theory and experiments; they allowed the following conclusions. If a laser giant pulse is sent through the liquid the beam diameter is reduced during its path through the cell due to self-focusing. The diameter at the exit window, which decreases with increasing laser power, follows quasistationarily the instantaneous laser power. For low incident laser power, the diameter increases again after the power has passed its peak value. At high laser power, stimulated Raman scattering in the forward and backward direction and stimulated Brillouin scattering occur, since the self-focused beam diameter is strongly reduced leading to a drastic increase of intensity. These scattering processes in the backward direction attenuate rapidly the laser power and limit the time duration of the self-focusing action.

The authors wish to thank Professor W. KAISER for his continuous interest in this work and for many valuable discussions and Dr. G. K. BORN for a reading of the manuscript.

A New Type of Apparatus for the Determination of the Thermal Diffusion Factor

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(Z. Naturforsch. **25 a**, 1879—1882 [1970]; received 11 September 1970)

In this article an apparatus is presented which gives a precisely known multiplication of the elementary effect in thermal diffusion experiments, avoiding the drawbacks of the swing-separator (Trennschaukel). This is achieved by using a different method of concentration nivellation than customary with the swing-separator, viz. thermosyphon action.

Introduction

Of the three types of apparatus, in regular use in thermal diffusion experiments, only two, the two-bulb apparatus and the swing-separator, designed by CLUSIUS and HUBER [1] are fitted for a precise determination of the thermal diffusion factor, whereas the thermal diffusion column, invented by CLUSIUS and DICKEL [2] is more or less a production apparatus, very useful for the attainment of high separations between the components of a gaseous mixture, but too complicated in its functioning to permit a precise determination of the thermal diffusion factor from these separations. The need for a second apparatus beside the basic and well understood two-bulb apparatus arises from the fact that thermal diffusion is a second order effect and as such can be very small, making the separation obtained in a two-bulb apparatus too small for the evaluation of the thermal diffusion factor with a reasonable accuracy.

The swing-separator, on the other hand, has its own drawbacks. It produces a separation which is meant to be an exactly determined power of the elementary separation as measured in a two-bulb apparatus. This is done by coupling a number of two-bulb apparatuses (tubes) by means of pieces of capillary tubing, which connect the cold side of tube number n to the hot side of tube $n+1$ and pumping the gas to and fro through these capillaries, so that a concentration nivellation takes place at both ends of each capillary. In this way an exactly known multiplication of the elementary separation takes place. However, as VAN DER WAERDEN [3] has shown, several disturbing factors make this type of apparatus less ideal than it looks at first sight. Under optimal conditions the finite pumping speed leaves a concentration difference at both ends of each capillary, due to back diffusion in the capillary. Raising the pumping speed would diminish this error, but introduces an other one: the gas masses flowing in and out each separation tube disturb the thermal and concentration equilibrium in these tubes. This can be seen in the following way: hot gas from the upper side of one tube is introduced into the cold side of the next one and vice versa and the entering gas causes turbulence in the (supposedly) stationary state of the mixture.

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[1] K. CLUSIUS and M. HUBER, Z. Naturforsch. **10 a**, 230 [1955].

[2] K. CLUSIUS and G. DICKEL, Z. Phys. Chem. **B 44**, 397 [1939].

[3] B. L. VAN DER WAERDEN, Z. Naturforsch. **12 a**, 583 [1957].

This happens at all pumping speeds but the disturbance increases with the pumping speed. Still another effect exists: as the pumping is done from both ends of the whole series arrangement of separation tubes, the amount of gas to be displaced before the gas is flowing through the capillaries connecting the middle tubes forms a kind of buffer so that the pumping in the middle tubes is done less effectively than in the tubes at both ends of the arrangement. This effect is especially notable when a large number of tubes has to be used to get a reasonable separation. The full quantitative treatment of these effects can be found in the article of VAN DER WAERDEN [3], together with the indication of the conditions under which they are minimized.

