THE DISSIPATION REACTION IN THE ASSIMILATION PROCESS I

by

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I. GENERAL CONSIDERATIONS

Notwithstanding the great amount of work dedicated to the assimilation process and its kinetics, one does not find in the literature a general analysis of the process from the viewpoint of theoretical chemical kinetics. All considerations on the subject start from special assumptions about the kind of molecules involved in different reactions, whereas, as will be shown, it is possible to make a kinetical analysis without referring to any special model. Such an analysis has the advantage that, so far as it really is complete, the results are completely general, which means that in some way or another it contains every special model. On the other hand, it has the disadvantage of not giving by itself any information about the exact mechanism of assimilation. In this respect the situation resembles that of thermodynamics in chemistry. In the next paper, however, we shall show that, as in thermodynamics, very little outside information suffices for the general considerations to lead to special conclusions.

II. THE BASIC REACTIONS

Without making any special assumptions one may state that every reaction in the assimilation process necessarily belongs to one of the following classes:

a. Assimilation reactions (types 1 and 2);
b. Saturation reactions (type 3);
c. Dissipation reactions (types 4 and 5).

The assignment of types to definite reactions depends to a certain extent on the measured quantities. We shall consider the following examples of measurable quantities: the intensity of incident light; the uptake of CO_2; the production of O_2; the production of "(CH_2O)"$_n$; and the concentration of excited chlorophyll (from the fluorescence)[1].

a. We call assimilation reactions those reactions which promote the assimilation. When the uptake of CO_2 is measured, they are the reactions which use the energy of the incident light either to react with CO_2 immediately or to produce new molecules or excited states which immediately or after a chain of intermediate states can bring about the consumption of a CO_2 molecule. When the production of O_2 is measured, the assimilation reactions are those reactions which use the energy of the incident light indirectly or immediately for the production of oxygen, and when the production of (CH_2O) is

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* Most of the work on this article was done when the author was engaged in the laboratory of Philips Gloeilampenfabrieken, Eindhoven.

measured the same holds for this product. Among the assimilation reactions we have to discriminate between two types: type 1 is monomolecular (first order) in the particles carrying light energy, type 2 is polymolecular (of higher order) in this respect. The idea of this definition is this: we know that incident light is absorbed in quanta; further, we know, that for the reduction of one CO_2 molecule more than one quantum is needed (see for instance[2, 3]: the quanta are about 42 Kal/mol. whereas the reduction of one CO_2 molecule requires at least 112 Kal/mol.). So besides reactions whereby the energy of the excited chlorophyll is given to the next participant in the reaction chain, sooner or later there must appear a reaction in which the energy originating from one absorbed quantum is transferred to a particle that has already energy which originated from another quantum of light. Such a reaction we call polymolecular, or of higher order in quanta. An example of a reaction of type 1 is

$$c^* + A_0 \rightarrow A_1^* + c \quad \text{with } v_1 = k_1 c^* A_0 \tag{1}$$

where c^* may be any particle that has received energy from a quantum of light (for instance, an excited chlorophyll molecule), A_0 is an acceptor of the energy before acceptance, A_1^* the acceptor after acceptance, and c is the initially excited particle after delivery of the energy. In the formula for V, the speed of the reaction, the symbols of the molecules stand for their concentrations. An example of a reaction of type 2 is:

$$2 A_1^* \rightarrow A_2^{**} \quad \text{with } v_2 = k_2 A_1^{*2} \tag{2}$$

The number of stars indicates from how many quanta the energy ultimately originates. When the number of stars on one particle increases we have a reaction of type 2 and when it remains constant the reaction is of type 1. For instance,

$$A_2^{**} + B \rightarrow 2 A_1 + C^{**} \text{ type 1}$$
$$D^{**} + E^* + F \rightarrow G^{***} + H \text{ type 2, and so on.}$$

The end-product of the assimilation chain, "CH_2O" or O_2, carries 4 stars or more, so somewhere in the chain there must be one or more quanta-collecting reactions (type 2).

