Radiation and vital phenomena

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Baas

L. B. BECKING

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PROEFSCHRIFT

TER VERKRIJGING VAN DEN GRAAD VAN
DOCTOR IN DE WIS- EN NATUURKUNDE
AAN DE RIJKS-UNIVERSITEIT TE UTRECHT,
OP GEZAG VAN DEN RECTOR-MAGNIFICUS
Dr. J. A. C. VAN LEEUWEN, HOOGLEERAAR
IN DE FACULTEIT DER GODGELEERDHEID,
VOLGENS BESLUIT VAN DEN SENAAT DER
UNIVERSITEIT, TEGEN DE BEDENKINGEN
VAN DE FACULTEIT TE VERDEDIGEN OP
DINSDAG DEN 11DEN OCTOBER 1921, DES
NAMIDDAGS TE VIJF UUR, DOOR

LOURENS GERHARD MARINUS
BAAS BECKING

GEBOREN TE DEVENTER

DRUKKERIJ F. W. HAJER — UTRECHT — 1921

AAN MIJNE MOEDER

Hooggeleerde Weevers, vòòr alles is het aan U dat ik een woord van oprechten dank wil richten. Uw onderwijs heeft de verdere richting van mijn studie bepaald.

Elk Uwer, Hoogleeraren in de Plant- en Dierkunde aan deze Universiteit, is een karakteristieke factor in mijne opleiding geweest.

Hooggeleerde Nierstrasz, gij toonde mij de kracht van de intuitie en de spot, twee niet te onderschatten factoren van het wetenschappelijk onderzoek, waar de laatste afbreekt dat wat de eerste te veel heeft uitgebouwd.

Hooggeleerde Jordan, ook Uw invloed op mijn ontwikkeling is meer in de richting van het denken zelve dan op de verrijking van feitenkennis gericht geweest. De wijsgeerige grond van de biologie zal daardoor steeds mijn levendige belangstelling bezitten.

Ook aan U, Hooggeleerde Westerdijk ben ik veel verplicht, ofschoon ik slechts korten tijd het voorrecht heb gehad onder Uw leiding te werken. Uw krachtig voorbeeld heeft steeds mijn eerbied afgedwongen.

Hooggeleerde Pulle, het werk eertijds onder Uw leiding verricht is voor mij een aansporing geweest om tijdens mijn verblijf in het buitenland de embryologie der Eusporangiaten tot onderwerp van onderzoek te maken. Uw vriendelijke hulp zal mij steeds in herinnering blijven.

Hooggeleerde Went, Hooggeachte Promotor! Moge het feit dat ik de eerst mogelijke gelegenheid heb aangegrepen om naar Nederland terug te keeren teneinde onder Uw leiding te promoveeren, genoegzaam uitdrukken welke gevoelens mij jegens U bezielen.

INTRODUCTION

ENERGY BALANCE OF VITAL PROCESSES.

Radiation is known to have a powerful effect on the many reactions, chemical and physical, which accompany — and possibly constitute — the phenomenon called life.

The maintenance of life on this planet is entirely dependant on a light-reaction; the synthesis of carbohydrates in the green leaf. The oxygen supply of the tissues in higher animals, that most important function of the haemoglobin, is influenced by radiation.

Zwaardemaker[1]), in a series of papers on physiological energetics, points out that the general form of the first law of thermodynamics; total energy equals heat exchange minus external labour, has no explicit physiological meaning. In order to obtain a more serviceable form of the first law he analyzes the total energy change in its different components; the last factor in this series being the radiant energy. This radiant energy can not be neglected in the equation, especially in the energy balance of green plants, and Zwaardemaker goes as far as to remark that:

> "Eine wirklich biologische Energetik hätte sogar letztere der Reihe von Energieformen (i. e. radiant energy) als erstes Glied an die Spitze zu stellen. Leider befindet sich das theoretische Studium hier noch ganz im Anfang und dürfen wir in unseren Formeln die Lichtenergie nur pro memoria führen".

Since all vital energy can be derived from radiant energy it seems unwarranted to exclude, or even to mention "pro memoria" this form of energy. In this paper radiation will be considered as a factor in the energy balance of the organism.

STATEMENT OF THE PROBLEM.

A living cell is an energy transformer. The diversity of its intricate mechanism allows for many different energy transformations. The transformations in which chemical and thermal energies are concerned can be studied with the help of thermodynamics and thermochemistry. A study on such processes has been carried out in several cases.

The transformations in which radiant energy is concerned are imperfectly known. A complete energy balance for the radiant energy of a physiological reaction has never been worked out.

Inasmuch as a living cell can be compared with a closed opaque container it may be assumed that a certain amount of heat radiation of any frequency is always present within the cell. Therefore every chemical reaction takes place in a bath of radiation.

Heat, the effect of molecular movement; radiation, the effect of electronic movement are coexisting phenomena accompanying every chemical (and physiological) reaction.

It is not improbable that in this bath of heat radiation there is radiation of a certain frequency, which frequency shows a definite relation to an electronic frequency within the chemical system. According to the principle of resonance, the chemical system would be *influenced* in that case by the radiation of that frequency.

Now Perrin[2]) advocates the idea that the radiant energy is the cause of the combination and dissociation of the molecules in every chemical reaction. The immediate consequence of this hypothesis would be that vital phenomena were caused by radiation.

Aware of the fact that Perrin's hypothesis has been the subject of severe criticism, his idea will be taken nevertheless as a working hypothesis and it will be assumed that *every physiological reaction is influenced, and possibly caused, by radiation. Every physiological reaction is accompanied by an absorption as well as by an emission of radiation.*

On this basis it will be tried to derive, at least partly, the energy balance of certain physiological processes. It must be kept in mind that the deductions from this unproven hypothesis are to be considered as a preliminary attempt to connect radiation-phenomena with thermodynamics. No claim will be made as to the absolute value of the statements expressed in the following chapters.

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¹) Zwaardemaker. Ergeb. d. Phys. V, **108**, 1906.

²) Perrin. Ann. de Phys. XI, **31**, 1919.

SYMBOLS

The symbols used in this paper are the usual letters. In a few cases, however, the symbols used by Arrhenius, Nernst and Perrin disagree. Therefore a list of the symbols used in this paper will be given below.

CONSTANTS

h = Planck's constant = $6{,}415 \,.\, 10^{-27}$ ergs/sec.
a = Radiation constant = $7{,}28 \,.\, 10^{-15}$.
k = Boltzmann constant = $1{,}34 \,.\, 10^{-16}$ ergs/sec^2 degree.
N = Avogrado constant = $6{,}8 \,.\, 10^{23}$.
R = gas constant = $N \,.\, k$.
S = Perrin's constant = $\frac{8 \pi h v^3}{c^3}$.
c = velocity of light in a vacuum = $3 \,.\, 10^{10}$ c.M./sec.
p = modification constant for Perrin equation = 0.27.

VARIABLES

λ = wavelength of light in 10^{-4} c.M.
v = frequency of light in vibrations/sec.
K = equilibrium constant.
K_1 and K_2 = reaction velocities.
u = energy change p. molecule during a reaction.
U = $N \,.\, u$ ergs (Q of Einstein, W of Perrin).
$A = \frac{u}{k}$; $A = \frac{U}{R}$.
W = work done bij a system (A of Nernst).
q = energy change *inside* a system during a reaction.
Q = temperature coefficient.
T = temperature.
t = time.

N. B. Quotation marks point to the end of the chapter.

CHAPTER I

THEORETICAL CONSIDERATIONS

BLACK RADIATION.

Assuming that temperature radiation must be the cause of reactions it can be expected that this radiation is determineable by Wien's law, according to which the wavelength of the maximum radiation intensity is inversionally proportional to temperature

$$\lambda . \mathrm{T} = 0{,}294 \text{ c.M. degree}$$

at "physiological temperatures" (plm. 300^0 abs.) the maximum will be situated in the infrared at

$$\frac{0{,}294}{300} = 9{,}8\ \mu$$

This maximum is also easily determineable by the luminosity equations of Planck[1]). Because of the fact that these equations will be used as a starting point for further deductions some of their properties will be considered here. The luminosity referring to wavelength can be expressed by equation

$$\mathrm{E} = \frac{c^2\ h}{\lambda^5} \cdot \frac{1}{\left(e^{\frac{c\ h}{k\ \lambda\ \mathrm{T}}} - 1\right)} \text{ ergs/c.M}^2\text{. sec.}$$

For different values of $\frac{c\ h}{k\ \lambda\ \mathrm{T}}$ this equation reduces to simpler forms.

According to the Maclaurin series

$$f(x) = f(o) + \frac{x}{1!} f'(o) + \frac{x^2}{2!} f''(o) + \ldots\ldots$$

$e^{\frac{c\,h}{k\,\lambda\,T}}$ can be written.

$$e^{\frac{c\,h}{k\,\lambda\,T}} = 1 + \left(\frac{c\,h}{k\,\lambda\,T}\right) + \frac{1}{2!}\left(\frac{c\,h}{k\,\lambda\,T}\right)^2 + \frac{1}{3!}\left(\frac{c\,h}{k\,\lambda\,T}\right)^3 + \ldots\ldots$$

when $\frac{c\,h}{k\,\lambda\,T} < 1$ this form approaches

$e^{\frac{c\,h}{k\,\lambda\,T}} = 1 + \frac{c\,h}{k\,\lambda\,T}$ and the original equation:

$$E = \frac{c\,k\,T}{\lambda^4} \text{ ergs/c.M}^2\text{. sec.}$$

However, when $\frac{c\,h}{k\,\lambda\,T} > 1$, and, accordingly, $e^{\frac{c\,h}{k\,\lambda\,T}}$ is large compared with 1, the luminosity equation reduces to

$$E = \frac{c^2\,k}{\lambda^5}\,e^{-\frac{c\,h}{k\,\lambda\,T}} \text{ ergs/c.M}^2\text{. sec.}$$

Fig I shows similar approximation formulae and their range of applicability as compared with the general relation. Immediately above the maximum the approximation formula coincides practically with the general equation.

For physiological purposes we always have to use small values of λ and T (low temperature, supra optimal frequencies). It will be seen at which place the maximum value of E in the equation

$$E = \frac{c^2\, h}{\lambda^5}\, e^{-\frac{c\, h}{k\, \lambda\, T}}$$ is situated.

Differentiation with respect to λ gives

$$\frac{\delta E}{\delta \lambda} = \frac{5\left(e^{\frac{c\, h}{k\, \lambda\, T}} - \frac{c\, h}{k\, \lambda\, T}\, e^{\frac{c\, h}{k\, \lambda\, T}}\right)}{\lambda^6 \,.\, e^{\frac{2\, c\, h}{k\, \lambda\, T}}}$$ or, for $\lambda_{\text{max.}}$;

$$5 - \frac{c\, h}{k\, \lambda\, T} = 0 \qquad \text{At } T = 300 \text{ abs.}$$

$$\lambda = \frac{3 \,.\, 10^{10} .\, 6{,}145 \,.\, 10^{-27}}{1{,}34 \,.\, 10^{-16} .\, 3 \,.\, 10^{2}}$$

$$\lambda_{\text{max.}} = 9{,}6\ \mu$$

The behaviour of the equation for the luminosity frequencies is entirely analogous to that of the luminosity referring to wavelengths.

$$K = \frac{h\, \upsilon^3}{c^2}\, \frac{1}{\left(e^{\frac{h\, \upsilon}{k\, T}} - 1\right)} \text{ ergs c.M}^2\text{. sec.}$$

reduces to

$K = \frac{k\, \upsilon^2\, T}{c^2}$ for small values of $\frac{h\, \upsilon}{k\, T}$ and to

$K = \frac{h\, \upsilon^3}{c^2}\, e^{-\frac{h\, \upsilon}{k\, T}}$ for large values of $\frac{h\, \upsilon}{k\, T}$, as is the case in physiological reactions. The maximum of this last equation is situated at 16 μ in the infrared.

