

The corresponding theorem for the problem of the representation of integers as a sum of powers of primes is rather more simple. Let ¹⁾

$$A'_q(n) = \sum'_{a \bmod q} \left(\frac{C_q(a)}{\varphi(q)} \right)^s e_q(-an), \quad \chi'_p = 1 + \sum_{\lambda=1}^s A'_{p^\lambda}(n).$$

Then we have the

Theorem. If $N'(p^\alpha, m)$ is the number of solutions of the congruence (1) for which all $h_i (i=1, 2, \dots, s)$ are prime to p , then

$$\chi'_p = p^\nu (\varphi(p^\nu))^{-s} N'(p^\nu, m).$$

Proof. From lemma 1 we get

$$\chi'_p = 1 + \sum_{\lambda=1}^{\nu} A'_{p^\lambda}(n).$$

We now consider the sum

$$\sigma' = \sum'_{h_i \bmod p^\nu} \sum_{a \bmod p^\nu} e_{p^\nu}((h_1^k + h_2^k + \dots + h_s^k - n)a).$$

Then in the same way as shown above for σ , we now find for σ' the two expressions

$$\sigma' = (\varphi(p^\nu))^s \chi'_p = p^\nu N'(p^\nu, m)$$

and the theorem follows immediately.

¹⁾ I. VINOGRADOFF, Einige allgemeine Primzahlsätze. Travaux de l'Institut math. de Tbilissi 3, 1-67 (1938) (in Russian and in German).

Chemistry. — On dissymmetrical synthesis in the case of complex metallic salts. III. By I. LIFSCHITZ ¹⁾. (Communicated by Prof. F. M. JAEGER.)

(Communicated at the meeting of January 28, 1939.)

§1. If a luteo-cobaltic salt be prepared from an optically inactive Co-salt and an optically active diamine — e.g. *l*-propylene-diamine (= *l*-pn), — a relatively-dissymmetrical reaction takes place and the obtained reaction-product is totally (or double) active. It might be expected to consist of a mixture of two optical isomers, viz. I. $[\text{Co}(l\text{-pn})_3]_D X_3$ and II. $[\text{Co}(l\text{-pn})_3]_L X_3$. However, in all cases so far examined only one single salt was obtained. Nevertheless, it may be easily demonstrated that a relatively dissymmetrical synthesis has, indeed, taken place. The obtained luteo-salt, namely, appears to possess a rotatory dispersion of a perfectly similar nature as $[\text{Co}(en)_3]_D X_3$, — which salt owes its activity exclusively to the axial symmetry of the complex ion. Moreover, already the occurrence of a COTTON-effect in the visible spectrum proves that the above-mentioned luteo-salt must be totally-active; for complexes, which are only partially-active with regard to the diamine, never manifest such a COTTON-effect ²⁾.

Totally different conditions are met with in the case of the complex cobaltic salts with three mol. of an optically-active α -amino-acid, e.g. $[\text{Co}(d\text{-alanine})_3]$. A comparison with optically-active $[\text{Co}(glycine)_3]$ is impossible here, as the latter salt has not yet been obtained in the optically-active form; while, on the other hand, it is not known whether a complex-bound, optically-active α -amino-acid present in of themselves racemic complexes, causes a COTTON-effect to display itself or not. The occurrence of a relatively-dissymmetrical synthesis, consequently, could only be considered as rigorously proved in the case of these tri- α -amino-acid cobaltates, if of the four theoretically possible reaction-products (α and β forms are geometrical isomers): III. α - $[\text{Co}(d\text{-alan})_3]_D$; IV. α - $[\text{Co}(d\text{-alan})_3]_L$; V. β - $[\text{Co}(d\text{-alan})_3]_D$; VI. β - $[\text{Co}(d\text{-alan})_3]_L$, either all four, or three, or at least III and IV or V and VI could be shown to be present in the reaction-product and could be isolated from it.

