

Index of Refraction of HCl from 1 to 10 μ

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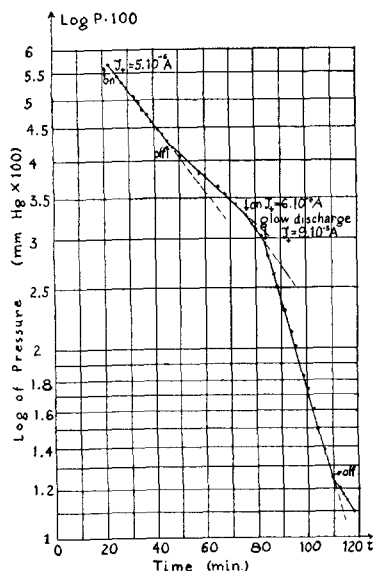


Fig. 2.

Finally to discover the described effect we had to choose the conditions (gas pressure, temperature of the source) so as to make the thermal dissociation on the source and the corresponding clean-up a minimum in comparison with the additional homogeneous effect. One must also remember, that the clean-up process of H atoms, generated only by thermal dissociation does not follow a linear, but rather a logarithmic law. Therefore, to find the additional clean-up due to the action of ions, and to calculate the efficiency of an ion, we must plot $\log p$ against t , and not simply p against t . In doing so with a part of curve (I) in Fig. 3 of the article of Kunsman and Nelson we get the curve, shown on Fig. 2 of the present article. Here we can see a rather marked increase of the clean-up rate at the time the field was turned on, and a slowing up of the clean-up at the time the field was turned off. Probably in this experiment of Kunsman and Nelson there happened to exist a sufficient coincidence of the required experimental conditions.

It appears therefore, that the experiments of Kunsman and Nelson do not entirely contradict our explanation of the effects we have observed, but on the contrary, seem, in part, to prove the correctness of our experiments.

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May 17, 1935.

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Index of Refraction of HCl from 1 to 10 μ

In view of the recent discussion in the literature concerning the effective charge of HCl,^{1,2} we believe it advisable to communicate immediately the results we have obtained from dispersion measurements between 1 and 10 μ . The dispersion curve is matched best by using a value of $1.00 \cdot 10^{-10}$ e.s.u. for the effective charge of the rotator-vibrator, and a value of $1.18 \cdot 10^{-18}$ e.s.u. for the electric moment of the rotator. The values for the effective charge and the electric moment are not mutually dependent to any great extent since the contribution of the pure rotation in the region near the rotation-vibration band is small, and *vice versa*. The uncertainty in the value of the effective charge of the rotator-vibrator is less than five percent. The value of the effective charge for the rotator-vibrator is in good agreement with Bourgin's³ result obtained from measurements of the absorption intensities in the band at 3.46 μ .

Beyond about 4.5 μ , the contribution of the rotator to the index of refraction exceeds that of the rotator-vibrator, and at 10 μ the effect of pure rotation is nearly as great as that of the rotator-vibrator as near the 3.46 μ absorption band as we could accurately measure it. The measurements between 5 and 10 μ thus afford an excellent check of the negative terms of the Kramers dispersion formula, since the majority of the molecules are in excited states and the number in each state can be accurately computed. If the negative terms are omitted and a reasonable value of the electric moment is used, one obtains by computation a contribution due to pure rotation which is more than twice as large as that obtained by experiment.

The value of the electric moment required to match the dispersion measurements is slightly larger than the value obtained by Zahn⁴ ($1.034 \cdot 10^{-18}$ e.s.u.) from dielectric constant measurements. This indicates that the low intensities obtained by Badger⁵ and by Czerny⁶ for the pure rotation spectrum are to be explained by the extreme difficulty of making absolute intensity measurements, especially in the far infrared. A complete report of the work will be published shortly.

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An Attempted Concentration of the Heavy Nitrogen Isotope

Urey and Greiff¹ have theoretically demonstrated that isotopic exchange reactions might be used for the separation or concentration of some of the isotopes of the lighter elements. The isotopic reaction,

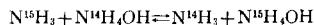


TABLE I.*

Sample	Ratio $N^{14}N^{14} : N^{14}N^{15}$
1	131 ± 2
3	135 ± 1
4	124 ± 1
-----	-----
5	134 ± 2
6	133 ± 2
7	134 ± 2
8	127 ± 2
9	138 ± 2

* Between analyses, conditions in the mass spectrograph changed so that the background correction for the first three samples was not the same as for the last five. Thus the first three samples are comparable, as are the last five.

was studied with the hope of concentrating the heavy nitrogen isotope. A twenty-five foot packed column, which was erected by Dr. W. G. Brown for the study of other exchange reactions, was used for this purpose. Gaseous ammonia was passed into the bottom of the column at a constant rate and water in at the top, at such a rate that the through-put of ammonia was very small. After six hours of continuous operation with as large a reflux ratio as possible to maintain, a small sample of forward flow ammonia was collected for analysis. This is designated as sample No. 3 and is to be compared with sample No. 1, a sample of tank ammonia.

