

## Origin of sodium in atmosphere

S. N. GHOSH

*J. K. Institute of Applied Physics and Technology, University of Allahabad,  
Allahabad, India*

AND

V. MITRA

*Moti Lal Nehru Regional Engineering College, Allahabad, U. P.*

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Equilibrium concentration of free Na atoms in the atmosphere has been calculated from photo-chemical reactions, diffusion and assuming that there is a constant influx of Na atoms from either the top or bottom side of the atmosphere. The analysis reveals the direction and magnitude of the flux of Na atoms in the atmosphere and hence settles the question whether these atoms have terrestrial or extraterrestrial origin.

### 1. INTRODUCTION

Certain metallic atoms and ions have been observed in the atmosphere. For example, the spectroscopic studies of the night and twilight airglows revealed the presence of Na, K, Li atoms (Blamont & Donahue 1964, Sullivan & Hunten 1964, Delannoy & Weill 1958). Mass spectrometers carried in rockets showed the presence of  $\text{Na}^+$ ,  $\text{Ca}^+$ ,  $\text{Mg}^+$  and probably  $\text{Fe}^+$  (Istomin 1963, Narcisi & Bailey 1965). The twilight of Na, which is comparatively richer in the atmosphere, has been extensively studied (Hunten 1967).

Many attempts have been made to interpret the sodium distribution in terms of the photochemical reactions in the upper atmosphere. In these investigations (Blamont & Donahue 1964, Sullivan & Hunten 1964, Gadsden 1964, Junge *et al* 1962), it is assumed that there is a constant mixing ratio of sodium (free, combined and ionized) to other constituents of the atmosphere, and that the concentration of free Na atoms is modified to different extent at different altitudes by oxidation and ionization processes. According to this assumption, one would expect scale height on the top side of the sodium layer nearly equal to that of the atmosphere. This is, however, in disagreement with recent observations (Donahue 1966, Hunter & Wallace 1967, Donahue & Meier 1967) of height distribution of sodium obtained by rocket measurements. The scale height of sodium on the topside of the layer is observed to be about 3 km, whereas the

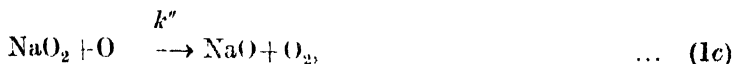
atmospheric scale height at the same altitude range is about 6 km. Recently, it has been suggested (Donahue 1966, Hunten & Wallace 1967, Donahue & Moier 1967, Hunten & Godson 1967) that sodium is released from dust particles. Gadsden (1967) pointed out certain implications in the dust hypothesis and suggested an alternative explanation on the basis of meteor ablation. Thus, the origin of sodium in the atmosphere is still a subject of controversy.

The height distributions of all metallic atoms and ions (Jones 1966) in the atmosphere reveal maxima approximately in the altitude range 90-100 km. This indicates that there is certain common process effective in producing these maxima. Since the vertical diffusion of free metallic atoms having a constant influx in the atmosphere can produce a maxima at a certain altitude, the diffusion process seems to play a role in establishing their equilibrium concentrations.

In the present paper, the equilibrium concentration of free Na atoms has been calculated from photochemical reactions, diffusion and assuming a constant influx of Na atoms from either top or bottom side of the atmosphere. Such an analysis will reveal the direction and magnitude of the flux of Na atoms in the atmosphere and hence will settle their origin from terrestrial or extra-terrestrial source.

## 2. EQUILIBRIUM PROCESSES

In considering the equilibrium processes, the following chemical reactions between sodium and oxygen atoms are considered.



In addition to these, the ionization (Bates & Soaton 1950) of Na atoms and their recombinations (Bates & Boyd 1956) are also considered, namely



where  $k_1'$ ,  $k_2'$ ,  $k''$ ,  $k'''$ ,  $Q_1$  and  $Q_2$  are the rate coefficients of the various reactions.

The equilibrium concentration  $n'$  of Na atoms,  $n''$  of  $\text{NaO}_2$  molecules,  $n'''$  of  $\text{NaO}$  molecules and  $\bar{n}'$  of  $\text{Na}^+$  ions (all these concentrations correspond to an

average atmosphere) are produced by the joint effect of the reactions (1a, b, c, d) and (2a, b) and diffusion of various sodium products.