b. Saturation reactions are reactions that are responsible for saturation of the reaction at high light intensities. It is assumed that saturation is caused by the fact that one species of the reacting molecules has to be absorbed by the assimilating system at a restricted number of places. This gives a special equation for the speed of the reaction; for instance,

$$B \rightarrow A_0 \quad \text{with } v_3 = k_3 B\, (N - A_0) \tag{3}$$

where B is the molecule in question before absorption; A_0, after absorption; and N, the number of "places", that is, the maximum number of molecules A_0 that can be absorbed at a time. This representation of the saturation phenomenon involves, of course, an assumption. It seems to be, however, the most simple and a very probable representation, and the argument will not be changed appreciably when we introduce a different type of saturation reaction. According to (3), the speed of the reaction never exceeds $V_{max} = k_3BN$. When we throw more than k_3BN quanta per second on the cell the surplus has to be dissipated. From this we see that a saturation reaction is always accompanied by a dissipation reaction. However, saturation reactions are distinctly different from dissipation reactions, since the former contribute essentially to the assimilation process, whereas the latter disperse energy that could have been used for assimilation.

c. Dissipation reactions are reactions by which energy originating from the absorbed light becomes useless for promoting assimilation. For instance,

$$c^* \rightarrow c + \text{heat with } v_4 = k_4\, c^* \tag{4}$$

Like assimilation reactions, dissipation reactions can be monomolecular in light quanta (type 4), which means that in one molecular process the energy of only one particle is dissipated; or polymolecular in quanta (type 5), when a meeting of more than one energy-carrying particle brings about the dissipation. For instance,

$$B^{**} + C^* \rightarrow D + E \text{ with } v_5 = k_5\, B^{**}C^* \tag{5}$$

as in the possible reaction:

$$HCOOH^{**} + 2\,OH^* \rightarrow CO_2 + 2\,H_2O \qquad \text{(type 5)}$$

(When formic acid is an intermediate product in the reaction chain, we very probably have to assign 2 stars to it, since it lies halfway between zero-star CO_2 and four-star CH_2O. Also, when we measure the assimilation as oxygen production, perhaps OH is a first one-star product. This type of polymolecular back-reactions appears in the analysis of ORNSTEIN et al.[4]).

Among the dissipation reactions of type 4 we discriminate between type 4a and type 4b since, as will be shown, these types influence the assimilation curve in different ways. Reaction 4a is a reaction of type 4, starting from a compound that reacts monomolecularly (type 1) in the assimilation chain; while reaction 4b is a reaction of type 4, starting from a compound that reacts polymolecularly (type 2) in the assimilation chain. We could discriminate similarly between reactions 5a and 5b, but we shall not go into such detail, since we may suppose reactions of type 5 rare.

III. DERIVATION OF THE ASSIMILATION EQUATION

The following is a complete set of reactions of all types:

$$\begin{array}{lllr}
c^* + A_0 & \rightarrow A_1^* + c & \text{with } v_1 = k_1 c^* A_0 & (1) \\
2\,A_1^* & \rightarrow A_2^{**} & \text{with } v_2 = k_2 A_1^{*2} & (2) \\
B & \rightarrow A_0 & \text{with } v_3 = k_3 B(N - A_0) & (3) \\
c^* & \rightarrow c + \text{heat} & \text{with } v_{4a} = k_{4b} c^* & (4a) \\
A_1^* & \rightarrow A_0 + \text{heat} & \text{with } v_{4a} = k_{4b} A_1^* & (4b) \\
A_1^* + A_2^{**} & \rightarrow 3\,A_0 + \text{heat} & \text{with } v_5 = k_4 A_1^* A_2^{**} & (5)
\end{array}$$

The essence of our argument is:

1. that such a set of reaction equations is sufficient to describe the kinetics of assimilation; and

2. that every molecular model of the assimilation process must, at least in principle, contain reactions of the types described here.

We cannot say that this set of equations is the most general form for a description of the kinetics of the process, since there may be more than one reaction of every type, and the sequence of the different reactions will also have some influence. However, the sequence appears to be only of secondary importance, and, as a first approximation, it is only the slowest assimilation reaction and the fastest dissipation reaction that count. To be more exact, it is not the reaction with largest k_4 but the reaction for which

$\frac{k_4^i}{k_1^i}$ is largest, where i denotes the i-th step in the chain. Qualitatively at least, nothing new would be added by a more complete treatment, and it is only the qualitative features of the problem that can be discussed up to now.

We shall now proceed to derive a general assimilation equation and in paragraph 5 apply our general considerations to certain molecular models.

