

1.1 Temperature and the rate of chemical reactions

1.1.1 The Q_{10} relation

The rate of all chemical reactions, cellular or otherwise, is dependent on temperature. The relationship can be expressed most simply in terms of a temperature coefficient, the Q_{10} value, derived from the equation

$$Q_{10} = \left(\frac{K_1}{K_2} \right)^{10/(t_1 - t_2)}$$

where K_1 and K_2 are the velocity constants (proportional to the rates of reaction) found at temperatures t_1 and t_2 respectively. The Q_{10} for a particular reaction is thus an expression of the predicted increase in rate for a 10°C increase in temperature. For most biological reactions the Q_{10} is between 2 and 3: a Q_{10} of 2.5 indicates an increase in reaction rate of 9.6% per $^\circ\text{C}$ increase in temperature.

Unfortunately, in biological systems the value of the Q_{10} itself varies with temperature. For since most metabolic processes virtually cease as the temperature approaches 0°C , the Q_{10} at such temperatures is often high, while as the upper ranges of temperature tolerance are approached, the Q_{10} drops.

1.1.2 The Arrhenius relation

The Q_{10} relationship cannot be explained on the simple basis of increased molecular agitation at higher temperatures, as a 10°C rise in temperature would only cause a 2% increase in the frequency of molecular collisions. However, an explanation for the Q_{10} relationship and a more precise formulation of the influence of temperature on reaction rates can be obtained from the Arrhenius equation:

$$K = A e^{-Ea/RT}$$

where K = velocity constant A = constant relating to molecular collision frequency

Ea = activation energy (see below)

R = gas constant $8.30 \text{ J mol}^{-1} \text{ K}^{-1}$ ($1.98 \text{ cal mol}^{-1} \text{ K}^{-1}$) and T = absolute temperature.

This relationship was first derived empirically by Arrhenius who later explained it by postulating that an 'activated' (high energy) complex lay

on the pathway from reactants to products. Under these circumstances, he argued, only those colliding molecules whose combined energy was in excess of the 'activation energy' (E_a) necessary to form the complex would be able to react (Fig. 1-1).

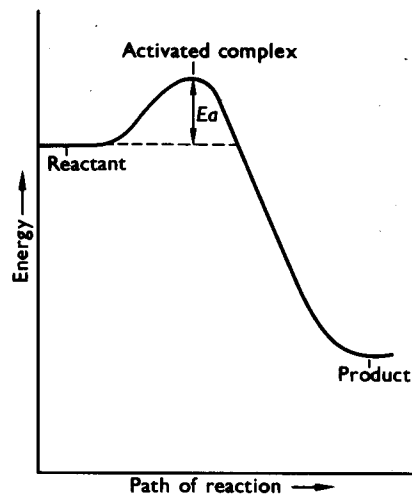


Fig. 1-1 Diagram showing the postulated energy changes during a reaction.

If this is the case, the effect of an increase in temperature can easily be explained. Let us suppose that in a population of colliding molecules at temperature T° (energy distribution being Gaussian) (Fig. 1-2), only a small proportion (diagonal hatching) have a combined energy sufficient to result in a reaction. If the temperature is increased to $(T+x)^\circ$ the energy distribution curve shifts to the right and thus the number of molecules with a combined energy exceeding E_a increases (stippled area). The number of molecules of combined energy exceeding E_a rises in an exponential way as the temperature increases and hence the reaction rate increases exponentially with temperature, as originally shown in the Arrhenius equation.

The Arrhenius equation can be written in logarithmic form:

$$\log_e K = \frac{-E_a}{RT} + A$$

$$\log_{10} K = \frac{-E_a}{2.303R} \cdot \frac{1}{T} + \frac{A}{2.303}$$

Hence a plot of $\log K$ against $\frac{1}{T}$ will give a straight line from whose gradient E_a can be found (slope = $-E_a/R$).

The activation energy (E_a) is measured in joules or calories and is sometimes known as the 'thermal increment', the 'temperature characteristic' or the 'Arrhenius constant' and is in this case often signified by μ . Its value may give an indication of the nature of the rate-limiting enzyme in a complex sequence of reactions.

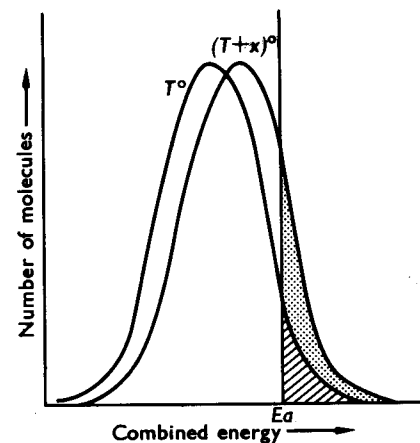


Fig. 1-2 Distribution energy in two populations of molecules at different temperatures.