### 3. EQUILIBIUM EQUATIONS

Suppose on the average  $S_0$  metallic atoms are continuously deposited per unit area per second from a certain agency (terrestrial or extra-terrestrial) in some layer of the atmosphere remote from the region of maximum sodium concentration. At the steady state of diffusion, the net current of the combined sodium products should be constant in each layer of the atmosphere and be equal to the flux  $S_0$ . Thus

$$a + b + c + d = a' + b' + c' + d' = S_0 \quad \dots (3)$$

or

$$a + b + c + d - S_0 = 0. \quad \dots (4)$$

Here the sign of  $S_0$  has been set such that if  $S_0$  is positive, the net flow of the combined sodium products is in the upward direction and the metallic atoms have their origin from the earth's side. If on the other hand  $S_0$  is negative, such atoms have their origin from the outside of the earth. During motion Na atoms may undergo any of the reactions — (1a, b, c, d) and (2a, b) but since all sodium products involve only one Na atom, the validity of equation (4) is always maintained.

A number of effects other than those considered in the present study, may modify the net steady current  $S_0$  of sodium products due to diffusion from one layer to another. For example, the dust particles or meteors carrying Na atoms may retain some of their initial velocity in addition to the diffusive velocity. The dust particles or meteors may continue to travel up to a considerable distance before they release Na atoms. Hence these atoms may be deposited directly in different amounts in different layers. Eddy diffusion due to vertical velocity of wind may also be effective. But all such processes are likely to subside before Na atoms reach the region of maximum concentration. Formation of a region of maximum concentration indicates accumulation of Na atoms due to slow movements indicating absence of all rapidly changing processes mentioned above. The assumed processes should, therefore, be applicable at least in a region close to the layer of maximum concentration.

If  $w'$ ,  $w''$ ,  $w'''$  and  $\bar{w}'$  be the upward vertical diffusion velocities of Na,  $\text{NaO}_2$ ,  $\text{NaO}$  and  $\text{Na}^+$ , respectively, in any layer of altitude  $Z$  then.

$$a = n'w'$$

$$b = n''w''$$

$$c = n'''w'''$$

$$d = \bar{n}'\bar{w}'.$$

Equation (4) then becomes

$$n'w' + n''w'' + n'''w''' + \bar{n}'\bar{w}' = S_0 \quad \dots (5)$$

The vertical velocity of diffusion  $w'$  of any minor constituent of concentration  $n'$  through a stable main atmosphere at an altitude  $Z$  is given by

$$w' = -D \left[ \frac{\partial(\ln n')}{\partial Z} \left( \frac{m'}{m} + \beta + \beta x \right) \frac{1}{H} \right]. \quad \dots (6)$$

where different symbols used in the equation are as follows :

- $D$  — coefficient of diffusion
- $m'$  — molecular mass of diffusing constituent
- $m$  — mean molecular mass of the main gas
- $H$  — scale height of the atmosphere
- $\beta$  — gradient of the atmospheric scale height
- $x$  — thermal diffusion factor.

Equation 6 shows that  $w'$  can be either negative, zero or positive. If the constituent concentration decreases slowly with altitude, the second term in the equation outweighs the first and the transport is in the downward direction. If on the other hand the constituent concentration falls off rapidly with altitude, the first term predominates and the transport is upward.

The continuity equation under the steady state of diffusion of all the sodium products together is given by

$$\frac{\partial(n'w')}{\partial z} + \frac{\partial(n''w'')}{\partial z} + \frac{\partial(n'''w''')}{\partial z} + \frac{\partial(\bar{n}'\bar{w}')}{\partial z} = 0 \quad \dots (7)$$

Each term in equation (7) represents the rate of change of concentration of certain sodium products due to diffusive velocity in a given layer. Each term is small compared to such rate of the product by photochemical reactions particularly in a region close to the maximum of sodium concentration. Therefore, it can be approximately assumed that the equilibrium in a layer among various products of sodium is proposed by photochemical reactions (1a, b, c, d) and (2a, b). Thus

$$k_1'n'n(O_2) + k_2'n'n(O_3) + Q_1n' = k'''n'''n(O) + Q_2\bar{n}'n(O^-), \quad \dots (8a)$$

and

$$k_1'n'n(O_2) = k''n''n(O), \quad \dots (8b)$$

Since on the average the concentration of Na and Na<sup>+</sup> remain constant in any layer we have also

$$Q_1n' = Q_2\bar{n}'n(O^-). \quad \dots (8c)$$

The concentration of various products of sodium in any layer can, therefore, be represented in terms of the concentration of Na atoms of the same layer.

