

further complication that the force acting on the particles is now velocity-dependent. However, the Chapman-Enskog method can be adapted to derive expressions for the diffusion velocity and the diffusion coefficients. In the presence of magnetic induction  $\mathbf{B}$  the relative velocity of diffusion is given by Chapman and Cowling (1952)

$$\bar{\mathbf{v}}_1 - \bar{\mathbf{v}}_2 = -\frac{n^2}{n_1 n_2} \frac{D_{12}}{1 + (\omega/\nu)^2} \mathbf{d}_{12} + \frac{n^2}{n_1 n_2} \frac{(\omega/\nu) D_{12}}{1 + (\omega/\nu)^2} \frac{\mathbf{B}}{B} \times \mathbf{d}_{12}, \quad (71)$$

where the notation corresponds to that used for (53). Here, however, the temperature is assumed uniform and

$$\mathbf{d}_{12} = \nabla \left( \frac{n_1}{n} \right) + \frac{n_1 n_2 (m_2 - m_1)}{n \rho p} \nabla p - \frac{\rho_1 \rho_2}{\rho p} (\mathbf{F}_1 - \mathbf{F}_2) - \frac{n_1 n_2}{\rho p} (m_2 \mathbf{e}_1 - m_1 \mathbf{e}_2) \nabla \times \mathbf{B}, \quad (72)$$

$$\omega = \frac{(e_1 m_2 \rho_2 + e_2 m_1 \rho_1)}{\rho m_1 m_2} B, \quad (73)$$

and

$$\nu = \frac{\rho k T}{m_1 m_2 n} \frac{1}{D_{12}}. \quad (74)$$

$D_{12}$  is the first approximation to the ordinary diffusion coefficient. The individual mean molecular velocities can be found, as well as electric current flow, with the help of (58) and (59). Comparing (71) with (53) we see that the effect of the magnetic field is to reduce the coefficient for direct diffusion in the ratio  $1:1 + (\omega/\nu)^2$  and to give rise to a transverse diffusion, at right angles to both  $\mathbf{B}$  and  $\mathbf{d}_{12}$ . A similar effect was found in the earlier discussion of the Lorentz gas permeated by a magnetic field but it is important to note the present meaning of the symbols  $\omega$  and  $\nu$ . Here  $\omega$  is a weighted mean of the gyrofrequencies  $\omega_1 = e_1 B/m_1$ ,  $\omega_2 = e_2 B/m_2$ . Further, if the particles are assumed to be smooth rigid spheres,  $\nu$  can be identified with a weighted mean of the collision frequencies of each type of particle with the opposite species; thus we have the well-known formulae in kinetic theory,

$$\nu_1 = 2n_2 \left( \frac{2\pi k T}{\mu} \right)^{\frac{1}{2}} \sigma_{12}^2, \quad \nu_2 = 2n_1 \left( \frac{2\pi k T}{\mu} \right)^{\frac{1}{2}} \sigma_{12}^2,$$

$$D_{12} = \frac{3}{8n\sigma_{12}^2} \left( \frac{kT}{2\pi\mu} \right)^{\frac{1}{2}},$$

in which  $\sigma_{12}$  represents the mean diameter of the two species. Hence

$$\nu = \frac{4\mu}{3} \left( \frac{\nu_1}{m_1} + \frac{\nu_2}{m_2} \right). \quad (75)$$

If the plasma consists of positive ions  $m_1$  and electrons  $m_2$ , the values to be taken for  $\omega$  and  $\nu$  are easily seen to be approximately  $\omega_2$  and  $\frac{2}{3}\nu_2$ .

*Diffusion in a multiple fluid.* General formulae for the first approximation to the diffusion velocities in a plasma with  $N$  constituents have been derived by Cowling (1945). The importance of such an investigation is obvious in ionospheric studies, where, in addition to electrons, there may be two or more species of positive ions as well as neutral particles. The formulae are complicated and we shall merely quote the conclusions reached in two particular cases of a ternary mixture: (i) a *slightly ionized gas* in which the first and major component is neutral and the second and third components are oppositely charged minor components, the gas as a whole being neutral. The conclusion is simply that the charged particles diffuse as in a Lorentz gas; thus equation 52 holds if  $\nu_i$ ,  $\nu_e$  are interpreted as effective collision frequencies  $\nu_{12}$ ,  $\nu_{13}$  respectively, defined by

$$\nu_{qr} = \frac{(\rho_q + \rho_r) k T}{m_q m_r (n_q + n_r) D_{qr}} \quad (q = 1, r = 2, 3) \quad (76)$$

where  $D_{qr}$  is the ordinary coefficient of mutual diffusion of the  $q$ th and  $r$ th gases in the absence of the third gas.