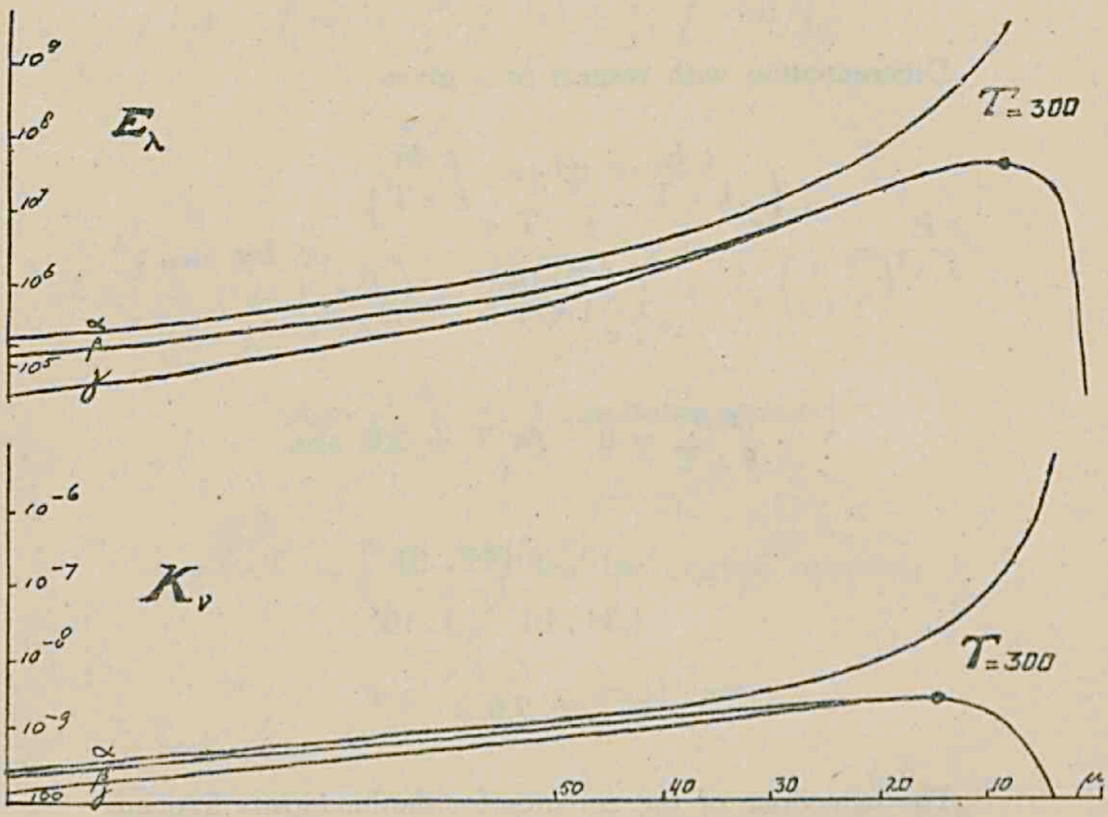

FIG 1.

As the luminosity equations serve for both emission and absorption it can be expected to find most of the chemical and physiological reactions excited by infrared light. The light emitted or absorbed during the reaction must belong also to the infrared region. In most physiological reactions, however, no infrared light seems to play a part. The light of the firefly is "cold" light. Its emission spectrum lacks the infra red part (Langley & Very; Langley; Ives [2]).

v. Gulik [11]) found for chlorophyll an absorption maximum at 3,4 μ. If this maximum should be situated at the position of the maximum black radiation it would correspond to a heat radiation of 800° abs! It is clear that the luminosity equations *as such* are not very well applicable on physiological processes.

THEORY OF J. PERRIN.

Perrin assumes that

> "toute reaction chimique est provoquée par une radiation lumineusé: sa vitesse est determinée par l'intensité de cette radiation et ne dépend de la température que dans la mesure où cette intensité en dépend."

The consequences of this assumption will be derived in different ways.

A reaction velocity K_1 is assumed to be a function of a light intensity I:

$$K_1 = f\,(I)$$

The proportion of two light intensities at different temperatures T_1 and T_2 ($T_2 > T_1$) will be

$$Q = \frac{E_2}{E_1} = \frac{I_2}{I_1} = e^{\frac{h\,v}{k}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)} \qquad (1)$$

or

$$ln\ Q = \frac{h\,v}{k}\left(\frac{1}{T_1} - \frac{1}{T_2}\right).$$

This equation will hold for the reaction velocities if K_1 is directly proportional to I. If K_1 is proportional to a power of I [as is the case in absorption of light] equation (1) will change into

$$Q = e^{p\frac{h\,v}{k}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)} \qquad (2)$$

or

$$ln\ Q = p\,\frac{h\,v}{k}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$ in which $p < 1$ and a constant.

Both cases have been found experimentally. (1) Seems to hold in certain cases of photochemical equilibruim where reaction velocity is directly proportional to luminosity (Trautz[3]).

Equation (2) applies to the cases where the reaction velocity is proportional to the quantity of light absorbed (Plotnikow [4]).

In (1) and (2) Q is the acceleration of the reaction by the increase in temperature of $(T_2 - T_1)$ degrees. Q can also be derived without using Planck's equations in connection with Perrin's hypothesis. The equation of Gibbs—van 't Hoft

$$\frac{d\,ln\,K}{d\,T} = + \frac{A}{T^2}$$ in which K is the equilibrium constant can be modified into

$$\frac{d\,ln\,K_1}{d\,T} = + \frac{A}{T^2}$$ in which K_1 is a velocity constant (Arrhenius' approximation). Integration gives us the proportion of two such velocity constants at different temperatures (assuming A to be constant)

$$\int_{T_1}^{T_2} d\,ln\,K_1 = A \int_{T_1}^{T_2} \frac{d\,T}{T^2} \qquad \text{or}$$

$$ln\,Q = A\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad (3)$$

Combination of (1) and (3) gives

$$A = \frac{h\,v}{k}\ \text{ergs} \qquad (4)$$

Combination of (2) and (3) gives

$$A = p\,\frac{h\,v}{k}\ \text{ergs} \qquad (5)$$

This is a logical result, in harmony with the quantum theory. The energy per molecule being quantumized we can write u = const. $h\,v$, and, because $A = \frac{U}{R} = \frac{u}{k}$ we get, by simple substitution equation (5).

Perrin's starting point is also the temperature equation of Arrhenius. For a certain frequency v the intensity of supra maximal radiation depends on T proportional to

$$S \cdot e^{-\frac{h\,v}{k\,T}} \quad . \text{ This gives}$$

$$-\frac{A}{T} = \frac{h\,v}{k\,T} \text{ and the equation (4).}$$

N.B. Langmuir 5) critisizes Perrin's attempt to combine luminosity and dissociation heat. The similarity between the Arrhenius' equation and the Planck equation is, according to Langmuir, due to the fact that both are probability equations. This may be the case, but still their relation may hold true because of the fact that the probabilities are, in both cases, taken from comparable elements (energy quantities). The similarity between the two equations was, long before Perrin, pointed out by E. Rasch 6), who, nevertheless, reached no applicable deductions.

In the following pages the quotient between two reaction velocities at different temperatures, Q, wil be used. This number has the advantage of a quotient: common discrepancies in numerator and denominator will disappear. Besides this it is easily determineable experimentally.

Equation (2) can be written:

$$ln\ Q = p\,\frac{h\,v}{k}\left(\frac{T_2 - T_1}{T_1\,T_2}\right),$$

and most determinations being carried out at temperature intervals of 10°:

$$ln\ Q_{10} = p\,\frac{h\,v}{k}\left(\frac{10}{T_1^{\,2} + 10\,T_1}\right) \text{ or,}$$

in wavelengths;

$$\lambda = p \, \frac{10 \,.\, 6{,}415 \,.\, 10^{-27} \;\; 3 \,.\, 10^{10}}{1{,}34 \,.\, 10^{-16} \;\; 2{,}3 \,.\, T_1 \,.\, (T_1 + 10) \,.\, log\ Q_{10}} \qquad \text{or;}$$

$$\lambda = p \, \frac{1{,}43}{\frac{2{,}3}{10} \; T_1 \, (T_1 + 10) \; log\ Q_{10}} \qquad \text{From (3) we get}$$

$$\lambda = p \, \frac{1{,}43}{A} \quad \ldots \text{ (6) and from the foregoing;}$$

$$\lambda = p \, \frac{6{,}2}{T_1 \, (T_1 + 10) \; log\ Q_{10}} \qquad (7)$$

In the analogous Perrin equation $p = 1$ and we get

$$\lambda = \frac{1{,}43}{A}$$

and for the temperature coefficient

$$\lambda = \frac{6{,}2}{T_1 \, (T_1 + 10) \; log\ Q_{10}}$$

It must be remarked that Perrin's equations are only rigidly true for black radiation, where any absorption or emission of radiation is counterbalanced by emission and absorption in surrounding sheaths.

PERRIN'S THEORY IS INADEQUATE.

The optimum black radiation, for which Perrin's equations hold, is, at physiological temperatures, situated at about 10 μ in the infrared. Between 290—300^0 abs.

$$log\ Q_{10} = \frac{6{,}2 \,.\, 1{,}0 \,.\, 10^3}{290 \,.\, 300} \qquad \text{or}$$

$$Q_{10} = 1{,}18$$

This temperature coefficient is of the order of the thermal acceleration of photechemical processes; reactions accelerated by the visible light! The absolute values as derived from Perrin's equations don't hold for photochemical processes.

Langmuir has calculated the available energy for such a photochemical reaction with the aid of $\lambda = \frac{1,43}{A}$. The dissociationheat of phosfine, corresponds, according te Perrin, at 948⁰ abs. with an exciting wave of 392 $\mu\mu$. The measured reaction velocity constant at this temperature proved to be $1,2 . 10^{-2}$. The required energy to keep up this velocity is $4,65 . 10^{5}$ ergs/c.M^2. sec. The total energy radiated from a black body of 948⁰ abs. with a wavelength less than 400 $\mu\mu$ is $1,3 . 10^{-5}$ ergs/c.M^2. sec. This is only $4 . 10^{-10}$ of the amount of energy required to cause the reaction in 1 c.M^3. of phosfine.

> "In other words, a black body at 948⁰ abs. radiates so little energy in the neighborhood of 392 $\mu\mu$ that this energy would only be sufficient to activate molecules of phosphine in a layer having a thickness not greater than $3 . 10^{-10}$ c.M. even if all the radiation were absorbed within this layer".

Lewis has calculated the velocities of the same reaction at the same temperature. On the assumption of a quantumized emission and continuous absorption (Planck) the discrepancy reaches the value of 10^7. On the assumption of a quantumized emission and absorption (Einstein) the discrepancy factor is reduced to plm. 10.

Still, black body radiation is not sufficient to account for the energy requirements of systems bathed in this radiation.

It has been shown before that heat radiation at physiological temperatures does not correspond with the position of the exciting frequency in different cases where these frequencies are known experimentally.

> Harvey[2]) remarks that organisms emit visible radiation much below the temperature of heat radiation of corresponding frequency. He confuses, however, in his statements the Boltzmann law and Wien's law.

Langmuir has applied the principle of the exciting wave on many reactions, the calculated values, however, show no coincidence with actual absorption bands for the compounds. Langmuir holds that this fact disproves Perrin's theory entirely. It is more probable, however, that it only demonstrates the inadequacy of the equation

$$\lambda = \frac{1{,}43}{A}.$$

There are more reasons for this fact. In the first place, a reaction will be considered which is photochemically sensitive to violet light. From equation (1) Q can be calculated. This proves to be a number in the neighborhood of fifty at room temperature. This means that this reaction will be explosive. Now there are many colourless compounds which react photochemically on violet rays. The vast majority of these substances, however, is not explosive. Lindemann [7]) has pointed out this fact, and Perrin himself remarks:

> "Toujours au voisinage de la température ordinaire considérons l'action d'une lumiére visible, d'un violet par exemple. Il vient $\frac{K_{310}}{K_{300}} = 50$. Si donc une réaction est assez prodigieusement sensible à la lumière violette pour être déjà notablement provoquée par ce qu'il y a de lumière violette dans une enceinte opaque à la température ordinaire, elle sera explosive si du moins elle est exothermique. Car 20° C. suffiront déjà pour multiplier la vitesse par 2500, et la température s'élévant forcément par le progrès de la réaction, la vitesse ira s' accélérant de plus en plus".

It is clear that Perrin's equation, the black radiation equation, gives no satisfactory expression of the experimental results. This was a priori evident, because it is the infrared part of the spectrum his equations deal with. Cane sugar inversion will be accelerated, according to Perrin, by a wavelength of 1,12 μ, rays which are utterly inactive on this reaction!

An application of equation (2), on the other hand, may lead to a preliminary estimate of p. because in

$$ln\ Q = p\frac{h\ v}{k}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Q and v for a certain reaction being known, p can be calculated. It will be seen later that as an average of all determinations $p = 0{,}27$.

Substituting this value for Q_{10} 1,5—3; which are the normal temperature coefficients at room temperature, v varies from the extreme red to the extreme violet of the visible spectrum.

Similar results are obtained by Richardson and Compton [8] for the mean energy of emitted photo-electrons from metal surfaces

$$E_{av} = K_{av}\ (v—v_0)$$

in which

$$K_{av} < h\ ,\ \text{about } 2{,}46.10^{-27}$$

in average. This would give

$$p < 1\ ,\ \text{about } 0{,}38.$$

POSSIBLE CAUSES OF THE DISCREPANCY.

1) The equations which are better applicable are derived on the assumption that a reaction velocity is proportional to a power of the intensity. This statement, which shows a superficial analogy to the so-called Schwartzschild law, cannot imply the assumption of an absorption unless it is not applicable on heat radiation. In heat radiation any absorption should be balanced bij emission in a surrounding layer. It is rather doubtful if an equation, originally derived for black radiation may, by simple multiplication with a constant become adapted to other conditions.