Thus

$$n'' = n' \left[ \frac{k_1' n n(O_2)}{k'' n(O)} \right], \quad \dots \quad (9a)$$

$$n''' = n' \left[ \frac{k_1' n n(O_2)}{k''' n(O)} + \frac{k_2' n(O_3)}{k''' n(O)} \right], \quad \dots \quad (9b)$$

$$\bar{n}' = n' \left[ \frac{Q_1}{Q_2 n(O^-)} \right]. \quad \dots \quad (9c)$$

In the absence of any reliable measurement of the concentration of  $O^-$  another simplifying assumption may be made. The assumption is that

$$n' = \bar{n}' \quad \dots \quad (9d)$$

Thus each product of Na atoms should satisfy equations (9a, b, c, d) as well as equation (5) under the joint effect of the chemical and diffusive equilibrium of the atmosphere. Substituting in equation (5) the values of  $w'$ ,  $w''$ ,  $w'''$  and  $\bar{w}'$  we have

$$\begin{aligned} D' \frac{\partial n'}{\partial Z} + D'' \frac{\partial n''}{\partial Z} + D''' \frac{\partial n'''}{\partial Z} + 2D' \frac{\partial \bar{n}'}{\partial Z} + \frac{D'n'}{H} \left( \frac{m'}{m} + \beta + \beta\alpha' \right) \\ + \frac{D''n''}{H} \left( \frac{m''}{m} + \beta + \beta\alpha'' \right) + \frac{D'''n'''}{H} \left( \frac{m'''}{m} + \beta + \beta\alpha''' \right) \\ + \frac{2D'\bar{n}'}{H} \left( \frac{\bar{m}'}{2m} + \beta + \beta\alpha' \right) + S_0 = 0. \quad \dots \quad (10) \end{aligned}$$

In case an ion-electron plasma diffuses through a neutral gas, ambipolar diffusion coefficient (which is double of the diffusion coefficient of  $Na^+$ ) is used in the expression of  $\bar{w}'$ . Also for the mass of  $Na^+$  the mean molecular mass of ion-electron i.e.,  $(m'/2)$  is to be used. Because below  $F$  layer of the atmosphere any ion will suffer collisions mainly with the neutral particles, the diffusion coefficient of  $Na^+$  can be calculated with the help of the same formula which is used for the neutral particles. Again substituting the values of  $n''$ ,  $n'''$  and  $\bar{n}'$  in terms of  $n'$  and neglecting the effect of thermal diffusion in equation (10).

$$\begin{aligned} \frac{\partial n'}{\partial Z} \left[ D' + \left( \frac{D''k_1'}{k''} + \frac{D'''k_1'}{k'''} \right) \frac{nn(O_2)}{n(O)} + \frac{D'''k_2'n(O_3)}{k'''n(O)} + 2D' \right] \\ + n' \left[ \left( \frac{D''k'}{k''} + \frac{D'''k_1'}{k'''} \right) \frac{\partial}{\partial Z} \left( \frac{nn(O_2)}{n(O)} \right) + \frac{D'''k_2'}{k'''} \frac{\partial}{\partial Z} \left( \frac{n(O_3)}{n(O)} \right) \right] \end{aligned}$$

$$\begin{aligned}
 & + \frac{1}{mH} \left\{ D'm' + \frac{D''m''k_1'n n(O_2)}{k''n(O)} + D''''m'''' \left( \frac{k_1'n n(O_2)}{k''''n(O)} + \frac{k_2'n(O_3)}{k''''n(O)} \right) + D'm' \right\} \\
 & + \frac{\beta}{H} \left\{ D' + \frac{D''k_1'n n(O_2)}{k''n(O)} + D'''' \left( \frac{k_1'n n(O_2)}{k''''n(O)} + \frac{k_2'n(O_3)}{k''''n(O)} \right) + 2\bar{D}' \right\} + S_0 = 0.
 \end{aligned}
 \tag{11}$$

