REACTIONS OF STATE SELECTED $Ar^{++}(^3P)$ AND $Ar^{++}(^1S)$ AND OF Ne^{++} IONS WITH VARIOUS NEUTRALS.

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ABSTRACT
In a drift experiment the energy dependences of the reactions of state selected $Ar^{++}(^3P)$ with He, Kr, H_2, O_2, CO_2, CH_4, C_2H_2 and NO, of $Ar^{++}(^1S)$ with He, H_2,N_2, O_2, CO_2, CH_4 and C_2H_2 and of $Ne^{++}(^3P)$ with H_2, N_2, O_2, CO, CO_2 and C_2H_2 have been investigated in the energy range below a few eV. The results indicate the Landau-Zener-Stückelberg model to be valid for these reactions.

INTRODUCTION
According to the Landau-Zener-Stückelberg model /1/ one would expect nearly all single charge transfer reactions of doubly charged ions with molecular neutrals to be fast. Because of the wide variety of energy levels present in molecular systems in most cases curve crossings can be found for the potential curve of the reactants and the constant repulsion curve of the products, in a favorable internuclear distance of a few Å, where a high transition probability leads to high reaction rate constants.
In order to get experimental proof for that, we investigated a wide variety of reactions of the doubly charged ions

$Ar^{++}(^3P)$, $Ar^{++}(^1S)$ and $Ne^{++}(^3P)$ with many molecular reactants.In the cases where rare gases and the exception among the molecules, H_2, are used as reactants, the chance for curve crossings to happen in a proper internuclear distance is reduced due to the smaller number of excited states which are available in these system. Therefore we also investigated some reactions of the above doubly charged ions with H_2 and some rare gases to get further evidence for the validity of the Landau-Zener-Stückelberg model.

EXPERIMENTAL

The present investigation was performed using a drift-apparatus, described in detail elsewhere /2/. Ions are produced in a hollow-cathode ion source, from where they enter the drift tube through a hole probe. After traversing the drift section these ions, which enter a quadrupole chamber through a sampling orifice are mass selcted and counted. Adding reactant gas in variable amounts to the buffer gas in the drift tube leads to a decline of the reactant ion signal from which the reaction rate constant is then calculated in the usual way /2,3,4/. The electric field strength in the drift section and the buffer pressure determine the relative kinetic energy KE_{cm} of the reactants. Thus the stepwise variation of those two parameters and measuring a rate constant at each step allows the investigation of the energy dependences of reaction rate constants. For the measurements of $Ar^{++}(^3P)$ reactions argon was used in the hollow cathode ion source,as well as in the drift section. From the three states $Ar^{++}(^3P)$, $Ar^{++}(^1D)$ and $Ar^{++}(^1S)$ all produced in the hollow cathode source only the (^3P) state survives in argon /3,5,6/ thus all the reactions of Ar^{++} measured in an argon buffer can be attributed to the $Ar^{++}(^3P)$ state. On the other hand helium buffer was used for measuring reactions of $Ar^{++}(^1S)$ as only the (^1S) state survives in helium.

For the investigation of Ne^{++} reactions Neon was used in the hollow cathode ion source as well as in the drift section. Only a single decline of the Ne^{++} signal was observed in each measurement and as the ^3P state is stable in Neon /6/ and is also the most abundant one we attribute all our measurements of Ne^{++} reactions to the $Ne^{++}(^3P)$ state. For the reduction of the data we used the mobilities of Johnson et al. /6/ in the case of the $Ar^{++}(^3P)$ and of the $Ne^{++}(^3P)$ reactions and of Störi et al. /2/ in the case of the $Ar^{++}(^1S)$ reactions.

