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REACTIONS OF NA$^+$, K$^+$, AND BA$^+$ IONS WITH O_2, NO, AND H_2O MOLECULES

BY

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Reactions of Na^+, K^+, and Ba^+ Ions with O_2, NO, and H_2O Molecules

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Reactions of Na^+, K^+, and Ba^+ Ions with O_2, NO, and H_2O Molecules*

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Abstract

Ion molecule reactions of sodium, potassium, and barium ions with O_2, NO, and H_2O have been studied in a drift tube - mass spectrometer apparatus. The following rate constants or upper limits were obtained:

Na^+, K^+, Ba^+ + O_2 (NO) → products

$$k < 10^{-13}\ \mathrm{cm^3/sec}\ (0.04\ \text{to} \sim 5\ \mathrm{eV})$$

$Na^+ + H_2O + M \rightarrow Na^+ \cdot H_2O + M$

$$k^{(3)} = 1.0\ (+\ 0.5,\ -\ 0.3) \times 10^{-28}\ \mathrm{cm^6/sec}\ \text{for}\ M = H_2O$$

$$k^{(3)} = 4.7\ (+\ 1.2,\ -\ 1.0) \times 10^{-30}\ \mathrm{cm^6/sec}\ \text{for}\ M = He$$

$K^+ + H_2O + M \rightarrow K^+ \cdot H_2O + M$

$$k^{(3)} = 4.5\ (+\ 2.3,\ -\ 1.5) \times 10^{-29}\ \mathrm{cm^6/sec}\ \text{for}\ M = H_2O$$

$$k^{(3)} = 2.6\ (0.7,\ -\ 0.5) \times 10^{-30}\ \mathrm{cm^6/sec}\ \text{for}\ M = He$$

The consequences of these results for the D and E region of the upper atmosphere are briefly described.

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I. Introduction

Recently attempts have been made to calculate the rate of charge neutralization in the metal ion layer[1,2] of the upper atmosphere at 93 km. Of potential importance to such calculations are the rates at which these ions are converted from atomic to molecular species which can undergo rapid dissociative recombination with electrons. Consequently, we have searched for reactions involving oxidation of the metal ions Na^+, K^+, and Ba^+ during energetic collisions with O_2 and NO molecules and have determined clustering reaction rates of Na^+ and K^+ ions with water molecules. Inasmuch as the binding energies of the metal oxide ions are expected to be rather small compared to the dissociation energies of O_2 and NO molecules, the oxidation reactions are expected to be endothermic, requiring substantial kinetic or internal energy in the colliding partners. As will be shown in Section III, up to ion kinetic energies of ~ 5 eV the 2-body oxidation reaction rates remain below our detection capabilities.

It appears that the formation of metal ion - water clusters is not likely to be an important metal ion loss process in the metal ion layer, as a result of the small concentration of water molecules in this region. Even in the D region, where a positive ion of mass 41 (tentatively identified as $Na^+ \cdot H_2O$) has been observed with a rocket-borne mass-spectrometer,[3] a three-body clustering reaction of the type described in Section IV appears too slow to account for the formation of this ion.

II. Experimental Apparatus

The drift tube-mass spectrometer apparatus has been described in an earlier paper[4] and was used essentially unchanged except for the ion source. The metal ions were produced by a hot filament coated with the oxide of the alkali (or barium) metal. The filaments were prepared according to the description of Blewitt and Jones[5] and were found to have a satisfactory lifetime in the case of Na^+ and K^+ sources (~ 100 hr). For Ba^+ emission the required temperature was much higher and most filaments burned out after a few hours. The filaments intended for Na^+ ion emission contained enough potassium impurities so that the sodium and potassium experiments could be carried out simultaneously with the same filament. Pulsing of the ion source was achieved by applying a negative pulse to a draw out electrode located in front of the filament.

In order to inhibit diffusion of the ions to the walls of the drift tube, all experiments were made with helium as a buffer gas. The water vapor pressure was measured before addition of the buffer gas by means of a millitor ion gauge which had been calibrated at higher pressures against a capacitance manometer - McLeod gauge system. It was found that the water vapor pressure in the drift tube decreased by up to 50% when the buffer gas (~ 1.5 torr of helium) was added. This effect had also been observed in earlier measurements with nitrogen, oxygen and carbon dioxide in helium as buffer gas and is attributed to the "sweep-out effect", i.e. the interaction of the two gases flowing with different velocities to the ion sampling orifice and into the differentially pumped mass spectrometer. The small mobility of sodium ions in water vapor (μ_0 was found to be 0.85 cm^2/V sec in H_2O vs 21 cm^2/V sec in helium) causes even a small water vapor concentration to have a significant effect on the measured drift times. With the help of Blanc's law[6] describing the mobilities in gas mixtures, the water vapor concentration in the presence of helium was determined and used for the analysis of the reaction rate measurements. The uncertainty of this concentration determination is estimated to be ~ ± 25%.