The maximum concentration of sodium  $n'$  (max) is obtained from the following equation

$$\begin{aligned}
 n'_{max} & \left[ \frac{1}{mH} \left\{ D'm' + \frac{D''m''k_1'n n(O_2)}{k''n(O)} + D''''m'''' \left( \frac{k_1'n n(O_2)}{k''''n(O)} + \frac{k_2'n(O_3)}{k''''n(O)} \right) + \bar{D}'m' \right\} \right. \\
 & + \frac{\beta}{H} \left\{ D' + \frac{D''k_1'n n(O_2)}{k''n(O)} \right\} + D'''' \left\{ \left( \frac{k_1'n n(O_2)}{k''''n(O)} + \frac{k_2'n(O_3)}{k''''n(O)} \right) + 2\bar{D}' \right\} \\
 & \left. + \left( \frac{D''k_1'}{k''} + \frac{D''''k_1'}{k''''} \right) \frac{\partial}{\partial Z} \left( \frac{n n(O_2)}{n(O)} \right) + \frac{D''''k_2'}{k''''} \frac{\partial}{\partial Z} \left( \frac{n(O_3)}{n(O)} \right) \right] + S_0 = 0. \dots (12)
 \end{aligned}$$

#### 4. VALUES AND COMPUTATION

From the observed height distribution of Na atoms, the maximum concentration of sodium  $n'_{max}$  and its altitude are known. From equation (12)  $S_0$  can be determined if other quantities belonging to this altitude are known. Values of  $S_0$  obtained from equation (12) can be used in equation (11) for computing the height distribution of Na atoms in the atmosphere in a region of maximum sodium concentration *viz.*, 80 to 120 km

At Saskatoon the average value of  $n'_{max}$  may be taken about 900 atoms/cm<sup>3</sup> and it is at an altitude of about 93 km (Sullivan & Hunter 1964). Values of  $n$ ,  $n(O_2)$ ,  $n(O)$ ,  $m$ ,  $T$ ,  $H$  and  $\beta$  at different altitudes are available at an interval of one kilometer from COSPAR International Reference Atmosphere (Champion 1965). Such values for  $n(O_3)$  are also available (U.S.A. Airforce Handbook of Geophysics 1961). All these atmospheric data belong to an average atmosphere. The values of  $n'_{max}$  and its altitude which are mentioned above belong to Saskatoon (52°N), therefore all the data of the atmosphere should have also been taken at the same latitude. In the lack of such precise latitudewise data, the average atmospheric data is being used here. In the absence of known values of the rate coefficient of reactions between sodium and oxygen, the values of the corresponding reactions between hydrogen and oxygen may be used as was done by Blamont & Donahue (1964). Present authors (1966) have also used rate coefficient of reactions between hydrogen and oxygen for those between lithium and oxygen. Hunter (1967) has applied correction to the rate coefficients of hydrogen

and oxygen reactions to obtain best guesses for the rate coefficient of sodium-oxygen reactions. His values are

$$k_1' = 2 \times 10^{-33} \text{ cm}^6 \text{ sec}^{-1}$$

$$k_2' = 6.5 \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1}$$

$$k'' \geq 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$$

$$k''' = 4 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$$

Treating the molecules to be rigid elastic spheres, their diffusion coefficients can be calculated by the following formula (Chapman & Cowling 1952)

$$D = \frac{3}{8n\sigma_{12}^2} \left[ \frac{kT(m_1 + m_2)}{2\pi m_1 m_2} \right]^{1/2} \quad (13)$$

where  $\sigma_{12} = \frac{\sigma_1 + \sigma_2}{2}$ .

various symbols used are as follows:

$\sigma_1, \sigma_2$  — molecular diameter of the minor and main gases

$k$  — Boltzman constant

$T$  — absolute temperature

$m_1, m_2$  — masses of the two kinds of molecules

$n$  — molecular density of the main gas.