2) There is, however, quantitative evidence in this direction. Einstein's photochemical theory has recently been modified by Ornstein & Burger [9]). These authors have been able to derive a condition, which approaches closely to what is called in this paper "the modified Perrin equation". Ornstein & Burger

have considered the conditions of a binary reaction, accelerated by light in both ways

$$(1.2) \rightleftarrows (1) + (2) \text{ at } T^0 \text{ abs.}$$

The energy per molecule N_{12} be ε, N_1 and N_2 be ε^1. Statistical mechanics gives, according to the Maxwell-Boltzmann law, for the equilibrium condition

$$\frac{N_{12}}{N_1\, N_2} = p\, \frac{e^{-\varepsilon/\theta}}{e^{-\varepsilon^1/\theta}} = p\, e^{\frac{\varepsilon^1-\varepsilon}{\theta}}$$

in which

$\varepsilon = \frac{R\,T}{N}$, p = quotient of the a priori possibilities of the system.

Now $N_{12} \longrightarrow N_1 + N_2$ is only accelerated by radiation, no spontaneous dissociation taking place.

$N_1 + N_2 \longrightarrow N_{12}$ may be caused by both collision and radiation. The velocity of dissociation is:

$B_1 \,.\, \partial \,.\, N_{12}$ in which ∂ = density of radiation,
B_1 is a constant.

The velocity of association is:

(by collision) $A_2 \,.\, N_1 \,.\, N_2$ + (by radition) $B_2 \,.\, \partial \,.\, N_1 \,.\, N_2$.

Equilibrium gives:

$$B_1 \,.\, N_{12} \,.\, \partial = A_2 \,.\, N_1 \,.\, N_2 + B_2 \,.\, N_1 \,.\, N_2 \,.\, \partial \qquad \text{or}$$

$$\left[B_1\, \frac{N_{12}}{N_1\, N_2} + B_2\right] \partial = A_2 \qquad \text{or}$$

$$\partial = \frac{A_2}{B_1\, \frac{N_{12}}{N_1\, N_2} + B_2}$$

Now, according to

Maxwell-Boltzmann:

$$\frac{N_{12}}{N_1 N_2} = p\, e^{\frac{\varepsilon^1-\varepsilon}{\theta}} .$$ Substitution gives

$$\delta = \frac{A_2}{B_1\, p\, e^{\frac{\varepsilon^1-\varepsilon}{\theta}} - B_2}$$

If θ increases, δ increases as the first power of T. A_2 only increases as $\sqrt{T}$ (kinetic theory of gases). Therefore at $\theta\ \infty$, $\delta\ \infty$;

$B_1\, p - B_2 = o$, and, all these factors being constant;

$$\delta = \frac{A_2/B_2}{e^{\frac{\varepsilon^1-\varepsilon}{\theta}} - 1}$$ or, substituting Planck's value for the radiation density

$$A_2/B_2 = \frac{8\,\pi\, h\, v^3}{c^3}\ \frac{e^{\frac{\varepsilon^1-\varepsilon}{\theta}} - 1}{e^{\frac{h\,v}{\theta}} - 1}$$

For T = o, A_2 will be zero and it is necessary that in this case $h\,v > \varepsilon^1 - \varepsilon$, or

The chemical active frequency must be situated *above* a certain frequency which is aequivalent to the reaction heat per molecule. This limiting frequency is given by the Einstein equation

$$v_0 = \frac{\varepsilon^1-\varepsilon}{h} .$$

For $\varepsilon^1 - \varepsilon$ we can write u, dissociation energy per molecule. Now because

$h\,v > \varepsilon^1 - \varepsilon$, it follows that

$h\,\dot{v} > u$ or

$\frac{h\,v}{k} > \frac{u}{k}$ or $\frac{u}{k}$ being equal to $\frac{\mathrm{U}}{\mathrm{R}} = \mathrm{A}$

$\frac{h\,v}{k} > \mathrm{A} \;\ldots.\; (8)$

If v be assumed a definite frequency, it follows that

$$\mathrm{A} \quad p\,\frac{h\,v}{k}\text{, in which } p < 1 \;\ldots..$$

This is obviously equation (6)

The Ornstein—Burger equation, however, gives only a partly solution of the problem. According to these authors any frequency $v > v_0$ will be active. There will be occasion to consider this fact more closely in the next chapter.

Ornstein's deductions have given a theoretical explanation of the factor p in the equations derived in the preceding paragraphs. They are of no help, however, in determining the absolute magnitude of this factor.

A similar idea, a little more restricted however, has been developed bij Tolman [10]). Tolman assumes an active region of frequencies, which is limited at both sides, (not, as Ornstein finds, at one side).

Prof. Dr. H. A. Lorentz has had the kindness to point out to me the relation between Perrin's and Tolman's theories. Dr. Lorentz's remarks will be translated almost literally in the following lines:

"According to Perrin a photochemical reaction may be caused by a frequency v, and the velocity of this reaction proportinal to the energy of the "black radiation" at the corresponding temperature. According to Planck the energy of black radiation belonging to the frequencies v and $v + d\,r$ (p. c.M^3.) is

$$\frac{8\,\pi\,h\,v^3}{c^3}\;\frac{1}{e^{h\,v/k\,\mathrm{T}} - 1}\,d\,v \qquad \text{(a)}$$

and (neglecting the factor $d\,r$) Perrin puts therefore K proportional to

$$\frac{8\ \pi\ h\, v^3}{c^3} \quad \frac{1}{e^{h\, v/k\, T} - 1} \qquad \text{or}$$

$$K = \frac{S}{e^{h\, v/k\, T} - 1} \qquad \text{(b)}$$

in which, for a certain v, S will be a constant; independant of temperature; hence (b) shows K as a function of T.

Neglecting the term -1

$$K = S\, e^{-\frac{h\, v}{k\, T}}, \text{ or}$$

$$\frac{dln\ K}{d\ T} = \frac{h\ v}{k\ T^2} \qquad \text{(c)}$$

Now Tolman assumes that the reaction may be caused by all frequencies within a spectral region of larger or smaller dimensions. This region may be devided into infinitely small parts, corresponding to interval $d\ v$. For each interval the radiant energy is given by equation (a) and each interval will cause a proportional reaction velocity K_v.

In this connection it must be mentioned that Tolman does not derive the proportionality of K_v to the energy of black radiation for the corresponding frequency interval from his theoretical considederations. He *assumes*, as Perrin does, this proportionality to exist.

Assuming the radiation of frequency v (energy 1 per unit volume) to cause a reaction velocity K_v; we get for a black radiation of intensity (a) a reaction velocity of:

$$\frac{8\ \pi\ h\, v^3}{c^3} \quad \frac{1}{e^{h\, v/k\, T} - 1} \ K_v\ d\, v$$

and, totally

$$K = \int \frac{8\ \pi\ h\, v^3}{c^3} \quad \frac{1}{e^{h\, v/k\, T} - 1} \ K_v\ d\, v \qquad \text{(d)}$$

The factor K_v stands for the "sensibility" of the system for rays of the frequency v. This sensibility will be maximal for rays of a certain frequency and will drop off more or less steeply at both sides. The integral in (d) must be extended over the entire active spectral region where $K_v > 0$. This factor K_v plays the same part as S in Perrin's equation (b). Assuming K_v to be independant of temperature, equation (d) can be changed so that an equation will be obtained analogous to Perrin's equation (c). Neglecting the term —1 in ($e^{hv/kT}$ —1), (d) will change into:

$$K = \int \frac{8 \pi h v^3}{c^3} \frac{1}{e^{hv/kT}} K_v \, d_v \tag{f}$$

In this equation $e^{hv/kT}$ depends on T. The differential quotient of this factor with respect to T is

$$\frac{h v}{k T^2} \, e^{-\frac{h v}{k T}}$$

and (f) gives accordingly

$$\frac{d K}{d T} = \int \frac{h v}{k T^2} \cdot \frac{8 \pi h v^3}{c^3} \, e^{-hv/kT} K_v \, d_v \tag{g}$$

Putting, at a certain temperature:

$\frac{8 \pi h v^3}{c^3} e^{-hv/kT} K_v = f(v)$, we can write for (f)

$$K = \int f(v) \, d v \tag{h}$$

and for (g)

$$\frac{d K}{d T} \int \frac{h v}{k T^2} f(v) \, d v \tag{i}$$

When we plot v against $f(v)$, a certain area will represent integral (h). Integral (i) will be represented by an area outside of which

$f(\nu) = 0$; the limiting curve of this area can be obtained by multiplying each ordinate of curve (h) with $\frac{h\nu}{kT^2}$. This factor is no constant, but increases with increasing ν. The maximum in the curve (i) will therefore be shifted to the region of the higher frequencies. $\frac{h\nu}{kT^2}$ will be the largest in the upper limiting frepuency $\left(\frac{h\nu^1}{kT^2}\right)$; the smallest in the lower limiting frequency $\left(\frac{h\nu''}{kT^2}\right)$. It is clear that

area (i) $<$ area (h) $\times \frac{h\nu^1}{kT^2}$; but that

area (i) $>$ area (h) $\times \frac{h\nu''}{kT^2}$.

Therefore:

$$\frac{h\nu''}{kT^2} < \frac{\frac{dK}{dT}}{K} < \frac{h\nu'}{kT^2}$$

and there must exist a frequency ν somewhere between ν'' and ν' that satisfies the condition

$$\frac{\frac{dK}{dT}}{K} = \frac{h\nu}{kT^2} \quad \text{or}$$

$$\frac{d\ln K}{dT} = \frac{h\nu}{kT^2} \tag{k}$$

in which ν will be not far from $\nu_{\max.}$ in $K = f(\nu)$.

Perrin's equation is therefore valid over an entire range of frequencies. There will be an average active frequency representing this region and which can be expressed by the Perrin equation. In order to apply this equation, however, the reaction velocity as a function of the frequency must be known. The average frequency ν' will be situated in the neighborhood of the maximum of this function.

Tolman's theory leaves the position of ν' undetermined. It may be said that this $\nu' > \nu''$, the lower frequency limit, and which is the frequency found by the original Perrin equation. About the *size* of the factor p these equations are silent.

Prof. Dr. D. L. Webster called my attention to the fact that in the case of an external light source, which is true for the majority of photochemical reactions, the temperatures T_1 and T_2 in the equations have no definite meaning, because one could as well substitute the temperature of the emitter as well as that of the absorber. The uncertainty of these factors may also contribute to the discrepancy between Perrin's equations and the actual experimental data. Summarizing it may be said that Perrin's equation

$$A = \frac{h\,v}{k}$$ only gives a lower limit

of active frequencies. That the equations as derived by Ornstein & Tolman give evidence that the active radiation must be of higher frequency. Tolman's deductions point to a definite maximal activity, while, according to Ornstein all frequencies $> v$ will be found active.

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CHAPTER II

EXCITING FREQUENCIES AND TEMPERATURE COEFFICIENT.

Equation (7)

$$\lambda = p \frac{6{,}2}{T_1 \ (T_1 + 10) \log Q_{10}}$$

expresses, at a given temperature, $\lambda = f\ (Q_{10})$. In the first place the real meaning of this fact will be considered.

EXCITING FREQUENCY.

Perrin calls λ the exciting wavelength. In Chapter I it has been shown that according to Ornstein & Burger λ may have any value as long as it suffices

$$\lambda = f\ (p\,,\ Q_{10}) \text{ in which } p < 1\,.$$

As soon as $p = 1$; the original Perrin equation is reobtained, in which λ is the limiting wavelength. This idea is similar to that expressed by Richardson 1) in his theory of photo-electric emission in which there is a limiting frequency below which no photo-electric emission takes place. The emission intensity plotted against frequency shows a curve with its convex side turned towards the frequency-axis. It is doubtful if such curves exist in chemical and physiological reactions. For, when the colour-sensibility of a photographic plate, the eye, or some other substance is considered, it can easily be seen that there is no definite limiting wavelength, no discontinuity in the curve which fades out gradually in the region of the longer waves. This state of things may be compared with the equations of Tolman, in which the reaction velocity is dependent on the frequency in the same way as the radiation density in Planck's equations. In photo-electricity such curves are known for the so-called selective photo-electric effect, which reaches its maximum at a certain critical wavelength. Pohl & Pringsheim[2]) have shown that the photo-electric activity depends on the angle at which the light is incident on the surface, and on the orientation of the plane of polarisation. When the light falls normally on the surface, the electric vector is parallel to the surface, and the photo-electric activity increases continuously as te wavelength decreases. But when the light is incident at an angle with the normal, the electric vector which is parallel to the plane of incidence produces a maximum effect for a particular wavelength. This maximum is taken to indicate a resonance phenomenon. The position of light sensitive organs in relation to incident radiation (transverse phototropism of the euphotometric leaf etc.) may have something to do with this fact. As every photochemical process starts with electron emission there is evidence that the distinction between normal and selective effect may hold true for these processes.