The rate constants for clustering of Na^+ and K^+ in H_2O at thermal energies were obtained by the "additional residence time" technique, which has been described in some detail in a previous paper[4]. In this technique the reaction rate is determined at thermal energies by admitting a pulse of metal ions to the drift region, turning the drift field off for specified intervals, then turning the field back on again to carry the ions to the collector end of the drift tube and into the differentially pumped mass spectrometer. By measuring the decrease in metal ion signal with increasing field off-time, both in the presence and in the absence of the reactant gas (H_2O), one can separate reaction and diffusion effects and so obtain the desired reaction rate.

III. Search for Reactions of Na^+, K^+, Ba^+ Ions with O_2 and NO

A thorough search was made for oxide ions formed in reactions of energetic Na^+, K^+, and Ba^+ ions with O_2 and NO. The binding energy of alkali ions (having a closed outer electron shell) with O atoms is expected to be quite small, so that reactions such as $Na^+ + O_2 \rightarrow NaO^+ + O$ are endothermic. At higher ion energies, however, their reactions may be energetically possible, and the search for oxide ions was therefore extended to ion energies up to ~ 5 eV. No ions that could be identified as reaction products were observed in this energy range, indicating that the corresponding rate coefficients must be very small. The rate coefficients for $K^+ + O_2(NO) \rightarrow KO^+ + O(N)$ were estimated to be less than 10^{-14} cm^3/sec.

In the corresponding sodium ion studies, NaO^+ ions having the same mass as K^+ ions could be distinguished from them only by their different dependence on the reactant gas concentration and their different times of flight (Na^+ has a slightly higher mobility in He than K^+ so that reaction products of Na^+ should exhibit a characteristic arrival spectrum with the onset at the time of flight of Na^+). The detection sensitivity for NaO^+ was therefore somewhat smaller. The upper limit for the rate coefficients of $Na^+ + O_2(NO) \rightarrow NaO^+ + O(N)$ were estimated to be $\sim 10^{-13}$ cm^3/sec. In addition to the absence of product ions, no attenuation of the parent ion signal was ever observed. (The upper limits on these reaction rates are arrived at by noting that a product ion counting rate equal to ~ 1% of the parent ion count rate could have been detected.)

The NO and O_2 pressures were varied between 10^{-3} and 0.5 torr with ~ 0.2 to 1.5 torr of helium present. Three body association reactions of the form $Na^+ + O_2 + M \rightarrow NaO_2^+ + M$ could have been observed if the rate coefficients were greater than $\sim 10^{-31}$ cm^6/sec. No indication of such reactions was found.

IV. Clustering of Na^+, K^+ Ions with H_2O

The existence of alkali ion water clusters has been known ever since Munson and Tyndall[7] discovered the strong effect of water traces on the mobility of alkali ions in rare gases. In our studies we tried to establish the mechanism and rate coefficients for the formation of the first cluster, i.e., the reaction $Na^+ + H_2O + M \rightarrow Na^+ \cdot H_2O + M$ (and $K^+ + H_2O + M \rightarrow K^+ \cdot H_2O + M$).

The reactions are thought to proceed in two-step collision processes, involving three particles. In the first step a water molecule attaches to the ion, leaving the intermediate complex with an excess energy. The complex may either break up again with a characteristic lifetime τ or the excess energy may be removed in a second collision rendering the cluster stable.

The stabilization can be described by a two body rate constant k_2 which depends on the nature of the third body M. If the lifetime τ is large compared to the time $(k_2\ M)^{-1}$ required for stabilization, almost all clusters will be stabilized, and the reaction will be limited by the rate of formation k_1 of the unstable complexes. An increase of the third body concentration will have no influence on the reaction ("saturated three body reaction"). If, on the other hand, $\tau \ll (k_2\ M)^{-1}$, the rate of clustering depends on the third body concentration $[M]$, and the reaction can be described by a three body rate constant $k^{(3)} = k_1\ k_2\ \tau$. This case was realized in the experiment, as is shown below.

In the experiment, both the water molecules and the helium atoms can act as stabilizing third bodies, although with different efficiencies. In this case the measured loss rate ν of K^+ or Na^+ ions due to clustering can be described as

$$\nu = d\ \ln\ [P^+]/dt = k_w{}^{(3)}\ [H_2O]^2 + k_{He}{}^{(3)}\ [H_2O]\ [He]$$

where P^+ refers to K^+ or Na^+, and $k_w{}^{(3)}$ and $k_{He}{}^{(3)}$ refer to the rate constants with M = H_2O or He.