(ii) a *ternary gas* in which the particles of the first two constituents (1, 2) are different kinds of ions and of the third (3) are electrons. The electrons again diffuse according to the elementary theory, the effective collision frequency now being  $\nu_{13} + \nu_{23}$ , in the notation of (76). The ion conductivity (see (52)) is expressed conveniently by the complex equation

$$\sigma^I + i\sigma^{II} = \frac{n_1 n_2 (e_1 m_2 - e_2 m_1)^2}{\rho m_1 m_2 (\nu_{12} + i\omega_{12})} \quad (77)$$

where (see (73))

$$\omega_{12} = \rho_1 \omega_2 + \rho_2 \omega_1. \quad (78)$$

Thus the ionic diffusion leads to an ion conductivity which is independent of the electrons and is given by the solution for a binary gas.

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**DIFFUSION IN THE NEUTRAL ATMOSPHERE.** If we consider the general equation of the diffusion of gases in the field of gravity determined by Chapman and Cowling (1939, 1952), we can deduce a simple expression for transport by diffusion in a planetary atmosphere if we consider that the equation of statics applies:

$$\frac{\delta p}{\delta r} = -g\rho. \quad (1)$$

In this equation,  $p$  is the pressure,  $g$  is the acceleration due to gravity, and  $\rho$  is the density at distance  $r$  from the centre of the planet. If the equation of perfect gases is used, i.e.

$$p = nkT \tag{2}$$

where  $n$  is the concentration,  $T$  is the absolute temperature, and  $k$  is Boltzmann's constant, we can write with full generality (1),

$$\frac{dp}{p} = \frac{dn}{n} + \frac{dT}{T} = \frac{d\rho}{\rho} + \frac{dT}{T} - \frac{dm}{m} = -\frac{dz}{H} \tag{3}$$

where  $H$  is the scale height defined by

$$H = kT/mg, \tag{4}$$

$m$  being the mean molecular mass.

For a mixture of two gases, Chapman's equation is written in the following form:

$$w_1 - w_2 = -D_{12} \left\{ \frac{n^2}{n_1 n_2} \frac{\partial(n_1/n)}{\partial r} - \frac{m_1 - m_2}{m} \frac{1}{p} \frac{\partial p}{\partial r} + \alpha_T \frac{1}{T} \frac{\partial T}{\partial r} \right\} \tag{5}$$

where  $\alpha_T$  is the thermal diffusion factor and  $D_{12}$  is the coefficient of diffusion. In this equation, the vertical flux at an altitude  $z$  is given by the balance

$$n_1 w_1 + n_2 w_2 = 0, \tag{6}$$

i.e. the molecules considered have equal and opposite diffusional fluxes. It can be seen that the rate of diffusion  $w_1$  of particles of mass  $m_1$  and concentration  $n_1$  is given by

$$w_1 = -D_{12} \left\{ \frac{1}{n_1/n} \frac{\partial n_1/n}{\partial r} + \frac{n_2(m_2 - m_1)}{nm} \frac{1}{p} \frac{\partial p}{\partial r} + \alpha_T \frac{n_2}{n} \frac{1}{T} \frac{\partial T}{\partial z} \right\}. \tag{7}$$

Equation 7 shows that the rate of diffusion of a constituent of concentration  $n_1$  and mass  $m_1$  depends on the three gradients of concentration, of pressure, and of temperature.

The introduction of relation (3) into (7) can be carried out easily if it is considered that the gradient of the scale height  $H$  given by

$$\beta = dH/dz \tag{8}$$

leads to the general relations

$$\frac{1}{n} \frac{\partial n}{\partial r} = -\frac{1 + \beta - 2H/r}{H} \tag{9a}$$

and

$$\frac{1}{T} \frac{\partial T}{\partial r} = \frac{\beta - 2H/r}{H} \tag{9b}$$

The use of (3) in (7) expresses the fact that the accelerations due to diffusion are neglected in comparison with the acceleration due to gravity.