The ammonia molecule was not satisfactory for analysis in the mass spectrograph, so all the samples were converted to nitrogen by the reaction of ammonia with sodium hypobromite. The results of the analyses are recorded in Table I, together with the analyses of other samples described below.

It is evident that the distribution of N^{15} is slightly favored in the NH_4OH molecule; however, either the fractionation factor for this reaction is almost unity, making this reaction most impractical for the concentration of heavy nitrogen, or the column did not contain nearly as many theoretical plates as we had anticipated.

Since a large Dewar flask filled with anhydrous ammonia served as a source of ammonia for the above experiment, it was possible at the same time to determine the ratio of vapor pressures of the molecules $N^{14}H_3$ and $N^{15}H_3$. The residue from this distillation is sample No. 4. The factor by which the sample was taken down in this experiment is somewhat uncertain. It may be as small as 76 and certainly not any larger than 800. If we use the first figure, a value of 1.012 is obtained for the ratio of vapor pressures, and using the second the ratio becomes 1.0082.

The experiment was repeated taking care to measure the volume of the residue more accurately. The factor by which the sample was reduced in this case was approximately 32,800. The residue is designated as sample No. 8 and is to be compared with No. 7, a sample of tank ammonia. The ratio calculated from data obtained in this experiment is 1.0052. This value is not in good agreement with those obtained above. In this experiment, a four-liter Dewar of liquid ammonia was evaporated under atmospheric pressure to 4 liters of ammonia gas. This gas was then condensed in a small trap and again evaporated till only the trap filled with gas remained. It seems probable that when the liquid residue becomes small, spattering and lack of stirring defeat the concentration that should result from continued dis-

tillation. In any case, the value 1.0052 is the minimum to be expected for the ratio of vapor pressures, and it is possible that the values obtained in the first experiment are more nearly correct.

The mean deviations recorded in Table I are somewhat larger than those actually calculated. We have been somewhat liberal in these estimates, since they are calculated from only five or six determinations in each case. The ratio of vapor pressures given as 1.0052 may be in error by about 0.0013 because of the errors in analysis. Incidentally it may be remarked that these values for the nitrogen isotope ratio are in excellent agreement with that of Vaughan, Williams and Tate² who found $N^{14} : N^{15} = 265 \pm 8$.

A ten-foot vacuum-jacketed packed column one inch in diameter, was constructed for the distillation of liquid ammonia. A dry ice condenser was installed at the top of the column and the ammonia was boiled at the rate of two liters per hour. After several hours operation at total reflux a sample (No. 9) was taken by passing a slow stream of inert gas through the condenser. The analysis shows the column to have approximately six theoretical plates. This is less than the number expected, but is in accord with the findings of Cryder, Fenske and co-workers³ on the distillation of water with packed columns of this type.

Samples of ammonia were obtained from the commercial stills of the Mathieson Alkali Works and analyzed to ascertain whether there might be a commercial source of ammonia containing an increased concentration of $N^{15}H_3$. Sample No. 5 is the starting material and No. 6 is a sample of the 3000-lb. residue obtained from 70,000 lbs. of ammonia which was distilled in four batches, each batch being added to the preceding residue. It is apparent that the distillation is carried out so rapidly at such a small reflux ratio that the concentration is almost negligible.

The vapor pressure ratio $N^{14}H_3 - N^{15}H_3$, although not particularly encouraging, indicates that the distillation of liquid ammonia may be a means of obtaining increased concentrations of $N^{15}H_3$. The difference between these vapor pressures is similar to that in the case of the H_2O^{16} and H_2O^{18} waters.⁴

We are indebted to Professor H. C. Urey for suggesting this problem and for suggestions offered during the course of the work, and to Professor Walker Bleakney for much helpful advice and the use of his apparatus in making the analyses. We also wish to thank the Mathieson Alkali Works, Inc. for sending us samples of ammonia from their large stills.

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