ESTIMATED ION MOBILITIES FOR SOME AIR CONSTITUENTS

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ABSTRACT

Estimates, based on available experimental data and on theory, are given for the mobilities of the ions O^+ , N^+ , O_2^+ , and NO^+ in the neutral species He, O, N, O_2, and N_2 from 0° to 2500°K .

INTRODUCTION

Knowledge of ion mobilities for air constituents is basic to the understanding of several upper-atmosphere phenomena and several problems concerned with re-entry physics. We here present estimates of the mobilities of the ions O^+ , N^+ , O_2^+ , N_2^+ , and NO^+ in the neutral constituents He, O, N, O_2, and N_2 from 0° to 2500°K .

Since reliable experimental data are very scarce, we are forced to rely heavily on theory. As a consequence, the uncertainty in our final estimates is quite variable, ranging from perhaps ± 25% in a favorable case to a factor of 2 in an unfavorable one. The crucial step in the theoretical calculations is the selection of the mechanism presumed to dominate the ion-neutral scattering. We consider the ion mobilities to be dominated by two mechanisms only: elastic collisions between ions and neutrals, and resonant charge-exchange collisions between ions and neutrals. The variation of the mobility with temperature can be radically different for different mechanisms. For charge-exchange collisions, the mobility decreases with increasing temperature, rapidly at first and then rather slowly. For elastic collisions, the temperature dependence of the mobility depends on the nature of the short-range force between ion and neutral. If this force is repulsive, the mobility rises with increasing temperature to a broad maximum, and then decreases. If the force is attractive, as in the case of a chemical valence force, the mobility probably decreases slowly with increasing temperature.

These are not the only mechanisms which may dominate ion mobilities. Consideration of alternative mechanisms and their effect on the present calculations is postponed to the discussion section at the end of this paper.

For all cases considered, we expect that a classical calculation of the collision trajectories is adequate (MUNN et al., 1964). The present calculations are restricted to low electric fields; the effects of higher field strengths can be estimated (KIHARA, 1953; MASON and SCHAMP, 1958), but are probably within the uncertainty of the zero-field estimate.

BASIC ASSUMPTIONS

A good general review and survey of ion mobilities and ion-neutral collisions has been given by McDANIEL (1964). At very low temperatures $(T \rightarrow 0°K)$, the mobility is dominated by the long-range r^{-4} ion-induced dipole energy, which is easily calculated if the charge on the ion and the polarizability of the neutral are known. The calculated polarizability-limited mobilities needed are listed in Table I, referred to a standard gas density of 2.69×10^{19} molecules/cm^3 (corresponding to 0°C and 1 atm), according to the formula

$$K_o = 13.88/(\alpha\mu)^{\frac{1}{2}} , \tag{1}$$

where K_o is the mobility in cm^2/sec-volt at standard density, α is the polarizability of the neutral in Å^3, and μ is the reduced mass of the ion-neutral pair in g/mole.

Also listed in Table I are the mechanisms assumed to dominate the mobilities at higher temperatures. In some cases there is good theoretical or experimental evidence for the assumption, in other cases the assumption is based on analogy, and in a few cases the assumption amounts only to an educated guess. These will be discussed after the available experimental evidence is summarized.

Table II summarizes the few mobility values which we take as known experimentally. Comparing these values with those in Table I, and recalling how the temperature dependence of the mobility is influenced by the collision mechanism, we conclude the following: $N_2^+ - N_2$ and $O_2^+ - O_2$ are controlled by resonant charge exchange, $NO^+ - N_2$ is controlled by short-range repulsion, and $N^+ - N_2$ is probably controlled by short-range valence attraction, analogous to $H^+ - H_2$ mobility (MASON and VANDERSLICE, 1959).