In the preceding communications the presence of a relatively-dissymmetrical synthesis could, indeed, in this way be proved in the case of the complex-formation with three mol. *d*-alanine or *d*-glutaminic acid. The results of these and not yet published researches ³⁾ now justify the

¹⁾ Cf. Proc. Kon. Akad. v. Wetensch., Amsterdam, 27, Nos. 9 and 10 (1924); *ibid.* 39, Nr. 10 (1936).

²⁾ Cf. A. WERNER, *Helv. Chim. Act.*, 1, 5 (1918).

³⁾ From not yet completed experiments it was found, that also in the case of complexes with asparaginic acid a similar argumentation is feasible. ☉

conclusion, that also in the case of cobaltic compounds with three mol. of arbitrarily chosen optically-active α -amino-acids, a relatively-dissymmetrical synthesis really takes place. This, however, does not alter the fact that, for the investigation of the laws of the relatively-dissymmetrical synthesis in general, and those in complexes containing amino-acids in particular, — it would be of fundamental importance to find an accurate criterion for the origin and nature of the optical activity observed. If, on the ground of determinations of the rotation and rotatory dispersion, we were able to decide immediately whether a given cobaltic complex is totally — or only partially-active (with regard to the coordinated groups), — then the always troublesome and sometimes even quite impossible isolation of the isomers present would become unnecessary.

Besides, such a criterion, also from a purely polarimetric point of view, might perhaps lead to somewhat broader views, as will be seen later.

§ 2. However, on the ground of the results obtained so far concerning the rotatory dispersion of complex compounds, such an activity-criterion *cannot* be given. We have by no means been able even to demonstrate that in a totally-active complex the rotations of the optically-active coordinated groups and those of the complex, — at any rate only upon first approximation, — are immediately superimposed; neither is it known, whether a special and characteristic contribution to the total rotation may be ascribed to an optically-active group, — at least in constitutively comparable complexes⁴⁾. The results of TSCHUGAEFF and SOKOLOW are of only limited importance in this respect, as will be discussed in another connection.

In numerous cases, however, it will be sufficient if, with some certainty, the order of magnitude of that contribution of the active group to the rotation can be estimated. In special cases it may already be of great value to know, whether the complex-bound group alone can produce a COTTON-effect or not. Examples of this may be found in the case of the α -amino-acid-complexes of *copper*, *nickel*, bivalent *cobalt*, etc.

According to an empirical rule proposed by the author and afterwards more generally confirmed, — complexes of these metals with optically-active, coordinatively-bivalent, organic substitutes always show such a COTTON-effect, when the ring of secondary valencies ("chelate"-ring) simultaneously encloses the "asymmetrical" carbon atom. However, *why* particularly in these cases a COTTON-effect manifests itself, had to be left undecided. The presence, namely, of a COTTON-effect might either be

⁴⁾ Comparable complexes are those, which spectroscopically — and, therefore, also constitutively, — have analogous structures (both molecular compounds or both real complexes) and which in the first place possess an equal and similar charge; e.g. $[\text{Co}(\text{en})_3]\text{X}_3$; $[\text{Co}(\text{en})_2(\text{l-pn})]\text{X}_3$; $[\text{Co}(\text{en})(\text{l-pn})_2]\text{X}_3$ and $[\text{Co}(\text{l-pn})_3]\text{X}_3$; not however e.g. $[\text{Co}(\text{d-alan})_3]$ and $[\text{Co}(\text{en})_2(\text{d-alan})]\text{X}_2$. An elaborate discussion of this problem will be given elsewhere.

based on a particularly strong linkage of metallic and carbon electrons, or it might have its origin in the "total" activity of the mentioned complexes themselves; in other words, — e.g. in the formation of a complex *d-alanine-copper* salt, — a relatively-dissymmetrical synthesis truly might have taken place.

P. PFEIFFER and W. CHRISTELEIT⁵⁾ recently have accepted the latter conception. However, the conclusion of these experimenters can only be maintained, if it could be demonstrated that complex-bound, optically-active amino-acids themselves, — i.e. in undeniably partially-racemic complexes, — do *not* give rise to such a COTTON-effect. Thus far nothing is known on this subject either.