After $k_{He}{}^{(3)}$ had been determined by varying the helium density at constant water vapor density (see Fig. 1), a plot (Fig. 2) of $k_w{}^{(3)} = \{\nu - k_{He}\ [He]\ [H_2O]\}/[H_2O]^2$ vs. $[H_2O]$ was made and showed no systematic variation with $[H_2O]$. This and the linear dependences of ν on $[He]$ indicates that we are indeed dealing with a true (unsaturated) three body reaction.

The measured rate constants are:

$Na^+ + H_2O + M \rightarrow Na^+ \cdot H_2O + M$

$k^{(3)} = 1.0\ (+\ 0.5,\ -\ 0.34) \times 10^{-28}\ cm^6/sec$ for $M = H_2O$

$k^{(3)} = 4.7\ (+\ 1.2,\ -\ 1.0) \times 10^{-30}\ cm^6/sec$ for $M = He$

$K^+ + H_2O + M \rightarrow K^+ \cdot H_2O + M$

$k^{(3)} = 4.5\ (+\ 2.3,\ -\ 1.5) \times 10^{-29}\ cm^6/sec$ for $M = H_2O$

$k^{(3)} = 2.6\ (+\ 0.7,\ -\ 0.5) \times 10^{-30}\ cm^6/sec$ for $M = He$

The rate constants were obtained at $T = 300°K$ and at $E/p = 0$. Although the ion energy can be varied easily in a drift tube, it becomes very difficult to establish the three body nature of the process due to the smaller range over which the densities can be varied at a higher E/p. Furthermore, since the unclustered ions and the intermediate ion complex acquire different energies in the electric field, the results could hardly be expressed in terms of a single parameter equivalent to an ion temperature for the reactions. Therefore data were taken only in the absence of a drift field, where all particles have the same, well defined temperature. The quoted uncertainties in the rate coefficients, approximately ± 50% when $M = H_2O$ and ± 25% when $M = He$, reflect the large uncertainty in the water vapor concentration determinations. All other sources of error in the determinations are much smaller and have therefore not been discussed in detail.

Heavier clusters of the form $Na^+ \cdot (H_2O)_n$ with $n = 1 - 5$ and $K^+ \cdot (H_2O)$ with $n = 1 - 4$ were also observed. Their presence could have disturbed the rate constant determinations (based on the loss rate of the alkali ion) only if the heavier clusters would lose all of their water molecules and replenish the unclustered ions. The energy required to detach one water molecule from a potassium ion water cluster has been determined by Searles and Kebarle[8] to be 0.78 eV for $K^+ \cdot H_2O$ and to decrease to 0.5 eV for n = 4. These energies are very much higher than the ions' drift energies so that a complete break up of clusters seems unlikely.

The only other determination of similar alkali ion clustering reactions was reported by Fehsenfeld et al[9]. They obtained a value of 3×10^{-30} cm^6/sec for $Na^+ + H_2O + He \rightarrow Na^+ \cdot H_2O + He$, in fair agreement with the present result.

V. Discussion

The absence of detectable 2-body oxidation reactions for the ions Na^+, K^+, and Ba^+ colliding with O_2 and NO molecules, even up to ion energies of ~ 5 eV, suggests that such processes are not likely to contribute to eventual charge neutralization in the metal ion layer.

The results of our studies suggest that the 3-body clustering reactions of the form

$$I^+ + H_2O + M \rightarrow I^+ \cdot H_2O + M \quad ,$$

where I^+ is a metal ion and M a third-body molecule such as N_2 or O_2, offer rate coefficients in the range 10^{-29} to 10^{-28} cm^6/sec. Thus, loss of **E region** metal ions by clustering ought to proceed very slowly (assuming an H_2O density of 3×10^7 at 93 km, one obtains a lifetime against clustering of 10^7 to 10^8 sec). At 82 km altitude, where a small concentration of positive ions of mass 41 ($Na^+ \cdot H_2O$) has been observed, the lifetime of Na^+ ions against direct water cluster formation is reduced to ~ 10^5 sec, which is still rather long. Thus, it seems likely that the mass 41 ion either is not $Na^+ \cdot H_2O$ or else the $Na^+ \cdot H_2O$ is formed indirectly, perhaps by the switching reaction $Na^+ \cdot CO_2 + H_2O \rightarrow Na^+ \cdot H_2O + CO_2$ after 3-body formation of $Na^+ \cdot CO_2$ in the presence of the more abundant CO_2[10].

