

Homogeneous Dissociation of Hydrogen Molecules by Collision with Positive Ions

A. Schechter

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Homogeneous Dissociation of Hydrogen Molecules by Collision with Positive Ions

In a series of recent articles! we have shown that positive ions, emitted from heated sources, and accelerated by an electric field produce, after reaching certain critical potentials, a sharp reinforcement of the hydrogen as well as nitrogen clean-up. Calculations of the energy which under optimal conditions can be absorbed by a given molecule on collisions with the ions showed, that at different critical potentials, corresponding to ions of different masses, the molecule is always able to absorb the same definite quantity of energy corresponding to some excited state of the molecule (12.4 v for hydrogen).

These data were further developed in a paper from our laboratory published in the Reports of the Academy of Science (USSR), (1934),2 concerning the synthesis of ammonia by bombardment of a hydrogen-nitrogen mixture with positive ions from synthetic spodumen-sources. For every sort of ions used there was found a definite critical potential, required for the synthesis of ammonia. The presence of the latter was shown both by means of pressuremeasurements, and chemically by means of Nessler's reagent. The calculation of energy that could be absorbed in the optimum case by the molecules of the mixture shows, that for all sorts of ions used (Li+, Na+, K+, Rb+, Cs+) the nitrogen molecule was able to take up about 22 volts. Fig. 1 illustrates the sharpness of the effect. All these investigations without exception indicate the possibility of sharp chemical effects resulting, at critical potentials, from collisions of molecules with ions. The observation of the effects described requires very careful control of experimental conditions. These were described rather briefly in the foregoing articles, a circumstance which was perhaps the principle cause of some misunderstandings arising from attempts of Mitchell³ and of Kunsman and Nelson⁴ to repeat our experiments. These authors, on the basis of their negative results, deny the correctness of our explanation of the data of H2.

In order to indicate possible causes of this disagreement, we shall describe some of the chief experimental conditions without which the observation of the observed effects is very difficult.

It is very important to keep the level of liquid air in the Dewar flask constant, because the smallest oscillations of the latter sharply change the rate of pressure fall (because of the change in area of the cooled surface). We were forced to build an apparatus for automatic control of the constancy of the liquid air level, and for the enlargement of the observed effect, to keep the whole reaction vessel in a Dewar flask. It seems that these two conditions were not fulfilled in the work of Kunsman and Nelson. The form of the collector in the apparatus of Kunsman and Nelson (Fig. 1 of their article), indicates that hydrogen atoms had greater chance to recombine on the surface of the collector, than to arrive into the tube end cooled by liquid air, a circumstance which also should diminish the effect observed.

It is further necessary to take into account that at pressures of the order of some tenths of a mm Hg the mean free path is $2-10\,$ mm. Therefore, to secure a suitable probability of collisions of an ion with an H₂ molecule the distance grid-cathode must be taken of the order of $4-5\,$ cm. A smaller distance does not prevent thermal dissociation of H₂, but it may diminish strongly the efficiency of the ions. From Fig. 1 of the article of Kunsman and Nelson one can assume, that in their arrangement this condition was not fulfilled.

Further, before every experiment we had to outgas the ion source (by heating it to 750–800°C) and the vessel (by heating it to 350°C) by constant pumping for several hours. Only after our Pirani gauge no longer registered any pressure increase on heating the ion source could we begin our experiment. In the article of Kunsman and Nelson nothing is said about outgasing before experiments.

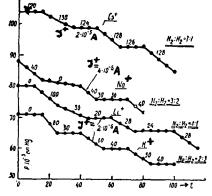
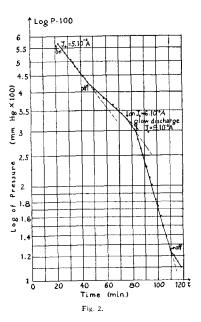


Fig. 1. The data on the curves indicate the voltages used



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 cleanup 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.

A. SCHECHTER

Institute for Chemical Physics, Leningrad, 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 10μ . The dispersion curve is matched best by using a value of 1.00 · 10-10 e.s.u. for the effective charge of the rotatorvibrator, and a value of 1.18 · 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's result obtained from measurements of the absorption intensities in the band at 3.46μ .

Beyond about 4.5μ , the contribution of the rotator to the index of refraction exceeds that of the rotator-vibrator, and at 10µ 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 · 10-18 e.s.u.) from dielectric constant measurements. This indicates that the low intensities obtained by Badgers and by Czernys 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.

> R. Rollefson A. H. ROLLEFSON

Physical Laboratory, The University of Wisconsin, Madison, Wisconsin, May 18, 1935.

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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,

 $N^{15}H_3 + N^{14}H_4OH \rightleftharpoons N^{14}H_3 + N^{15}H_4OH$