§ 3. As a first attempt to solve the described problems, an examination was made of complexes of the general formula $[\text{Co}(\text{en})_2(\text{A}m\text{ac})]\text{X}_2$ — where (A*m*ac) represents an optically-active α -amino-acid. The *glycine*-salt VII was already obtained by J. MEISENHEIMER, both in the racemic and the optically-active form. At my request, Dr. F. L. M. SCHOUTEDEN repeated these experiments, wholly confirmed them and at the same time completed them by a determination of the rotatory dispersion (see fig. 2, curves 1 and 2). Analogous salts with other, and in particular with optically-active amino-acids, could not be prepared by MEISENHEIMER: according to his observations these complexes are so strongly soluble and do crystallize so imperfectly, that he refrained from further attempts to isolate them. Indeed the *chlorides*: VII. $[\text{Co}(\text{en})_2(\text{glycine})]\cdot\text{Cl}_2$; VIII. $[\text{Co}(\text{en})_2(\text{d-alan})]$; IX. $[\text{Co}(\text{en})_2(\text{l-leucine})]\text{Cl}_2$ cannot be obtained in a pure and crystallized form; the *leucine*-salt also offers great difficulty in purification. On the other hand, the *nitrate* corresponding to VIII and the *d- α -bromine-camphor- π -sulphonate* may be obtained in fine, red-orange crystals; while of the complex containing *leucine* a splendidly crystallized *iodide* could be prepared; with great difficulty also a *chloride* and more easily the pure *d-tartrates* and the *d- α -bromine-camphor- π -sulphonate* were prepared. The accurate prescriptions for their preparation and the results of the analyses made will be communicated elsewhere; here only the result of the polarimetric measurements will be discussed in detail.

In fig. 1 besides the rotation-curves of the employed amino-acids, those of the complexes directly obtained from *praseo-cobalti-chloride* and *d-alanine* or *l-leucine*, are represented. One is struck by the fact, that the rotation of the latter is of a totally different order of magnitude than that of the active *glycine*-salt VII; and already here there is an indication of the fact, that these complexes truly must be *partially-racemic*. Indeed, it soon became apparent, that both salts can themselves easily be resolved: VIII by means of *d- α -bromine-camphor- π -sulphonic-acid*, IX by *d-tartaric*

⁵⁾ P. PFEIFFER and W. CHRISTELEIT, Z. f. physiolog. Chem. (H. S.), 245, 197 (1938).

acid. Finally, from the totally active *bromo-camphor-sulphonates* or *tartrates*, as well the *nitrate* corresponding to VIII as the totally-active