We now discuss the evidence for the assumed mechanisms listed in Table I. Resonant charge exchange for $N_2^+ - N_2$ and $O_2^+ - O_2$ is indicated not only by the mobility measurements, but also from beam measurements above 30 eV , which indicate a large cross section for charge exchange (STEBBINGS *et al.*, 1963; NICHOLAS and WITTEBORN, 1966). Resonant charge exchange is also indicated for $O^+ - O$ by both experiment (STEBBINGS *et al.*, 1964) and theory (KNOF *et al.*, 1964), the case of $N^+ - N$ is entirely analogous (KNOF *et al.*, 1964).

Short-range repulsion is clearly indicated for $NO^+ - N_2$ by the mobility measurements; it is assumed by analogy that the same holds true for $NO^+ - O_2$, $N_2^+ - O_2$, and $O_2^+ - N_2$. Whether $O^+ - N_2$ should come under this same analogy or whether it should be considered analogous to $N^+ - N_2$, which has a valence attraction, is not clear; we have calculated the $O^+ - N_2$ mobility according to both assumptions. The cases of $O_2^+ - O$ and $NO^+ - O$ are even less clear. Any serious electronic rearrangement to produce a valence attraction seems unlikely because the ionization potential of O is greater than the electron affinities of O_2^+ and NO^+ . We have therefore assumed short-range repulsion, but confess this is largely a guess. Fortunately, these two systems are probably only of minor importance in most phenomena of interest. The system O^+ - He is probably also only of minor importance, but there are good theoretical reasons for expecting it to show short-range repulsion and not valence attraction.

Short-range valence attraction seems indicated for N^+ - N_2 by the mobility measurements, and is supported by the fact that N_3^+ is known to be a stable species (KELLER et al., 1965, and papers referred to therein). It seems reasonable to consider O^+ - O_2 an analogous case, especially since the ion O_3^+ is known (MENTZONI, 1964, and papers referred to therein).

CALCULATIONS

The results of all the mobility calculations are collected in Table III. Values are usually given to three significant figures for the sake of smoothness, although in most cases the uncertainty is much greater than this would seem to imply. Details of the calculations are discussed below.

A. Resonant Charge Exchange

Diffusion collision integrals for O^+ - O and N^+ - N have been calculated by KNOF, MASON, and VANDERSLICE (1964), from which the mobilities are readily calculated (McDANIEL, 1964).

The computation of the O_2^+ - O_2 and N_2^+ - N_2 mobilities follows the methods used by KNOF, MASON, and VANDERSLICE (1964). It has been shown that the mobility (or diffusion) cross section is approximately twice the charge-exchange cross section when charge exchange is probable (HOLSTEIN, 1952; DALGARNO and McDOWELL, 1956; DALGARNO, 1958), and that a nearly linear relation holds between the square root of the charge-exchange cross section and the logarithm of the relative energy of collision. Thus two values of the charge-exchange cross section suffice to predict all values. One value can be obtained from the mobility measurements at 300°K , and another from beam experiments (STEBBINGS _et al._, 1963; NICHOLS and WITTEBORN, 1966). The transition between mobility dominated by charge exchange and mobility dominated by polarization was estimated by graphical interpolation (KNOF, _et al._, 1964). The results are shown in Fig. 1.

B. Short-Range Repulsion

The system $NO^+ - N_2$ furnishes the basic example for all the cases involving short-range repulsion forces. The system $NO^+ - O_2$ is sufficiently similar that it is simplest to combine both, and report the results as NO^+ - air . The values of the mobility in Tables I and II can be used to estimate mobilities at higher temperatures, provided we assume something specific about the interaction forces. The simplest assumption which has any hope of approximating physical reality is that the interaction potential has a long-range r^{-4} attractive component and a short-range r^{-8} or r^{-12} repulsive component. The necessary numerical integrations have been made for the 8-4 potential by HASSÉ and COOK (1931), and for the 12-4 potential by MASON and SCHAMP (1958). The fact that the ratio of the mobility at 300°K to that at 0°K is 1.16 determines the depth of the potential well, which is 0.12 eV according to the 8-4 potential and 0.11 eV according to the 12-4 potential. Either absolute mobility then gives the position of the potential minimum, which is 2.67Å for the 8-4 potential and 2.93Å for the 12-4 potential. The whole curve of mobility vs. temperature can then be calculated from these parameters. The results are shown in Fig. 1.