RESULTS

The results obtained for the reactions of $Ar^{++}(^3P)$,$Ar^{++}(^1S)$ and $Ne^{++}(^3P)$ are shown in the Figures 1 through 4 . In addition to that an upper limit of $k \leq 10^{-13} cm^3 sec^{-1}$ can be given for the reactions of $Ar^{++}(^3P)$ with Ar, $Ar^{++}(^1S)$ with He an $Ne^{++}(^3P)$ with Ne, and an upper limit of $k \leq 5x10^{-12} cm^3 sec^{-1}$ was found for $Ar^{++}(^3P)$ reacting with H_2. All the reactions with molecular neutrals, with the exception of H_2 are fast as expected from the Landau-Zener-Stückelberg model mentioned above. Most of the other rate constants also can be explained in terms of this model. The reaction of $Ar^{++}(^1S)$ with the He is exothermic by more than 7eV thus leading to curve crossing at a very small internuclear distance R_x of less than 2 Å. As expected from this, the rate constant is small. On the other hand $Ar^{++}(^3P)$ reacts much faster with He, the respective curve crossing being at a favorable distance $R_x \sim 4$ Å.
In the case of the slow reaction of $Ar^{++}(^3P)$ with H_2 the curve crossing is at $R_x \leq 1.4$ Å, whereas the energy of $Ar^{++}(^1S)$ is high enough, so that this fast reaction can proceed via the $^2\Sigma_u$ repulsive state of the H_2^+ (R_x = 7 to 8Å). This repulsive state cannot be reached in the Franck-Condon regime in the reaction of $Ar^{++}(^3P)$ with H_2.

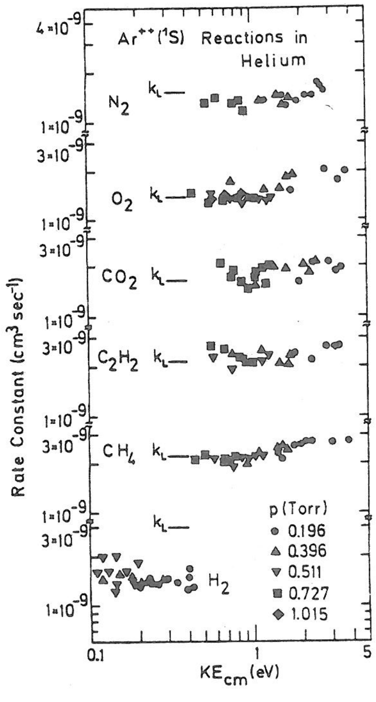

Fig. 1

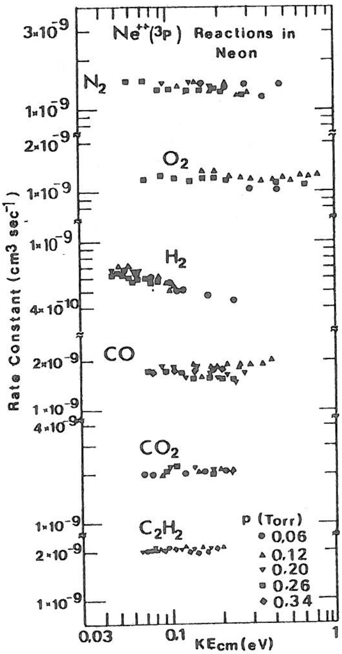

Fig. 2

The present results strongly indicate the Landau-Zener-Stückelberg model to be applicable in the low energy regime of reactions of doubly charged ions so that this model may be used to predict whether yet unmeasured rate constants are fast or slow.

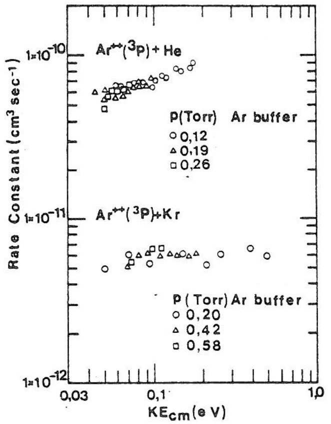

Fig. 3

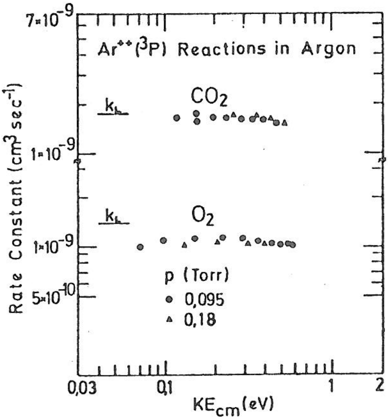

Fig. 4

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