Thus, the equation expressing the rate of diffusion  $w_1$  is written

$$w_1 = -D_{12} \left\{ \frac{1}{n_1} \frac{\partial n_1}{\partial r} + \frac{1}{H} \left[ \frac{m_1}{m} + \left( \beta - \frac{2H}{r} \right) \left( 1 + \alpha_T \frac{n_2}{n} \right) \right] \right\} \tag{10}$$

On considering the expression (9a) for the vertical distribution of the total concentration, it can be assumed that the vertical distribution of the constituent of concentration  $n_1$  is written

$$\frac{1}{n_1} \frac{\partial n_1}{\partial z} = -\frac{X}{H} \left( 1 + \beta - \frac{2H}{r} \right) \tag{11}$$

where  $X$  is considered as the factor of the vertical distribution of a constituent of mass  $m_1$  and of concentration  $n_1$ .

Thus, in place of (10), we have

$$w_1 = \frac{D_{12}}{H} \left[ \left( X - \frac{m_1}{m} \right) + \left( \beta - \frac{2H}{r} \right) \left( X - 1 - \alpha_T \frac{n_2}{n} \right) \right] \tag{12}$$

This equation shows what the nature of the vertical transport by diffusion is. In an isothermal atmosphere,

$$\beta = \frac{2H}{r} \tag{13}$$

and equation 12 reduces to

$$w_1 = \frac{D_{12}}{H} \left( X - \frac{m_1}{m} \right) \tag{14}$$

Moreover, if the constituents are in perfect mixture,

$$X = 1 \tag{15}$$

and (14) becomes

$$w_1 = \frac{D}{H} \left( 1 - \frac{m_1}{m} \right) \tag{16}$$

In this case, the transport by diffusion takes place upwards if the mass  $m_1 < m$  and the converse arises if  $m_1 > m$ . When the atmosphere is not isothermal, it is appropriate to consider the effect of the thermal diffusion factor  $\alpha_T$ . It is generally negligible for constituents the masses of which do not differ greatly. But for a light element diffusing in a heavy gas,  $\alpha_T \approx -0.4$  and it is therefore not negligible in comparison with unity, particularly when the light element is a secondary constituent ( $n_2 \approx n$ ).

The importance of the diffusion equation written in form (12) resides in the fact that, in many cases, it is certain that the vertical distribution factor is very different from unity. This is the case, for example, when dissociation is involved or when chemical reactions modify the vertical distribution of secondary constituents. In order to obtain numerical values, it is sufficient to in-

introduce into (12) the expression for the coefficient of diffusion  $D_{12}$ . This can be written

$$D_{12} = \frac{3}{8} \frac{1}{\pi \sigma_{12}^2 f} \left( \frac{m_1 + m_2}{m_1} \right)^{\frac{1}{2}} \left( \frac{\pi k T}{2 m_2} \right)^{\frac{1}{2}} \frac{1}{n} \quad (17)$$

where  $\sigma_{12}^2$  is the effective collision section for rigid elastic spheres of diameters  $\sigma_1$  and  $\sigma_2$ , i.e.

$$\sigma_{12} = \frac{1}{2} (\sigma_1 + \sigma_2) \quad (18)$$

and  $f$  is a correction factor which takes account of the fact that the effective section may depend on the temperature. In this case,  $D_{12}$  is not directly proportional to  $T^{1/2}$ .

By substituting (17) in (12), we obtain for the flux of particles of mass  $m_1$ ,  $F(m_1)$ :

$$F(m_1) = \frac{3}{8} \frac{fg}{\pi \sigma_{12}^2} \left( 1 + \frac{m_2}{m_1} \right)^{\frac{1}{2}} \left( \frac{\pi m^2}{2 m_2 k T} \right)^{\frac{1}{2}} \frac{n_1}{n} \times \left[ \left( X - \frac{m_1}{m} \right) + \left( \beta - \frac{2H}{r} \right) \times \left( X - 1 - \alpha_r \frac{n_2}{n} \right) \right]. \quad (19)$$