A more realistic physical model includes an r^{-6} attractive component of the potential, which is a combination of the London dispersion energy and the ion-induced quadrupole energy, and which is seldom completely negligible (MARGENAU, 1941; MASON and SCHAMP, 1958). Mobility calculations have been carried out for such a 12-6-4 potential, which can be written in the form (MASON and SCHAMP, 1958)

$$\phi(r) = \frac{1}{2}\varepsilon\,[(1+\gamma)(r_m/r)^{12} - 4\gamma\,(r_m/r)^{6} - 3(1-\gamma)(r_m/r)^{4}]\ , \qquad (2)$$

where $\phi(r)$ is the potential energy, ε is the depth of the potential minimum, r_m is the position of the minimum, and γ is a dimensionless parameter which serves as a measure of the importance of the r^{-6} energy. An approximate value of the coefficient of the r^{-6} term can be calculated quantum-mechanically by the approximate London formula (HIRSCHFELDER <u>et al.</u>, 1964), and leads to a value of $\gamma \approx 0.25$. With this value of γ , the mobility values at 0° and 300°K lead to $\varepsilon = 0.065$ eV and $r_m = 3.62$Å , from which the whole mobility vs. temperature curve can be calculated. The result is shown in Fig. 1; it is evident that the addition of r^{-6} energy lowers the mobility at high temperatures.

From Fig. 1 it can be seen that the various assumptions about the NO^+ - air interaction potential have little effect on the calculated mobilities up to about 400°K , but the values then diverge, and the spread of values increases to about ±25% at 2500°K . Another interesting point to be noticed in Fig. 1 is that the mobilities of NO^+ - air , $O_2^+ - O_2$ and $N_2^+ - N_2$ are similar at 0°K , but at 2000°K the mobility of

NO^+ - air has risen to about four times that of $N_2^+ - N_2$, because of the different natures of the ion-neutral collisions.

The systems $O_2^+ - N_2$ and $N_2^+ - O_2$ are presumably similar to NO^+ - air and have similar interaction potentials. Their mobilities are therefore obtained from those for NO^+ - air by scaling with a factor inversely proportional to $(\alpha\mu)^{1/2}$; this assures that the correct polarization limit is obtained, according to Eq. (1). The 12-4 curve for NO^+ - air was chosen as a reasonable compromise. A similar procedure was followed for $O^+ - N_2$, $O_2^+ - O$, and $NO^+ - O$; for these systems the scaling is more drastic, and the results accordingly more uncertain.

The system O^+ - He is too different from NO^+-air for direct scaling. The most similar system for which mobility data are available is Na^+ - He , and for this system the potential parameters of Eq. (2) have been determined (MASON and SCHAMP, 1958). We assume that the values of γ and ε will be similar for O^+ - He , and choose $\gamma = 0.15$, $\varepsilon = 0.040$ eV . The known polarization limit for O^+ - He then requires that $r_m = 2.32Å$, from which the mobility as a function of temperature can be calculated.

C. Short-Range Valence Attraction

The system $H^+ - H_2$ serves as a model for the calculation of mobility where strong valence forces are important. The mobility of $H^+ - H_2$ was calculated by MASON and VANDERSLICE (1959), who determined the interaction potential from available quantum-mechanical calculations of the energy of H_3^+ and from experimental data on the elastic scattering of low-energy protons in H_2 . These calculations are in reasonable agreement with the experimental mobility at 300°K (PERSSON and BROWN, 1955;

SAPOROSCHENKO, 1965). The mobilities of $O^+ - O_2$ and $N^+ - N_2$ are obtained from those of $H^+ - H_2$ by scaling with the factor $(\alpha\mu)^{-1/2}$, which assures the correct polarization limit. The measured mobility of $N^+ - N_2$ at 300°K then serves as a check on the scaling procedure. The agreement is quite reasonable, as is shown in Fig. 2. This is perhaps a fortuitous consequence of the fact that the temperature dependence of the mobility in these cases is weak, and so almost any sensible scaling procedure will work fairly well. However, more recent work (KELLER et al., 1965) on nitrogen ion mobility indicates a value for $N^+ - N_2$ at 300°K which is 25% lower than the higher one of the two shown in Fig. 2.

