Comment on the Homogeneous Exchange Reaction Between Hydrogen and Deuterium

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longing to the ionic and the two covalent functions must cross near 10 a.u., but must interact strongly near 10 a.u., the actual V state, though to a large extent ionic below 10 a.u., nust become pure covalent above 10 a.u. and dissociate to one normal and one excited H atom.

In our communication[1] we assumed without checking, that our two-parameter (ζ_g, ζ_u) variation function would tend as $R \rightarrow \infty$ toward the closed-shell H^- approximate pure ionic function. However, Hurley[4] has recently pointed out that our variation function for energy-minimizing values of ζ_g and ζ_u actually goes as $R \rightarrow \infty$ into a linear combination of an open-shell H^- pure ionic and a $1s2s$-like covalent function. Hurley has also pointed out[5] that on introducing an additional parameter (namely, the ratio of the ionic and covalent terms), the function goes over smoothly as $R \rightarrow \infty$ into a rather good approximation to a $1s2s$ covalent function. (Presumably, however, it should go into a $1s2hy$ function, where $2hy$ is a $2s - 2p\sigma$ hybrid.)

While the indicated behavior of our function as $R \rightarrow \infty$ is very interesting, we feel that the main significance of our function is in the framework of MO theory, at small and moderate R values. But also, we have found, in calculations made subsequent to our original communication, that in a range of R values greater than R_e, but less than the crossing point of the pure ionic and covalent zeroth order potential energy curves near 10 a.u., the energy of our function is actually minimized with $\zeta_g = \zeta_u \approx 0.7$. In other words, the closed-shell ionic function is in this range the best wave function obtainable within the limitations of our two-parameter variation function. These calculations show that at 2.5 A (4.73 a.u.) the energy of our function is mnimized with $\zeta_g = \zeta_u \approx 0.7$, but also indicate an incipient second minimum of *higher* energy for $\zeta_g \approx 0.9$, $\zeta_u \approx 0.5$. At 4.0 A (7.56 a.u.) we find two definite minima, one for $\zeta_g = \zeta_u \approx 0.7$, the second near $\zeta_g = 0.1$, $\zeta_u = 0.3$, but this time the second minimum is appreciably (0.15 ev) *lower* than the first.[6] In other words, the $R \rightarrow \infty$ asymptotic behavior described by Hurley has now begun to take over. Nevertheless, our results indicate that there is a definite range of R where the pure ionic function with $\zeta_g = \zeta_u$ represents the best approximation within the limitations of our variation function. Our calculations are being continued in order to explore more thoroughly the behavior of ζ_g and ζ_u for the two minima in this range and to delineate more precisely the boundaries of this range.

We wish to thank Dr. Hurley for his suggestions and enlightening communications with us.

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[1] P. Phillipson and R. S. Mulliken, J. Chem. Phys. **28**, 1248 (1958).
[2] S. Huzinaga, Progr. Theoret. Phys. **19**, 125 (1957).
[3] For relevant calculations, see J. T. Lewis, Proc. Phys. Soc. (London) **68**, 632 (1955).
[4] A. Hurley, J. Chem. Phys. **32**, 301 (1960).

[5] This is implied in footnote reference 4 and was made clear in a private communication to us from Dr. Hurley.
[6] The energy at 4.0 A for $\zeta_g = \zeta_u = 0.7$ is 10.79 ev, and not 10.98 ev as reported in footnote reference 1. This is to be compared with 10.64 ev with $\zeta_g = 1.0$, $\zeta_u = 0.3$.

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IN a recent theoretical paper by I. Shavitt[1] on the elementary reactions of the type $H + H_2 = H_2 + H$, existing experimental data are reviewed, including our previous work on the hydrogen-deuterium exchange.[2]

A comment seems appropriate on some remarks by Shavitt regarding the perturbing action of oxygen, since our experiments have been discussed further, together with additional data, in a previous paper.[3] At the same time we wish to correct a trivial arithmetical error present in our paper, which leads to·an inconsistency, as pointed out by Shavitt.

In our paper[2] we stated that the experiments by Farkas and Farkas[4] (F and F), and by Van Meersche (VM)[5] were effected by the diffusion of oxygen through the walls of the reaction vessel. Shavitt comments on this point by remarking that some of the measurements of VM were obtained at temperatures low enough to exclude any oxygen diffusion through the walls. These measurements are in good agreement with VM's measurements at higher temperatures, as well as with F and F's measurements. It would therefore appear that oxygen diffusion at high temperature must be irrelevant for the exchange reaction. We wish to point out that a heterogeneous effect of the oxygen can actually be present at all temperatures. In order to eliminate the oxygen adsorbed on the walls, the reaction vessel must be outgassed at around 1100°C with a vacuum jacket around it. If this precuation is not taken, higher reaction rates are obtained, yielding, however, the same activation energy. The effect clearly showed up in our case[2] with a vessel which had been partially degassed; measurements were reproducible, and yielded the same activation energy, but higher exchange rates were observed than after further outgassing. The cause for the observed higher rates has been attributed by us to a higher stationary concentration of atoms. We recall that atoms are produced by a heterogeneous process. In addition to the above-mentioned effect, a heterogeneous production of HD molecules, characterized by an activation energy of about 17 kcal/mol, becomes increasingly important at lower temperatures.[3]

Thus, of the whole temperature interval studied by us (from 800 to 1010°K), only the interval 910 to 1010°K is free from heterogeneous production of HD molecules, and can be examined for the homogeneous reaction.

