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The Kinetic Theory of Planetary Atmospheres

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PHILOSOPHICAL TRANSACTIONS.

I. *The Kinetic Theory of Planetary Atmospheres.*

By G. H. BRYAN, *Sc.D., F.R.S.*

1. THE possibility of applying the Kinetic Theory to account for the presence or absence of different gases in the atmospheres surrounding the various members of our Solar System, and in particular to explain the absence of any visible atmosphere from the Moon, was first discussed by WATERSTON in 1846, in his memorable paper on "The Physics of Media," that so long remained unpublished in the archives of the Royal Society.* This application of the theory is distinctly mentioned in the abstract of WATERSTON's paper published in 1846,† which is reproduced by Lord RAYLEIGH as an appendix to the paper itself. Hence we may say that the kinetic theory of planetary atmospheres is as old as the kinetic theory of gases.

The present subject received the attention of Dr. JOHNSTONE STONEY somewhere about the year 1867. It was brought under my notice by a note written by Sir ROBERT BALL in 1893,‡ and in that year I read a paper before the Nottingham meeting of the British Association on "The Moon's Atmosphere and the Kinetic Theory," in which numerical results were obtained sufficing to account for the absence of a visible atmosphere on the Moon and the existence of such gases as hydrogen in presence of the Sun. At that time, however, I did not see clearly how to take account of axial rotation, which evidently might play an important part in whirling off the atmospheres from certain planets, and thus the results given only represented the state of affairs at points along the polar axes of the bodies in question. Owing to this objection I did not deem it desirable to publish a more detailed paper than the abstract which appeared in the Nottingham Report.§

In the following year I published a note "On the Law of Molecular Distribution in the Atmosphere of a Rotating Planet," as an appendix to my Report on the Kinetic

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* 'Phil. Trans.,' A, 1892.

† 'Proc. Roy. Soc.,' vol. 5, p. 604.

‡ 'Science,' February 24, 1893.

§ 'British Association, Nottingham Report, 1893, p. 682.

Theory ;* but various circumstances have prevented me from following up the line of investigation thus started. In the interval, the new elements discovered by Professor RAMSAY have supplied fresh material for discussion, and in 1897 a paper "Of Atmospheres upon Planets and Satellites" was published by Dr. JOHNSTONE STONEY.†

The latter paper, however, does not in any way anticipate the methods that I had contemplated using, and there are so many points on which further investigation appeared desirable that a continuation of the present work seemed to me fully justified.

Since the present investigation was completed, I have seen Mr. S. R. COOK's paper,‡ the method of which is closely analogous with that adopted in the calculations of my Nottingham paper.

2. WATERSTON's *Method.*

WATERSTON's investigations take no account of the fact that the molecular speeds of the molecules of the gas are distributed about a mean, according to such an arrangement as the BOLTZMANN-MAXWELL distribution. Hence in dealing with planetary atmospheres it is assumed that at any point all the molecules are moving with the same speed. On such an assumption the conditions for the existence of an atmosphere are very simple, especially if no account is taken of axial rotation. For supposing the celestial body under consideration to be a sphere of radius a, and that the acceleration of its attraction at distance r is μ/r^2, then v being the translational speed of a molecule at the surface of the body, it is evident that if

$$\tfrac{1}{2}v^2 > \frac{\mu}{a}$$

the molecules will describe hyperbolas, and will ultimately fly off to infinity, so that the body will lose its atmosphere ; while if

$$\tfrac{1}{2}v^2 < \frac{\mu}{a}$$

the atmosphere will not extend beyond a concentric sphere whose radius r is given by

$$\tfrac{1}{2}v^2 = \mu \left(\frac{1}{a} - \frac{1}{r} \right).$$

If WATERSTON's hypothesis were correct it would have the following advantages :—

(i.) It would enable an exact limit to be fixed for the temperature at which any gas could exist in the atmosphere of a planet.

(ii.) It would enable an exact limit to be fixed for the height of that atmosphere.

(iii.) It would account for the decrease of temperature of the atmosphere with increase of height.

WATERSTON concluded that the Moon was capable of retaining an atmosphere of air provided that its temperature was not greater than 2405° F.

* 'British Association Report,' 1894, p. 100.

† 'Trans. Roy. Dublin Soc.,' vol. 6, p. 305.

‡ 'The Astrophysical Journal,' vol. 11, 1.