The mobility of $O^+ - N_2$ was calculated both on the assumption of short-range attraction and of short-range repulsion, and the results are shown in Fig. 2. This illustrates the important influence of the short-range interactions at even moderate temperatures.

DISCUSSION

Some estimate of the uncertainty in our final results can be obtained from the internal evidence on the sensitivity of the results to changes in the assumptions about the ion-neutral potential. At 2000°K this amounts to about ± 20% for NO^+ in air and over a factor of 2 for O^+ in N_2. There is a ± 15% uncertainty in the high-temperature mobilities of O_2^+ in O_2 and N_2^+ in N_2, caused by uncertainty in the ion-beam measurements of the charge-exchange cross section. In addition, there is the uncertainty caused by possible error in the experimental results at 300°K, on which some of our extrapolations are based. This could add another 10% uncertainty to the NO^+ in air mobilities

(YOUNG et al., 1965), and 20% to the N_2^+ in N_2 mobilities (KELLER et al., 1965).

Thus our estimated uncertainties are at least ± 25% for most of the systems listed in Table III, and must be put at a factor of 2 for those systems for which the nature of the interaction is doubtful (O_2^+ - O, NO^+ - O, O^+ - N_2) .

Finally, it should be stressed that the results might be totally wrong if any mechanism is important other than elastic collisions or resonant charge exchange. A classic example is the mobility of H_3^+ in H_2 . Assuming elastic collisions only, MASON and VANDERSLICE (1959) calculated a K_o vs. T curve much like that for NO^+ in air. Subsequent work (VARNEY, 1960; BARNES et al., 1961) showed that the proton-exchange reaction, $H_3^+ + H_2 = H_2 + H_3^+$, dominated the mobility, and completely changed the course of the K_o vs. T curve. Analogous possibilities are by no means unlikely for O_2^+ and N_2^+ . For instance, MENTZONI (1964) reports ambipolar diffusion results in oxygen plasmas which he interprets in terms of the mobility of O_2^+ in O_2 rising to a maximum of about 5.0 cm^2/sec-volt around 600°K , and then falling slightly from 600° to 900°K . Our reason for rejecting these results in the present calculations is the evidence from the direct beam measurements that O_2^+ - O_2 resonant charge exchange is highly probable (STEBBINGS et al., 1963; NICHOLS and WITTEBORN, 1966). Similarly, our calculations on N_2^+ require that the N_2^+ ion maintain its identity in collisions with N_2 , and not form other ions, such as N^+ , N_3^+ , or N_4^+ . It is by no means sure that this is the case (KELLER et al., 1965; McKNIGHT et al., 1967), and our results must be accepted with this reservation in mind.

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Table I. Polarization - limited (T = 0°K) mobilities, and assumed mechanisms for higher-temperature mobilities (*exch.* = resonant charge exchange; *rep.* = elastic collisions, short-range repulsive force; *val.* = elastic collisions, short-range attractive valence force).

Mobility, K_o, cm^2/sec-volt

ion \ gas	He	O	N	O_2	N_2
O^+	17.1 rep.	5.64 exch.		3.36 val.	3.28 rep.,val.
N^+			4.93 exch.		3.42 val.
O_2^+		4.84 rep.		2.74 exch.	2.71 rep.
N_2^+				2.84 rep.	2.80 exch.
NO^+		4.91 rep.		2.78 rep.	2.75 rep.

