

Die Streuung in der Nähe von 80° erreicht die Werte:

	m	M	Mittel
im aufsteigenden Aste:	0 ^m .308	0 ^m .354	0 ^m .331
im absteigenden Aste:	0 .211	0 .305	0 .258
Mittel	0 .259	0 .329	

Die Streuung ist wieder grösser beim Maximum, und grösser im aufsteigenden Aste. Das Verhältnis der Streuungen 0.331 und 0.258 ist 1.28, das Verhältnis der durchschnittlichen Geschwindigkeiten des Lichtwechsels bei Auf- und Abstieg ist 1.06.

Utrecht, April 1937.

Chemistry. — *Flow potentials on platinum.* (Preliminary communication).

By H. R. KRUYT and J. OOSTERMAN.

(Communicated at the meeting of April 24, 1937).

Flow potentials occur if a liquid, flowing along a wall, carries ions from the double layer which is situated on the boundary wall-liquid. In principle, therefore, we may also expect flow potentials on a platinum capillary. They are, moreover, described by QUINCKE¹). However, the influence of the conducting wall should be taken into consideration²).

For the technique of flow potential measurements we refer to the publication of KRUYT and RUYSSSEN³).

Already the very first measurements, performed on the system platinum-twice distilled water made us distinguish the following deviations from the more normal systems isolator (glass, quartz, etc.)-aqueous solution:

a. The potential which sets in is not strictly constant, as e.g. is the case with Jena glass 397^{III} within 0,1 %.

b. After elimination of the difference in pressure on the ends of the platinum capillary, the E.M.F. decreases slowly (in case of glass it decreases, within the time required for an E. M. F. measurement, to the so-called electrode-potential).

c. The electrode-potential (the potential difference which we measure if no liquid flow occurs and which in normal cases has its origin in the inequality of the two potential differences platinum electrode-liquid) shows large variations, in contrast with the corresponding potential difference in the system glass-water.

¹) G. QUINCKE, Ann. Physik (POGGENDORFF) 107, 1 (1859); 110, 38 (1860).

²) M. V. SMOLUCHOWSKI in GRAETZ's Handbuch der Elektrizität und des Magnetismus, II, p. 394 (1921).

³) H. R. KRUYT and R. RUYSSSEN, Proc. Royal Acad. Amsterdam, 37, 498 (1934).

These deviations are due to wall conductivity. For the occurrence of this wall conductivity it is required that the ions, being liberated at the ends of the capillary, are discharged on the metal wall. As a result of this discharge, the ends of the capillary are polarized into hydrogen- and oxygen-electrodes.

The E. M. F., which is measured as apparent flow potential, may be considered to be composed as follows:

Potential difference platinum electrode-liquid + pot. difference liquid-hydrogen electrode (in one vessel) + pot. difference oxygen electrode-liquid (in the other vessel) + pot. difference liquid-platinum electrode. The hydrogen- and oxygen electrodes have a conductive connection by means of the capillary wall.

From these observations we may draw the following conclusions:

I. The apparent flow potential is situated at the ends of the platinum capillary. If the capillary is turned over in the flow potential cell, the E. M. F. then should obtain the opposite sign. Experimentally this appeared indeed to be the case.

II. If we make the capillary wall into an unpolarizable electrode, no E. M. F. is observed in the liquid flow. We actually find this in the case that the flow is brought about with 10^{-4} n HCl + 0.1 % quinhidrone.

III. It must be possible to imitate the phenomena on the platinum capillary by means of the following arrangement: Flow potential cell with glass capillary and in each vessel, by the side of the measuring-electrode, yet a platinum plate. When they are connected by a copper wire, the same discharge and polarization phenomena must occur on these plates as before on the platinum capillary. The two arrangements appear indeed to yield corresponding results.

IV. The potential is not constant because, owing to the continuous discharge of ions, during the pressure, the amount of gas bound by the electrode and consequently the potential differences of the hydrogen- and oxygen-electrodes change continuously.

V. After elimination of the difference in pressure, the oxygen-hydrogen cell is discharged through the content of the capillary. After a measurement, therefore, the E. M. F. decreases slowly.

VI. The electrode-potential is for the platinum capillary completely determined by the potential differences of the hydrogen- and oxygen-electrode with the liquid. According to the more or less far proceeded discharge of the cell, the electrode-potential is smaller or larger.

When we perform a flow measurement on a platinum capillary, then the amount of gas bound by the electrodes, the ε potential and consequently ζ are altered. If we keep that amount constant, a condition for a sharply defined ε and ζ , no polarization phenomena can occur.

From this follows the fundamental impossibility to determine the electrokinetic potential of platinum accurately by means of flow potential measurements.

Similarly in the determination of the isoelectric point with the multivalent ions Al^{+++} and Th^{++++} the amount of gas bound by the capillary plays a predominant part. Since it appears to be very difficult to reproduce this gas amount exactly, ζ also is subject to alterations and consequently the electrolyte concentration at which reversion of charge takes place. At the same time care should be taken that the amount of adsorbed gas on the capillary is in equilibrium with the amount of oxygen in the solutions which are used.