The Syphon-Separator

The apparatus we would like to introduce now avoids all of the aforementioned effects by using a different way of equalizing the concentrations between the hot and cold sides of neighbouring tubes, viz. thermo-syphon action. Figure 1 shows a part of the experimental arrangement. A number of tubes are arranged side by side, exactly as in the swing-separator, the upper parts being kept on the higher, the lower parts on the lower temperature. The cool side of one tube is connected with the hot side of the next one by means of two pieces of tubing, one of which can be heated, while the other one can be cooled. The temperature difference between the two connection tubes causes the gases in the apparatus to rise in the heated tube and to flow down in the cold one (thermosyphon action), thus assuring a thorough mixing of the gases at opposite ends of neighbouring tubes. That the mixing thus obtained can be sufficient has been shown already in the work of CLUSIUS [4] and VELDS [5]. They both used a thermosyphon arrangement for concentration-nivellation purposes: Clusius for the coupling of thermaldiffusion columns, Velds for a modified two-bulb apparatus, used for experiments at elevated pressures. The first advantage of our method can be seen immediately: as each connection has its own driving unit, the number of tubes can be made as high as desired without the occurence of a buffer-effect. The second problem which is circumvented in our arrangement is that of the thermal disturbance: by making the temperature of the heaters high enough, the gas flowing past them can attain during the passage the same temperature as is present in the high temperature part of the next tube, whereas the coolers may be made cold enough to give the downcoming gas the right temperature for the cool side of the arrangement. The thermal disturbance was no real problem however, as the temperature can be measured inside the tubes of the swing-separator, thus giving the right (disturbed) temperature. Such a measurement has to be done also in our arrangement for the adjustment of the heaters and coolers.

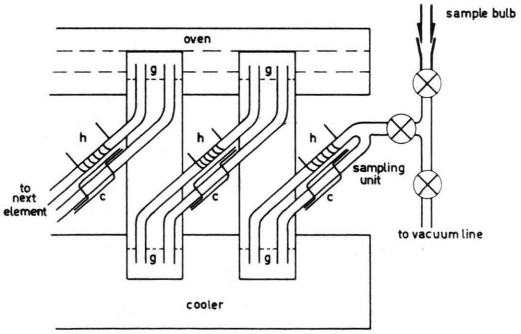

Fig. 1. Part of the syphon separator. The last tube on the other end of the aparatus has identical sampling facilities, connected however to the opposite end of the tube. h = heating coil; c = cooler; g = grid.

In the apparatus as described hitherto turbulence is still present and even necessary for a good concentration nivellation and in this respect the apparatus needs another refinement. The connection tubes, which run for a part of their length inside the separation tubes (once again for the attainment of thermal equilibrium) are led inside the separation tubes through a fine mesh grid that separates the thermo-syphon flow (which takes place here in a space of uniform temperature) from the part in which the temperature gradient is present and in which the thermal diffusion takes place. This grid is based on the following philosophy: as the resistance of the grid to viscous flow is inversely proportional to the fourth power of the diameter of its meshes, whereas its resistance to diffusion is inversely proportional to the second power of this diameter, the grid forms an effective barrier against flow (and so against the turbulency disturbance) while the dif-

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[4] K. CLUSIUS, Helv. Chim. Acta **33**, 2134 [1950].

[5] C. A. VELDS, J. LOS, and A. E. DE VRIES, Physica **35**, 417 [1967].

fusion still can take place by making the number of meshes (the area of the grid) big enough.

Sampling is done in the same fashion as the concentration nivellation: by means of thermo-syphon systems the mixtures at both ends of the whole system are brought at room temperature in the sampling system.