Table II. Experimental mobilities at 300°K.

System	Mobility cm^2/sec-volt	Ref.
$N^+ - N_2$	3.3 3.1	(a) (b)
$N_2^+ - N_2$	1.8	(a,b)
$O_2^+ - O_2$	2.25	(c)
$NO^+ - N_2$	3.2	(d)

(a) MARTIN *et al*. (1963); however, see KELLER *et al*. (1965).

(b) McKNIGHT *et al*. (1967).

(c) VARNEY (1953); this value has subsequently been confirmed by a number of workers.

(d) GATZ *et al*. (1963); see also YOUNG *et al*. (1965).

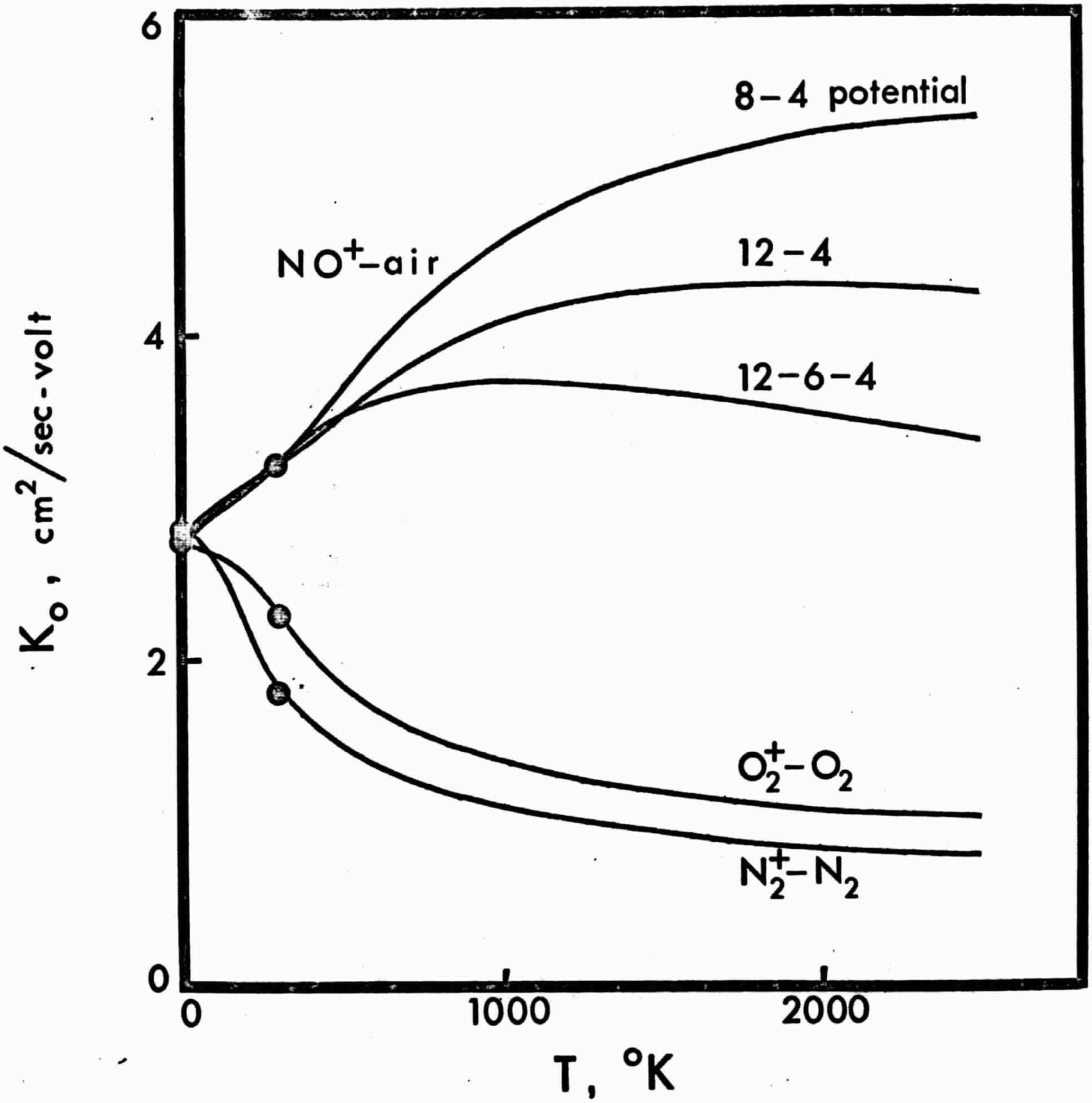
Table III. Estimated ion mobilities in cm^2/sec-volt at standard density.