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Figure Captions

Fig. 1 Effect of helium as third body on the observed reaction frequency at a constant water vapor density ($[H_2O]$ = 8.4×10^{15} cm^{-3}). Data points have been corrected for the "sweep out" effect (see Sec. II). Note that the intercept at $[He] = 0$ corresponds to $k_w^{(3)}$.

Fig. 2 Three body coefficient $k_w^{(3)}$ as function of water vapor density, reduced to $[He] = 0$.

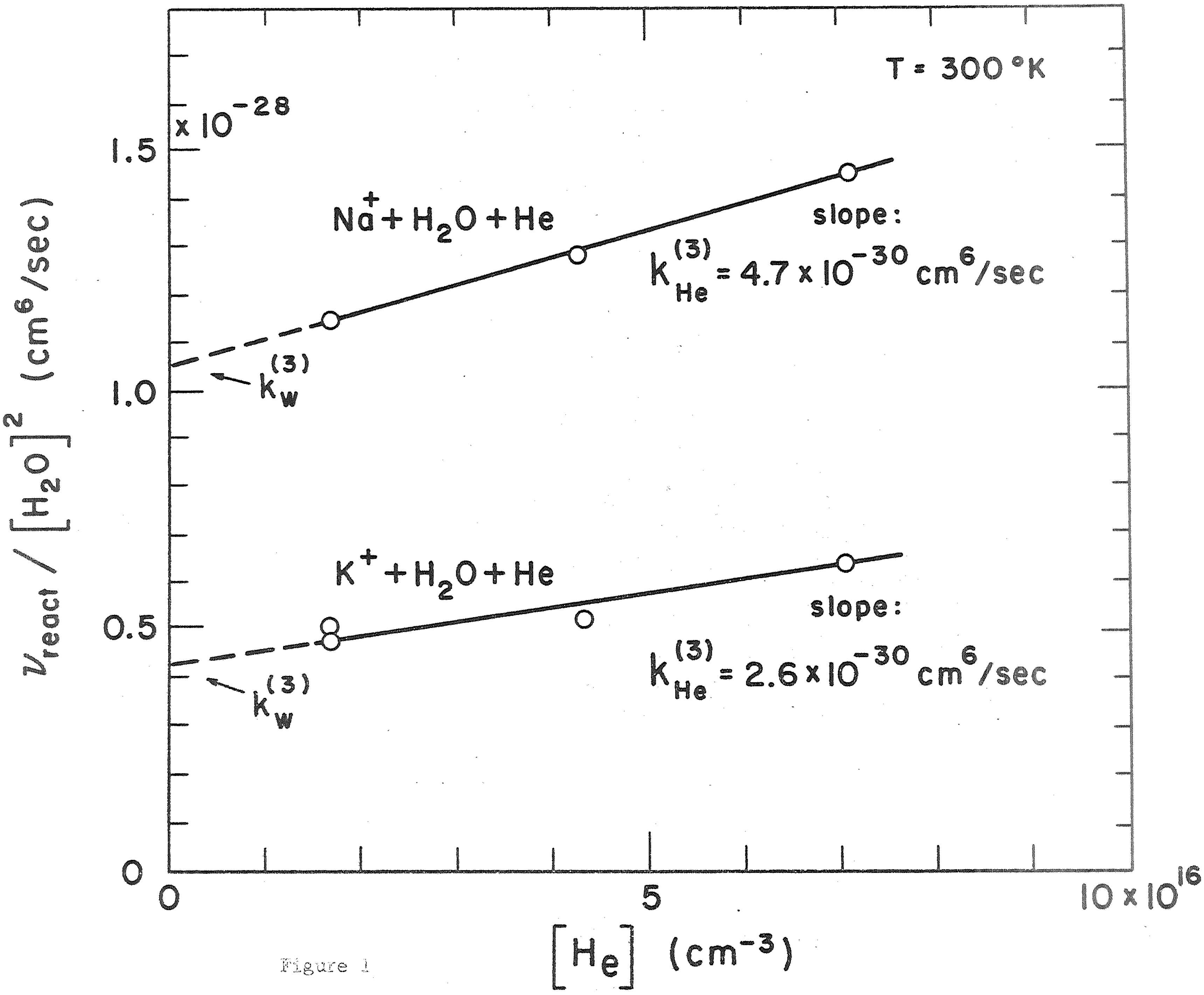
T = 300 °K
x 10^-28
1.5
1.0
0.5
0
$\nu_{react} / [H_2O]^2$ (cm^6/sec)
$Na^+ + H_2O + He$
slope:
$k^{(3)}_{He} = 4.7 \times 10^{-30}$ cm^6/sec
$k^{(3)}_w$
$K^+ + H_2O + He$
slope:
$k^{(3)}_{He} = 2.6 \times 10^{-30}$ cm^6/sec
$k^{(3)}_w$
0
5
10 x 10^16
[He] (cm^{-3})

