Journal of Atmospheric and Terrestrial Physics, 1960, Vol. 18, pp. 65 to 70. Pergamon Press Ltd. Printed in Northern Ireland

Ion-atom interchange

D. R. BATES and M. NICOLET
Queen's University, Belfast, and Department of Radiation, R. Meteorological
Institute, Brussels 18

(*Received* 3 *December* 1959)

Abstract—It is argued that the ion–atom interchange processes of importance in the upper atmosphere (e.g. $O^+ + N_2 \rightarrow NO^+ + N$ and $O^+ + O_2 \rightarrow O_2^+ + O$) are very much slower than simple collision theory has led some aeronomists to suppose. The rate coefficients involved are thought to be sensitive to the temperature. Ion–atom interchange does not, as has been suggested, exercise an appreciable direct influence on the degree of dissociation of the nitrogen.

1. INTRODUCTION

WHEN attention was first drawn to the importance of ion–atom interchange

$$X^+ + YZ \rightarrow XY^+ + Z \tag{1}$$

in the upper atmosphere (BATES, 1955) it was pointed out that the rate coefficient is likely to be quite large in many instances since such interchange does not necessitate an electronic transition. Steric hindrance can scarcely be a major factor in simple rearrangements but it was thought that the activation energy might be significant in some instances and therefore quantitative estimations of rate coefficients were not attempted.

Several experimental studies of ion–atom interchange have now been made (POTTER, 1955; STEVENSON and SCHISSLER, 1955, 1958; LAMPE and FIELD, 1957). They relate mainly to cases involving the isotopes of hydrogen. For these rather special cases the interchange process is very fast indeed. Neither steric hindrance nor activation energy appear to be appreciable.

Following some early work by EYRING *et al.* (1936), FIELD *et al.* (1957) and GIOUMOUSIS and STEVENSON (1958) have developed a theory based on the assumption that all close encounters lead to interchange. Account is taken of the long-range forces between the colliding systems. According to this theory the rate coefficient for process (1) is

$$k = 2\pi(e^2\mathscr{P}/\mu)^{\frac{1}{2}} \tag{2}$$

where e is the electronic charge, $\mathscr{P}$ is the polarizability of the neutral molecule and μ is the reduced mass. Comparisons which have been made demonstrate that the accord with the results of the experimental studies mentioned above is satisfactory.

Calculation using formula (2) gives the rate coefficient for any exothermic ion–atom interchange process between simple systems composed of only the main atmospheric constituents to be as large as about 1×10^{-9} cm^3/sec. This value has therefore been adopted by some aeronomists (e.g. KRASOVSKY, 1957). However, the absence of appreciable steric hindrance and activation energy for a process involving the isotopes of hydrogen should not be taken to imply their absence for a similar process involving nitrogen and oxygen. It will be argued in Section 5 that certain of the interchange processes of interest to aeronomists must in fact be very slow.

2. ATMOSPHERIC MODELS

No attempt will be made here to survey current views on the structure of the thermosphere. However, information on a representative model constructed by NICOLET (1959) is presented in Table 1 for later reference. The model is in close accord with what has been learnt about the total air density from satellite drag data (GROVES, 1959). This does not of course mean that its accuracy is high for the altitude distributions of the temperature and of the number-densities of the individual constituents.

Table 1. Properties of thermosphere
(NICOLET, 1959)

Altitude (km)	Temperature (°K)	Number densities (particles/cm^3)			Total density (g/cm^3)
		O	N_2	O_2	
150	1186	$3{\cdot}3 \times 10^9$,	$2{\cdot}5 \times 10^{10}$	$5{\cdot}2 \times 10^9$	$1{\cdot}5 \times 10^{-12}$
200	1467	$1{\cdot}3 \times 10^9$,	$6{\cdot}2 \times 10^9$,	$1{\cdot}1 \times 10^9$	$3{\cdot}8 \times 10^{-13}$
250	1580	$7{\cdot}0 \times 10^8$,	$2{\cdot}0 \times 10^9$,	$3{\cdot}2 \times 10^8$	$1{\cdot}3 \times 10^{-13}$
300	1580	$4{\cdot}1 \times 10^8$,	$6{\cdot}5 \times 10^8$,	$1{\cdot}1 \times 10^8$	$4{\cdot}7 \times 10^{-14}$
400	1580	$1{\cdot}4 \times 10^8$,	$7{\cdot}7 \times 10^7$,	$1{\cdot}2 \times 10^7$	$7{\cdot}9 \times 10^{-15}$