For simplicity we first omit all plural-quanta reactions (types 2, 4b and 5), so our whole assimilation chain consists of one assimilation reaction (1), one saturation reaction (3), and one dissipation reaction (4a). In this simplified case A_1 is at once the „product", so $\frac{dA_1^*}{dt} = v_1 = V$, the speed of the assimilation

$$v_1 = k_1 c^* A_o = V \qquad (I)$$

Further, $\frac{dc^*}{dt} = I - v_1 - v_{4a} = 0$, where I is the intensity of the incident light, so

$$I - V = k_{4a} c^* \qquad (II)$$

and $\frac{dA_o}{dt} = v_3 - v_1 = 0$, and therefore

$$k_3 B (N - A_o) = v_1 = V \qquad (III$$

When we write (III) in the form $k_3BN - k_3BA_o = V_{max} - k_3BA_o = V$, we can take A_o from this and c^* from II and substitute both in (I) to find

$$V = k_1 \frac{I - V}{k_{4a}} \cdot \frac{V_{max} - V}{k_3 B} = \frac{k_1}{k_{4a} k_3 B} (I - V)(V_m - V)$$

$$\text{or } CV = (I - V)(V_m - V)$$

$$\text{or } V = I - \frac{CV}{V_m - V} \quad (X) \qquad \text{with } V_m = k_3 BN$$

$$\text{and } C = \frac{k_3 k_{4a} B}{k_1}$$

This equation, derived from a very simple reaction "chain", shows already most of the characteristics of the experimental assimilation curve (fig. 1). It is a hyperbola starting from the origin with a slope $\frac{V}{I} = \frac{v_1}{v_1 + v_{4a}} = \frac{k_1 N}{k_1 N + k_{4a}}$ and approaching asymptotically to the value $V = V_m$ for large I. Whether the curve remains straight for some distance or soon bends depends on the value of C; that is, principally upon the ratio of the dissipation constant k_{4a} and the assimilation constant k_1. When C is very small V equals I up to V-values near to V_m; only when V is very nearly equal to V_m does the second term in (X) become important, and from there on V remains very nearly equal to V_m. When C is large the curve bends soon. It follows from the experimental curves that C is generally very small; they are rather "straight" in any case, but owing to decrease of intensity in a suspension of cells the experimental curves are always more curved than the theoretical curve for one "apparatus".

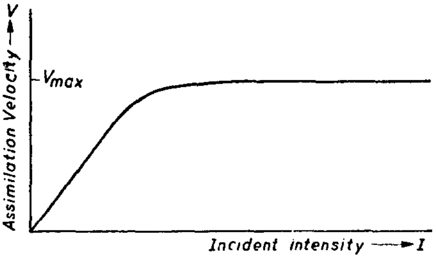

Fig. 1. Assimilation curve, when quanta-collecting reaction (2) is very rapid (eq. X)

So far we have omitted the bimolecular reaction (2) $2\,A_1^* \rightarrow A_2^{**}$ and the appropriate dissipation reaction (4b) $A_1^* \rightarrow A_0$ + heat. When we add these two reactions formula X is only slightly changed:

$$V = V_{\max} - \cfrac{C}{\cfrac{I}{V + qV^{\frac{1}{2}}} - 1}$$

or

$$V + qV^{\frac{1}{2}} = I - \frac{C(V + qV^{\frac{1}{2}})}{V_m - V} \qquad \text{(Y)}$$

with $V_{\max} = k_3BN \qquad C = \frac{k_3k_{4a}B}{k_1}$ and $q = \frac{k_{4b}}{k_2^{\frac{1}{2}}}$

(Y) is identical with (X) when $qV^{\frac{1}{2}}$ is negligible compared with V. When q is very small (so small that $qV^{\frac{1}{2}}$ is negligible for all measurable values of V) (Y) yields the same assimilation curve (fig. 1); when q is somewhat greater, this becomes perceptible in the regions of smallest V, where the term $qV^{\frac{1}{2}}$ bends the assimilation curve as shown in fig. 2 (part a). This is the S-shaped curve as found in experiments on bacteria[6, 7], and which is discussed by WOHL[8] and WASSINK *et al.*[7].