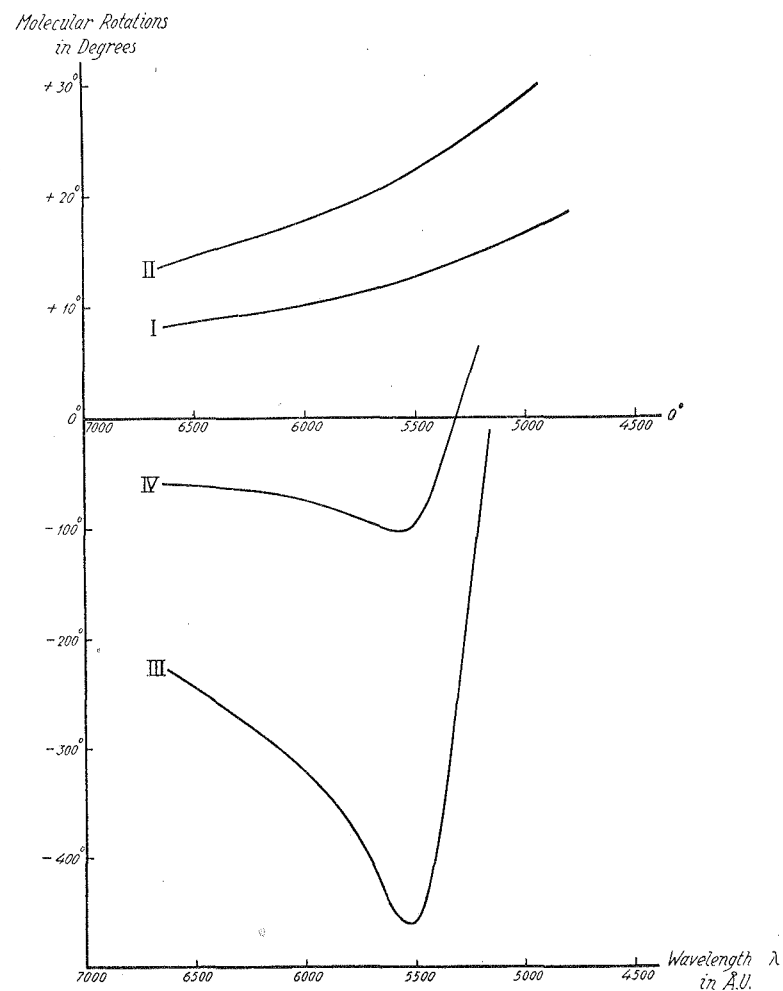


Fig. 1.

- I. *d*-Alanine (Conc. 1.65 gr. in 100 cc. 1 N. HCl)
 II. *L*-leucine (Conc. 1.42 gr. in 100 cc. 1 N. HCl)
 III. $R\text{-[Co(en)}_2(l\text{-leucine)]I}_2 + 1 H_2O$
 IV. $R\text{-[Co(en)}_2(d\text{-alanine)](NO}_3)_2 + 1.5 H_2O$ } in water.

chloride IX could be prepared. The rotations of these complexes have been graphically represented in the figs. 2 and 3.

Consequently, of the complexes of the type: $[\text{Co(en)}_2(\text{A}mac)] \cdot X_2$, we now have at our disposal: the active *glycine*-salt; the partially-active (with regard to the coordinated groups) and the totally-(double) active forms. From the shape of their rotation-curves, immediately a number of conclusions may be drawn.

§ 4. A. In the first place it is seen that by the introduction of one molecule optically-active α -amino-acid, no dissymmetrical synthesis occurs.

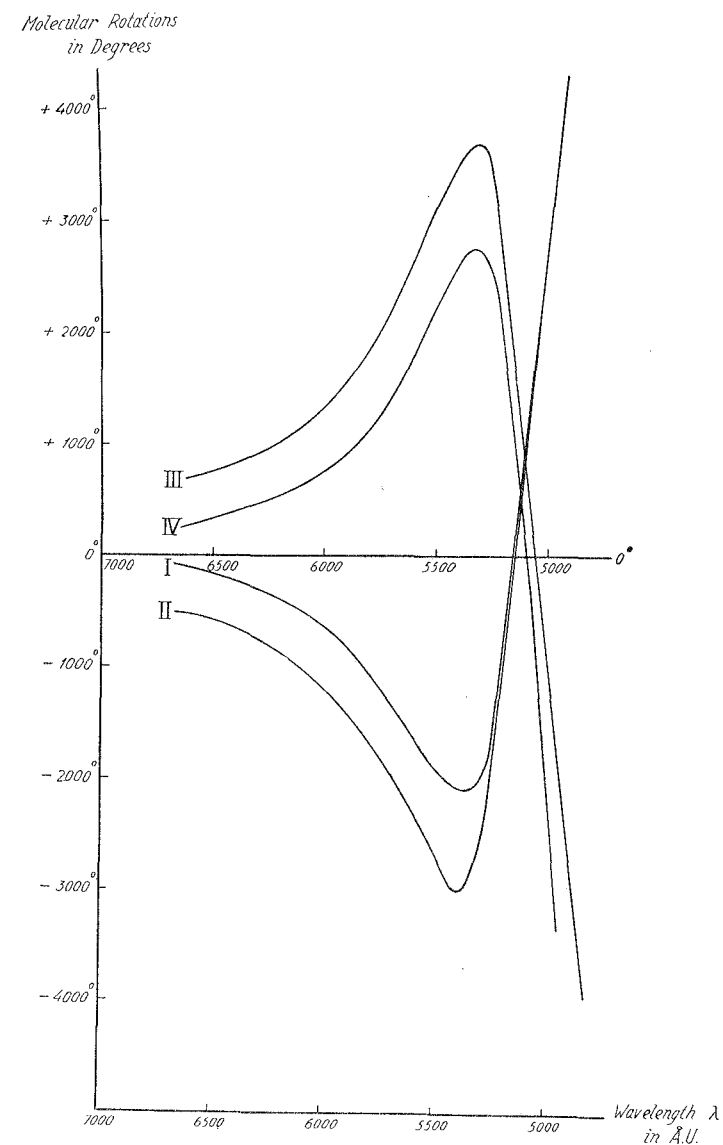


Fig. 2.