In our paper, the ratio k_3/k_4 between the velocity constants of the reactions $D+H_2$, and $H+D_2$, because of a trivial arithmetical error, was given as 1.6 at 1000°K. The value for k_3/k_4 should be corrected as 1.31. This correction leaves the values of the over-all rate a (Table I of footnote reference 2) unchanged within 2%. The ratio between the values of F and F and our values therefore remains 2. The same factor may be assumed for the *ortho-para* reactions, as already discussed.[2] The only values which are affected are the experimental k's for the exchange reaction.

We would like, however, to comment briefly on this point. It can be verified that in our kinetic treatment the expansion in series and the limiting condition (24), which allowed us to calculate the value of k_3/k_4, are in fact equivalent to imposing the additional condition $[H]/[D] = \text{const} = (K_{H_2}/K_{D_2})^{\frac{1}{2}}$ ($=1.31$ at 1000°K). In fact, substitution of $k_3/k_4 = (K_1/K_2)^{\frac{1}{2}} = (K_{H_2}/K_{D_2})^{\frac{1}{2}}$ in the equation $[H]/[D] = (k_3[H_2]+k_6[HD])/(k_4[D_2]+k_5[HD])$ [Eq. (10)] which gives the variation of $[H]/[D]$ in the course of the reaction shows that $[H]/[D]$ becomes constant (K_{H_2}, K_{D_2} dissociation constants of H_2 and D_2; $K_1 = k_3/k_5$; $K_2 = k_4/k_6$). If the assumption $[H]/[D] = \text{const}$ is removed, and if no other assumption is made, then it becomes impossible to calculate the above ratio from experimental data alone. The same considerations apply to the k_3/k_4 values given by F and F and by VM. The only significant quantities which can be derived from this type of experiment are the over-all rate [proportional to $k_3k_4/(k_3+k_4)$] and the activation energy. .

We can summarize our comments as follows:

(a) In the temperature interval 910 to 1010°K, where the heterogeneous production of HD molecules has become negligible, elimination of the perturbing effect of oxygen adsorbed at the walls of the reaction vessel leads to values of the over-all rate constant, for the exchange reaction, which are lower by a factor of 2 with respect to the values previously determined by F and F and by VM.

(b) The kinetics to which the reaction conforms is such as to make the determination of the ratio k_3/k_4 impossible, unless additional assumptions are introduced. From the theoretically determined values of the rate constants, a comparison can be made with the over-all rate of exchange $k_3k_4/(k_3+k_4)$, which has been experimentally determined at various temperatures.

We wish to express our thanks to Professor J. O. Hirschfelder and to Dr. I. Shavitt for helpful discussions on this subject.

[1] I. Shavitt, J. Chem. Phys. **31**, 1359 (1959).
[2] G. Boato, G. Careri, A. Cimino, E. Molinari, and G. G. Volpi, J. Chem. Phys. **24**, 783 (1956).
[3] A. Cimino, E. Molinari, and G. G. Volpi, Gazz. chim. ital. **86** 609 (1956).
[4] A. and L. Farkas, Proc. Roy. Soc. (London) **A152**, 152 (1935).
[5] M. Van Meersche, Bull. soc. chim. Belg. **60**, 99 (1951).

Erratum: NMR Spectra of Some Simple Epoxides

[J. Chem. Phys. **32**, 1378 (1960)]

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O N page 1383, the captions for Figs. 3 and 4 should be interchanged.

Erratum: Infrared and Raman Spectra of Fluorinated Ethanes XII. 1,1,2,2-Tetra-fluoroethane

[J. Chem. Phys. **32**, 899 (1960)]

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T HE last two sentences preceding the Discussion section on page 906 should read as follows:

Taking $a=2.6$ A, one finds

$$E_p \text{ (gauche)} = 1020 \text{ cal/mole}, \quad E_r \text{ (trans)} = 0.$$

These values agree quite well with those observed.

Erratum: Mechanics of Atomic Recombination Reactions

[J. Chem. Phys. **32**, 1001 (1960)]

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E QUATIONS (5) and (6) should be corrected to read

$$\mu\ddot{r} - \mu r\dot{\theta}^2 + dV/dr = 0 \tag{5}$$

and

$$\tfrac{1}{2}\mu\dot{r}^2 = E(1-b^2/r^2) - V. \tag{6}$$