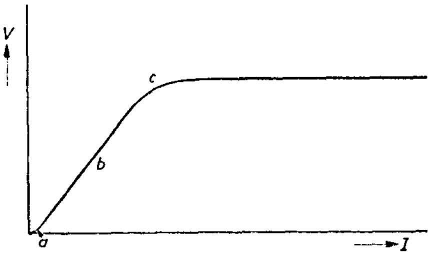

Fig. 2. General type of assimilation curve with quanta-collecting reaction just perceptible (eq. Y)

If we complete the set of reactions by adding type 5 (high order dissipation reactions), nothing new is added since these reactions have their greatest influence at higher intensities where dissipation always dominates. So we conclude from our argument *that the S-shaped curve is the most general form of assimilation curve;* indeed, more general than the straight curves which are more commonly found by experiment. The S-shape is always present, since for very low light intensities there must be a concentration of light quanta (for instance, one quantum per cell) where the monomolecular dissipation reaction (4b) dominates over the corresponding polymolecular assimilation reaction. However, the S-shape becomes imperceptible when q is very small, which means when the ratio of dissipation to assimilation constant $(q = \frac{k_{4b}}{k_2^{\frac{1}{2}}})$ is very small, so small that the region where $V = q^2$ is not measurable.

Now it is clear that dissipation constants must be small, otherwise the complicated mechanism of assimilation would not be possible at all with reasonable efficiency. On the other hand, one cannot expect the various „excited" states between CO_2 and H_2CO to be all very stable. It is true that apparently certain stable intermediate products exist, since cells can behave differently according to their „reduced state", depending on their pre-treatment*; but for a chemist it is difficult to believe that *all* the stages in the chain, the one-quantum, the two-quantum, and the three-quantum-states, would be stable. Especially for the odd states (1 and 3 quanta) is it difficult to devise stable compounds. Besides, the phenomenon of saturation of assimilation without accumulation of stable compounds proves that real dissipation reactions exist.

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* For this remark I am indebted to Dr. WASSINK.

Anyhow, the degree of stability can always be accounted for by a suitable choice of k_{4b}, consequently the above considerations are always valid.

IV. DERIVATIÒN WITH DIFFERENT CHAINS

As stated above the general results of our argument are not influenced by such changes in the chain as adding more reactions of the same type or changing the sequence of the reactions. To explain this we may consider two different types of chains.

First, we take the case of a dissipation reaction competing with the saturation reaction (3) in such a way that the N places on the absorption system are occupied either by the regular acceptor A_0 or by the dissipating acceptor A_0' (Accents indicate the new reaction $4_a'$). We find:

$$\begin{array}{lll}
c^* + A_0 \rightarrow A_1^* + c & v_1 = k_1 c^* A_0 & (1) \\
c^* + A_0' \rightarrow \text{heat} & v_4' = k_4' c^* A_0 & (4') \\
c^* \rightarrow c + \text{heat} & v_{4a} = k_{4a} c^* & (4a) \\
B \rightarrow A_0 & v_3 = k_3 B\,(N - A_0 - A_0') & \\
B' \rightarrow A_0' & v_3' = k_3 B'(N - A_0 - A_0') &
\end{array}$$

For simplicity we omit quanta-collecting reactions.

Straightforward calculations give for this system an assimilation curve as in fig. 1 (without the S-shape, because quanta-collecting reactions are omitted) that can be considered as the sum of two "simple" assimilation curves, one for assimilation and one for dissipation, according to (4').

Next, we consider a case where saturation is not caused by the limited supply of A_0 but by the restricted number of places available to A_2^{**}, the first bimolecular product:

$$\begin{array}{llll}
c^* + A_0 \rightarrow A_1^* & \text{with } v_1 = k_1 c^* A_0 \ (A_0 \text{ present in abundance}) & & (1) \\
2A_1^* \rightarrow A_2^{**} & \text{with } v_2 = k_2 A_1^{*2}\,(N - A_2^{**}) & (2) & \\
A_2^{**} \rightarrow A_3^{**} & \text{with } v_1' = k_1' A_2^{**} & (1') & \\
c^* \rightarrow c + \text{heat} & \text{with } v_{4a} = k_{4a} c^* & (4a) & \\
A_1^* \rightarrow A_0 + \text{heat} & \text{with } v_{4b} = k_{4b} A_1^* & (4b) &
\end{array}$$

For this chain we find an equation somewhat different from (Y):

$$I_{\text{eff}} = V + q\sqrt{k_1'} \cdot \sqrt{\frac{V}{V_m - V}} \qquad (Z)$$

with $I_{\text{eff}} = \dfrac{k_1}{k_1 + k_{4a}}\, I \qquad q = \dfrac{k_{4b}}{\sqrt{k_2}}$ and $V_m = Nk_1'$.