Because Perrin considers chemical reactions as resonance phenomena, the selective effect must play the most important part in these cases. The negative outcome of Ursprung's experiments on photo-electric emission of green leaves[3]) do not indicate that such emission is absent. The emitted electron may react again before it leaves the system (see Bodenstein theory of photochemical reaction in Chapter III of this paper). Another fact in favour of the connection between photochemical and photo-electric processes is Richardson's equation for the influence of temperature on electron emission which shows a close relation to Perrin's equation (7).

The exciting frequency will, therefore, be considered as an average frequency, situated in the neighborhood of the maximum of a selective photo-chemical process.

TEMPERATURE COEFFICIENT

The temperature coefficient will be defined as the proportion between two reaction velocities of this reaction at two temperatures. van 't Hoff has introduced the expression Q_{10} in physical chemistry. This temperature coefficient for 10° C. difference lies, at room temperature, usually between 2 and 3. This statement of van 't Hoff has caused much confusion. Usually it is assumed that, if a reaction is not 2—3 times accelerated by a temperature increase of 10° C., this reaction is not taking place according to van 't Hoff's "law".

Now equation (3)

$$ln\ Q = A \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

can be written

$$Q_{10} = e^{\frac{{}_{10}A}{T^2 + {}_{10}T}}$$

It is clear that when $T = 0$ $Q_{10} = \infty$ and that when
$T = \infty$ $Q_{10} = 1$. It is evident also that in the range of physiological temperatures ($T = 273—303$) Q_{10} will decrease.

> Krogh[4]) seems to think that the Q_{10} is a rigid constant. Pütter[5]) tries to explain the decrease of the Q_{10} by a complex system of processes, each with a certain definite Q_{10}. This is unnecessary.

Cohen Stuart[6]) has derived an expression for this decrease, assuming a certain reaction velocity to be a linear function of the temperature. This assumption leads him to the following connection

$$(Q_{10} - 1)\ T = \text{constant.}$$

This formula does not apply. Within the range of physiological temperatures Q_{10} varies usually 30—50 %, therefore

($Q_{10} - 1$) still more. T varies from 273°—303° abs. little more than 10 %. This change carmot compensate the large variation in the Q. In order to compare the applicability of this equation and

$$Q_{10} = e^{\frac{A}{T^2 + {}_{10}T}}$$

the constant will be calculated from an actual set of experimental data by both methods. The reaction time of phototropic response in Avena is a temperature function. This temperature function is studied by Miss de Vries [7]). The constant from Cohen-Stuart's equation (= c) as well as A will be calculated

T	$T^2 + {}_{10}T$	Q_{10}	$Q_{10}-1$	*log* Q_{10}	$c/_{10^2}$	$A/_{10^3}$
273	77230	3,0	2,0	0,478	5,46	8,06
278	79780	2,8	1,8	0,447	5,04	8,02
283	82930	2,6	1,6	0,415	4,52	7,95
288	85780	2,6	1,6	0,415	4,71	8,03
293	88830	2,5	1,5	0,398	4,39	7,91

Columm 7 proves to be constant. Therefore equation (3) holds.

Analyzing the Q_{10} in its components; two reaction-velocities, it may be asked if the reaction velocities themselves can be analyzed further. For a reaction velocity a similar equation as Ohm's law seems to hold

$$\text{velocity of reaction} = \frac{\text{chemical resistance } (f)\ (r)}{\text{chemical force } (r)\ (f)} \qquad \text{or,}$$

$$Q_{10} = \frac{f^{\circ} \cdot r'}{r^{\circ} \cdot f'}$$

Chemical force *f* is a function of the free energy; very little is known about chemical resistance, except that it is greatly demmished by rise of temperature. Factors as internal friction etc., undoubtedly have something to do with chemical resistance, and are perhaps directly proportional to this factor. For aqueons solutions $\frac{r'}{r''}$ is small, and, in order to make $Q_{10} = 2-3$, there must be an increase in the free energy of the system. But for protoplasmatic processes, where $\frac{r'}{r''}$, the thermal coefficient of an emulsoid, is very large, the free energy must decrease in order to keep Q_{10} in the range of known experimental values. Generally spoken it can be said that there are Q_{10}'s chiefly related to a) reaction velocities, b) chemical forces or c), chemical resistances.

a) Q_{10} RELATED TO REACTION VELOCITY.

Longitudinal growth of plants and animals; retinal current and reaction times are different factors connected with reaction velocities. Reaction time is a good index for reaction velocity, in asmuch the velocity constant can be represented by

$$\frac{1}{a^{n}} - \frac{1}{x^{n}}$$

a. being available- and
x. decomposed amount.

When the reaction is practically finished the reaction velocity is inversionally proportional to the reaction time, as in that case the equation limits to

$$\frac{c}{t}.$$

The intensity of an electric current can be compared directly with a velocity. And it is clear that the Q of congitudinal growth, being the Q of a reaction *rate* belongs to this group.

b) Q_{10} RELATED TO CHEMICAL FORCE.

Heat-, light- and electron emission, heat-, light- and electron absorption belong to this group. As these processe~~n~~s take place mostly at surfaces, the resistance does not change very much with temperature and $\frac{r'}{r''}$ will be small. The small Q_{10} for many of these cases has been explained is this way (diffusion theory of Nernst).

c) CHEMICAL RESISTANCE. is a function of the internal friction of a system. The internal friction of an emulsoid changes quite perceptibly with the temperature. The rate of the protoplasmic current, a velocity is so much influenced by temperature that it seems to be dependant on the internal friction only. The change in the free energy of the system *d f* must, accordingly, be almost nil. The long latency times (praesentationtime or refractory period) of many physiological reactions are probably connected with internal frictions.

d) OTHER CASES. In most of the physiological reactions the origin of the Q_{10} is obscure. Q_{10} of respiration or assimilation, measured by the amounts of carbondioxide given off or absorbed are made up of many factors. Only when the intake or output is constant during a long period of time it is warranted to assume the velocity to be proportional to the amount of CO_2. Another complex case is the time required for seeds to germinate at different temperatures. Here the Q_{10} of absorption, viscosity, respiration and all kind of enzym actions play a role. The same can be said about the Q_{10} of the time needed for larvae to develop (Krogh) or for ants .to walk a certain distance (Shapley).

There are several cases in which equation (3) is not applicable. Instead of decreassing continuonsly with increassing temperature, an initial increase may be observed in certain cases, as the saponification of esters. Several explanations of this fact have been attempted, but the real cause of this curions phenomenon is not known as yet. In many reactions Q_{10} decreases very rapidly and becomes < 1; which means that the reaction velocity decreases with increasing temperature. The so-called optimum reactions in physiology, and the reactions the influence of temperature on catalytic activity of metal soles belong to this group. The theory of limiting factors, as proposed by Blackman (8) has given an explanation for this fact. In optimum curves it is no longer warranted to assume a temperature relation with *one* variable; a second variable, the observation time, comes in. Only when, at a given temperature, the intensity is independant of the observation time, the van 't Hoff law is directly applicable.

When the intensity varies with the observation time, Blackman suggests that an extrapolation to the observationtime = zero may lead to the construction of the van 't Hoff curve in this case. An actual extrapolation was carried ont for a set of experimental data on plant respiration. The results will be published in a separate paper. It will only be pointed out here that the extrapolated curve can be represented by a van 't Hoff curve.

In this paper cave will be taken to exclude all Q_{10}'s situated at abnormally hich temperatures.

EXCITING FREQUENCY AND TEMPERATURE COEFFIENT.

For a certain temperature interval dT

$$\lambda \; log \; Q_{10} = \text{constant.}$$

At room temperature it may be expected to find the $\frac{\text{violet}}{\text{red}}$ sensitized reactions to have a $\frac{\text{high}}{\text{low}}$ temperature coefficient. According to equation (6)

$$\lambda = p \, \frac{1{,}43}{A} \, ,$$

in which A is assumed to be constant. This is not always the case.

$$T_1 \; T_2 \; ln \; Q_{10} \text{ is not always constant.}$$

If it is constant the reaction will be sensitized by the same wavelength at different temperatures. These reactions will be called stenophotic (στενός = narrow). In other cases Q_{10} decreases too fast to be balanced entirely by the increase of T_1 T_2. A will decrease, and the exciting frequency will shift to the red end of the spectrum. If this shift is considerable the reaction will be called euryphotic (ευρ'ύς = broad). *The broad absorption bands of many coloured compounds may provide the means to resist the action of this shift.*

An absorption band be expected to shift to the red with increasing temperature. Appreciable results have been obtained with solutions of chlorophyll, aurine und eosine, also with potassium permanganate. The amount of the possible shift cannot, however, be calculated by the equations developed in Chapter I, as A is assumed to be constant.

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CHAPTER III

THE MAGNITUDE OF THE TEMPERATURE COEFFICIENT

A. *Low Temperature Coefficient*

PHOTO-CHEMICAL PROCESSES.

It has been assumed by different authors that photochemical processes have a small Q_{10}. It is assumed generally that in "photochemical" processes the temperature coefficient is much lower than in "chemical" or "physical" processes. Bayliss [1]) remarks that;

> "This follows from the fact that the rate of the photochemical change depends on that of the absorption of the light, which varies only slightly with temperature".

Apart from the fact that the rate of photochemical change is in many cases *not* dependant on that of the light absorption, it is a dangerous thing to ascribe the size af the Q_{10} to the same cause in all cases. Different other authors, as e. g. Tolman and Bodenstein [2]) hold a different opinion as that expressed above. Nernst holds that the low Q_{10} is caused by diffusion. Recently this idea has been opposed by Hecht [3]) for the bleaching of the visual purple in the light. So it can be seen that there is no unanimous opinion about the direct cause of the size of the Q_{10} in photochemical processes. In this paper photochemical reactions will be considered as photoelectric in their nature and the concequencis of this idea will be considered. Allen[4]) has developed a photo electric theory of the photographic plate, in which he assumes the silver halides to shoot off an electron from one of the outer (valency) rings, because, according to Richardson, the photo-electric processes take place in the outer rings. If, moreofer, a ringstructure, similar to the Bohr atom, is assumed to represent the structure of the substance — it is clear that it will take less labour to remove an electron from a distant ring than to remove an electron which circulates nearer to the nucleus. The labour to remove such an electron is the equivalent of the dissociation heat of the reaction. This is $U = \frac{A}{R}$, and, according to equation (3) this labour must, at a certain temperature interval be proportional to $ln\ Q_{10}$. *Therefore it can be expected that large atoms and atom-aggregates possess a smaller* Q_{10} *for their photo-chemical reactions than small atoms or atom aggregates.* As the accurate determination of these small thermal coefficients is very difficult it is impossible to test this result quantitatively. It will therefore be tested only if, in general, the simpler compounds (as measured by atomic — and molecular weight) will have a smaller photochemical Q_{10} as the heavier atoms or compounds. From the book of Plotnikov, as well as from the article of Bodenstein and others the following data were obtained:

REACTION	AUTHOR	Mol. weight	$E_{10} . 10^2$
$H J + O_2$	Plotnikov	128	142
$C H_3 J + O_2$	Plotnikov	145	142
Toluole + Br	Bodenstein	92	140
Styrole — meta-S.	Lemoine	104	139
$S O_2 + O_2$	Bodenstein-Fink	64	136
$Cl_2 + H_2$	Bodenstein	71	134
$Ti + H^{\cdot}$	Denham	48	129
$H_2 O_2$	Teletov	34	128
$Cr + H^{\cdot}$	Jablczynski	52	127
$S O_2 + O_2$	Coehn-Becker	64	120
Ozone + Cl_2	Weigert	48	117
Anthracene	Luther	178	116
Oxalic acid	Eder	108	111
m-Anthracene	Weigert	191	110
K – Co – oxalate	Vrânek	234	110
Orginac dyes	Svezov	300–600	107–104
Quinine	Goldberg	312	104
Ag Br	Lumière	196	102

Subsequently the correlation coefficient between molecular weight and Q_{10} was determined in the usual way and found to be $r = 0{,}84 \pm 0{,}05$; which is strong negative correlation. Several reactions could not be treated because of the incertainty of the Q_{10} or the uncertainty of the molecular weight. Aware of the fact that the molecular weight is a poor index for the number of electron-rings, it is clear that heavy atom-aggregates or heavy atoms will have more rings as light ones.

M. Bodenstein has given a general photochemical theory, derived from equilibrium considerations. This theory holds that the first phase of light action (absorption) is photoelectric. A valency electron is shot off. The "primary" reaction takes place in the remaining positive nucleus, the "secundary" reactions are caused by the photoelectron.

