**Physics.** — *On an apparatus for rectifying small quantities of liquefied gas, and on the purification of krypton.* By H. VAN DIJK, J. MAZUR and W. H. KEESOM. (Communication N°. 228 from the KAMERLINGH ONNES Laboratory at Leiden.)

(Communicated at the meeting of September 30, 1933).

*Summary.* An apparatus is described with which it is possible to purify a relatively small quantity of gas by rectification according to CLAUDE's principle of "retour en arrière". This method has been tested for the purification of krypton and satisfactory results have been obtained.

§ 1. *Introduction.* A method which is much used for the purification of gases that cannot easily be separated by chemical means, is that of condensation followed by fractional evaporation. In this method condensation is performed at a temperature at which the gas to be separated has a small, the more volatile admixtures, however, still have an appreciable vapour pressure. The latter are then drawn off by exhausting, after which the condensate is evaporated slowly, the fraction which evaporates last being eliminated.

If necessary the process can be repeated with the middle fraction. This method has, however, the difficulty that the middle fraction, which is evaporated at a higher temperature, will contain on one hand that portion of the more volatile admixtures that was solved or occluded in the (in most cases solid) condensate, on the other hand a part of the heavier impurities that already have again an appreciable vapour pressure at that temperature. This difficulty can be avoided if at a properly chosen temperature a rectification is performed. Theoretically, to obtain this result completely, one should need an infinitely long rectification column, and the different fractions should have to be drawn off infinitely slowly. Hence in practice a certain compromise has to be chosen. It may appear, however, that in many cases one can obtain a quite satisfactory result with an apparatus of practical dimensions and within a practical time.

The desirability to test this became evident when in behalf of measurements of saturated vapour pressures of krypton, to be followed by determinations of liquid and vapour densities, it was needed to separate a quantity of very pure krypton from a sample of gas which by the kind intermediary of Prof. MATHIAS was put at the disposition of the KAMERLINGH ONNES Laboratory by G. CLAUDE. It had appeared that the method of condensation and fractional evaporation did not yield the desired result. A happy circumstance was that in behalf of the further separation of hydrogen isotopes by rectification [1]) an apparatus had been designed

[1]) Cf. W. H. KEESOM and H. VAN DIJK, These Proceedings **36**, 248, 1933. Comm. Leiden, N°. 224*a*.

and already tested with which rather small quantities of liquefied gas can be rectified. We decided to undertake with it the purification of the quantity of krypton at hand, partly as a test and a first application of this method of purification of gases, and further in order to obtain in this way a quantity of krypton of the desired purity.

§ 2. *Purification of krypton by fractional evaporation.* The apparatus is represented in Fig. 1. The krypton from the bulbs *A, B* etc. in which it was furnished by the Société l'Air Liquide, was slowly passed through the

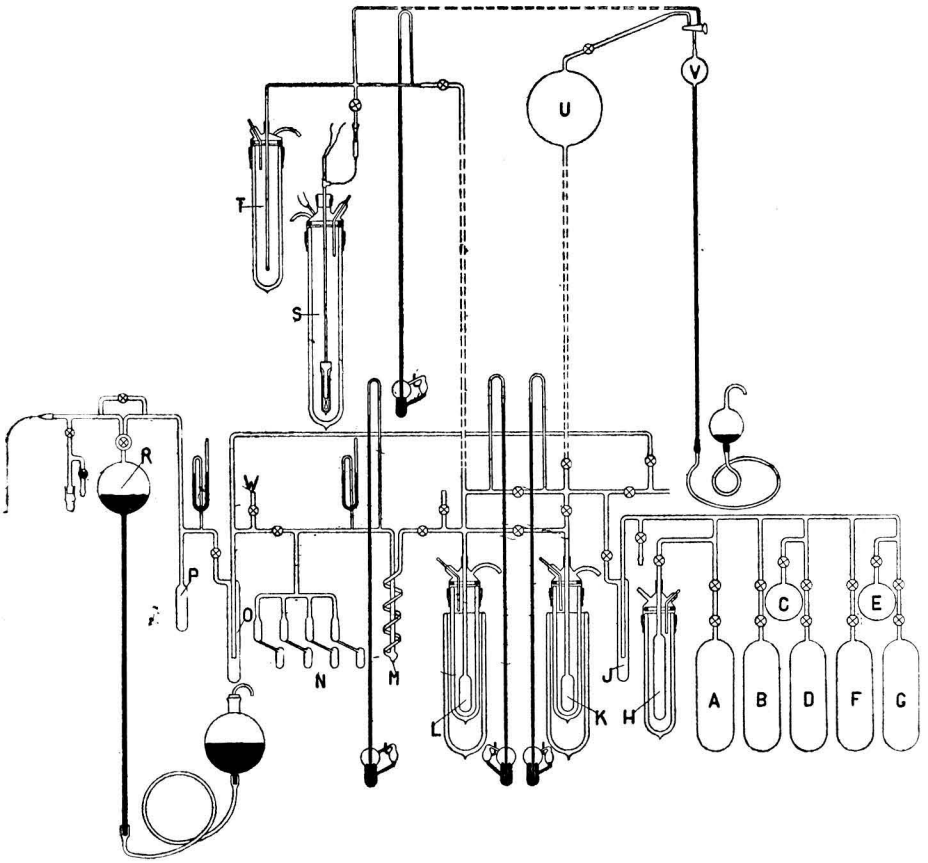


Fig. 1.

trap *J* refrigerated by alcohol cooled by liquid air to a temperature of —115° C, in order to freeze out water and carbon dioxide, and condensed into *K* kept cold by liquid oxygen. After lowering the temperature to —205° C by reduction of the pressure above the liquid oxygen, the pressure above the solid krypton was 2 cm mercury. The gas above the solid krypton was then exhausted during 10 minutes, after which the remaining pressure was 0.5 cm. Then *L* was slowly cooled with liquid oxygen and the middle fraction from *K* condensed into it. The gas above the solid krypton in *L*

was exhausted at —210° C till no measurable pressure remained. The middle fraction evaporating from $L$ was collected in $R$. This process was repeated after having transferred the gas to $H$ with the aid of liquid hydrogen.