When the dissipation constant k_{4b} is small, this equation represents a curve like fig. 2 (eq. Y) characterised by 3 parts:

part *a*, curved tangential to the X-axis in O for $V < \dfrac{q^2 k^1_{1b}}{V_m}$;

part *b*, straight part of the equation $V = I_{\text{eff}}$; and

part *c*, curved and approaching asymptotically the line $V = V_m$ for $V_m - \dfrac{q^2 k_1'}{V_m} < V < V_m$.

Therefore, though equation (Z) appears rather different from (Y), owing to the peculiar circumstance that we have chosen a chain in which the product that causes the

S-shape is identical with the product that accumulates when saturation begins, nevertheless the same type of curve results.

V. COMPARISON WITH MOLECULAR MODELS

In paragraph 1 it was stated that our analysis is concerned with only the type of reaction and assumes nothing special about the reacting molecules. If the analysis is general, every reaction of any proposed reaction scheme must belong to one of our types.

For instance, some of the so-called back-reactions, by which molecules lose one or more of their quanta, belong to our dissipation reactions. Also, the reactions with intracellular donors of MULLER[8] (see also par. 12 of [7]) have to be considered as dissipation reactions when the assimilation is measured as uptake of CO_2 or as production of O_2, but as assimilation reactions if production of "CH_2O" is measured.

The mechanism of GAFFRON and WOHL[10] assumes closed units of about 2000 chlorophyll molecules. When a quantum falls on such a unit that has lass than 4 quanta, the quantum is used for assimilation; when a quantum falls on a unit that has collected 4 quanta and is in its BLACKMAN period, the quantum is dissipated. From such a model it follows at once that when the cell works at half its maximum speed, one half of the units are permanently occupied by 4 quanta, one half of the incident quanta bring lost, so that the yield of the assimilation, V, is half its original value. In the same way, for $V = 3/4\ V_{max}$, I V/I is three-quarters its initial value. Thus we find the strongly curved graph b in fig. 3 according to the equation

$$I = \frac{KV}{V_m - V} \quad \text{(W)}$$

SMITH[11] showed that experimental curves are decidedly "straighter" than equation (W) predicts (exp. fig. 3a, W: fig. 3b). It appears that Nature works more efficiently than according to the theory of GAFFRON and WOHL. When a quantum of light finds the nearest reduction place occupied, it travels to the next one and so on, since apparently (see the straight lines of fig. 3) the dissipation constant k_4 is small enough to give the quantum (or whatever excited particle migrates) a fair chance of surviving several "deceptions" without losing the possibility of contributing to an assimilation chain.

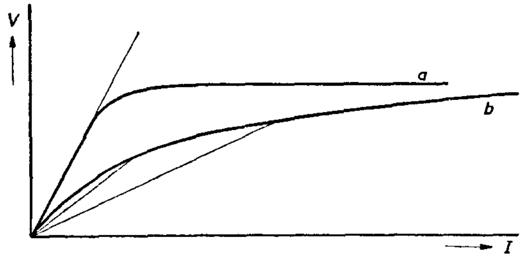

Fig. 3. Curve b of GAFFRON AND WOHL compared with experimental curve a

Theoretically, GAFFRON and WOHL made the mistake of not considering dissipation as a definite reaction with a speed depending upon a reaction constant and the concentration of the reacting particles:

$$v_{4a} = k_{4a}c^{\star}.$$

The concept of an assimilation reaction that always proceeds when there are four quanta on a unit and a dissipation reaction that always proceeds when there are more than 4 quanta is incompatible with chemical kinetics, which requires a certain chance for both reactions, numerically accounted for by reaction constants.

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The unit concept of GAFFRON and WOHL served to explain saturation. However, we have shown that saturation can be easily accounted for by the restricted number of places available to a certain reactant. So the result mentioned by GAFFRON and WOHL that the same number of assimilation centres is calculated from the experiments of ARNOLD and EMERSON with intermittent light on one hand, and from V_{max} in continuous light in combination with the experimental BLACKMAN time on the other, follows readily from our formulae. In fact, the BLACKMAN time is $\tau = {}^1/k_3B$, the number of assimilation spots is N (see our eq. 3), while V_{max} according to GAFFRON and WOHL is N/τ and according to our equations it is $k_3BN = N/\tau$ also.