The primary reactions are caused by a small number of quanta. The secundary reactions are more complicated. In the latter reactions the same quantum may act this way on a large number of molecules.

Prof. Dr. H. A. Lorentz was so kind to call my attention to the fact, that Tolman still holds another opinion about the temperature coefficient of photochemical reactions. In his theory Tolman introduces the "sensibility" factor K_r; a reaction velocity belonging to a frequency range d_v. This factor is probably a temperature function; the internal condition of the molecules may change during the reaction, and this may cause a change in the "sensibility" for certain frequencies. This also makes it clear, why a temperature shift of an exciting frequency is possible. Tolman has derived the K_v—T relation for black radiation by means of statistical mechanics.

There are cases, however, in which the crucial point is *the sensibility of the molecules only*. It is possible to imagine a photochemical reaction starting not under the influence of black radiation of its environment; but under the influence of a controlable external light source. Keeping this light constant, it is possible to change the temperature of the illuminated object. Tolman remarks about this case:

"As far as the author knows, this is the first theoretical treatment of the temperature coefficient of photochemical reactions."

CATALYSTS. From the Arrhenius equation:

$$\frac{d \ln K'}{d T} = \frac{A}{T^2}$$

it is possible, with the aid of equation (5) to substitute $p \frac{h \cdot v}{k}$ for A. The reaction be accelerated or retarded by a catalyst and its reaction velocity be K''.

For the uninfluenced reaction

$$\frac{d \ln K'}{d T} = p \frac{h v'}{k T^2}$$

For the influenced reaction at the same T;

$$\frac{d \ln K''}{d T} = p \frac{h v''}{k T^2}$$

It follows that

$$\frac{d \ln K'}{d \ln K''} = \frac{v'}{v''} \qquad (9)$$

or, in words;

If a reaction is $\frac{\text{positively}}{\text{negatively}}$ catalyzed, the exciting light frequency will shift to the $\frac{\text{red}}{\text{violet}}$ end of the spectrum.

Now v is inversionally proportional to $ln\, Q_{10}$. From this it can be concluded that;

if a reaction is $\frac{\text{negatively}}{\text{positively}}$ catalyzed, the temperature coefficient will $\frac{\text{decrease}}{\text{increase}}$.

Perrin's theory therefore gives an explanation of the fact, observed by Winther [5]), that the decomposition of the so-called Eder oxalate solution by light is catalyzed by $Fe\,Cl_3$ and that, the more the reaction is catalyzed, the more the optimum activity shifts to the red end of the spectrum.

Dhar [6]) found that, with a great many reactions, the temperature coefficient was $\frac{\text{decreased}}{\text{increased}}$ as this reaction was $\frac{\text{negatively}}{\text{positively}}$ catalyzed.

Therefore the second cause of the infra normal temperature coefficient may be catalysis.

CHANGES
N INTERNAL
FRICTION.

Temperature has little or no influence on the change in internal friction of suspensoids. As far as we are aware, no important physiological reactions exist where this factor can play a role, as nearly all physiological reactions can be considered as emulsoid systems.

HEAT
RADIATION.

Heat radiation intensity at physiological temperatures has also a small Q_{10}. As the optimum frequency in this case is an infrared radiation it can better be treated in the next group of reactions, which are also characterized by a small temperature coefficient.

RED
SENSITIVE
REACTIONS.

Equation (7)

$$\lambda = p \, \frac{6{,}2}{T_1\,(T_1 + 10) \log Q_{10}}$$

shows the relation between an optimal exciting light wave and the temperature-coefficient of a certain reaction at certain temperature. In chapter I it has been shown that, at room temperature, there is a corresponding variation of λ (visible spectrum) and Q_{10} (average values) if $p = 0{,}27$.

T_1 may be taken between 0°—30° C., as higher temperatures imply the influence of limiting factors. The determination of the Q_{10}, especially in older investigations, has often been carried out in a very inaccurate way. The majority of experimental values had to be rejected for this reason. It may be asked if equation (7) expresses satisfactorily the results in cases where both optimal exciting frequency and temperature coefficient are known.

PHOTO-SYNTHESIS.

The initial process, the intake of carbon dioxide, is notably influenced by light and by temperature. Recent investigations of Ursprung (l. c.) have confirmed the view held by the earlier authors: the optimum frequency for the activity of the assimilation is situated near the optical axis of the red absorption band of the green leaf. The temperature influence has been studied by Blackman and Miss Matthei [7]) and recently by Warburg [8]).

As the results of the latter author confirm those of Blackman, there is evidence that the values for the Q_{10} are trustworthy.

Blackman's value $\frac{K'_{20}}{K'_{10}} = 2{,}05$ gives

$$\lambda = \frac{0{,}27 \, . \, 6{,}2}{283 \, . \, 293 \, . \, 0{,}312}$$

$$= \frac{1{,}67}{2{,}95} \cdot 10^{-4} \text{ c.M.}$$

$$= 644 \ \mu\mu \, .$$

$\frac{K'_{30}}{K'_{20}} =$ is probably a little too small, because of the limiting factor.

$$\lambda = \frac{1,67}{303 \, . \, 263 \, . \, 0,256} \text{ c.M.}$$

$$= 734 \; \mu\mu$$

According to equation (7) the exciting frequency for CO_2 assimilation is situated at the red end of the spectrum. The average frequency between 10—30° C. = 689 $\mu\mu$, probably a little too high, because of the influence of the limiting factors on $\frac{K'_{30}}{K'_{20}}$.

This value is close to that for the maximum absorption in the green leaf (678 $\mu\mu$) and to that for the assimilation maximum.

LONGITUDINAL GROWTH.

The action of red and infrared light on longitudinal growth has recently again been demonstrated by Klebs[9]). This influence has been observed by different authors on different plants. According to these facts the process can be expected to have a low temperature coefficient. This is actually the case, as an investigation of Miss Talma[10]) shows. The growth velocity of Lepidium sativum can be assumed to be proportional to a reaction velocity. The most constant series of data $\frac{K'_{27}}{K'_{17}} = 1,81$ will be used.

$$\lambda = \frac{1,67}{290 \, . \, 300 \, . \, 0,257} \text{ c.M.}$$

$= 750 \; \mu\mu$, or about the red limit of the visible spectrum.

SUPRA-OPTIMAL TEMPERATURES.

In chapter II it has been pointed out that, at supra-optimal temperatures, the temperature coefficient will decrease and become abnormally small.

ONCLUSION FOR SMALL TEMPERATURE COEFFICIENTS.

Contrary to the prevailing opinion that the cause of a small temperature coefficient is either light absorption or diffusion, it has been shown that there are many other instances, as; the size of the reacting molecule or atom, the temperature, the sensibility to low frequency radiation etc., wich may cause the Q_{10} to be small.

B. *High temperature coefficients.*

As it has been pointed out in chapter II, high temperature coefficients are typical for processes connected with changes in the internal friction (viscosity) of emulsoïds.

The viscosity of colophonium in terpineol, for example, decreases $92 . 10^5$ to $4{,}8 . 10^5$ units from 7,1° C. — 11,8° C.

v. Schroeder[11]) found a decrease in the viscosity of gelatin from 31° C. — 21° C. from 13,76 to 1,42 units. According to equation (7) this high coefficient would point to an exciting wavelength in the ultraviolet, situated at

$$\lambda = \frac{1{,}67}{294 \,.\, 304 \,.\, \log \dfrac{13{,}76}{1{,}42}}$$

$$\lambda = 200 \; \mu\mu \,.$$

In this chapter it will be tried to prove that *reactions with a high temperature coefficient absorb U. V. light and are sensitized by it.*

INTERNAL FRICTION.

Friction is a very important factor in protoplasmatic processes, in as much it determines the rate of the plasmatic current and many enzymatic reactions. In this chapter coagulation, heat destruction, oxydation of haemoglobin and protoplasmic current will serve as examples.

v. Schroeder's value for the viscosity of gelatin pointed to an exiting light wave of plm. 200 $\mu\mu$. *We can, therefore, expect, if equation* (7) *holds true, that proteins absorb quite generally the ultraviolet part of the spectrum, and that their reactions are excited by the ultraviolet light.*

Now Soret[12]) found that nearly all proteins absorb about the same region in the ultraviolet. The work of Hertel[13]) has shown that the inactivation of enzymes and toxins is caused by ultraviolet waves.

COAGULATION AND HEAT DESTRUCTION.

Chick and Martin[14]) found an enormous Q_{10} for the coagulation of haemoglobin. It has been shown by Bovie[15]) that haemoglobin can be coagulated by ultraviolet light. Dreyer & Hansen[16]) coagulated different proteins in the ultraviolet.

The values, published by Tammann[17]), on heat destruction of emulsin, are still classical examples of high temperature coefficients.

Tammann found between 65° and 75° C. a Q_{10} of $\frac{14,7}{2,86}$.

According to (7) this would point to

$$\lambda = \frac{1,67}{338 . 348 . 0,712} \text{ c.M.}$$

$$\lambda = 202\ \mu\mu.$$

Hertel (l.c.) Green[18]) and Schmidt—Nielsen[19]) have destroyed and inactivated enzymes by U - V light of short wavelength.

In this connection it is interesting to see that dyphteria-toxin is destroyed by the U - V light while the antitoxin is not affected. Similar antagonisms will be treated in chapter IV.

PROTOPLASMIC CURRENT.

Already Velten[20]) has published data on protoplasmic current. Between 0°—10° C. he found for the rate of this current in cells of Nitella $Q_{10} = 9,33$. Accordingly;

$$\lambda = \frac{1{,}67}{273 \, . \, 283 \, . \, log \, 9{,}33} \text{ c.M.}$$

$$\lambda = 225 \ \mu\mu .$$

This reaction is markedly affected by light; the optimum reaction can be expected in that region which the protoplasm absorbs. This is, according to V. Henri[21]) between 240—214 $\mu\mu$.

OXIDATION OF HAEMOGLOBIN.

From the data of Barcroft and Hill[22]) the Q_{10} of reaction velocities can be exterpolated; giving analogous results for two series of experiments.

$$Q_{\frac{26}{16}} = 5{,}0 \qquad\qquad Q_{\frac{40}{30}} = 4{,}7$$

Corresponding to

$$\lambda = \frac{1{,}67}{289 \, . \, 299 \, . \, log \, 5{,}0} \text{ c.M.}$$

$$\lambda = 284 \ \mu\mu \qquad \text{and}$$

$$\lambda = \frac{1{,}67}{303 \, . \, 313 \, . \, log \, 4{,}7} \text{ c.M.}$$

$$\lambda = 278 \ \mu\mu .$$

Now oxyhaemoglobin posesses a strong U-V absorption, which has an optimum at 275 $\mu\mu$ (Dhéré)[23]). And the third link in the chain gives Hertel (l.c.), who finds oxyhaemoglobin to become reduced by the magnesiumline 280 $\mu\mu$ (2803 Åö).

CONCLUSIONS FOR HIGH TEMPERATURE COEFFICIENT

High temperature coefficients are invariably connected with a) changes in internal friction,

b) Ultra violet absorption,

c) Ultra violet excitation.

A variety of causes, as for the low temperature coefficients, could not be traced. The modified Perrin equation (7) expresses satisfactorily the actual state of affairs. The results can be tabulated as follows:

SUBJECT	λ from equation (7) in $\mu\mu$	λ from absorption in $\mu\mu$	λ from activity in $\mu\mu$
viscosity of gelatin	200	ultraviolet	?
coagulation of Hglb.	200	ultraviolet	ultraviolet
destruction of emulsin.	202	ultraviolet	ultraviolet
protoplasmic current	225	240—114	240—214
oxidation of Hglb.	284—278	275	280

N. B. The excitability of protoplasm is greatly affected by the ultraviolet. Still the initial phase of this process is not influenced by temperature. The probable reason of this fact will be traced in the next chapter.

C. *Normal temperature coefficients.*

PHOTOTROPIC SENSIBILITY IN PLANTS.

Avena sativa has been the object of many investigations both on the spectral sensibility and temperature coefficients of this process. Blaauw[24]) has found the spectral position of the optimum sensibility at 467 $\mu\mu$. The temperature coefficiënt of the phototropic reation time has been studied by Miss de Vries (l. c.). It has been shown in chapter II that the A in Arrhenius' equation remains practically constant throughout a wide range of temperatures. Equation (7) gives for the exciting frequencies;

TEMPERATURE	Q_{10}	λ calculated in $\mu\mu$
0°—10° C.	3,0	439
5°—15° C.	2,8	452
10°—20° C.	2,6	470
15°—25° C.	2,6	455
20°—30° C.	2,5	461
Average λ,	calculated	456
Optimal λ,	found	467

It may be remarked in this connection that in Avena the yellow colour of the coleoptile may be the cause of the blue-violet absorption.

If the determination had been carried out in two decimal places instead of one, no doubt the approximation would have been closer.

RETINAL PROCESSES.

