

Dissection is of value only for the study of the general structure of the proboscis and its various components; the relation of these to each other, especially in the guttered part of the labium, can only be studied in complete series of transverse sections. It is, moreover, misleading to base any generalisation upon the study of a single species of this large order of insects.

B. JOBLING.

Wellcome Entomological Field Laboratories,
Claremont, Esher, Surrey.
June 26.

¹ NATURE, 135, 915; 1935.
² Jobling, *Bull. Ent. Res.*, 1928.

Kinetics of Heterogeneous Catalysis and of Enzyme Action

THE activation of the adsorbate recently described in NATURE¹ was explained by the formation of an adsorption complex $E-S^+$ in which the adsorbed molecule S has gained a quantum of rotation-vibrational energy from the surface molecule E . This complex will be dissociated into $E+S^+$ by the supply to it of a quantity of energy equal to that transferred from E to S in the formation of the complex. If the energy of activation of the free molecules S^+ be the critical increment of one of the reactions of the substance S , that reaction will be promoted by the surface of E molecules.

If now the number of molecules in the available surface be represented by E and the molecular concentration of the reactant (assumed to be constant) be represented by S , the initial velocity of formation of the adsorption complex will be k_1SE and at time t the velocity will have fallen to $k_1S(E-x)$, where x is the number of adsorption complexes which have been formed. The velocity of dissociation of these complexes at time t will be $k_2xe^{-Q_1/RT}$, where Q_1 is the amount of energy transferred from surface to adsorbate in forming the complex. If the concentration of S be constant, a stationary state will be established at which the velocity of the reaction promoted by the surface will be given by

$$r = k_1S(E-x) = k_2xe^{-Q_1/RT}.$$

By the elimination of x we have

$$r = \frac{k_1SEK}{k_1S+K}, \text{ where } K = k_2e^{-Q_1/RT}, \text{ and}$$

$$\log \frac{r}{k_1SE-r} = \log \frac{k_2}{k_1S} - Q_1'/T, \text{ where } Q_1' = Q_1/2 \cdot 303R.$$

If now the substance E be itself adsorbed as a unimolecular layer on a surface C with the formation of the adsorption complex $C-E^+$, the molecules of E will now be activated, the energy of activation being denoted by Q_2 . When these activated molecules adsorb the reactant S there will be formed the adsorption complex $C-E-S^+$, in which the total energy of activation of S^+ is Q_1+Q_2 . This complex will be resolved by the absorption of the energy Q_1 into $C-E+S^+$ and the de-activated catalyst $C-E$ will be reactivated to $C-E^+$ by the absorption of the energy Q_2 . In this manner a reaction with a total critical increment of Q_1+Q_2 can be promoted by an adsorbed catalyst, the total energy being absorbed from the surroundings in two separate and distinct stages.

By analogy with the above simple case a stationary state will be established, if the concentration of the reactant S be maintained constant, the reaction velocity being given by

$$r = k_1S(E-x-y) = k_2xe^{-Q_1/RT} = k_3ye^{-Q_2/RT}.$$

By the elimination of x and y we obtain the same expression as before, namely:

$$r = \frac{k_1SEK^1}{k_1S+K^1};$$

$$\text{but } K^1 = \frac{k_2k_3e^{-(Q_1+Q_2)/RT}}{k_3e^{-Q_1/RT} + k_2e^{-Q_2/RT}}.$$

$$\text{Since } \frac{e^{-(Q_1+Q_2)/RT}}{e^{-Q_1/RT} + e^{-Q_2/RT}} = \frac{e^{-Q_2/RT}}{1 + e^{(Q_1-Q_2)/RT}},$$

the exponential term has a maximum value of $\frac{1}{2}e^{-Q_2/RT}$ when $Q_1=Q_2$. If $Q_1=Q_2$, there will be two exactly similar processes taking place under identical conditions and hence it is legitimate to assume that $k_2=k_3$. On these two assumptions the expression for the reaction velocity is much simplified and may be written in the forms

$$r = \frac{k_1SE \times 0.5k_4e^{-Q_3/RT}}{k_1S + 0.5k_4e^{-Q_3/RT}}$$

$$\text{and } \log \frac{r}{k_1SE-r} = \log \frac{k_4}{2k_1S} - Q_3'/T,$$

where $k_4=k_2=k_3$, $Q_3'=Q_3/2 \cdot 303R$ and Q_3 is one half the total critical increment of the reaction promoted by the adsorbed catalyst.

It may be suggested that enzyme reactions are of this two-stage activation type, since there is little doubt that the enzyme is adsorbed on the co-enzyme. The virtue of such an enzyme system is due to the fact that it is able to promote within a living organism a reaction the critical increment of which is so large that it cannot otherwise take place with measurable velocity at the temperature of that organism.

The equations and the specificity of enzyme systems will be described more fully in a further communication, but one important conclusion may be stated. Neither the critical increment of a heterogeneous reaction nor that of the de-activation of an enzyme system can be determined directly from measurements of the reaction velocity at two different temperatures, since it is $\log \frac{r}{\text{const.}-r}$ and not $\log r$ which is linear with the reciprocal of the absolute temperature.

E. C. C. BALY.

University,
Liverpool.
June 11.

¹ NATURE, 136, 28, July 6, 1935.

Shape of the NO₂ Molecule

IN a recent paper¹, one of us has shown that the available data² on the contours of the infra-red bands of NO₂ are most consistently interpreted by a ring-like structure for the molecule, with the O-N-O angle approximately 60°. The theory of directed valency was employed there to provide a possible electronic configuration for this model. Closer investigation of the electronic structure, however,