the credit for this relationship should be given instead to Jacobus Henricus van't Hoff.

The latter had shown (8) that if one combined with the van't Hoff isochore a kinetic expression for the condition of equilibrium one obtained eqn. (3).

$$\frac{d \ln k_{\mathrm{f}}}{dT} - \frac{d \ln k_{\mathrm{r}}}{dT} = \frac{d \ln K_c}{dT} = \frac{\Delta H^{\circ}}{RT^2} \qquad (3)$$

This suggested that both k_{f} and k_{r}, the rate constants for the forward and reverse reactions, might show a temperature dependence of a form analogous to that of the equilibrium constant, K_c. Accordingly, van't Hoff proposed the equation,

$$\frac{d \ln k}{dT} = \frac{C}{T^2} + B \qquad (4)$$

as the necessary form of the relationships between k and T. However, in seeking to apply eqn. (4) to his experimental results, he admitted the possibility that C might be zero and B

The Data Considered by Arrhenius

Author	Reaction	Temperature range/°C	Authors' Equation
Hood (1885)	Oxidation of Fe II by ClO_3^-	10–32	$k = a \cdot b^{\theta}$
Warder (1881)	Alkaline hydrolysis of EtOAc	4–38	$(a + k)(b - \theta) = c$
Urech (1884)	Inversion of sucrose	1–40	$\cdots$
Spohr (1888)	Inversion of sucrose	25–55	$\cdots$
Hecht and Conrad (1889)	Reaction of ethoxide with MeI	0–30	$k = a \cdot 10^{b\theta}$
van't Hoff (1884)	Decomposition of aqueous chloracetic acid	80–130	$\log_{10} k = \dfrac{a}{T} + b$
van't Hoff (1884)	Decomposition of chloracetate ion in alkaline solution	70–130	$\log_{10} k = a\theta - b$
van't Hoff (1884)	Dehydrobromination of dibromosuccinic acid	15–101	$\log_{10} k = a\theta - b$

non-zero. This leads to the logarithm of the rate constant being a linear function of temperature, which was the relationship used by van't Hoff in respect of two reactions. Thus, Arrhenius was the first to assert that eqn. (2) was generally applicable to all reactions, and the equation is justly named after him, although he did not originate the relationship.

It has been claimed (9) that the Arrhenius equation was first discovered in 1878 by Hood. In that year John J. Hood of Glasgow, Scotland, reported (10) on the reaction of ferrous ions with chlorate in acidic media. His work includes a study of temperature effects over the range 18–22°C leading to the suggestion that the rate increased in proportion to θ^2, which was probably the earliest attempt to describe the effect of temperature. Subsequently, Hood proposed (11) that a better function was b^θ, where the value of the constant b was 1.093. Thus, it does not seem reasonable to assert that the eqn. (2) was discovered by Hood, and even less so to say that he did so in 1878, though he did remark, in one of his papers in 1885, that "the temperature function is of an exponential form." More than one exponential function involving temperature can be envisaged, and since none was actually proposed but a different equation was, claims on Hood's behalf based merely on this remark seem quite unjustified. Consequently, it would appear premature to celebrate the centenary of eqn. (2) until 1989.

But if the equation made famous by Arrhenius was one previously (but not consistently) employed by van't Hoff, the former's reasoning for its validity was quite different from that outlined above. Discussing this in relation to the inversion of sucrose, he proposed (3) that the actual substance with which acids reacted to bring about the inversion process was not simple cane sugar but a substance "active cane sugar" which, to use more contemporary terminology, he envisaged as being a tautomeric form of ordinary "inactive" cane sugar, formed endothermally from it and in rapid equilibrium with it. Thus, using the van't Hoff isochore, he deduced eqn. (5),

$$\frac{d \ln k(T)}{dT} = \frac{q}{RT^2} \qquad (5)$$

where q represented what would now be called the standard molar enthalpy of the "active" form less that of the much more abundant "inactive" tautomer. (A further implicit assumption made here was that the rate of reaction of the "active" form did not vary with temperature.) Thus the empirical constant C in eqns. (1) and (2), with dimensions of reciprocal temperature, was equated to q/R, where q has dimensions of energy per mole.

Although this reaction model did not for long hold sway, as there evolved the more familiar expression for the Arrhenius equation,

$$k(T) = A \exp(-E_a/RT) \qquad (6)$$

the constant E_a was labelled the "activation energy" on the historical basis that it represented, on the Arrhenius model, the energy required to convert the reacting substance into the "active" form.

