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Unconventional Applications of the Arrhenius Law

In two recent semi-popular lectures I referred to a few applications of the Arrhenius law that are not included in modern physical-chemistry texts. A number of people have requested further details, and have suggested that the modern student, with his devotion to "relevance," might appreciate the Arrhenius law better if he saw it applied to a process such as the chirping of crickets rather than to some dull chemical reaction. I have therefore collected a few such unconventional processes, and have prepared some diagrams from which the reader may easily prepare slides and transparencies.

In this connection two valuable reviews are an article by Crozier (*1*) and a chapter by Hoagland in "The Voices of Time" (*2*).

Chirping of Tree Crickets

Several workers (*3–5*) have measured rates of chirping of tree crickets (*Oecanthus*) over a range of temperatures, and have found the Arrhenius law to apply. One set of data is plotted in Figure 1; the activation energy is 12.2 kcal/mole.

Creeping of Ants

The velocity of creeping of the ant *Liometopum apiculetum* was measured by Shapley (*6*) over a temperature range, and the results fitted to an empirical equation. Crozier (*1*) showed that a plot of log rate against $1/T$ gave two intersecting straight lines, corresponding to $E = 25.9$ kcal/mole below 16°C and $E = 12.2$ kcal/mole above that temperature.

Flashing of Fireflies

Snyder and Snyder (*7*) measured the frequency of flashing of fireflies, and Crozier (*1*) gives a plot of their data; his plot is reproduced in Figure 2. There is more scatter than for the crickets, but the activation energy is the same, 12.2 kcal/mole.

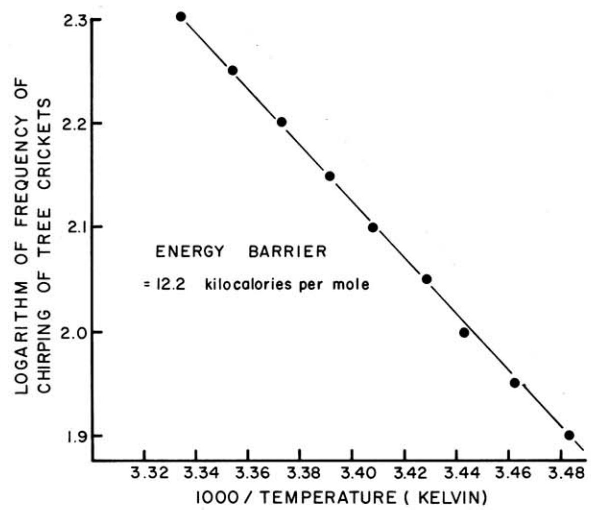

Figure 1. Arrhenius plot for the chirping of tree crickets.

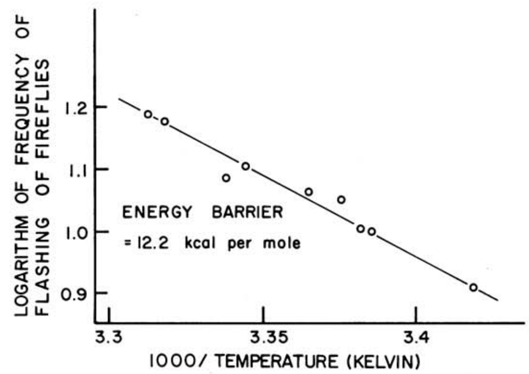

Figure 2. Arrhenius plot for the flashing of fireflies.

Rate of Terrapin Heart Beat

Martin (*8*) made measurement of the frequency of heart beat of a terrapin, under a variety of conditions. Figure 3 shows an Arrhenius plot of one of his sets of observations, which relate to perfusion of the heart with a solution containing 0.08 per cent of potassium chloride. From 18 to 34°C the Arrhenius law is obeyed very satisfactorily, with an activation energy of 18.3 kcal/mole. Below 18°C the apparent activation energy is much higher; here the terrapin was presumably not feeling quite himself, and his heart beat was being controlled by some other chemical process.

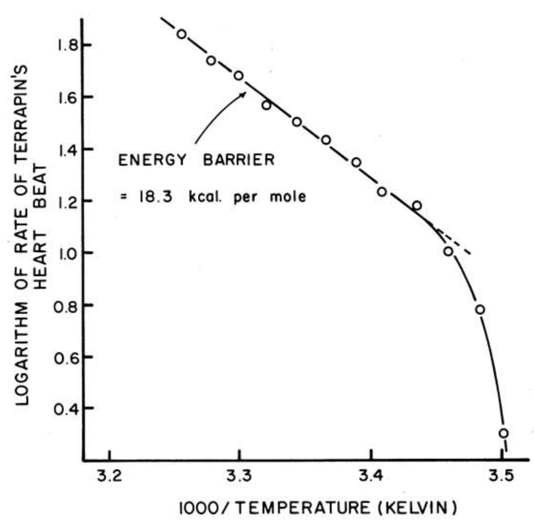

Figure 3. Arrhenius plot for the rate of a terrapin's heart beat.

Alpha Brain-Wave Frequencies

Jasper (*9*) made (but did not reproduce) an Arrhenius plot of the human alpha brain-wave rhythm, and obtained an activation energy of about 7 kcal/mole. Similar plots have been made by others (*2, 10, 11*).

Psychological Rates

Of special interest are some applications of the Arrhenius law to rates of psychological processes. For example, Hoagland (*12, 2*) made studies of patients whose body temperatures varied over a few degrees. He had them count at what they believed to be one a second, and found the rates to be higher the higher the temperature. His Arrhenius plot is reproduced in Figure 4; the activation energy is 24.0 kcal/mole.

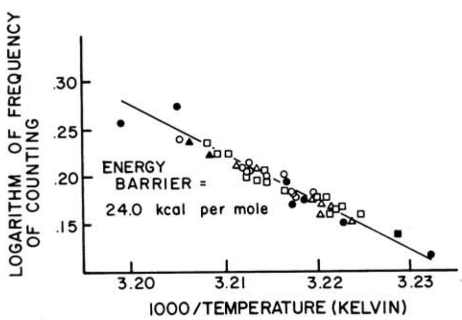

Figure 4. Arrhenius plot for rates of counting.

Our subjective sense of time thus obeys the Arrhenius law, with a substantial activation energy, and Hoagland suggests that it is controlled by an oxidation process in the brain.. Shakespeare (*13*) was aware of this variation in subjective time

> Time travels in divers places with divers persons. I'll tell you who Time ambles withal, who Time trots withal, who Time gallops withal, and who he stands still withal.

The temperature effect, however, escaped him.

A somewhat related investigation was carried out by H. von Foerstler, who measured rates of forgetting over a range of body temperatures. Persons were asked to remember a string of nonsensical syllables, and measurements made of the times for which they could keep this material in their minds. Details have apparently not been published, but Hoagland [ref. (*2*), pp. 323–324] quotes a letter from von Foerstler in which the activation energy is given as 24.0 kcal/mole, exactly the same as for the counting rates; possibly the same chemical process controls both effects.

Comments

Besides being of pedagogical value, the above examples are useful in illustrating two important kinetic principles. The first is that even when a process is quite complex it may, under certain conditions, obey the Arrhenius law within the experimental error. This can arise if, for example, one step in a series of elementary processes is much slower than the rest, but it can also arise in many other ways.

The second principle is that if the energy barrier (activation energy) for a process is greater than about 5 kcal/mole it is almost certain that chemical processes, involving the breaking of primary chemical bonds, are involved. Physical processes, e.g., plastic flow, usually have lower energy barriers. It is therefore extremely likely that all of the processes mentioned above, including the psychological ones, are essentially chemical ones.

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