Figure 1

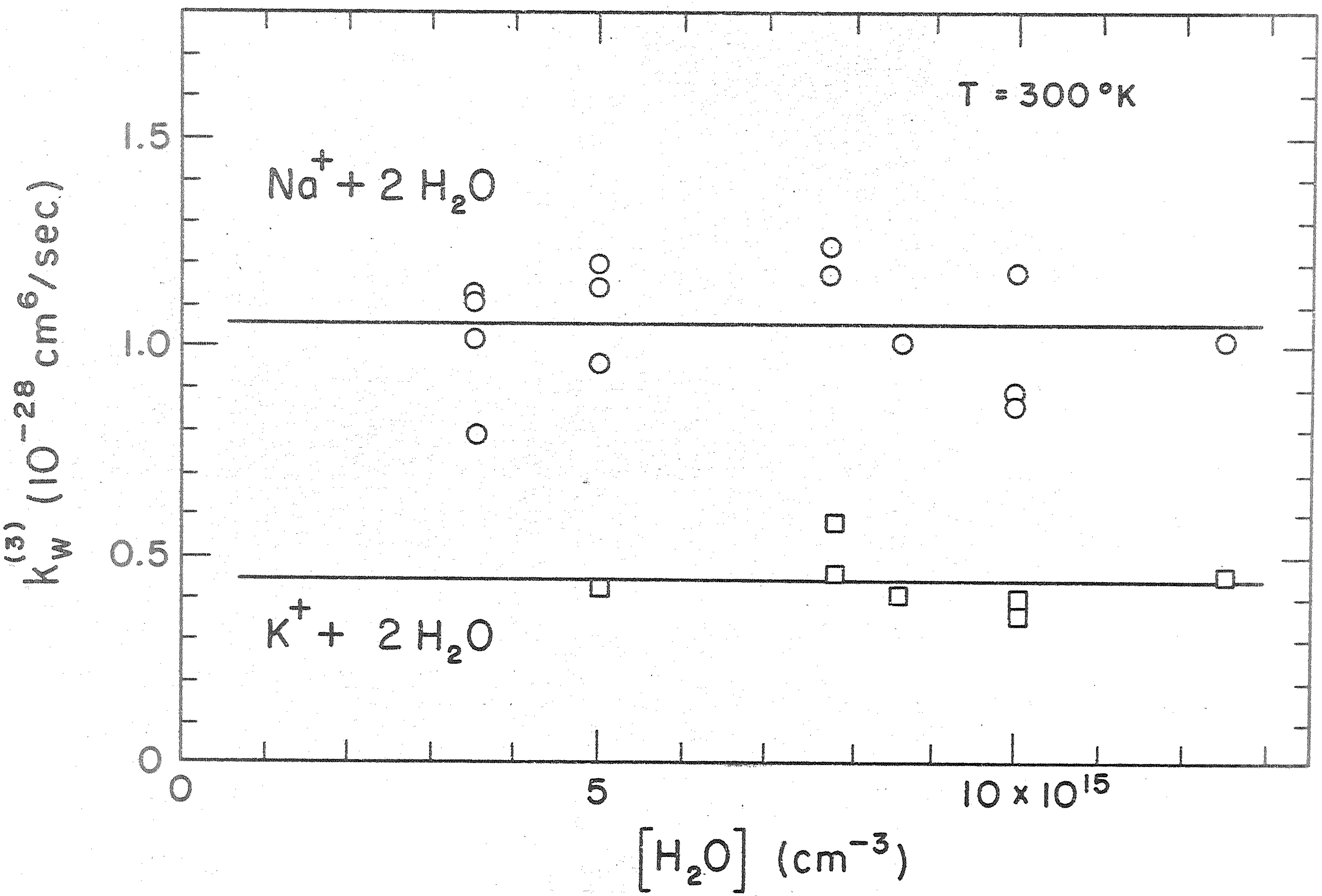
T = 300 °K
$Na^+ + 2\,H_2O$
$K^+ + 2\,H_2O$
$k_w^{(3)}$ (10^{-28} cm^6/sec)
0
0.5
1.0
1.5
0
5
10×10^{15}
[H_2O] (cm^{-3})

Figure 2