

Chemistry. — “*The Use of the ZEISS Waterinterferometer (RAYLEIGH-LÖWE) for the Analysis of Non-Aqueous Solutions*”. By Prof. ERNST COHEN and H. R. BRUNS.

(Communicated at the meeting of June 25, 1921).

1. Among the methods for a quantitative determination of the concentration of solutions, the optical methods excel the others in many cases in accuracy and rapidity of execution. With very careful regulation of the temperature (constant down to 0.01) it is possible to determine with the most practical measuring instrument, the refractometer, indices of refraction accurate to 1 or 2 units of the fifth place of decimals, which about corresponds in aqueous salt solutions with an error in the determination of the concentration of 0.02% .

In some cases, e.g., for the analysis of exceedingly diluted solutions, this accuracy is, however, not sufficient. An instrument, which is eminently fit for such determinations, is the waterinterferometer according to RAYLEIGH-LÖWE, put on the market by the firm ZEISS. It enables us to measure the index of refraction of a solution down to 2 units in the 7th place of decimals, corresponding to an error in the determination of the concentration of at most 0.0002% . This interferometer is, however, as its name indicates, constructed for the use of water as solvent, and all the investigations which have been executed by the aid of it up to now, concerned aqueous, or very diluted alcohol, solutions.

In connection with an investigation, of which we hope soon to give further details, it was necessary to carry out accurate analyses of exceedingly diluted solutions in organic liquids. It then appeared that if the interferometer is to be used also in this case, a number of precautions must be observed, which will be set forth more at length in what follows.

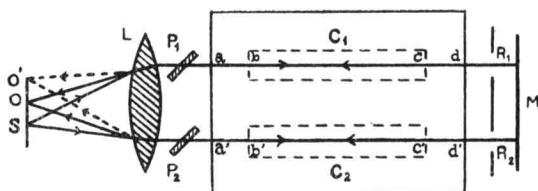


Fig. 1.

We will, however, first give a short description of the interferometer with the aid of figures 1 and 2¹⁾.

2. Fig. 1 gives a schematic representation of the instrument. The rays furnished by a source of light S, made parallel by lens L, pass through the identical vessels C_1 and C_2 filled with the same liquid, and then through a screen provided with two slits R_1 and R_2 , are reflected as two separate beams by mirror M, and after having been united again by lens L, they form an interference image in O. When white light is used this image consists of a central bright band bounded by two dark ones; the bright bands following on them on either side have coloured edges. When now C_1 is filled with a solution which has a greater index of refraction than the pure solvent in C_2 , this interference image is displaced in consequence of the lengthening of the optical path, e.g. to O' . It can be brought back to the zero position O by turning the compensator plate P_1 (P_2 is immovable), through which the optical path is again artificially shortened. The angle, over which P_1 has been rotated, is a measure for the difference of index, hence indirectly for the concentration of the solution in C_1 .

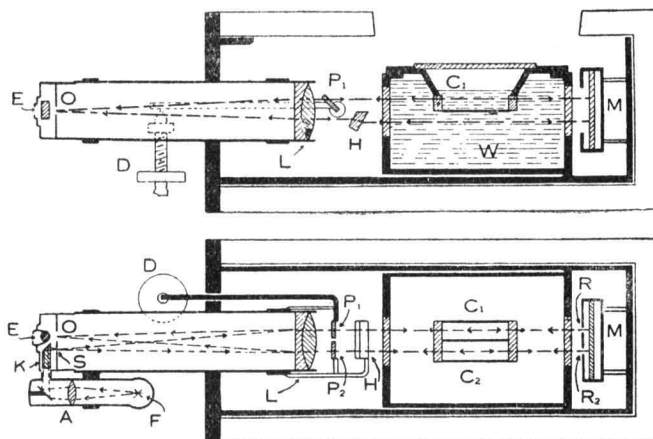


Fig. 2.