3. RELATIVE ABUNDANCE OF THE IONS IN THE UPPER ATMOSPHERE

Radio scientists have established that the effective recombination coefficient in the *E*- and *F1*-layers is large, and is almost independent of the gas or electron density, whereas the effective recombination in the *F2*-layer is moderate in magnitude, and is an increasing function of the gas density and a decreasing function of the electron density (RATCLIFFE and WEEKES, 1960). According to the theory which BATES and MASSEY (1947) put forward to explain the observations, the ions in the *E*- and *F1*-layers are mainly molecular. They disappear by dissociative recombination

$$XY^+ + e \rightarrow X' + Y' \tag{3}$$

which is very rapid. As one ascends through the *F2*-layer the relative abundance of the slowly recombining atomic ions rises, due to the diminution in the frequency of the ion–atom interchange collisions* which convert them into molecular ions. Atomic ions predominate at and above the peak of the *F2*-layer.

The measurements carried out at Churchill by JOHNSON *et al.* (1958), using mass spectrometers mounted on rockets, support the general theoretical deductions on the ion composition. Table 2 shows some of their results. Similar results have been obtained in the Soviet Union (see KELLOGG, 1959).

---

* The collision process operative was originally thought to be charge transfer.

4. Interchange Processes

The only ion–atom interchange processes which need be considered here are those which are exothermic and which do not involve an electronic transition. In the following the values given for the reaction energies have been computed with the relevant ionization and dissociation energies taken to be as recommended by Watanabe (1958). The symbol x denotes the excitation energy of the lowest state of NO$^+$ which can be formed from an N$^+$ ion and an O atom. This energy is doubtless great enough to render endothermic some of the processes leading to the excited state (designated below, by an asterisk).

Table 2. Observed ion composition
(Johnson *et al.*, 1958)

Altitude (km)	Day 1207 CST, 23 March 1958 Fractional abundance			Night 2321 CST, 20 November 1956 Fractional abundance		
	O^+	O_2^+	NO^+	O^+	O_2^+	NO^+
100	$0{\cdot}0_0$	$0{\cdot}4_0$	$0{\cdot}6_0$	$0{\cdot}0_0$	$0{\cdot}0_0$	$1{\cdot}0_0$
150	$0{\cdot}1_0$	$0{\cdot}2_5$	$0{\cdot}6_5$	$0{\cdot}0_5$	$0{\cdot}3_0$	$0{\cdot}6_5$
200	$0{\cdot}6_5$	$0{\cdot}1_0$	$0{\cdot}2_5$	$0{\cdot}3_5$	$0{\cdot}2_5$	$0{\cdot}4_0$
250				$0{\cdot}8_5$	$0{\cdot}0_5$	$0{\cdot}0_5$

Atomic oxygen ions may be transformed to molecular ions through

$$O^+ + N_2 \rightarrow NO^+ + N + 1{\cdot}0_9\,\mathrm{eV} \qquad (4)\dagger$$

$$O^+ + O_2 \rightarrow O_2^+ + O + 1{\cdot}5_3\,\mathrm{eV} \qquad (5)$$

$$O^+ + NO \rightarrow NO^+ + O + 4{\cdot}3_6\,\mathrm{eV} \qquad (6)$$

or

$$\rightarrow O_2^+ + N + 0{\cdot}1_6\,\mathrm{eV} \qquad (7)$$

and atomic nitrogen ions may be transformed similarly through

$$N^+ + O_2 \rightarrow NO^{+*} + O + (5{\cdot}7_6 - x)\,\mathrm{eV} \qquad (8)$$

$$N^+ + NO \rightarrow NO^{+*} + N + (4{\cdot}3_6 - x)\,\mathrm{eV} \qquad (9)$$

or

$$\rightarrow N_2^+ + O + 2{\cdot}2_4\,\mathrm{eV}. \qquad (10)$$

If the colliding systems may be taken to be unexcited then the only interchange process transforming molecular ions into atomic ions is

$$N_2^+ + N \rightarrow N^+ + N_2 + 1{\cdot}0_3\,\mathrm{eV} \qquad (11)$$

---

† Potter (1955) has inferred from mass-spectrometric investigations in the laboratory that k_4 is $1{\cdot}0 \times 10^{-8}$ cm^3/sec. This can scarcely be accepted since the expected value of the rate coefficient describing all O$^+$ — N$_2$ close encounters is an order of magnitude smaller. It is to be doubted if (4) were responsible for the NO$^+$ ions observed and, therefore, if the investigations even provide evidence that the process is rapid.