Again it will be tried to find three sets of data. The purple of the rods is bleached by light. de Haas[25]) found a maximum absorption for the visual purple of fishes at 540 $\mu\mu$, of mammals at 500 $\mu\mu$. This is probably the place of the maximum action; Piper[26]) found the the maximum retinal current of the frogs eye at 544 $\mu\mu$.

Hecht (l. c.) could find no temperature influence on the bleaching of the visual purple. Here again is an example of a series of processes, of which the initial process is not influenced by temperature (see next chapter).

The Q_{10} of the retinal current has been determined by Riedel[27]) for the cray fish between 0—30° C. Equation (7) gives

$$\lambda = \frac{1{,}67}{273 \,.\, 283 \,.\, \log 2{,}5} \text{ c.M.}$$

$$\lambda = 537 \ \mu\mu .$$

Hecht (l. c.) studied phototropic responce in Mya. The temperature coefficient of the latent period $Q^{20}/_{10} = 2{,}4$

$$\lambda = \frac{1{,}67}{283 \,.\, 293 \,.\, \log 2{,}4} \text{ c.M.}$$

$$\lambda = 525 \ \mu\mu .$$

CONCLUSIONS

The equation (7):

$$\lambda = p \frac{6{,}2}{T_1 \ (T_1 + 10) \log Q_{10}} \text{ c.M.}$$

seems to hold in a good many cases. About twenty different temperature coefficients yielded values for λ which are in agreement with the experimental data. In the case of low temperature coefficients the relation is not so clear.

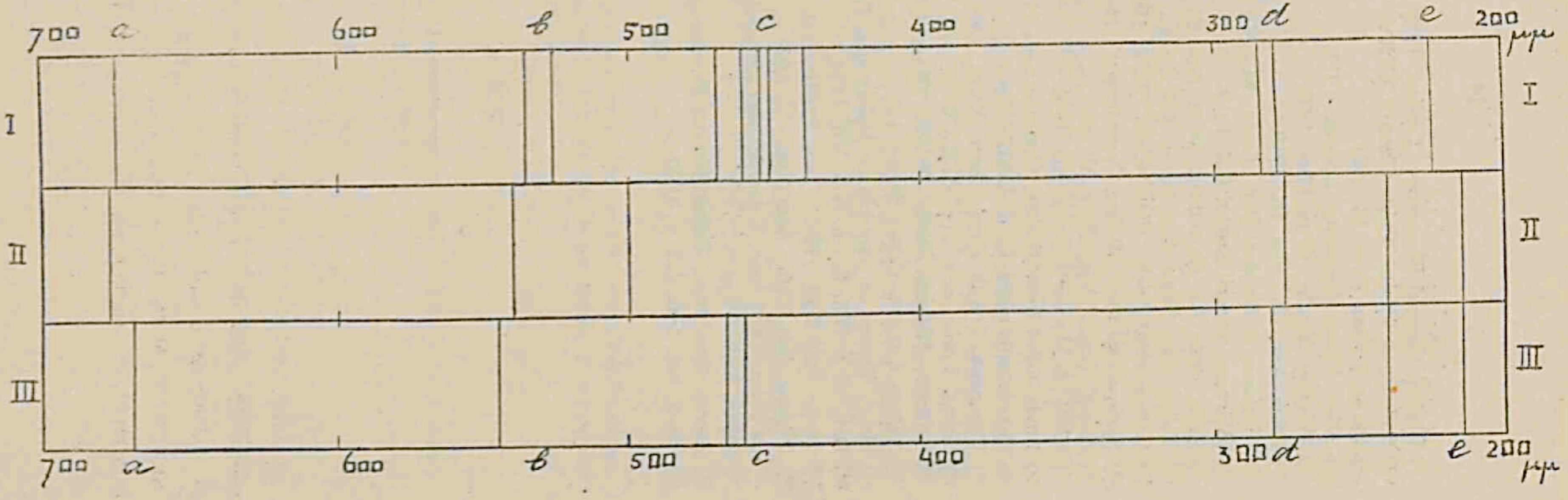
FIG. II. SHOWS THREE SPECTRA.

I shows the calculated exciting frequencies for
- a) photosynthesis.
- b) retinal processes.
- c) phototropic response.
- d) haemoglobin oxidation.
- e) protoplasmic current.

II shows the absorption maxima for the media, in which these processes take place.

III shows the optimal spectral activity for the different processes. The value at c. 467 $\mu\mu$ is calculated from data of Miss Hurd[28]).

A satisfactory agreement between the three spectra is evident.



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CHAPTER IV

RADIATION AND REVERSIBLE REACTIONS.

INTRODUCTION.

An endothermic reaction will be considered, which takes place under absorption of a light quantum $h\nu$. Now there are two possibilities. Either the entire quantum $h\nu$ is used in the reaction, or the quantum $h\nu$ is "degraded" to a quantum $h\nu'$, in which $h\nu' < h\nu$. The same idea can be applied on exothermic reactions; either an entire quantum $h\nu$ is emitted, or the quantum $h\nu'$ is absorbed and "promoted" to $h\nu$; in which $h\nu > h\nu'$. The absorbed or emitted energy in the above cases will be $h(\nu-\nu')$ ergs.

Perrin expresses this idea as follows;

> "Toute réaction implique deux mouvements inverses d'énergie rayonnante, sav. absorption de la lumière qui la provoque, et émission de la lumière qui la renverserait".

Or
$$A + \nu \rightleftarrows A' + \nu'.$$

> "Toute énergie de réaction se mésure par l'excès de la fréquence absorbée sur la fréquence rayonnée".

Or
$$h\nu - h\nu'.$$

This statement enables us to derive a reaction heat in terms of frequencies. This reaction heat is for one molecule

$$h(\nu - \nu').$$

for a gramme molecule

$$N \, . \, h\,(v-v') \text{ ergs} \qquad \text{or}$$

$$4{,}3 \, . \, 10^{-3}\,(v-v') \text{ ergs} \qquad \text{or}$$

$$1{,}0 \, . \, 10^{-10}\,(v-v') \text{ calories}$$

in which v corresponds to

$$\frac{k\,A}{p\,h} \qquad (5)$$

The idea of two frequencies becomes more clear when illustrated by Ostwald's metastable photochemical equilibrium. A wedge shaped block rests on one of its rectangular planes. On tipping this block over at first energy is required to raise the centre of gravity till it is situated perpendicularly above the line of support, than it will be lowered till the block lies on its next rectangular plane. The loss in potential energy may be larger in each turn than the amount of spent energy. If the energy be expressed by $h\,v$, equation (10) can be obtained immediately and it becomes clear why different frequencies may play a role.

Ornstein & Burger found, and their results are in agreement with many photochemical data, that the active radiation has a frequency v which is larger than the

$$\frac{[\text{energy of bound molecules} - \text{energy of dissociated molecules}]}{h}$$

and in the case of the lower limit of the active frequency

$$h\,v_0 = \varepsilon' - \varepsilon \,,$$

this frequency is directly proportional to the difference of energies in the bound-and the dissociated molecules, in other words, proportional to the reaction heat. Inasmuch the reaction heat is a fixed quantily ε' and ε can be written $h\,v'$ and $h\,v$ respectively and the lower energy limit becomes

$$\pm\, h\,(v-v') \text{ which is equation} \qquad (10)$$

This being a *lower* limit the Perrin equation must be modified in

$$U = N \, . \, p \, . \, h \ (v - v') \qquad \text{or}$$

$$U = 0{,}27 \, . \, 10^{-10} \ (v - v') \ \text{calories} \qquad (10)$$

REVERSAL BY LIGHT.

Now, if a system of two exciting frequencies exits, the reaction heat can be calculated. In a "dark" reaction the limiting frequency will be low. In that case $v' - v$ will be maximal. According to Perrin's idea, there are no real "dark" reactions. This dualistic point of view, as proposed by Trautz (l. c.) and Bodenstein (l. c.) becomes superfluous and reactions of the type

$$A + \text{light} \overset{\longrightarrow}{\cancel{\longleftarrow}} B$$

$$B \text{ in dark} \longrightarrow A \qquad \text{can be written}$$

$$A + v \rightleftarrows A' + v'$$

It was known long ago that opposite parts of the spectrum may have opposite effects (Luther [1]). The latent image of a photographic plate is destroyed by infrared radiation (Millochau [2]). Stobbe's fulgides [3] are a very striking example of this reversible action. The bleaching of the visual purple by light is counteracted in the dark (Kühne [4]). Ba-Pt-cyanure becomes brown in x-rays, bleached again by visible light. Guaiacum becomes green in the light, but is bleached in the dark.

A powerful antagonism between the red end and the blue end of the spectrum exists in the case of plant growth (Klebs l.c.). While the long waves stimulate longitudinal growth and inhibit cell division, the short waves stimulate cell division and inhibit longitudinal growth.

As in the dark reaction a large value of $h \, (v' - v)$ might be expected, the Q_{10} must be large — in the light reaction the Q_{10} must be small.

This is actually the case, as the following table shows.

Q_{10} light	Q_{10} dark	AUTHOR	T
anthracene $\leftrightarrows$	dianthracene	Luther 1)	60—160° C.
1,1	2,8		
methyl-anthr. $\leftrightarrows$	dimeth-dianth.	Weigert 5)	60—170° C.
1,1	2,6		
HJ $\leftrightarrows$	HJO_3	Bodenstein	—
1,4	2,86	l. c.	
toluole + Br $\leftrightarrows$	Br toluole	do	—
1,85	4,0	l. c.	
K—Co—Oxalate	Co—Ox + K—Ox	Vránek 6)	20—30° C.
1,1	4,56		

The difference in Q_{10}'s can be accounted for thermodynamically. Considering a reactionisochore

$$\frac{d\,ln\,K}{d\,T} = +\,\frac{A}{T^2}$$

The reaction is reversible, one reaction velocity

being K_1 ; the other K_2 .

$$Q_1 = \frac{K_{1\,.\,T}}{K_{1\,.\,t}} \qquad Q_2 = \frac{K_{2\,.\,T}}{K_{2\,.\,t}}$$

Now $K = d\,ln\,K_1 - d\,ln\,K_2$ or

$$ln\,K = ln\,\frac{Q_1}{Q_2}\text{, between } t \text{ and T} \qquad \text{or}$$

$$ln\,\frac{Q_1}{Q_2} = \pm\,A\,.\,\frac{T-t}{T\,.\,t} \qquad (11)$$

If A is positive, $Q_1 > Q_2$

" " " negative; $Q_1 < Q_2$.

With the help of equations (10) and (11) it will now be tried to investigate the influence of radiation on physiological reactions. The Perrin hypothesis in its general form

$$A + v \leftrightarrows A + v'$$

implies an emission of radiation, either as fluorescence or luminescence, in every chemical reaction.

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CHAPTER V

RADIATION AND PHYSIOLOGICAL REACTIONS.

INTRODUCTION. Physiological reactions vary from comparatively simple processes — as protoplasmic movements and vacuole pulsotions to the complex phenomena as growth, assimilation. There are, however, general laws which govern both simple and complicated phenomena; the principles of thermodynamics.

Notwithstanding the many criticisms on the applicability of the second law of thermodynamics there is no reason to raise serious doubts as to its applicability on physiological systems (Zwaardemaker [1])).

In the preceding chapters it has been tried to modify and extend the hypothesis of Perrin, which advocates the importance of radiation as the cause of combination and dissociation of molecules. One easily measurable factor, the temperature coefficient, has given certain clues as to the nature of the influencing radiation.

There is evidence that radiation influences a good many physiological reactions. It is unlikely, however, that is *causes* these reactions. Organisms in caverns or deep sea are only reached by heat radiation of a low energy value, unsufficient to account for the energy changes within the system. The same is the case for cells inside the organism. It is, however, possible that in the case of heat radiation there is sufficient energy available to initiate the destruction of a mestastable equilibrium (comp. the wedge-shaped blok in the preceding chapter).

In certain cases, part of the work is done by the radiant energy.

The equilibrium of a radiation system would involve absorption as well as emission of light. This emission has only been studied in the range of the visible spectrum. It is possible that, in the majority of cases, the emission will be of an infra red character and has sofar escaped attention. Up till this time, it is mainly the high frequency radiation that has called the attention of the investigators. Especially the specific action of the ultra violet rays on the living cells has been the subject of many investigations.

The Perrin theory requires in many cases an exciting ultra violet frequency. This radiation, when emitted, will be absorbed immediately by the surrounding protoplasm; as protoplasm possesses broad absorption bands in the ultra violet. This occurrence of ultra violet frequencies in living tissues has been assumed also by von Tappeiner[2]) and his school to account for certain peculiarities in the action of sensitizing dyes on the organism. It is not difficult to ascribe this role to a great many natural pigments.

> The fact that the effect of radioactive metals as well as radioactive emission on the heart can be modified by fluorescent dyes may have some connection with Tappeiner's assumptions (Zwaardemaker[3])).