Ten years after the publication of this classic paper, Arrhenius' equation met and passed another test when Max Bodenstein published (12) his study of the second-order reaction between H_2 and I_2 in the gas phase and showed that, over a range of 200 K, $\log_{10} k$ was a linear function of T^{-1}. Despite this, the equation did not acquire immediate universal acceptance, especially in England. A. G. Vernon Harcourt of Christ Church, Oxford, the subject of a recent article (13) in the JOURNAL OF CHEMICAL EDUCATION and President, 1895–97, of The Chemical Society of London, continued to discuss the effect of temperature in terms of an equation equivalent to the explicit relationship,

$$k(T) = bT^m \qquad (7)$$

where b and m were constants. Of this relationship Harcourt wrote (14) in 1913, "The discovery of this natural law seems

to have attracted less attention than it deserved."

The conspicuous success of the Arrhenius equation with Bodenstein's data has been described (15) as "raising it to canonical status for over half a century." In this process, the development of the two main theories of bimolecular reactions during the opening decades of the twentieth century was undoubtedly relevant, since each theory produced a rate equation containing an exponential expression involving T in a manner analogous to that in eqn. (6). At the same time, it was soon realized that in special circumstances the Arrhenius equation might fail, for example (16), because of concurrent mechanisms for a reaction, with quite different dependences on temperature. Other special circumstances leading to gross non-linearity of an Arrhenius plot were irreversible changes to a catalyst on carrying out a reaction at high temperatures or the approach to an explosion limit.

In later years there also developed among those studying the kinetics of reactions in solution an awareness of a more general shortcoming of the Arrhenius equation in that experimental data, obtained with improved precision and over wider ranges of temperature, showed that in certain cases Arrhenius plots were undeniably curved. Ironically, one of the first reactions for which this was proved was the inversion of sucrose (17). When the rates of such reactions came to be interpreted in terms of the transition state theory formulated in thermodynamic terms (18), the significance of these varying slopes was recognized as a variation with temperature of the enthalpy or the entropy of activation, quantities which, of course, reflect the role of the solvent in the reaction process.

For truly elementary processes, i.e., bimolecular reactions in the gas phase, reservations about the Arrhenius equation were not evident until much later, even though both the main theories of bimolecular reactions (collision theory and transition state theory) predicted that the rate equation should contain, within the pre-exponential factor, T raised to some or other power. Even in the 1950's it was claimed that "the simple Arrhenius equation was satisfactory for almost all known sets of data on individual processes in the gas phase, if due allowance is made for experimental error" (19).

This situation quickly changed as the newer techniques for the study of fast reactions vastly extended the temperature range over which the rate constants of elementary gas reactions could be measured, and as the accumulated data on various reaction systems were subjected to critical evaluation. (In this connection, it is relevant to point out that above 1000 K, RT is both a quantity which cannot readily be neglected and one whose value changes rapidly with reciprocal temperature.) For example, for the reaction, $OH + CH_4 \rightarrow CH_3 + H_2O$, E_a increased from 15 kJ mol^{-1} at 300 K to 32 kJ mol^{-1} at 1000 K (20). However, such data do not invariably conflict with the activated complex theory, despite the appreciable curvature of the Arrhenius plot.

Two further groups of reactions may be listed among these not obeying eqn. (6). For diffusion-controlled reactions in aqueous glasses, the rate constant varies as $\exp\{-E/(T - T_0)\}$, where T_0 is the effective temperature below which there is no molecular mobility in the glass (21). For such reactions, the Arrhenius plot is by no means linear. Also in solution, for several proton-transfer reactions the Arrhenius plots are appreciably curved because at low temperatures the rate does not fall off to the expected extent. This is widely attributed (22) to the contribution from proton tunnelling becoming, at the lower temperatures, far in excess of that from the normal reaction process.

Thus, it is now widely accepted that although, over a limited range of temperature, plots of $\ln k(T)$ against T^{-1} are acceptably linear and may quite reasonably be used for purposes of interpolation, eqn. (6) is not in general obeyed, even by elementary chemical reactions, in the sense that unique constants A and E_a do not exist for each reaction. Thus, it is now

widely recognized that even when the Arrhenius plot is apparently linear, E_a is best regarded as an empirical or a phenomenological quantity, defined as in eqn. (8),

$$E_a = -R \frac{\mathrm{d} \ln k(T)}{\mathrm{d}(1/T)} \qquad (8)$$

and, to minimize misunderstandings, termed "the Arrhenius activation energy" (23). In many instances, such as the cases cited in the previous paragraph, it is a quantity with no (not even approximate) physical significance. Thus, although at the end of his paper, Arrhenius attempted to justify his equation theoretically, it has now been re-located, in the spirit of the opening section of his paper, to that part of the framework of reaction kinetics which deals with the empirical treatment of reaction data.

In 1903, Svante Arrhenius was awarded the third Nobel Prize for Chemistry. The citation did not mention his contributions to reaction kinetics, nor did his Nobel Lecture. Both concentrated on his formidable achievements in electrochemistry. But there can be no doubt that this distinguished scientist was also responsible for a most significant advance in reaction kinetics, for which he is justly commemorated.

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