and the only other interchange process suffered by molecular ions is

$$O_2^+ + N \rightarrow NO^+ + O + 4{\cdot}2_0 \text{ eV}. \qquad (12)\dagger$$

5. DISCUSSION

By equating the rate at which O^+ ions are destroyed by (4) and (5) to the rate at which they are produced by the *inverse* of (7), which he believes has no reaction energy, HERTZBERG (1958) obtained an expression purporting to give the equilibrium night value of the ratio $n(O^+)/n(O_2^+)$ in which n denotes the number-densities indicated. Using the data of JOHNSON *et al.* (1958) (Table 2) he hence deduced that the degree of dissociation of the nitrogen in the region of the F-layers is very high. He attributed this high degree of dissociation to (4) which, he argued, must be a much more important source of *odd* nitrogen atoms than

$$N_2^+ + e \rightarrow N' + N''. \qquad (13)$$

The reasoning is incorrect. It would be permissible to equate the rates of destruction and of production of O^+ ions if (5) and the inverse of (7) were the only processes operating; but it is not permissible to equate these rates in the presence of (6) since this process causes the *permanent* loss of O^+ ions. Equilibrium between the interchange processes listed clearly requires NO^+ to be the sole species of positive ion.

Provided no mechanisms of importance have been ignored the disappearance of O^+ ions during the night is determined by the equation

$$dn(O^+)/dt = -\gamma n(O^+) \qquad (14)$$

with

$$\gamma = k_4 n(N_2) + k_5 n(O_2) + [k_6 + k_7] n(NO) \qquad (15)$$

(from which terms due to recombination have been omitted as negligible). Letting $n_0(O^+)$ denote the number-density at sunset, the number-density t sec later is hence

$$n_t(O^+) = n_0(O^+) \exp(-\gamma t). \qquad (16)$$

For this relation to be consistent with the data of JOHNSON *et al.* (1958), given in Table 2, the numerical value of γ obviously must be extremely small compared with unity. Referring to Table 1 it may be seen that if k_4 and k_5 were indeed some 1×10^{-9} cm^3/sec as has been supposed (Section 1) then near the 200 km level γ would be at least about 3 sec^{-1}.

To explain why almost all the O^+ ions are not replaced by NO^+ ions within a few seconds of sunset, while retaining the supposition that k_4 and k_5 are some 1×10^{-9} cm^3/sec, it might be suggested that O^+ ions are continually being reformed from the NO^+ ions by

$$NO^+ + R \rightarrow O^+ + NR \qquad (17)$$

where R is some unidentified radicle. A systematic search has not revealed any species of radicle for which (17) is exothermic. The most favourable case appears

---

† It is assumed that

$$N_2^+ + O \rightarrow NO^{+*} + N + (2{\cdot}1_2 - x) \text{ eV}$$

is endothermic.

to be when R is an N atom. Even in this case the process is endothermic by $1{\cdot}0_9$ eV. The possibility that some of the NO^+ ions resulting from (4) may carry the requisite $1{\cdot}0_9$ eV does not appreciably affect the position: thus, since a considerable fraction of them must carry less energy, there would still be a rapid irreversible drain on the O^+ ions. It does not seem that the conclusion that k_4 and k_5 are very much smaller than 1×10^{-9} cm³/sec can be avoided.

According to the theory of BATES and MASSEY (1947), outlined in Section 3, γ is to be identified with the coefficient describing the rate of loss of electrons in the *F2*-layer. Several groups have carried out determinations of this coefficient using radio data. The most thorough work is that of RATCLIFFE *et al.* (1956), who recognized in their analysis that there may be important vertical movements of the electrons. They derived values of $2{\cdot}7 \times 10^{-4}$, $1{\cdot}0 \times 10^{-4}$ and $3{\cdot}7 \times 10^{-5}$ sec^{-1} at the 250, 300 and 350 km levels, respectively (see also YONEZAWA *et al.*, 1959).