If the constituent of mass  $m_1$  is a secondary constituent, i.e. if  $n_1 \ll n_2$ , expression (19) becomes

$$F(m_1) = \frac{3}{8} \frac{fg}{\pi \sigma_{12}^2} \left( 1 + \frac{m_2}{m_1} \right)^{\frac{1}{2}} \left( \frac{\pi m_2}{2 k T} \right)^{\frac{1}{2}} \frac{n_1}{n_2} \times \left[ \left( X - \frac{m_1}{m_2} \right) + \left( \beta_2 - \frac{2H_2}{r} \right) (X - 1 - \alpha_r) \right] \quad (20)$$

With a view to determining practical conditions, we adopt a mean effective section of  $2.8 \times 10^{-15} \text{ cm}^2$ , corresponding to a collision diameter  $\sigma_1 = \sigma_2$  of 3 Å. Thus, the effective diffusion section is not over-estimated. On introducing, in addition, the physical masses, i.e.  $M(O) = 16$ , the diffusional flux is given by  $F(M_1) \text{ cm}^{-2} \text{ sec}^{-1}$

$$F(M_1) = 1.823 \times 10^{11} g_0 \left( \frac{r_0}{r} \right)^2 \left( 1 + \frac{M_2}{M_1} \right)^{\frac{1}{2}} \left( \frac{M_2}{T} \right)^{\frac{1}{2}} \frac{n_1}{n_2} \times \left[ \left( X - \frac{m_1}{m_2} \right) + \left( \beta_2 - \frac{2H_2}{r} \right) (X - 1 - \alpha_r) \right]. \quad (21a)$$

It will be seen that in the homosphere, i.e. in the part of the atmosphere where the main constituents are in the same proportions, we have

$$F(M_1) = 1.823 \times 10^{11} g_0 \left( \frac{r_0}{r} \right)^2 \left( 1 + \frac{M_2}{M_1} \right)^{\frac{1}{2}} \left( \frac{M_2}{T} \right)^{\frac{1}{2}} \frac{n_1}{n_2} \times \left[ \left( 1 - \frac{m_1}{m_2} \right) - \alpha_r \left( \beta_2 - \frac{2H_2}{r} \right) \right]. \quad (21b)$$

This expression shows that the diffusional flux in the homosphere does not vary greatly as a function of the altitude, since it depends essentially on the ratio  $(r_0/r)^2$  and the variation in  $T^{-1/2}$ . For simplification, we may adopt an altitude of the order of 100 km corresponding to  $(r/r_0) = 0.985$ , a temperature of 200°K, and a low gradient. Thus, we have, in the case of the terrestrial atmosphere,

$$F(m_1) = 1.7 \times 10^{13} \left( 1 + \frac{M_2}{M_1} \right)^{\frac{1}{2}} \left( \frac{M_2}{T} \right)^{\frac{1}{2}} \left( 1 - \frac{M_1}{M_2} \right) \frac{n_1}{n_2}. \quad (22)$$

For the various planets, expression (22) is applicable if the numerical factor is multiplied by the following figures:

Mercury	Venus	Mars	Jupiter	Moon	Titan
0.36	0.858	0.40	2.64	0.165	0.176

If we adopt molecular nitrogen,  $M = 28$ , as the main constituent, we very frequently approach actual conditions. We thus obtain, from (22), the following diffusional fluxes:

hydrogen:  $F(H) = 3.4 \times 10^{13} [n(H)/n_2] \text{ cm}^{-2} \text{ sec}^{-1} \quad (23)$

deuterium:  $F(D) = 2.3 \times 10^{13} [n(D)/n_2] \text{ cm}^{-2} \text{ sec}^{-1} \quad (24)$

helium-3:  $F(^3\text{He}) = 1.9 \times 10^{13} [n(^3\text{He})/n_2] \text{ cm}^{-2} \text{ sec}^{-1} \quad (25)$

helium-4:  $F(^4\text{He}) = 1.6 \times 10^{13} [n(^4\text{He})/n_2] \text{ cm}^{-2} \text{ sec}^{-1} \quad (26)$

oxygen-16:  $F(O) = 4.6 \times 10^{12} [n(O)/n_2] \text{ cm}^{-2} \text{ sec}^{-1} \quad (27)$

oxygen-32:  $F(O_2) = -7.6 \times 10^{12} [n(O_2)/n_2] \text{ cm}^{-2} \text{ sec}^{-1}. \quad (28)$