3. *Application of* MAXWELL'S *Law.*

The results tabulated in my British Association paper of 1893 were based on the assumption that the speeds of the molecules were grouped according to MAXWELL'S Law, so that out of any N molecules at any point the number whose speed lies between c and $c + de$ is

$$\frac{4Nh^{\frac{3}{2}}}{\sqrt{\pi}} e^{-hc^2} c^2 dc \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad .(1),$$

where $2/\sqrt{(\pi h)}$ is the mean speed, and $3/2h$ the mean square of the speeds of the molecules (WATSON, ' Kinetic Theory of Gases,' p. 6).

If v be the least velocity required to carry off a molecule to infinity, and given by the relation $\frac{1}{2}v^2 = \mu/a$, then the number of molecules having sufficient speed to fly off from the atmosphere will be

$$= \frac{4Nh^{\frac{3}{2}}}{\sqrt{\pi}} \int_{v}^{\infty} e^{-hc^2} c^2 dc,$$

which on putting $hc^2 = t^2$ gives

$$\frac{4N}{\sqrt{\pi}} \int_{v\sqrt{h}}^{\infty} e^{-t^2} t^2 dt \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2).$$

To calculate the integral, we have on integration by parts

$$\int_{t}^{\infty} e^{-t^2} t^2 dt = \tfrac{1}{2} t e^{-t^2} + \tfrac{1}{2} \int_{t}^{\infty} e^{-t^2} dt$$

$$= \tfrac{1}{2} t e^{-t^2} + \tfrac{1}{2} \text{Erfc } t . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3),$$

where Erfc t denotes the complement of the error function of t.

The values of $2\pi^{-\frac{1}{2}}$ Erf t are tabulated for small values of t in WOOLSEY JOHNSON'S ' Method of Least Squares,' p. 153, but in the present problem the values of t are necessarily large. Employing the series for Erfc t given in WOOLSEY JOHNSON, p. 46, Ex. 11, we deduce that the number of molecules moving with speed greater than the critical speed is

$$\frac{2N}{\sqrt{\pi}} e^{-t^2} t \left\{ 1 + \frac{1}{2t^2} - \frac{1}{2^2 t^4} + \frac{1 \cdot 3}{2^3 t^6} - \frac{1 \cdot 3 \cdot 5}{2^4 t^8} + \cdots \right\} \quad . \quad . \quad .(4),$$

where $t = v\sqrt{h}$.

For very large values of t, such as occur in many of the calculations, the first term of the series need alone be taken into account for purposes of rough approximation.

From this formula were calculated the results given in Table I. of my Nottingham paper, and which it may be convenient to reproduce here. This table shows the values of N when the number of molecules given by the above formula is taken to be unity ; in other words, the number of molecules of oxygen or hydrogen at different temperatures out of which there is, on an average, *one* molecule moving with sufficient

speed to overcome the attraction of the Earth, the Moon, Mars, or the Sun, as the case may be.

The wide difference in the numbers, due to the presence of the exponential factor, is sufficient to account for the practical permanence of the atmospheres of certain planets and the non-existence of certain gases in the atmospheres of others.

TABLE of Average Number of Molecules of Gas to every one whose Speed is sufficiently great to overcome the Attraction of the Corresponding Body.

Hydrogen at Temperature.		Oxygen at Temperature.		Surface of Moon.	Surface of Mars.	Surface of Earth.	Earth's atmosphere at height of 80 miles.	At Earth's distance from Sun.
Absolute.	Cent.	Absolute.	Cent.					
273°	0°	4368	4095°	3·6	3920	$6·0 \times 10^{19}$	$2·3 \times 10^{19}$	$2·7 \times 10^{307}$
68	−205	1092	819	610·0	$5·0 \times 10^{15}$	$3·3 \times 10^{81}$	$7·6 \times 10^{79}$	$6·6 \times 10^{1233}$
17	−246	273	0	$2·7 \times 10^{12}$	$1·0 \times 10^{65}$	$2·3 \times 10^{329}$	$5·7 \times 10^{322}$	$2·0 \times 10^{4740}$
$4\frac{1}{4}$	−269	68	−205	$6·9 \times 10^{51}$	$1·8 \times 10^{263}$	$4·5 \times 10^{1322}$	$1·5 \times 10^{1296}$	$1·7 \times 10^{19767}$

4. *Mr.* COOK's *Method.*

Mr. COOK has employed a method almost identical with that explained above. He uses the formula (4), and proceeds to calculate the number of molecules crossing a unit of surface with velocity exceeding the critical velocity, which would just suffice to carry a molecule to infinity. For the Earth the number of molecules is computed under the following conditions :—

(1) For a spherical shell at the Earth's surface at a mean temperature of 5° C.

(2) For a spherical shell 200 kiloms. from the Earth's surface at a temperature of −66° C.