1.1.3 Enzyme catalyzed reactions

Reactions which rely upon the presence of enzymes are, like all other reactions, dependent upon temperature, as discussed above. However, in the case of enzymes, another temperature related factor must be considered: *thermal inactivation*. Enzymes are very susceptible to thermal inactivation: the higher the temperature, the more rapidly an enzyme is damaged and loses its catalytic properties. The *optimal temperature* for an enzyme-driven reaction is that at which the maximum amount of chemical change is catalyzed. Although an increase in temperature increases the reaction rate, it also shortens the life of the enzyme, so it follows that the optimal temperature must be expressed in relation to the time available for the reaction. Thus, for reactions lasting a few seconds, the optimal temperature may be very high, as thermal inactivation of the enzyme is not important. On the other hand, for reactions lasting much longer, the optimal temperature will be considerably lower since the integrity of the enzyme must be maintained for a greater period of time.

In general, the enzymes involved in metabolic processes in mammals and birds have optimal temperatures in the range 30-40°C at which they are relatively stable, whereas many enzymes found in reptiles, fish, amphibia

and invertebrates have optimal temperatures more appropriate to the animals' commonly prevailing temperatures.

The adaptation of the properties of enzymes to make them compatible with an animal's internal thermal environment is probably largely the result of long-term evolutionary processes. However, some remarkable metabolic changes can be instituted within short periods of time during the process of acclimatization.

1.2 Nomenclature

It is common practice to divide the animal kingdom into 'warm-blooded' and 'cold-blooded' species. However, such a subjective segregation of the birds and mammals simply because the surface of their bodies normally feels warm to the touch is grossly unsatisfactory. The terms *homeothermic* (or *homiothermic*: Greek *homiois* = like) and *poikilothermic* (*poikilos* = various) will be used in this book. Homeothermic forms (birds and mammals) have evolved complex and metabolically expensive means of maintaining the temperature of their body core (see p. 22) within narrow limits. Poikilothermic forms (invertebrates, fish, amphibia and reptiles) have no such mechanisms, thus their temperature generally approximates to that of their environment. Homeothermic animals are sometimes termed *endotherms* since their relatively high metabolic heat production coupled with their low thermal conductance means that their body temperature is largely dependent upon their own oxidative activity. Conversely, poikilothermic animals have a low rate of heat production and a relatively high thermal conductance. Therefore metabolic heat is of less significance than heat from the environment in determining their temperature and they are termed *ectotherms*.

1.3 Animals and their thermal environment

Energy exchange between an animal and its environment is exceedingly complex. At its simplest, it includes on the one hand the exploitation of the chemical energy in the diet and on the other hand the heat exchange with the environment determined by the physical processes of conduction, convection, radiation and evaporation.

Figure 1-3 demonstrates qualitatively the direction of thermal energy exchanges for a homeothermic animal in a moderately warm environment. It is important to remember, however, that in *general* terms very similar considerations will prevail in the case of poikilotherms. This will be discussed in the following chapter.

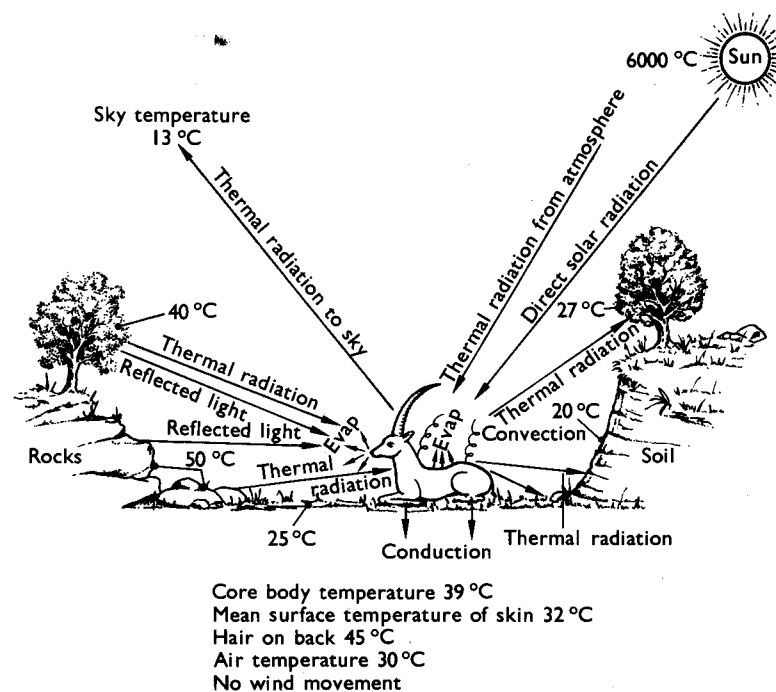


Fig. 1-3 Qualitative representation of the energy exchanges between a homeothermic animal and a moderately warm environment. (From GORDON, M. S. et al. (1968). *Animal Function: Principles and Adaptations*. Macmillan, New York and London).