Experiments

As thermo-syphon action and its resulting flow are not well enough understood to permit a mathematical analysis of the working of the apparatus we have restricted ourselves to a series of experiments with a specimen of the new apparatus. As experimental mixtures we chose mixtures of the gases Ar and He. This combination was chosen because thermo-syphon action is easier brought about with gases with a high atomic weight than with light gases such as He. So a succesfull operation with a mixture containing a high He concentration would show that no restrictions do exist on the gases that can be used. The combination with Ar was chosen because here the elementary effect is big enough to permit the evaluation of the thermal diffusion factor in a two-bulb apparatus, thus making possible control experiments. The apparatus was made out of pyrex glass and consisted of four separating tubes, each with a length of 15 cm and a diameter of 2.5 cm. Two tubes were interconnected by two smaller ones (approximate length 35 cm, diameter 0.7 cm) which were either heated by a few windings of resistance wire or cooled by a small cooler. The upper part of each separating tube was thermostated in the following way: each tube extended for about 3.5 cm through two aluminum plates, while a third plate covered the whole system. In between the aluminum plates resistance wire for heating had been installed; a platinum resistance sensor connected to a Thermosistor thermostating arrangement switched the current on and off.

The temperature in the separation tubes, showed fluctuations of the order of 0.01 °C during the time of one experiment due to the gas that was streaming through it. The duration of an experiment was about one day, though calculations with the formulae given by SAXENA and MASON[6] showed that equilibrium to within one permille could be expected in a shorter time.

The thermostating of the colder side of the separation tubes was done in a far less sophisticated way, viz. by immersion of the lower parts of the tubes in running tapwater. This simple procedure gave a temperature fluctuation of less than 2 °C during a single experiment. The tapwater was also used for the small coolers in the connection tubes. The grid was a commercially available electrically deposited plate with tapered holes with mean diameter $20 \cdot 10^{-3}$ cm, thickness $80 \cdot 10^{-3}$ cm. The area of the holes was approximately 2% of the total area of the grid.

Two types of He/Ar mixtures were used: one with about 80% He and one with 10% He. Most of the experiments were performed with mixtures with 80% He as these were the most crucial ones. The temperature of the upper parts of the tubes was between 196 and 200 °C inside the tubes and 207 °C in the aluminum block; the lower temperature varied from 8.8 to 14.5 °C inside the tubes. The pressure ranged from 650 to 700 Torr.

The analysis of the samples was performed on an Atlas CH_4 mass-spectrometer. For the determination of the real percentage of each component in the samples the mass-spectrometer had been calibrated on its relative efficiency for Ar and He with Ar/He samples of known and varying composition.

The results of the experiments are given in Table 1. The reproducibility in all three cases for which a mean value and a standard error could be computed can be considered as excellent: the standard error in the separation Q is 0.5% in the case of the mixture II and III and 0.2% in the case of mixture IV, which is as good as can be expected with a conventional mass-spectrometrical analysis.

Mixture	$c_{\mathrm{He, in.}}$	$c_{\mathrm{He, f, exp.}}$	$c_{\mathrm{He, f, calc.}}$	Q_{exp}
I	81.4	89.8	90.0 ± 0.2	2.00
II	80.9	89.7	89.7 ± 0.2	2.04
II	80.5	89.3	$89.4\,^{+0.3}_{-0.2}$	2.02
II	81.4	89.9	90.0 ± 0.2	2.03
II	81.0	89.8	89.7 ± 0.2	2.07
III	80.7	89.9	89.8 ± 0.2	2.13
III	80.4	89.6	$89.6\,^{+0.3}_{-0.2}$	2.09
III	80.2	89.5	89.5 ± 0.2	2.12
III	79.6	89.1	$89.1\,^{+0.3}_{-0.2}$	2.09
III	79.4	89.0	89.0 ± 0.2	2.09
IV	8.4	14.2	$13.4\,^{+0.6}_{-0.5}$	1.82
IV	8.3	14.0	13.3 ± 0.5	1.81
IV	8.1	13.8	$13.0\,^{+0.6}_{-0.5}$	1.81
IV	8.1	13.8	$13.0\,^{+0.6}_{-0.5}$	1.81

Table 1. Comparison between the experimentally obtained and calculated endconcentrations in the syphon-separator. Values in columns 2, 3 and 4 are percentages. $c_{\mathrm{He, in}}$: initial value of the He-concentration; $c_{\mathrm{He, f, exp.}}$: experimental value of the final He-concentration; $c_{\mathrm{He, f, calc.}}$: calculated value of the final He-concentration; Q_{exp}: experimentally obtained value for the separation.