It seems to us that the chief justification of Perrin's hypothesis lies in the fact that it will prove to be an excellent working hypothesis; which calls the attention to a great many possibilities which, hitterto, have remained unnoticed.

VERSIBLE
ACTIONS.

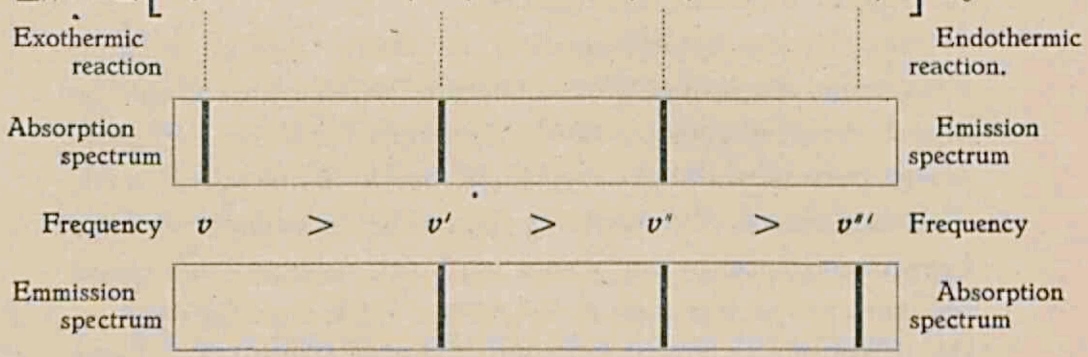
A complex series reaction as underlies most physiological phenomena may be considered as excited or inhibited by different frequencies, corresponding to different temperature coefficients. The temperature coefficients of these subsequent reactions may either express the magnitudes of the exciting frequencies, or they may express the *relation* between two exciting frequencies.

As the Einstein equation $U = N h v$ expresses the relation between light frequency and energy; the Perrin equation $U = N h (v - v')$ between frequency *surplus* and energy.

The Einstein equation may be compared with an expression of the combustion heat, the Perrin equation with the expression of a reaction heat. Only when v' is sufficiently small both equations express the same thing.

Now for a complex series reaction the whole process of radiation exchange can be examplified as follows.

$$U = \pm \overset{h}{\cancel{\vartheta}}\, N h \sum \left[(v - v') + (v' - v'') + (v'' - v''') \right] \text{ ergs}$$

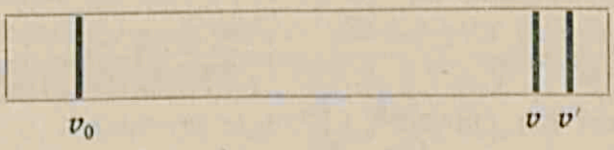


In this schematical representation the energy change in one reaction ΔU takes place between two frequencies, e. g. v and v'. In the exothermic process v is the initial optimal frequency absorbed by the system, usually an ultra violet wave. ΔU ergs is liberated when $h v$ is degraded to $h v'$ in other words, there is fluorescence or luminescence of a frequency range with the average v'. This same frequency can initiate a second jump in potential energy, degrading to v''. This wil go on, and if the process is brought to an end by the 3^d energy jump, a frequency average v''', very often an infra red frequency, will be emitted. The endothermic reaction will go the other way; in this case with an initial absorption of v''', a final emission of v.

This schematical representation suggests absorption and emission spectra of the reaction systems in which absorption bands are emission bands and in which Stoke's law (frequency of fluorescent light is smaller than the frequency of the exciting light) doesn't seem to hold. *Such spectra exist in the living cell.*

> V. Henri 1) has recently developed a formula which shows a connection between the different absorption bands of many complex organic dyes. The absorption spectra consist of equidistant bands; obeying the formula
>
> $\nu = \nu_0 + na + mb$, n and m being integers.
>
> This gives
>
> $\nu - \nu_0 = na + mb$, or according to Perrin the equidistance of the bands expresses:
>
> $dU = na + mb$, the energy jumps being the same between two arbitrarily chosen bands.
>
> Henri remarks that ν_0 usually possesses a strong fluorescence, corresponding to the lowest energy level in the Perrin equation (10).

A series reaction will have different Q_{10}'s for the different processes and these values will differ considerably when the energy changes in the different stages of the process will be very unequal. In physiological processes there are several instances known in which the initial temperature coefficient is very small. This may point to the destruction of a metastable equilibrium. (Retinal processes, sensibility of protoplasm). The theoretical spectrum of this reaction will be:



The system takes in $h\nu$, and changes this into $h\nu'$. Energy *loss* is $pNh\,(\nu' - \nu)$ p . gram-molecule, corresponding to a small Q_{10} ($\nu' - \nu$ is small). The system degrades $h\nu'$ into $h\nu_0$.

Energy *gain* is $pNh\,(\nu' - \nu_0)$ p . gram-molecule, corresponding to a larger Q_{10} . $(\nu' - \nu_0)$ is larger).

The considerations developed in the above pages will now be applied on different physiological reactions. This influence of radiation will considered on

(1) Oxidation, respiration, light emission.

(2) Carbon dioxide assimilation.

(3) Enzym action.

OXIDATION, RESPIRATION LIGHT EMISSION.

Luther[5]) remarks that nearly every photochemical reaction has the nature of an oxidation or a reduction. Therefore radiation seems to be a powerful agent in changing the oxidation potential, either in a chemical or physiological medium. Some authors (Hertel l.c.) hold that the reactions in a certain part of the spectrum are either oxidations or reductions. In the light of the developed theory this would seem untenable, as, for a certain frequency v all rays $v + n\,d\,v$ must induce a higher, all rays $v - n\,d\,v$ a lower oxidation potential. The experimental evidence shows that the ultraviolet can induce both reductions (methylene blue) and oxidations (sugars etc.). Generally, however, it is clear that, if $v - n\,d\,v$ induces an oxidation potential which is much lower than v; $v - n\,d\,v$ will be shifted considerably to the red end of the spectrum, and it can be said that the violet end of the spectrum *is more liable* to cause oxidation, the red end to cause reduction. It will be seen that the two important physological reductions are caused by the red end of the spectrum.

The equilibrium Haemoglobin $\rightleftarrows$ *Oxyhaemoglobin.*

The reaction $Hb \rightleftarrows O_2Hb$ is exothermic in the lungs and gills, exothermic in the tissues; accompanied by oxidation and reduction respectively. The thermal coefficient for the oxidation is very high. The theoretical position of the average exciting wavelength for this dissociation is situated at about 280 $\mu\mu$; a value quite close to the ultraviolet absorption band of the haemoglobin (275 $\mu\mu$) and the maximum of the actual reaction as found by experiment (280 $\mu\mu$).

endo-

It may be asked now if it is possible to calculate the average frequency of the light which will be emitted during this reacton, if this reaction is thought to be sensitized by 280 $\mu\mu$.

In order to carry out this calculation the reaction heat of the system $Hb \longrightarrow O_2Hb$ must be known. The values of du Bois Reymond[5]) and Barcroft & Hill[6]); plm. 28 K.G. calories, will be taken.

In Equation (10)

$$U = 0{,}27 \; 10^{-10} \; (v - v')$$

$$v' = v - \frac{U \, . \, 10^{-10}}{0{,}27}$$

$$v' = 1{,}07 \, . \, 10^{-15} - 1{,}04 \, . \, 10^{-15}$$

$v' = 3 \, . \, 10^{-13}$, corresponding to a wavelenght of about **10** μ.

This means that, according to the modified Perrin theory, the exothermic reaction $Hb \longrightarrow O_2Hb$ will emit infrared radiation; the endothermic reaction $O_2Hb \longrightarrow Hb$ will be excited by this radiation.

Now this excitation occurs. Hartridge and Hill[7]) have found that the system $Hb \longrightarrow O_2Hb$ is sensitive to infrared light. The equilibruim constant changing in this light from

$$K \text{ to } \frac{K}{20} .$$

According to them, the labour done by the light is, per gramme molecule (formula of Nernst)

$$R\,T \; ln \; 20 \text{ ergs} \qquad \text{or}$$

$$\frac{2{,}3 \, . \, 6{,}8 \, . \, 1{,}34 \, . \, 1{,}3 \, . \, 3{,}1}{4.27} \, 10^2 \text{ calories} = 1{,}97 \text{ K.G. cal.}$$

Hartridge & Hill find 1,85 calories, because of the N of Avogadro, which they take to be $6{,}5 \,.\, 10^{23}$ instead of the more recent value $6{,}8 \,.\, 10^{23}$.

Now, according to Ornstein & Burger the chemical active frequency gives

$$h\nu > \varepsilon' - \varepsilon \;.$$

In this case the active radiation must have a frequency higher than

$$v = \frac{1{,}97 \,.\, 10^{3} \,.\, 4{,}27 \,.\, 10^{7}}{h \,.\, N} \qquad \text{or}$$

$$v > 1{,}94 \,.\, 10^{13}$$

corresponding to a wavelength of **15** μ.

The consequence of Hartridge & Hill's data is therefore that any ware shorter than 15 μ will be active so sensitize the reaction $O_2Hb \longrightarrow Hb$.

This is about the place calculated from the Perrin equation (7) and about the optimum of the heat radiation at the body temperature of poikilothermic animals.

Now this would mean a remarkable coincidence, the more so because the values of Hartridge & Hill seem very trustworthy.

Unfortunately this is not the case with the experimental values of Barcroft & Hill for the reaction heat. According to these authors this reaction heat will be about 28 calories. Now there are other investigations which give much smaller values. (Berthelot 8), Torup 9), Camis 10), Meyerhof 11))). The average value from their work is 13,6 calories (10,8 – 15 cal). According to (7)

$$v' = v - \frac{U \,.\, 10^{10}}{0{,}27}$$

$$v' = 1{,}07 \,.\, 10^{15} - 0{,}5 \,.\, 10^{15}$$

$$= 0{,}57 \,.\, 10^{15}$$

corresponding to a wavelength of plm 530 μ μ, in the neighborhood of the maxima of absorption of O_2H b in the visible part of the spectrum (540 μ μ).

The energy jump from this place to the infrared maximum is also 13,6 calories. It is therefore possible that most of the authors have measured the energy jumps between 275 μ μ and 540 μ μ or between 540 μ μ and 10 μ, both corresponding to the intake of one molecule of oxygen.

The reaction haemoglobin $\rightleftarrows$ *oxyhaemoglobin may be, therefore, compared to a dark* $\rightleftarrows$ *light equilibrium, as in the case of the photo-polymerisation of anthracene. The position of the main absorption bands as calculated by the Perrin equation is in agreement with the actual facts.*

OXIDATIONS.

In order to acconnt for the exciting frequencies outside the visible spectrum, the existence of a fluorescent substance has been assumed by von Tappeiner and his school. Recently Noack [12]) has developed a theory in which the Palladin system peroxydase — oxygenase is replaced by fluorescent substance — M n-salt. In the light of the theory developed in in the preceding chapters his ideas can be interpreted as follows.

The fluorescent substance changes the incident light into photochemically active light, which action is catalyzed by the M n-salt. Noach has worked with the colour changes in press juices from Aloe and Vicia. It is possible that in these complex solutions the M n-salt was already present. Therefore his experiments were repeated, using phenoles instead of press juices. 1 % Pyrogallol, pyrocathechin and hydrochinon proved to react in a similar way as the press juices; their oxidation was accelerated by eosin in the light. Addition of M n-salt had no effect on the hydrochinon; it accelerated the eosin-light oxidation of pyrocathechin and pyrogallol. No effect could be traced on 1 % phloroglucin, 0,5% o-cresole and a saturated solution of tyrosin. One cannot expect the different phenoles to react in the same way with the same sensitizer, as they possess a different light absorption. As far as the evidence goes the oxidation of phenoles is influenced by light and optical sensitizers, and as these phenoles can be compared to a Palladin system, there is no reason to assume that respiration would prove independant of radiation.