Fig. 2 represents a horizontal and a vertical cross-section of the interferometer more in details. The white light of an Osram lamp F is concentrated by lens A and prism K, on the very narrow slit S, which forms the secondary source of light. The passage of the

¹⁾ A fuller description is found in the following places:

F. LÖWE, *Zeitschr. für Instrumentenkunde* **1910**, 321; F. LÖWE, *Physikalische Zeitschr.* **11**, 1047 (1910).

P. HIRSCH, *Fermentforschung* **1**, 33 (1914).

L. H. ADAMS, *Journ. Amer. Chem. Soc.* **37**, 1181 (1915).

rays is further quite as in fig. 1. The lower part of the beam leaving lens L, however, does not traverse the vessels, but passes under them through the water in reservoir W, which serves as "Temperier bad" of the vessels. Also these rays of light interfere in O, where they form a fixed image lying below the former, separated from it by a narrow line, and serving as "point de repère" of the zero position. Both images are examined by means of the greatly magnifying cylinder ocular E. The compensator plate P_1 is rotated by means of a lever, which is worked by a micrometer screw with drum D; on this drum a scale is drawn of a hundred divisions. With the instrument used by us one interference band corresponds to 21 scalar divisions. The uncertainty in the adjustment with regard to the coinciding of the two interference images is, after some practice, about half a scalar division.

For the analysis of solutions one has only previously to construct a gauging curve comprising the concentration region used. On the shifting of the central band which seems to take place in this case, compare ADAMS¹⁾.

3. When it is tried to analyse in this way solutions in organic liquids (for which, of course, the use of so-called "säurefest verschmolzen" vessels consisting entirely of glass, is necessary) the following phenomena are in general observed in the interferometer. The upper interference image is blurred and shifted with regard to the lower one. The bands are permanently oblique and curved, or for a long time. Shaking of the liquid in the vessel (by tapping against the interferometer) indeed promotes the rapidity with which the image is formed, but reproducible results cannot be obtained, and after some time the lines become again shifted and curved.

The causes of these deviations, which render an accurate measurement of course impossible, appeared to be due to the following circumstances:

- A. the nature of the bath-liquid.
- B. the influence of the temperature on the index of refraction of the solvent;
- C. evaporation and distillation against the glass covering-plates of the vessels;
- D. absorption of water during the conveying and the staying of the liquid in the vessels.

4. Ad A. *The nature of the bath liquid.*

Compared with by far the majority of the organic liquids the

¹⁾ ADAMS, Journ. Amer. Chem. Soc. **37**, 1181 (1915).

water used as bath liquid possesses a very small index of refraction. For the substances examined by us we have e.g. at 20°:

tetrachlorethane	: $n_D = 1.496$
benzene	: $n_D = 1.501$
whereas for water:	$n_D = 1.333$

It is easily seen that on use of such solvents with greatly deviating indices of refraction, an exceedingly small departure from the parallel position of the plane-parallel front and back wall of the vessels, brings about a very great displacement of the upper interference image. Let us call the index of refraction of the bath liquid n_1 , that of the liquid in the vessel n_2 ; let further the path in the bath-liquid (a b + c d in fig. 1) passed over by the beam of light which passes C_1 , be l_1 , that in the vessel l_2 . The optical path is then for vessel C_1 , the beam passing over the path twice¹⁾:

$$2(n_1 l_1 + n_2 l_2).$$

With perfect parallelism of the plane-parallel plates, this path has the same length for the other beam. If, however, the length of vessel C_2 is e.g. σ more than that of C_1 , the optical path is here: $2[n_1(l_1 - \sigma) + n_2(l_2 + \sigma)]$.

Accordingly the difference in optical path is:

$$\Delta = 2\sigma(n_2 - n_1),$$

and the displacement of the interference image brought about by this and expressed in bands:

$$N = \frac{\Delta}{\lambda} = \frac{2\sigma(n_2 - n_1)}{\lambda},$$

if λ represents the wave-length of the light used.

In the case of water and tetrachlorethane $n_2 - n_1$ is = 0.16.

From this follows for $\lambda = 0.00058$ mm.:

$$N = 550 \sigma, \text{ or expressed in scalar divisions:}$$

$$N' = 21 \times 550 \sigma = 11550 \sigma \text{ scalar divisions.}$$

If the deviation from the parallel position σ is e.g. 0.001 mm., the shifting amounts to no less than ± 12 scalar divisions. The displacement observed with the vessel used by us appeared to be about 40 scalar divisions. Besides this displacement also the imperfect form of the upper image is partly due to the non-parallelism of front and back wall of the vessels.

5. To obviate this difficulty, a liquid must be chosen as "Tempe-

¹⁾ We may disregard here the thickness of the plane-parallel plates, the result not being affected by this.

rierbad", whose index of refraction lies as close as possible to that of the liquids to be investigated. Aqueous solutions with strong refractivity (e.g. of cane-sugar or cadmium salts), which are preferable to organic substances, because they do not attack the cement with which the windows are fastened in the reservoir **W**, proved unsuitable, on account of their high viscosity. After also a number of mixtures of little volatile organic liquids (paraffin-oil-methylsalicylate and methylonyl-ketone-methylsalicylate) had been tried, in which, however, difficulties also presented themselves, tetrachlorethane itself was taken for it. Previously the rims of the windows had, however, to be protected, for which purpose a layer of an aqueous glue appeared to be very effective, and the paint had to be removed from the reservoir.