Next we have to interpret the nominal values of the separation obtained. The simplest way to handle the values would be, in conformity with general practice with swing-separators, to extract the fourth

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[6] S. C. SAXENA and E. A. MASON, Mol. Phys. **2**, 264, 379 [1959].

root (the apparatus has four separation tubes) of the separation and compare this value with the separation obtained in a two-bulb apparatus under identical conditions. This comparison would be incorrect, however, as no account has been taken of the fact that the composition of the mixture in all four tubes is different, due to the separation. This effect is not negligible as both the separation in each tube and the concentration dependence of the thermal diffusion factor for Ar/He mixtures are fairly large. Therefore we used a step-by-step procedure in which we calculated the separation in each tube and combined these values to obtain the overall separation. To do this we needed an analytic function for the concentration dependence of the thermal diffusion factor. We obtained this function by performing a number of thermal diffusion experiments on Ar/He-mixtures of varying composition in a two-bulb apparatus and then supposing the theory of LARANJEIRA[7] to be valid to a sufficient accuracy i.e. we supposed that the reciprocal of the thermal diffusion factor has a linear concentration dependence. Starting from the experimentally determined initial concentration ratio on the cold side of tube number 1 we can calculate now the final concentration ratio to be expected on the hot side of tube number 4 and compare this value with the experimentally obtained result. Both values, the experimental and the calculated one, are given in the third and fourth column of Table 1, together with the error that can be expected, due to the uncertainty in the experimental values from the two-bulb apparatus.

Comparison of the values in these columns shows that in all cases with a high He concentration the experimental value lies within the limits of error of the calculated one. With a low He concentration, however, the calculated value is always too low; we do not contribute this effect to malfunctioning of the syphon apparatus but to the value obtained with the two-bulb apparatus. The values for the thermal diffusion factor α for the experiments with a low He concentration from this apparatus are on the average somewhat lower (approximately 5%) than would be expected on the basis of the results of other experimenters. Should the value of α be somewhat higher, then the slope of the line for $1/\alpha$ should diminish, resulting in a better agreement between the calculated and the observed values of the final concentrations. It was not possible, due to circumstances, to repeat the two-bulb measurements, so that this rather unsatisfying result can not be corrected. The values for the two-bulb experiments with high He-concentrations are in good agreement with those of other experimenters.

Conclusion

Although the experiments with mixtures with a low He content have not produced satisfactory results, the very good agreement between predicted and experimentally found concentrations in the other experiments, gives us the conviction that the combination of thermo-syphon action and a grid for the prevention of turbulence can be used for an exactly determined multiplication of the elementary separation. This makes the apparatus a valuable tool for a precise determination of the thermal diffusion factor in mixtures where a multiplication of the elementary effect is desired in view of the smallness of the separation obtained in a two-bulb apparatus.

Acknowledgements

The authors would like to thank Mr. J. VAN WEL for advice and design of the glass parts of the apparatus and Dr. A. E. DE VRIES for his criticism.

This work is part of the research program of the "Stichting voor Fundamenteel Onderzoek der Materie" (Foundation for Fundamental Research on Matter) and was possible by financial support of the "Nederlandse Organisatie voor Zuiver-Wetenschappelijk Onderzoek" (Netherlands Organization for the Advancement of Pure Research).

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[7] M. F. LARANJEIRA, Physica **26**, 409, 417 [1960].