- I. $[\text{Co(en)}_2(\text{glycine})]_L\text{-d-}\alpha\text{-Bromine-Camphor-}\pi\text{-sulphonate}$
 II. $[\text{Co(en)}_2(\text{glycine})]_L \cdot J_2$
 III. $[\text{Co(en)}_2(d\text{-alanine})]_D\text{-d-}\alpha\text{-Bromine-Camphor-}\pi\text{-sulphonate}$
 IV. $[\text{Co(en)}_2(d\text{-alanine})]_D \cdot (\text{NO}_3)_2$ } in water.

This is in perfect agreement with the results found with optically-active diamines, — where by the introduction of a single molecule of an optically-

active diamine, neither a case of total optical activity, nor the occurrence of a dissymmetrical reaction was observed ⁶).

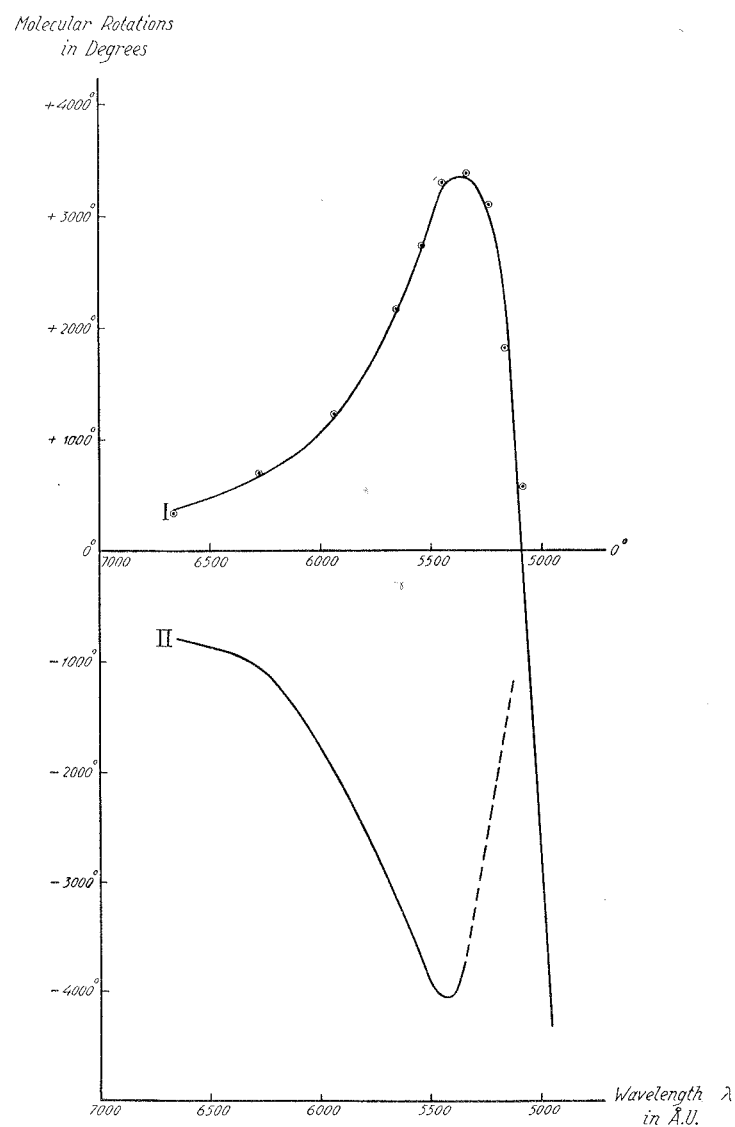


Fig. 3.