6. *Ad B. The influence of the temperature on the index of refraction of the solvent.*

The strong and always recurring curvatures of the bands are partially owing to the great value of the temperature coefficient of the index of refraction in organic liquids, accompanied with a very small specific heat.

From KANONNIKOFF's determinations¹⁾ $\frac{dn}{dt} = -0.0005$ may e.g. be calculated for tetrachlorethane at $\pm 20^\circ$.

Benzene has $\frac{dn}{dt} = -0.00065$ at 20° .

A change of temperature of 0.01° gives, therefore, rise to a change in the index of refraction of 6 units in the 6th place of decimals, which when a 2 cm. vessel is used, corresponds to a displacement of 10 scalar divisions. For water these values are about eight times smaller

Exceedingly slight temperature disturbances through addition of heat from outside, which occur especially on a prolonged stay of the observer in the neighbourhood of the apparatus, give much sooner rise to curvatures and displacements of the bands in such liquids than in water.

7. To prevent this:

1. the interferometer was surrounded by a large thermostat, filled with water.
2. a stirrer was placed in the bath liquid.

¹⁾ Journ. für prakt. Chemie, **32**, 520 (1885).

This last improvement at the same time also greatly accelerates the exchange of heat between vessel and bath, so that already after 10 or 15 minutes the reading can take place. To prevent currents in the liquid during the measurement, the stirrer was always stopped a minute beforehand.

8. *Ad C. Evaporation of the liquid in the vessels.*

Only in more concentrated solutions is the error brought about by evaporation, greater than the error of measurement. If e.g. from 2 cc. of a 0.1 N.-solution of $C_2H_2Br_4$ in $C_2H_2Cl_4$, 2 mgr. of $C_2H_2Cl_4$ evaporates, this gives rise in our apparatus to an error of 1.6 scalar divisions. Greasing of the rim of the glass cover can, however, prevent such an evaporation. Another source of errors, however, still continues to exist, viz. distillation against the glass cover. This can often be observed already soon after the filling of the vessel; the liquid which is distilled moves between glass cover and vessel rim on account of surface tension, and attacks the vaseline. To prevent this it is to be recommended¹⁾ in aqueous solutions to keep the temperature of the "Temperierbad" always some degrees lower than that of the room; in an investigation of more volatile liquids this is, however, not sufficient.

9. It is, however, possible, to avoid this source of error entirely by using for the closure of the vessel, instead of glass plates, massive closing bodies, which occupy the whole vapour space. For this purpose brass blocks were constructed provided with a flat rim, which fit very tightly in the vessel, and leave only a space of ± 2 cc. for the liquid. This is then conveyed to the vessel by the aid of a pipette of 2 cc. capacity, provided with a long capillary passed through a hole bored through the closing block. After the filling the bored hole is closed by a copper ground-in needle. Greasing of the rim of the vessel is now unnecessary; no evaporation takes place through the remaining capillary slits.

10. *Ad D. The influence of the water absorption.*

Dry, organic liquids absorb water vapour from the atmosphere exceedingly rapidly. On account of the great difference in index of refraction between water and those substances, added to the sensitiveness of the method of measurement, however, the presence of exceedingly small quantities of water causes already errors in the

¹⁾ HIRSCH, *Fermentforschung* 1, 38 (1914).

determination which exceed the error of measurement many times. Also when the liquids have not been previously expressly dried with a view to P_2O_5 , but when they have only been repeatedly fractionated after preliminary drying with $CaCl_2$ (which was the case with the substances used by us) they show already a strong absorption of water-vapour. Especially for $C_2H_2Cl_4$ this appeared to be the case, but though in a less degree, benzene gave also greatly varying values.

When the determinations are carried out with quite the same precautions as are observed for aqueous solutions, two successive determinations executed directly after each other, already in consequence of this source of error alone, yield greatly deviating values, which e.g. for $C_2H_2Cl_4$ can sometimes differ inter se no less than 40 scalar divisions. In order to ascertain the influence of the water content on the interferometer reading a previously weighed solution of 5 mgr. water in 35 gr. of $C_2H_2Cl_4$ dried on phosphoric acid was measured against this same $C_2H_2Cl_4$. The displacement was 85 scalar divisions. From this follows that the presence of 0.005 mgr. of water in 2 cc. of $C_2H_2Cl_4$ already causes an error of a scalar division.