T°K	O^+-O	O_2^+-O_2	N^+-N	N_2^+-N_2	NO^+-air			O_2^+-N_2	N_2^+-O_2	O^+-He	O_2^+-O	NO^+-O	O^+-N_2		O^+-O_2	N^+-N_2
	exch.	exch.	exch.	exch.	8-4	12-4	12-6-4	12-4	12-4	12-6-4	12-4	12-4	12-4	val.	val.	val.
0	5.64	2.74	4.93	2.80	2.75	2.75	2.75	2.71	2.84	17.1	4.84	4.91	3.28	3.28	3.36	3.42
100	5.58	2.67	4.86	2.63	2.92	2.92	2.89	2.87	3.01	19	5.1	5.2	3.5	3.2	3.33	3.39
200	5.36	2.55	4.74	2.15	3.02	3.08	3.00	3.04	3.18	21	5.4	5.5	3.7	3.2	3.29	3.35
300	4.88	2.25	4.58	1.80	3.19	3.19	3.19	3.14	3.29	23	5.6	5.7	3.8	3.2	3.26	3.32
400	4.49	2.01	4.37	1.61	3.41	3.33	3.36	3.28	3.44	24	5.9	5.9	4.0	3.2	3.23	3.29
500	4.18	1.84	4.14	1.47	3.63	3.49	3.49	3.44	3.61	24	6.1	6.2	4.2	3.1	3.21	3.26
600	3.92	1.72	3.89	1.37	3.82	3.63	3.58	3.58	3.75	25	6.4	6.5	4.3	3.1	3.19	3.24
800	3.54	1.54	3.53	1.23	4.24	3.88	3.68	3.82	4.00	24	6.8	6.9	4.6	3.1	3.14	3.19
1000	3.26	1.40	3.26	1.13	4.54	4.07	3.71	4.01	4.20	24	7.2	7.3	4.8	3.0	3.10	3.15
1500	2.77	1.20	2.77	0.97	5.00	4.26	3.63	4.20	4.40	22	7.5	7.6	5.1	2.9	2.98	3.04
2000	2.46	1.08	2.46	0.87	5.22	4.29	3.49	4.23	4.43	21	7.6	7.7	5.1	2.8	2.88	2.93
2500	2.24	0.99	2.24	0.80	5.31	4.24	3.33	4.17	4.37	19	7.5	7.6	5.1	2.7	2.82	2.87