- | | |
|--|----------------|
| I. $[\text{Co}(\text{en})_2(\text{l-leucine})]_D\text{-}d\text{-tartrate}$ | } in
water. |
| II. $[\text{Co}(\text{en})_2(\text{l-leucine})]_L\text{-}d\text{-tartrate}$ | |
| $\odot\odot\odot [\text{Co}(\text{en})_2(\text{l-leucine})] \cdot \text{Cl}_2$ | |

B. It further appears that a complex-bound, optically-active amino-acid may, — also in undoubtedly racemic, and, therefore, still fissable complexes,

⁶) Cf. Proc. Kon. Akad. v. Wetensch., Amsterdam, 27, Nos. 9 and 10 (1924); *ibid.* 39, Nr. 10; A. WERNER, *Helv. Chim. Acta*, 1, 5 (1918).

— produce a COTTON-effect. This is in agreement with the result of the previously made and published observations on *tri-d-alanine-* and *tri-d-glutamic-cobaltiates*. For if from the measured rotation curves of e.g. $\alpha\text{-}[\text{Co}(\text{d-alan})_3]_D$ and $\alpha\text{-}[\text{Co}(\text{d-alan})_3]_L$ or of the corresponding *glutaminates*, the rotations of $\alpha\text{-}[\text{Co}(\text{d-alan})_3]_{\text{Rac}}$ or of $\alpha\text{-}[\text{Co}(\text{d-glutam})_3]_{\text{Rac}}$ be calculated, it appears that also the latter salts must show a COTTON-effect ⁷).

Thus at the same time it has been demonstrated that the statement by PFEIFFER and CHRISTELEIT, — if not untenable, — at any rate must be considered as to be totally *unproved*; and this can be stated the more decidedly, as these partially-active salts show a rotation and a rotatory dispersion of about the same order of magnitude and of a similar character, as the complexes of the bivalent metals ⁸) containing *α -amino-acids*.

C. The rotation of the totally-active complexes VIII and IX, — but also that of VII, — is of another order of magnitude than that of the partially-active salts; and it proves to be higher than that of the latter.

This may be easily stated by a comparison of the maximal molecular rotations. The magnitude of the maximal molecular rotation consequently seems to enable us, — at any rate as a first conjecture, — to decide, whether a given complex salt must be considered as a totally- or partially-active one. For the present, this is only valid for *cobaltic* complexes of this kind.

D. The contribution of the optically-active group (*α -amino-acid*) to the rotation is, — upon first approximation, — equally large in the case of the totally-active complexes, as in that of the partially-active ones; in our cases, therefore, the rotations of the complex and the coordinated group are, upon first approximation, independent of each other. For if the rotations of $[\text{Co}(\text{en})_2(\text{l-leucine})]_D$ and $[\text{Co}(\text{en})_2(\text{l-leucine})]_L$ be — each with its own sign —, added then the sum be divided by *two* and the obtained rotation subtracted from that of the *d-tartrate-ion*, then, with a rough approximation, the rotations of the partially-racemic salt are, indeed, obtained ⁹).

E. Finally, it may be remarked that the maximal rotation of the complexes: $[\text{Co}(\text{en})_2(\text{A}mac)]X_2$ is superior as well to that of optically-active *triethylene-diamine-cobaltic-chloride* as to that of the *tri- α -amino-acid-cobaltiates*. Similar phenomena, i.e. that complexes of the types: $[\text{CoA}_2B]$ and $[\text{CoAB}_2]$ show a higher rotation than such like $[\text{CoA}_3]$ or $[\text{CoB}_3]$, are also found in other series of complexes; but the experimental material is as yet still very scarce. It is possible that this higher rotation

⁷) For this purpose we only have algebraically to add the rotations and to divide the result by two.

⁸) A comparison will be made in another connection. The *physiologically* important conclusions of PFEIFFER and CHRISTELEIT are not weakened by our results.