It has been shown (Golomb & McLeod 1966) that the values of the diffusion coefficients estimated by using the above formula are in good agreement with those measured from the radial growth of chemiluminous trails deposited in the upper atmosphere.

In the absence of known values of collisional diameters of atoms, molecules and ions (to be used in equation (13)), their size is obtained from the knowledge of their chemical bond and valency. The diameters of the sphere which circumscribe their chemically determined structure have been tentatively taken equal to their collisional diameters.

The radii of Na and Na<sup>+</sup> are, respectively, known to be 1.572 Å and 0.95 Å. Their collisional diameters may be taken equal to 3.14 Å and 1.90 Å respectively. The O-O distance in the molecule of NaO<sub>2</sub> has been reported to be 1.28 ± 0.01 Å (Pauling 1960). The oxygen atom (1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>4</sup>) has two unpaired p electrons which are oriented at right angles and therefore one might expect Na-O-O angle to be nearly 90° (Stator 1931). The approximate shape of NaO<sub>2</sub> molecule can be obtained by drawing two spheres (O<sup>2-</sup> molecules) each of radius 1.4 Å with a distance 1.28 Å between their centres and one of which is touched in a perpendicular direction by another sphere (Na<sup>+</sup> molecule) of radius 0.95 Å. Such

a molecule will be circumscribed by a sphere of radius 2.54 Å. Therefore the collisional diameter of  $\text{NaO}_2$  molecule may be taken equal to 5.62 Å. In a completely ionic linkage  $\text{NaO}$  molecule would contain  $\text{Na}^+$  and  $\text{O}^-$  ions. The radius of  $\text{Na}^+$  is 0.95 Å and in the absence of exact radius of  $\text{O}^-$  the radius of  $\text{O}^{2-}$  (1.4 Å) can be approximately taken. A sphere circumscribing two touching spheres of these radii would give the diameter of  $\text{NaO}$  molecule equal to 5.42 Å for the completely ionic linkage. For a single bond covalent linkage the diameter of  $\text{NaO}$  molecule would be the sum of the diameters of  $\text{Na}$  atom (3.144 Å) and  $\text{O}$  atom (1.48 Å) and is equal to 4.624 Å. As the linkage of  $\text{NaO}$  is 82 per cent ionic, the diameter of  $\text{NaO}$  would be equal to about 5.276 Å. Mean collisional diameters of air molecules at different altitudes between 80 and 120 km are obtained by taking the collisional diameters of  $\text{N}_2$ ,  $\text{O}_2$  and  $\text{O}$  equal to 3.15 Å, 2.98 Å and 1.49 Å respectively.

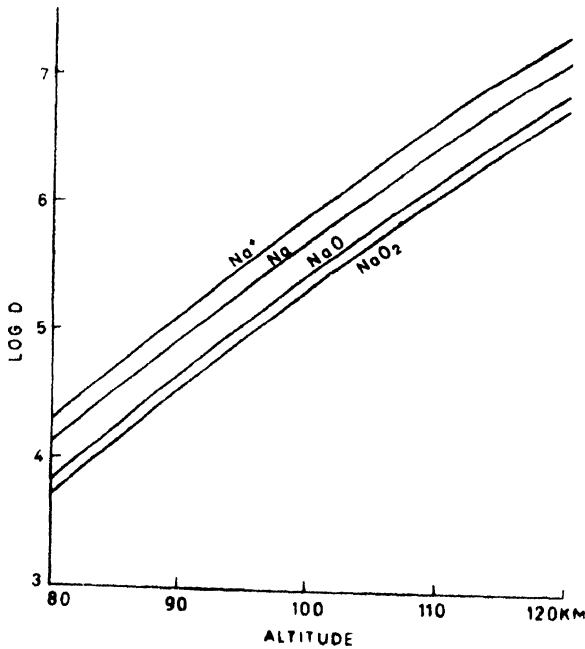


Fig. 1. Diffusion Coefficients of  $\text{Na}$ ,  $\text{Na}^+$ ,  $\text{NaO}$ , and  $\text{NaO}_2$  at different altitudes.