11. It is self-evident that with such sensitiveness the utmost care should be taken to prevent any contact of the liquid that is to be examined and water-vapour, if an accuracy is to be reached comparable with that in solutions in water. Therefore the liquids were always preserved over phosphoric acid which had been heated

at 160° for some days. The storing bottles had the shape as indicated in fig. 3. The conveyance into the vessel took place with the aid of pipettes J, which had been cleaned with benzene, heated, and filled with dry air.

These were filled from A by fastening them with a rubber tube on to the tube E, and pressing in dry air at F. The solutions were prepared by weighing in flasks B, which had also been previously rinsed with benzene, heated with evacuation, and filled with dry air. The small quantities of $C_2H_2Cl_4$ were conveyed into them by the

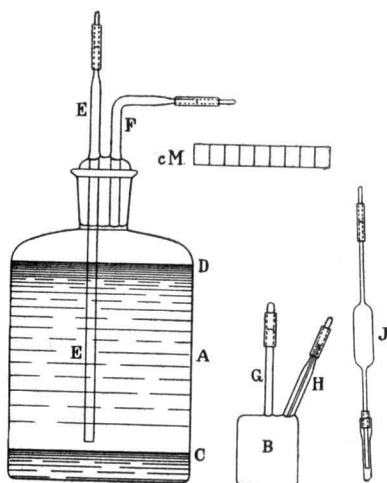


Fig. 3.

aid of a glass capillary. The solvent was directly pressed over from the storing bottle into B, after the tubes G and E had been connected

by means of a siphon-shaped tube. The filling of the pipettes J with the solution from B took also place by pressing in of dry air through tube H, after the capillary of the pipette had been immersed through G in the solution; a rubber ring, put round the capillary, ensured air-tight closure.

When the pipette is closed in the way as is seen in the figure, it is possible to preserve the liquid quite unchanged for 12 hours.

The vessels were always cleaned with benzene instead of alcohol and ether, because the latter causes water-vapour to condense on the glass in case of quick evaporation. Before the filling with liquid the vessels were filled with dry air.

The brass closing blocks also protect the liquid sufficiently against absorption of water-vapour from the atmosphere, so that the interferometer position does not appreciably change during the time taken up by a determination. It is true that in the course of some hours the zero position is slightly displaced in consequence of absorption of water by the pure solvent in vessel C₂; this displacement can, however, easily be determined and taken into account.

12. Only when the precautions described here are observed, is it possible to obtain an accuracy and reproducibility, almost equal to that which is reached for aqueous solutions.

In conclusion we may give a series of measurements referring to solutions of C₂H₂Br₄ and C₂H₂Cl₄ of different concentrations. With every solution two independent measurements were made (also the zero-position was determined every time anew). The measurements are reduced to vacuum. Just as before a vessel of 2 cm. was used.

concentration in percentages (weighed in)	observed number of scalar divisions		mean	corrected	concentration calculated (in percentages)
	1st measurement	2nd measurement			
0.1256	131.0	129.2	130.1	130.1	0.1262
0.1490	176.3	175.3	175.8	154.8	0.1500
0.2925	346.5	345.1	345.8	303.8	0.2920
0.3208	374.9	375.6	375.3	333.3	0.3199
0.4699	556.9	557.1	557.0	494.0	0.4700
0.5409	655.9	654.9	655.4	571.4	0.5413
0.7166	869.8	869.3	869.6	764.6	0.7166

In this table the concentration is expressed in grammes of $C_2H_2Br_4$ present in 100 gr. of solution. The values given under "corr." are the means, diminished by the correction for the shifting of the central band; it occurs here every time after ± 150 scalar divisions.

Under "calculated" are given the values satisfying the interpolation formula:

$$p = 0.0009772 n - 0.0000000523 n^2,$$

which has been calculated from the observations according to the method of least squares. In this p represents the concentration (expressed in percentages), n the corrected number of scalar divisions.

Hence it appears that the reproducibility of the measurements is ± 1 scalar division, corresponding to 0.0009 per cent.

SUMMARY.

The causes of the difficulties met with when it is tried to use the ZEISS waterinterferometer for the analysis of solutions in organic liquids, were discussed and the precautions were mentioned required to carry up the accuracy of the measurements to the same order as can be reached with aqueous solutions.

Utrecht, June 1921.

VAN 'T HOFF-Laboratory.