⁹) An accurate similarity is not to be expected, since here we have to deal with *small differences of large numbers*.

of complexes with *unequal* coordinated groups is more particularly connected with their *lower* symmetry. Among other things the fact, that the geometrically isomeric complexes with three mol. *α-amino-acid*, — which practically *only* differ as to their molecular symmetry, — qualitatively do not display any appreciable differences in their rotatory dispersion, but yet possess quantitatively highly different absolute rotations, — seems really to corroborate this suggestion. From this we perhaps might conclude, that of two comparable complexes, the one which possesses the lower symmetry, ever will show the greater rotation. To this and other problems we will soon return in another paper ¹⁰⁾.

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¹⁰⁾ This might supply us with a method of determining the sterical constitution of geometrical isomers, such as *α-* and *β-trialanine-cobaltic-salts*. So far this proved to be impossible.

Botany. — *Einige Bemerkungen über den Einfluss der Nitratreduktion auf die Atmung der Wurzeln.* Von W. P. POSTMA. (Communicated by Prof. J. C. SCHOUTE.)

(Communicated at the meeting of January 28, 1939.)

Von mehreren Untersuchern (STEWART, HOAGLAND, LUNDEGÅRDH u.a.) wurde ein Zusammenhang zwischen der Aufnahme von Salzen durch die Wurzeln und der Intensität der Atmung nachgewiesen. Immer wurde gefunden, dass mit einer grösseren Salzaufnahme auch eine kräftigere Atmung verbunden war. Um diese Beziehung zu erklären, wurden verschiedene Theorien aufgestellt.

Allein die Auffassung LUNDEGÅRDHS wird hier kurz besprochen.

Aus den Versuchen LUNDEGÅRDHS erhellt, dass die Atmung der Wurzeln von Weizen nicht durch das Aufnehmen von Kationen beeinflusst wird. Dagegen konstatiert er, dass bei einer Zunahme der Anionenaufnahme auch eine kräftigere Atmung stattfindet. Diese Zunahme der Atmung (Vergrößerung der CO₂-Abgabe) ist, wie sich zeigt, der Aufnahme der Anionen proportional. So weist LUNDEGÅRDH u.a. nach, dass beim Aufnehmen von 1 Mol. NO₃ etwa 2 Mol. CO₂ abgegeben werden; für Cl sind dies etwa 3 Mol. CO₂, für SO₄ etwa 6 Mol. CO₂.

Aus den von LUNDEGÅRDH erhaltenen Werten kann allein dann ein bestimmtes Verhältnis zwischen Anionenaufnahme und CO₂-Produktion gefolgert werden, falls eine etwaige weitere Verarbeitung dieser Anionen an Ort und Stelle keine CO₂-Produktion mit sich bringt. Besonders wenn man die Nitrataufnahme untersucht, muss man diese Möglichkeit berücksichtigen. Dass eine kräftige Nitratreduktion stattfinden kann, konstatierten bereits WARBURG und NEGELEIN bei der Grünalge Chlorella.

Anfangs meinten LUNDEGÅRDH und BURSTRÖM, dass die Atmung in der Wurzel durch die Reduktion des Nitrates erhöht werde, (*Planta* 18, '33, S. 698). Später kamen sie von dieser Ansicht zurück und glauben nun, dass diese Vermehrung der Atmung allein durch das Aufnehmen des Anions und nicht durch die weitere Verarbeitung verursacht wird. Ihr Schluss ist auf der Tatsache basiert, dass von ihnen bei Nitrataufnahme eine geringere Zunahme der Atmung gefunden wird als bei der Cl-Aufnahme, während bei der letzteren von keiner weiteren Verarbeitung die Rede sein wird (*Biochem. Z.* 261, '33, S. 250). Auch 1935 nehmen sie diesen veränderten Standpunkt ein, während sie betonen, dass die aufgenommenen NO₃-Ionen erst in den oberirdischen Teilen verarbeitet werden. In den Wurzeln können sie keine NO₃-Reduktion nachweisen; aber nähere experimentelle Daten fehlen.

In seiner letzten Publikation kommt LUNDEGÅRDH nochmals auf dieses