The conclusion is that in the terrestrial atmosphere the order of magnitude of diffusional flux is given by

$$F \approx 10^{13} (n_1/n_2) \text{ cm}^{-2} \text{ sec}^{-1}. \quad (29)$$

We must nevertheless take into account the fact that only a slight change of physical conditions is necessary to modify the direction of the diffusional flux. Let us take the oxygen molecule as an example. Formula (21 b) leads to

$$F(O_2) = 8.8 \times 10^{12} \frac{n(O_2)}{n_2} [(X - 1.14) + \beta(X - 1)] \quad (30)$$

Transport takes place towards high altitudes if the term between square brackets is positive, i.e. if

$$X > 1 + \frac{0.14 \beta}{1 + \beta} \quad (31)$$

or with a gradient  $\beta = 0.2$

$$H > 1.12 H(O_2). \quad (32)$$

Consequently, it is sufficient that the scale height of the molecular oxygen should become less than 1.12 times that of the atmosphere for diffusion to bring about a transport upwards. In particular, if we assumed a photochemical equilibrium, we should have:

$$F(O_2) = 2 \times 10^{13} n(O_2)/n_2 \text{ cm}^{-2} \text{ sec}^{-1}, \quad (33)$$

i.e. a flux which easily compensates for the photodissociation. In other words, a vertical flux of molecules exists which can compensate for the molecules photodissociated in the field of the Sun's radiation.

On the other hand, if we consider a constituent appearing in the heterosphere as a result of a dissociation, a concentration maximum appears. At the level of this maximum, there is always a transport downwards, the flux of which is obtained from (20) where  $X = 0$ . In particular, for atomic oxygen in nitrogen, we find:

$$F(O) = -6 \times 10^{12} n(O)/n_2 \text{ cm}^{-2} \text{ sec}^{-1}, \quad (34)$$

i.e. once again a very considerable flux which must affect the photochemical conditions. This is the more important in that it is a transport downwards which is not opposed by the mixing of the air due to turbulence or to any other atmospheric movement.

These examples show how the study of the structure of the upper planetary atmospheres cannot be determined within the elementary framework of photodissociation or photoionization equilibria. Transport by diffusion modifies the dissociation equilibrium as a consequence of the transport of the molecules upwards. The dissociation pro-

cesses would have to be extremely rapid for the diffusion process not to predominate. In the case of the distribution of atoms, it is a question of comparing the times for recombination and for diffusion. When recombination is due to a triple collision, the maximum concentration will always be displaced downwards with respect to the equilibrium conditions, and there will be a transport downwards of the atoms produced by dissociation or ionization.

The totality of the effects of dissociation and diffusion leads to a vertical distribution of the constituents such as is shown in the figure.

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**DILATATION.** When a material is deformed, the (cubical) dilatation is the ratio of the increase in volume of a small piece of the material to the original volume. If the associated dilatation is negative, the deformation is a compression.

**DILATATIONAL WAVE.** A wave in an elastic medium, the seismic *P* wave, in which a deformation of dilatational (or compressional) type is propagated. In fluid media, dilatational waves are identical with sound waves.

**DIP POLES, MAGNETIC.** The points at the Earth's surface where the horizontal component of the magnetic field vanishes. The geographic latitude of the North and South magnetic, or dip, poles is about 72°.

**DISTURBED DAYS.** Five days selected each month as international magnetic disturbed (or active) days on the basis of readings at many magnetic observatories.

**DOMAINS IN FERROMAGNETIC MATERIALS.** The characteristic feature of ferromagnetism is spontaneous magnetization. This is the almost complete parallel alignment of the spin magnetic moments of certain of the electrons in ferromagnetic materials, which occurs, even in the absence of an applied field, under the action of quantum mechanical exchange forces. The fraction of these electrons which is imperfectly aligned increases with increasing temperature until, at the Curie temperature, the spontaneous magnetization drops to zero. At room temperature the degree of alignment in iron, for example, is roughly that which would be induced in a paramagnetic material by a field of some ten million oersteds. Exchange forces are therefore equivalent to fields of this magnitude and it is clear that fields attainable in practice, which are very seldom greater than 10<sup>5</sup> oersteds, can change the magnitude of the spontaneous magnetization only by negligible amounts. The complicated changes in the overall magnetization of a ferromagnetic specimen when it is subjected to an