LUMINESCENCE. According to modern theories, luminescence is only a prolonged fluorescence. In organisms, this luminescence is caused by an oxidation (Dubois [13])). The production of this light is not accompanied by a measurable caloric effect. (Harvey l.c.). The three last sentences enable us

a) to apply the equation of Perrin

$$A + \nu \rightleftarrows A' + \nu'.$$

b) to connect lumniescence and oxidations,

c) to predict that

$$U = 0{,}27 \,.\, 10^{-10} \, (\nu - \nu')$$

will be very small. Accordingly $\nu - \nu'$ will be very small and, approximately, $\nu = \nu'$, or the exciting frequency for reduction is equal to the exciting frequency for oxidation. This oxidation is, according to Dubois and Harvey:

luciferin ⟶ oxyluciferin ,

a phenole derivative. Therefore the wavelength of the light emitted during this reaction may give us, according to (7), a clue as to the thermal acceleration of this oxidation process. It will be seen if the thermal accelerations of other oxidations in vegetable and animal cells are comparable to these calculated data. The value for the maximum wavelength for the emitted light in animals is by

Cypridina hilgendorfii	512 μμ
Pyrophoris noctilucus;	
thoracic segments	554
abdominal segments . . .	563
Photinus spiralis	540
Ph. pennsylvanica	550
Ph. consanguineus	585
Lampyris sp.	587
Photinus sp.	578
AVERAGE	555

while the values for plants show a considerable shift to the higher frequencies;

Bacteria	505 μμ
Bacteria	525
Bacteria	510
Agaricus melleus	520
Xylaria hypoxylon	500
AVERAGE	512

For these values we can calculate the corresponding Q_{10} at room temperature (15—25°), following:

$$\log Q_{10} = 0{,}39/0{,}23 \,.\, \lambda \,.\, T_1 \,.\, T_2 \,.$$

This gives for animal light;

$Q_{15/25} = 2{,}32$ and for plant light;

$Q_{15/25} = 2{,}52$

These calculated values for the temperature coefficient are of the same order as the known coefficient for other oxidation processes, as the following table shows;

AUTHOR	OBJECT	$Q_{15/25}$	Calculated $Q_{15/25.}$
Kuyper	peas	2,2	
	wheat	2,3	
	lupins	2,4	
	AVERAGE	2,3 . .	. . . 2,30
Krogh	AVERAGE (6 species)	2,27	
Lindstedt	fishes	2,1	
Vernon	Lumbricus	2,16	
	toad	2,15	
	AVERAGE ANIMALS	2,17 . .	2,30 . . . ~~2,52~~

If these values are true, the energy change during such a reaction can be calculated, on the assumption that there is a direct connection between respiration (or *part* of the respiration) and light emission.

This proves to be about 10 gram-calories, a quantity too small to detect, as luciferin must have a rather high molecular weight.

2) *The* CO_2 *assimilation of the green leaf.*

In the case of haemoglobin oxidation it has been seen that the light energy of an ultraviolet quantum corresponds to plm. 30 K.G. calories p. gramme-molecule. These values were sufficient to account for the energy changes in the haemoglobin, they are deficient to account for the increase in energy that takes place during the process of photosynthesis in the green leaf. Even the simplest possible product, formaldehyde, requires 137 K.G. calories per gramme-molecule. External illumination, however, may provide several light quanta per molecule before the first product of photosynthesis is formed. Light of very different wavelength is able to initiate this process, provided that it is absorbed.

According to recent investigations a strong red fluorescence takes place inside the chloroplastids (Stern 14)). The maximum red absorption in the leaf is also a maximum of fluorescence. This may point, according to Perrin's theory, to a series of processes. The first process may be initiated at higher frequency and absorbing this light, emitting radiation of about 678 $\mu\mu$; the other process absorbing light of 678 $\mu\mu$ and emitting an infra-red group of frequencies. And, since Ursprung (l. c.) has shown that the infrared radiation may cause photosynthesis it is possible that the infrared emission may take place at different parts of the infrared spectrum.

A series process, as it has been shown in the first paragraph of this chapter, implies, as a consequence of Perrin's theory, a series of absorption bands.

It suggests a series of equidistant bands, as expressed by Henri's formula

$$\nu = \nu_0 + na + mb\,.$$

The values of Willstätter 15) for the chlorophyll spectrum and the rather scanty data for the infra red (v. Gulik) and ultra violet (Ursprung) absorption may be related by the expression

$$\nu = 8{,}9 \,.\, 10^{13} + n,\ 8{,}9 \,.\, 10^{13}$$

as the following table shows;

$\nu = 8{,}9 \,.\, 10^{13} + n \,.\, 8{,}9 \,.\, 10^{13}$				
n	ν . calculated	ν . observed	DEV.	AUTHOR
0	$8{,}9 \,.\, 10^{13}$	$8{,}9 \,.\, 10^{13}$	$\pm\, 0 \,.\, 10^{13}$	v. Gulik
1	17,8 ..	—	—	—
2	26,7 ..	—	—	—
3	35,6 ..	35,2 ..	— 0,2 ..	v. Gulik
4	44,5 ..	44,3 ..	— 0,4 ..	Willstätter
5	53,4 ..	53,5 ..	+ 0,1 ..	Willstätter
6	62,3 ..	61,5 ..	— 1,2 ..	Ursprung
7	71,2 ..	72,4 ..	+ 1,2 ..	Ursprung

The deviations may partly be caused by the uncertainty in the determination of the determination of the optical axes of the bands.

$\nu = 8{,}9 \, . \, 10^{13}$ corresponds to about 2,5 K.G. calories; or, for the whole chlorophyll spectrum the energy jump is about 20 K.G. calories. It may be that Willstätters assumption, an initial reaction of the chlorophyll with the carbon dioxide will lead to a small value for the reaction heat of photosynthesis. The experimental data are as yet too scanty to allow similar deductions as in the case of the reduction of the oxihaemoglobin.

LIGHT EMMISSION OF THE GREEN LEAF

One conclusion, however, may be drawn in connection with Perrin's theory. Inasmuch as the green leaf *absorbs* chiefly red light during photosynthesis, there is evidence that light of about this frequency will be *emitted* during the reverse process; respiration.

This would mean, essentially, nothing else as a prolonged fluorescence.

Immediately after photosynthesis a green leaf can be brought into a dark room.

The light emitted can be shown by an image made on a photographic plate.

Care must be taken that the leaf is not in direct contact with the sensitive emulsion as different chemical compounds cause a reduction of the silver emulsion. We name here; carbon dioxide, formic acid, different ethereal oils, hydrogen peroxide.

A leaf in immediate contact with a photographic plate gives a visible image within 18 hours exposure, as I was able to verify on leaves of Tropaeolum, Escholtzia, Salix and many others. Ursprung & Gockel [16]) have not been able to get any image through a glass plate from Primula and Pinus leaves after seven days exposure with an orthochromatic plate.

Scheminsky, however, mentions that radiation, emitted by fermenting beans is able to penetrate through a glass plate.

In order to make the obstacle for the emitted light as small as possible 2 inch coverslides were used of homogeneous texture and thickness. Wratten panchromatic plates were used. The results were entirely negative with Salix, Lonicera and Malva leaves. Even after a four days exposure no trace of an image could be observed. With Tropaeolum, however, a distinct image was obtained within 18 hours. This same result could not be obtained by using "Seed 23" plates.

Nor could it, till now, be repeated. This failure is probably due to the fact that the emission takes place at the limit of the sensibility for the Wratten emulsion. The experiments will be continued with other sensitized emulsions.

SUGAR INVERSION. It is obvious that the final product of photosynthesis cannot be starch as this can be formed, independently from light, only by increasing the concentration of sugars in the cell. There is considerable evidence that the first product is sugar and we will take cane sugar as the end product of photosynthesis (Brown and Morris). The leaf must be able to invert and synthesize cane sugar under the influence of the visible light. Now the experiments show the result that cane sugar cannot be inverted bij U. V. light down to 200 $\mu\mu$.

Now, according to Perrin's equation (9), a catalyzer will influence the position of this frequency. Positive catalysis will lower the active frequency. Therefore there is evidence to assume that the addition of a catalyzer will sensitize the sugar solutions for visible rays. The experiments of Winther (l. c.) have shown that iron is a powerful photochemical catalyzer. It remained therefore to be investigated whether addition of iron salts could cause cane sugar inversion. The experiments, carried out in the Californian sunlight have shown that after 18 hours of sunlight more than 80% of a 0.5 N cane sugar solution become inverted by rather small amounts ($^1/_2$%) of iron. Ten Erlenmeyer flasks were prepared as follows:

FLASK

A and A^1 . . . . . . ; sterilized A in direct, A^1 in diffuse light.
100 cc. 0.5 N
cane sugar
25 cc. 10 % $Fe\,SO^4$

B and B^1 . . . . . . ; „ B „ B^1 „ „
100 cc. 0.5 N
cane sugar
25 cc. 10 % $Mn\,SO^4$

C and C^1 . . . . . . ; „ C „ C^1 „ „
100 cc. 0.5 N
cane sugar
25 cc. 10 % $Mg\,SO^4$

D and D^1 . . . . . . ; „ D „ D^1 „ „
100 cc. 0.5 N
cane sugar
no additions

E, F, G, controls, like A, B, and C, but kept in absolute darkness.

After ten hours illumination the controls gave a rotation (Schidt-Haensch polarimeter).

+ 19.89° average.

The flask, iron sunlight gave	+ 10.09°	
„ „ iron diffuse light	+ 14.45°	
„ „ manganese sunlight	+ 19.03°	
„ „ „ diffuse light . .	+ 19.75°	
„ „ magnesium sunlight . . .	+ 19.85°	
„ „ „ diffuse light. .	+ 20.12°	
„ „ no addition, sunlight. . .	+ 18.90°	contamination ?
„ „ „ „ subdued light	+ 20.08°	
„ „ controls dark	+ 19.98°	

Manganese and magnesium proved to be ineffective. An important deduction can be made from this. *If we assume the reaction invert sugar ⟶ cane sugar to be principally reversible, we can expect the plant to use a photocatalyzer to effect this reaction. This would lead us to believe that in the chloroplasid a catalyzer would act in a similar way as our iron catalyzer with the in vitro experiments.* Now, Moore [17]) has established the presence of inorganic iron compounds in the chloroplastids. He has been able to show the catalytic and synthetic action of iron on several compounds.

From equation (9) it will be seen that the temperature coefficient of a positively catalyzed reaction decreases. Therefore, the factor A in equation (3) will be decreased also. Now Euler and Laurin [18]) have determined the A for hydrogen ion- and for enzymatic cane sugar inversion, finding for A 25,600 and 9,400 respectively. The A is considerably decreased and corresponds now to a wavelength in the visible spectrum (415 $\mu\mu$).

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CONCLUDING REMARKS

Summarising the contents of this paper is not very well possible, the statements being made in a condensed form already.

The writer only wishes to emphasize once more that he is perfectly aware of the many shortcomings of his work. A short criticism on the preceding paper will make this clear.

1. The fundamental basis of this paper, the theory of Jean Perrin, is by no means a stable and recognized structure.
2. The quantitative changes in the original Perrin equation are entirely arbitrary.
3. The theory is incomplete, inasfar as it has ignored the large field opened by the heat theorem of Nernst.
4. There is a considerable disproportion between theory and experiment.

The, apparently, succesfull application of the theory, however, seems to justify the opinion that the Perrin theory will prove to be a convenient working hypothesis.

It enables the experimentator to synthesize a vast group of, hitherto disconnected, facts.

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EQUATIONS DERIVED IN THE PRECEDING CHAPTERS.

(1) $$ln\ Q = \frac{h\ v}{k}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

(2) $$ln\ Q = p\ \frac{h\ v}{k}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

(3) $$ln\ Q = A\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

(4) $$A = \frac{h\ v}{k}$$

(5) $$A = p\ \frac{h\ v}{k}$$

(6) $$\lambda = p\ \frac{1{,}43}{A}$$

(7) $$\lambda = p\ \frac{6{,}2}{T_1\ (T_1 + 10)\ \log\ Q_{10}}$$

(8) $$\frac{h\ v}{k} > A$$

(9) $$\frac{v}{v'} = \frac{d\ \log K}{d\ \log K_1}$$

(10) $$U = 0{,}27 \, . \, 10^{-10}\ (v - v')$$

(11) $$ln\ \frac{Q_1}{Q_2} = \pm\ A\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

STELLINGEN

I

Het levend protoplasma kan doorlaatbaar zijn voor enzymen.

II

Bij de quantitatieve bepaling van enzymwerking dient de latentietijd in aanmerking genomen te worden.

III

In de prikkelphysiologie dient de meterkaars-secunde vervangen te worden door de erg per secunde voor monochromatisch licht.

IV

Bij vrije paring treedt na eenige generaties een vaste numerieke verhouding op tusschen de eigenschappen eener populatie.

V

De proeven van Calvin Bridges zijn bewijzend voor de chromosoomhypothese der erfelijkheid.

VI

Het genus Botrychium dient in drieën gesplitst te worden.

VII

De stelairtheorie is van geen waarde bij phylogenetische beschouwingen.

VIII

Het voorkomen van bepaalde planten wijst op bepaalde samenstelling van den bodem, echter niet op een bepaalde geologische formatie.

IX

Tumoren kunnen worden veroorzaakt door injecties van hypotonische oplossingen.

X

De leerproeven genomen door Buitendijk op hoogere dieren zijn methodisch onverdedigbaar.

XI

Palaeospondylus gunni Traq. is waarschijnlijk een larvale vorm, bijvoorbeeld van Coccosteus.

XII

Het eiland Terschelling is geheel van alluvialen oorsprong.

XIII

Het vraagstuk der internationale uitwisseling van studenten en hoogleeraren dient krachtig ter hand genomen te worden.