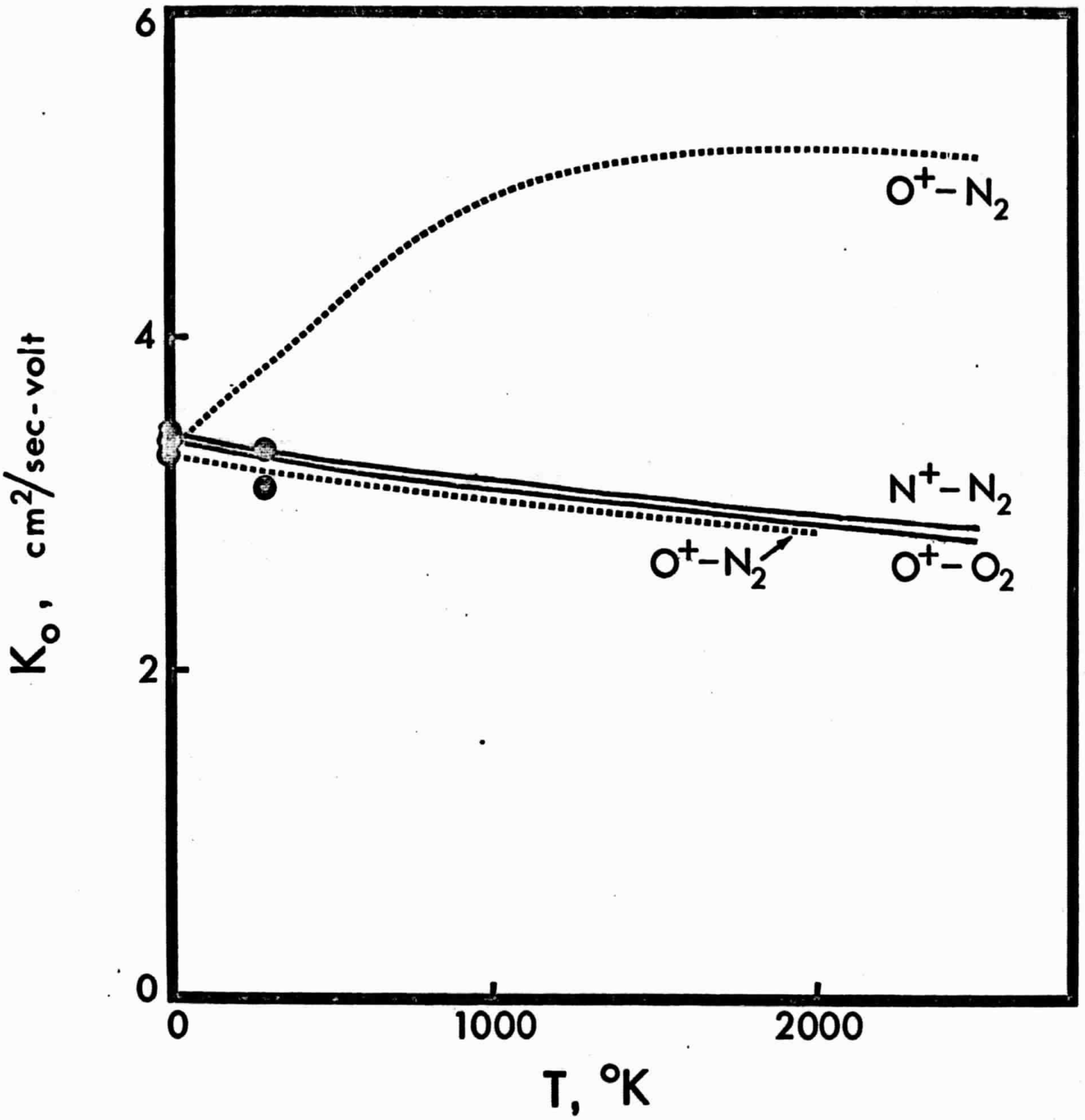
FIGURE CAPTIONS

Fig. 1. Mobilities as a function of temperature, showing the effect of resonant charge exchange (O_2^+ - O_2 and N_2^+ - N_2) and of the assumed form of the ion-neutral interaction (NO^+ - air).

Fig. 2. Mobilities as a function of temperature, showing the effect of short-range valence attractive (N^+ - N_2, O^+ - O_2, O^+ - N_2) and short-range repulsion (O^+ - N_2).



K_o, cm^2/sec-volt
6
4
2
0
0
1000
2000
T, °K
8−4 potential
12−4
12−6−4
NO$^+$−air
O_2^+−O_2
N_2^+−N_2


6
4
2
0
K_o, cm^2/sec-volt
O^+-N_2
N^+-N_2
O^+-N_2
O^+-O_2
0
1000
2000
T, °K

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