Diffusion coefficients of  $\text{Na}$ ,  $\text{NaO}_2$ ,  $\text{NaO}$  and  $\text{Na}$  as calculated with the help of the above values are plotted in figure 1 between altitude range 80 to 120 km.

### 5. RESULTS AND DISCUSSIONS

From equation (12) the values of  $S_0$  comes out to be—544 atoms/sec  $\text{cm}^2$ . The negative sign indicates that the influx of  $\text{Na}$  atoms is from outside the earth. Using this value of  $S_0$  in equation (11), the height distribution of  $\text{Na}$  atoms between the altitude range 80–120 km is computed and is plotted in figure 2.



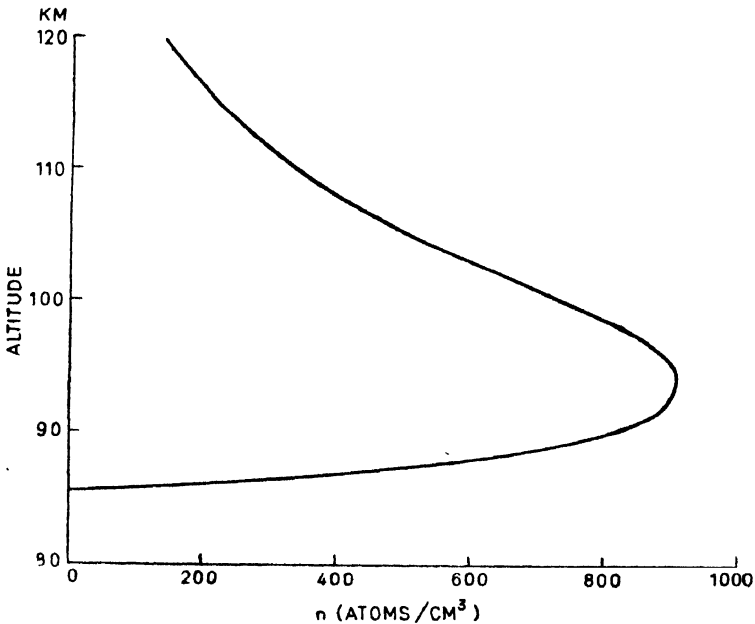


Fig. 2. The height distribution of Na atoms obtained from equation (11).

The extra-terrestrial source of Na atoms, as revealed in the present study, may be either the interstellar dust or meteors. It is assumed that there is a constant current of sodium flowing through all layers between 80 and 120 km. This assumption is true only when all Na atoms are released from the dust or meteors soon after their entry into the atmosphere. If meteors are the source of the atmospheric sodium, following Gadsden's suggestion, the release of Na atoms will not be complete until considerable depth of the atmosphere is penetrated. The assumption of constant vertical current of sodium products flowing through all layers, as assumed in our analysis, will not be true. However at 93 km which is the altitude of maximum sodium concentration the release of Na atoms should be nearly complete. Hence the topside of the computed curve of sodium distribution curve has a steeper rise compared to that of the observed curve. It is, therefore likely that the atmospheric sodium is of meteoric origin.

In any case, the arguments and assumptions of the present study are valid for the region of maximum sodium concentration and therefore, of the equations (11) and (12), at least the latter is valid. Moreover, substitutions of various quantities in equations (11) and (12) show, that very few terms namely

$$(D' + 2D'), \frac{1}{mH} (D'm' + \bar{D}'\bar{m}') \text{ and } \frac{\beta}{H} (D + 2D')$$

have significant contributions. It may be pointed out that all the quantities involved in these terms are known. Quantities having uncertain values, *e.g.*,

reaction coefficient, diffusion coefficients of  $\text{NaO}_2$  and  $\text{NaO}$  molecules are avoided. Therefore from these arguments, there is no uncertainty in the direction of the flux of Na atoms in the atmosphere as obtained from equation (12). The present study, inspite of having a limited and restricted use at all altitudes due to meteor ablation, definitely indicates the origin of atmospheric sodium to be from extra terrestrial source and most likely from meteors.

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