Information on the magnitude of γ may be obtained in another way. Denoting the rate coefficients for

$$NO^+ + e \rightarrow N' + O' \tag{18}$$

and

$$O_2^+ + e \rightarrow O' + O'' \tag{19}$$

by α_{18} and α_{19}, and assuming that these dissociative recombination processes and the ion–atom interchange processes (4) and (5) control the number-densities of the NO^+ and O_2^+ ions in the *F2*-layer during the night (which assumption should not cause serious error), it may be seen that

$$\gamma n(O^+) = \{\alpha_{18} n(NO^+) + \alpha_{19} n(O_2^+)\} n(e). \tag{20}$$

Since $n(O^+)$ and $n(e)$ are almost equal this reduces to.

$$\gamma = \alpha_{18} n(NO^+) + \alpha_{19} n(O_2^+). \tag{21}$$

Reliable laboratory measurements on the recombination coefficients have not yet been carried out, but the behaviour of the *E*-layer during the day and night (RATCLIFFE and WEEKES, 1960) when interpreted in conjunction with the data on the ion composition obtained by JOHNSON *et al.* (1958) suggests that perhaps α_{18} is about 3×10^{-9} cm³/sec and α_{19} about 3×10^{-8} cm³/sec*. Judging from their values relative to $n(O^+)$ it is likely that at 250 km both $n(NO^+)$ and $n(O_2^+)$ were some 1×10^4/cm³ during the nocturnal flight on which part of Table 2 is based. Substitution of these two pairs of estimates in (21) gives γ to be 3×10^{-4} sec^{-1} at 250 km. The closeness of the agreement with the corresponding result in the preceding paragraph is of course fortuitous.

Accepting the deduced value of γ at 250 km and taking $n(N_2)$ and $n(O_2)$ to be as in Table 1 it is seen that

$$k_4 + 0{\cdot}1_6\, k_5 = 1{\cdot}3 \times 10^{-13}\ \text{cm}^3/\text{sec}. \tag{22}$$

Remembering that the rate coefficient for all close encounters is about 1×10^{-9} cm³/sec it is hence apparent that (4) and (5) must be greatly inhibited by steric hindrance or, more probably, activation energy. An important consequence is

---

* The temperature dependence of neither coefficient is known.

that k_4 and k_5 are likely to be rapidly increasing functions of the temperature. Quantitative (as distinct from qualitative) prediction of how the effective recombination coefficient varies with altitude is not possible on present knowledge.

References

Bates D. R. 1955 *Proc. Phys. Soc. Lond.* A **68,** 344.

Bates D. R. and Massey H. S. W. 1947 *Proc. Roy. Soc.* A **192,** 1.

Eyring H., Hirschfelder J. O. and Taylor H. S. 1936 *J. Chem. Phys.* **4,** 479.

Field F. H., Franklin J. L. and Lampe F. W. 1957 *J. Amer. Chem. Soc.* **79,** 2419.

Gioumousis G. and Stevenson D. P. 1958 *J. Chem. Phys.* **29,** 294.

Groves G. V. 1959 *Nature, Lond.* **184,** 178.

Hertzberg M. 1958 *J. Geophys. Res.* **63,** 856.

Johnson C. Y., Meadows E. B. and Holmes J. C. 1958 *J. Geophys. Res.* **63,** 443.

Kellogg W. W. 1959 *Planet. Space Sci.* **1,** 71.

Krasovsky V. I. 1957 *Izv. Akad. Nauk. SSSR, ser. geofiz.* **4,** 504.

Lampe F. W. and Field F. H. 1957 *J. Amer. Chem. Soc.* **79,** 4244.

Nicolet M. 1959 *J. Geophys. Res.* **64,** in press.

Potter R. F. 1955 *J. Chem. Phys.* **23,** 2462.

Ratcliffe J. A., Schmerling E. R., Setty C. S. G. K. and Thomas J. O. 1956 *Phil. Trans.* A **248,** 621.

Ratcliffe J. A. and Weeks K. 1960 *Physics of the Upper Atmosphere* (Edited by Ratcliffe J. A.). AcademicPress, New York.

Stevenson D. P. and Schissler D. O. 1955 *J. Chem. Phys.* **23,** 1353.

Stevenson D. P. and Schissler D. O. 1958 *J. Chem. Phys.* **29,** 282.

Watanabe K. 1958 *Adv. Geophys.* **5,** 153.

Yonezawa T., Takahashi H. and Arima Y. 1959 *J. Radio Res. Lab.* **6,** 21.