It is doubtful whether WOHL's attempt to save the unit concept by introducing the idea of the kinetic unit has any meaning. We agree with DORRESTEIN et al.[12] that the only sensible meaning for the kinetic unit is that of a reaction area. But the concept of a unit implies boundaries (more or less permeable), whereas the chance for reaction may decrease rapidly with increasing distance from the absorption spot, but it does not change discontinuously or vanish completely anywhere.

We shall not consider all the many proposed mechanisms of photosynthesis in detail. A good survey of the literature up to 1935 is given by BURK and LINEWEAVER[13], with an attempt to include the facts known in 1935 in a general minimum mechanism. From our point of view their mechanism is a special one. They consider reactions of type I only, whereas their only dissipation reaction (the back-reaction of the light reaction) is supposed negligible, so they do not account for dissipation at all. However, as we have shown, the competition between assimilation and dissipation is an essential feature of the assimilation process. The same problem arises in the theory of fluorescence of crystals. Here the mechanism of dissipation is definitely more complicated from the theoretical point of view than the mechanism of fluorescence[14, 15, 16]. The problem of why some crystals are fluorescent is submerged in the more difficult problem of why not all crystals are fluorescent. It is possible that we have similarly to investigate dissipation before we can hope to understand assimilation.

SUMMARY

In a description of the kinetics of the assimilation process, besides different types of assimilation reactions, dissipation reactions also must be considered. The sequence of these reactions is of secondary importance. With the aid of such reactions, part of which may coincide or be without influence, a general equation for the assimilation curve is derived which is in agreement with experiment. It is shown that the theory of the assimilation unit of GAFFRON and WOHL is unsatisfactory and also that it does not agree with experiment. S-shaped assimilation curves are shown to be more general than straight curves, the absence of the S-shape being due to a special relation between certain reaction rate constants. In our considerations only the order of the reactions is of importance, and no *a priori* assumptions are made with respect to the molecules involved.

RÉSUMÉ

Dans l'étude cinétique du processus de l'assimilation, on doit considérer, à côté des différentes réactions d'assimilation, les réactions de dissipation. La suite de ces réactions ne présente qu'une importance secondaire. Tenant compte de ces réactions, dont certaines peuvent coincider ou ne pas avoir d'influence, on établit une équation générale permettant de représenter l'assimilation par une courbe en accord avec les données expérimentelles. Il apparait que la théorie de l'assimilation émise par GAFFRON et WOHL ne s'accorde pas avec les faits. L'assimilation est plus généralement représentée par des courbes en S que par des droites, l'absence de la forme en S étant due à un rapport spécial entre certaines constantes de vitesse de réaction. Il apparait ici que seul l'ordre des réactions a de l'importance, alors qu'aucune hypothèse *a priori* n'est faite concernant la nature des molécules mises en jeu.

ZUSAMMENFASSUNG

Bei der Beschreibung der Kinetik des Assimilationsprozesses müssen ausser den verschiedenen Typen von Assimilationsreaktionen auch Dissipationsreaktionen berücksichtigt werden. Die Reihenfolge dieser Reaktionen ist von sekundärer Bedeutung. Mit Hilfe solcher Reaktionen, von denen ein Teil möglicherweise zusammenfällt oder ohne Einfluss sein kann, wird eine allgemeine Gleichung für die Assimilationskurve abgeleitet, die mit dem Experiment übereinstimmt. Es wird gezeigt, dass die Theorie des ,,assimilation unit" von Gaffron und Wohl unbefriedigend ist und auch mit den experimentellen Resultaten nicht übereinstimmt. S-förmige Assimilationskurven sind, wie gezeigt wird, allgemeiner als gerade Kurven, und die Abwesenheit der S-Form wird durch eine besondere Beziehung zwischen gewissen Reaktionsgeschwindigkeitskonstanten verursacht. Bei unseren Betrachtungen ist nur die Ordnung der Reaktionen von Bedeutung, und keinerlei *a priori* Annahmen in Bezug auf die teilnehmenden Moleküle werden gemacht.

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