A spectroscopic test by means of a large STEINHEIL glass spectrograph, 2 mm pressure in the GEISSLER tube with external electrodes, revealed, in the range between 5876 and 4140 Å, some sixty lines which all were identified as krypton lines, except two which were due to xenon. Of oxygen or nitrogen no trace was found in this way.

The vapour pressure curve of the krypton so obtained showed, however, an anomaly at about —185° C (cf. § 3*b*). So it was decided to see whether by rectification possibly a purer sample of gas might be obtained.

§ 3. *Purification of krypton by rectification.*

*a. The rectifying apparatus* was taken up already in Fig. 1 and is represented in detail in Fig. 2. Its working principle is that of the socalled "retour en arrière" used by CLAUDE in the rectification of air. The vapour formed in the still $K$ by using the heating coil $S$ is condensed along the windings of a copper screw $R$. The liquid formed streams back along these windings and partly also along the inner wall of the DEWAR vessel. The condensation heat is conducted at the top of the apparatus to the liquid at the outside.

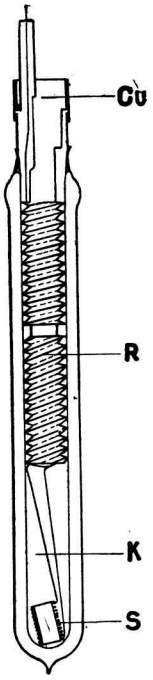

Fig. 2.

As the DEWAR vessel is unsilvered one can easily control the rectification process and properly adjust the heat production in the coil. The apparatus, which had been designed in behalf of the rectification of hydrogen (cf. § 1), was tested first by rectifying mixtures of oxygen and nitrogen [1]). Having been filled with a mixture containing about 5 % of nitrogen, after an hour's rectifying practically pure nitrogen could be taken off at the top. Chemical analysis of this product showed no oxygen to an amount of 1 %. Hence the rectifying effect was at least equivalent to that of a column of 5 or 6 ideal pans.

*b.* For a further purification of the sample of krypton mentioned in § 2 the apparatus described under *a* was surrounded by a bath of ethylene kept constantly at a temperature a little above the triple point of krypton. After half an hour's rectification the first fraction of 130 cm³ gas at standard conditions was slowly (2 cm³/min) drawn off. The next fraction (98.5 cm³) was put into the vapour pressure apparatus. A last fraction of 323 cm³ was collected.

The vapour pressure measurements showed clearly that the rectification

[1]) We wish to record our thanks to chem. cand. J. W. BOEHMER for performing this test.

had resulted in an appreciable increase of the purity of the gas. The *log p, $T^{-1}$*-curve (*p* in mm Hg.) now showed no abnormal variation of the slope, *vide* Fig. 3, where the dashed line (- - - -) refers to measurements on the sample purified by fractional evaporation, the full line (——) to those

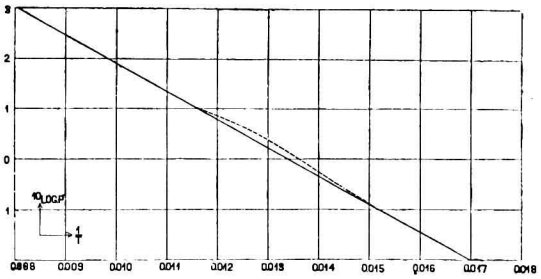


Fig. 3.

on the sample purified by rectification. Numerical data concerning the vapour pressures of krypton will be given in a subsequent paper.

To check the purity of the gas now obtained the middle and the last fractions mentioned above were added together [1]) and rectified again in an apparatus as described under *a*, but of smaller dimensions. In this apparatus the double-speeded screw was 4 cm long, diameter 8 mm, depth of the thread 1,5 mm. The vapour pressures of the middle fraction obtained by this new rectification coincided with those of the product of the first rectification. We conclude that rectification is a much more effective method of purification than fractional evaporation.

[1]) Rectifying the middle portion alone was prohibited by its small quantity.

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**Physics.** — *On the adsorption of neon on glass at liquid hydrogen temperatures.* By W. H. KEESOM and G. SCHMIDT. (Communication N°. 226*a* from the KAMERLINGH ONNES Laboratory at Leiden.)

(Communicated at the meeting of September 30, 1933).

*Summary.* Measurements have been made on the adsorption of neon on glass at four temperatures in the liquid hydrogen range. It appeared that in increasing the pressure the covering of the wall proceeds regularly and that complete covering with a monomolecular layer is reached at about the saturated vapour pressure. The adsorption isotherms are represented pretty well by the formula :

$$q^3 = \frac{p}{0.7\,(p_s - p) + p},$$

$q$ being the fraction of the wall covered, $p$ the pressure, $p_s$ the saturated vapour pressure.

§ 1. *Introduction.* When trying to measure temperatures below 1°K. by means of a helium thermometer with an ice point pressure of 1 mm mercury, it appeared that already below 4°K. the pressure decreased too rapidly, and that at 0.73°K. (derived from the vapour pressure of the liquid