Testing of the law of VON SMOLUCHOWSKI²⁾ was done as follows: The platinum capillary was replaced by a Jena glass filter 7N4. We imitated the wall conduction with two platinized platinum plates on either side of the filter, between which was a resistance box. The platinum plates were made into unpolarizable electrodes by taking $10^{-4} n$ HCl + 0.1 % quinhydrone as filling. With this arrangement the formula of VON SMOLUCHOWSKI appears to be applicable, within the experimental error (1 %), to an area of "wall conduction" of 400—100,000 Ω .

Utrecht, April 1937.

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Chemistry. — *On the Possibility of Distinguishing Right- and Left-handed Structures in Crystals by means of their LAUE-Patterns.* By J. TER BERG and F. M. JAEGER.

(Communicated at the meeting of April 24, 1937).

§ 1. In the chemical and crystallographical literature of to-day often still the opinion is held that, — according to FRIEDEL's principle¹⁾ of the superimposing of a centre of symmetry on the true symmetry of the crystal, when the latter is radiated through by X -rays, — it is in general impossible to distinguish the dextro- and the levogyatory crystals of optically active substances from each other by means of the LAUE-patterns obtained with them.

As a general rule this, of course, is true; however, in some particular cases there are exceptions to this rule and it is possible, by a suitable arrangement of the experimental conditions, yet to distinguish the right- and left-handed structures in this way. A general review of the problem, therefore, seems to be not out of place and is the aim of the present paper.

From FRIEDEL's principle the particular symmetry of the LAUE-pattern, obtained by means of a pencil of X -rays penetrating a crystal in a direction parallel to an axis of symmetry of the crystal, can in each case be predicted, if the proper symmetry of the crystal-species investigated and

¹⁾ G. FRIEDEL, *Compt. rend. Paris*, **157**, 1533, (1913).

the orientation of the photographic plate and the crystal with respect to the primary X -ray are accurately known. The results of the study of such LAUE-patterns have, — in all cases where the mutual orientation of plate and crystal were, indeed, faultless, — fully corroborated the exactness of those theoretical deductions¹⁾. Thus, for instance, it was stated, that the special distribution of the intensities of the diffraction-spots in the LAUE-patterns of uniaxial crystals, obtained by radiating through plan-parallel plates cut parallel to $\{001\}$ or $\{0001\}$ of such crystals, manifested the lack of symmetry with respect to definite planes perpendicular to the photographic film, if only the crystal did *not* possess either such planes of symmetry, or symmetry-axes of *even* period perpendicular to the direction of the principal binary, ternary, quaternary or senary axis. For this reason *dolomite* and *phenakite* [symmetry *): $A_3 \cdot C$ (also \bar{A}_6)]; *apatite* [symmetry: $A_6 \cdot \Sigma \cdot C$]; *nephelite* [symmetry: A_6]; *scheelite* and *erythrite* [symmetry: $A_4 \cdot \Sigma \cdot C$]; *wulfenite* [symmetry: A_4]; etc. all yielded LAUE-patterns on the basal face, the intensity-distribution of which proved only to have a single trigonal, hexagonal or tetragonal axis; and the same was stated in the case of *monoclinic* crystals, if radiated through in a direction perpendicular to $\{010\}$. On the other hand, a basal LAUE-pattern of *NiSO₄ + 6H₂O* [symmetry: $A_4 \cdot 2A_2' \cdot 2A_2''$]; of *quarz* and *cinnabar* [symmetry: $A_3 \cdot 3A_2$]; of *antimonylbariumtartrate + KNO₃* [symmetry: $A_6 \cdot 3A_2' \cdot 3A_2''$], yielded images of this kind, which proved to be symmetrical with respect to 2×2 ; 3; or 2×3 planes passing through the principal axis A_4 , A_3 or A_6 respectively.

Optically active substances which crystallize in one of the eleven²⁾ axially symmetrical classes: C_1 — C_6 ; D_2 — D_6 ; T and K , — will, therefore, in most cases yield LAUE-patterns which cannot be distinguished from their mirror-images, if the crystals are radiated through in a direction perpendicular to one or more symmetry-axes of even periods. More especially this holds for the crystals of the dihedral groups: D_2 , D_3 , D_4 and D_6 , — as these all possess binary axes perpendicular to their principal axis A_n , — if they are radiated through in the direction of this principal axis. The same is true for crystals of the classes T and O , if the pencil of X -rays traverses the crystals in the direction of their binary ($\perp \{100\}$; $\{110\}$) or quaternary ($\perp \{100\}$) axes. But an exclusively axial symmetry of the LAUE-pattern with crystals of one of the eleven classes mentioned will certainly appear in all cases, where *no* symmetry-axes of even period

¹⁾ F. M. JAEGER, *Proceed. R. Acad. Sc. Amsterdam*, **17**, 1204, (1915); H. HAGA and F. M. JAEGER, *ibid.*, **18**, 542, 1201, 1350, (1916).

*) The symbols used are: A_n = principal axis of period $\frac{2\pi}{n}$; A_2' or A_2'' are binary axes of two alternating sets; Σ is the principal plane of symmetry, perpendicular to A_n ; C = symmetry-centre.

²⁾ F. M. JAEGER, *Principle of Symmetry*, 2nd Ed., (1920), 81.