(3) For a spherical shell 20 kiloms. from the Earth's surface at a temperature of −66° C.

(4) For a spherical shell 50 kiloms. from the Earth's surface at a temperature of 180° C.

Apart from the fact that no account was taken of axial rotation in either my earlier calculations or those of Mr. COOK, the assumption of the BOLTZMANN-MAXWELL distribution prevents us from drawing any hard and fast line between gases which can exist, and gases which cannot exist, at any given temperature on any planet. It seems natural to think that, mathematically speaking, the condition of permanence would be satisfied if the number of molecules out of which one would attain the critical velocity were greater than the total number of molecules in the planet's atmosphere. But the loss of a good many cubic centimetres of air from our atmosphere in the course of a year might easily be taking place without producing any perceptible effects on its practical permanence.

5. Dr. STONEY'S *Method.*

If v be the critical velocity which would enable a particle to overcome the attraction of a planet, so that $\frac{1}{2}v^2 = \mu/a$, and u be the velocity of translation at the planet's equator due to axial rotation, it is clear that a particle moving in the proper direction with *relative* velocity $v - u$ would escape. If this relative velocity be a large multiple of the mean molecular velocity of the gas, then the escape of molecules will be of rare occurrence; if it be a comparatively small multiple, the gas cannot remain permanently on the planet. Dr. STONEY, in his paper of 1897, calculates the corresponding critical relative velocity $v' - u'$ at the top of the atmosphere of the planet; then, if w be the velocity of mean square in the gas, his condition of permanence is that the velocity-ratio $\dfrac{v' - u'}{w}$ must be great.

The limiting value of this ratio consistent with permanence might for convenience be called the critical velocity-ratio.

There being no well-defined theoretical limit to this velocity-ratio, Dr. STONEY has adopted the plan of judging the unknown from the known. Assuming that free hydrogen and helium could not exist in our atmosphere, while watery vapour does actually so exist, it is inferred that a velocity-ratio of 20 is consistent with permanence, while a velocity-ratio of 9·27 is incompatible with permanence. Applying these criteria to the case of other members of the Solar System, Dr. STONEY investigates the possibility of the existence of different gases in the atmospheres of the other members of the Solar System. Those for which the velocity-ratio falls between the two above limits are uncertain as constituents of the corresponding atmospheres, and any observations as to their actual existence or non-existence will enable closer limits to be fixed for the velocity-ratio. In making these calculations, Dr. STONEY assumes a temperature of $-66°$ C.

Now there are many circumstances which render a further investigation of the ocnditions of permanence of planetary atmospheres desirable. It is not obvious that inferences drawn from the value of the velocity-ratio in different planets are necessarily conclusive. Thus, for example, the relative velocity $v' - u'$ might be the same for two planets—one rotating very slowly and having the smaller gravitation potential, and the other rotating very rapidly and having the greater gravitation potential. The above velocity only determines the proportion of molecules *at the planet's equator moving in the direction of rotation* which would fly off. But it is clear that in the planet with the smaller potential and slower rotation a greater proportion of molecules at other points or moving in other directions would leave. For a non-rotating body, the velocity-ratio determines the proportion of *all* the molecules that would fly off, provided that they were moving away from the planet. A planet would get rid of its atmosphere much more quickly if the molecules flew off to infinity in all directions from all parts of its surface than if they were only whirled off near its equator.

Again, the molecules which at the *surface* of the planet happen to be moving with velocity greater than the critical velocity, so far from leaving its atmosphere, will only collide with other molecules, provided the atmosphere is of sufficient density to possess the attributes of ordinary gases, *i.e.*, is of density comparable with that of our atmosphere. It is only in media of extreme tenuity, possessing the properties of high vacua, where the mean free path of the molecules is very great, that there is practically any chance of a molecule, which possesses sufficient speed, escaping without coming into collision with other molecules. In the case of the Earth this circumstance is taken into account by Dr. STONEY, where he calculates the critical velocity-ratio at a certain distance from the Earth's surface, this distance being assumed to represent the limit of height of the atmosphere. But this bring us to the question as to what is to be regarded as the limit of a planet's atmosphere, and we are thus brought to consider the problem of the law of stationary distribution of the molecules in the atmosphere of a rotating planet.

The original object of the present investigation was to clear up a number of obscure points such as those mentioned above, and at the same time to replace considerations of the critical velocity-ratio by results of a more statistical character. But the calculations have led to the result that certain gases believed by many physicists to escape from our atmosphere either do not so escape, or, if they do, that their escape takes place under different conditions as to temperature, &c., to those commonly assumed, or is a result of causes lying outside the principles of the Kinetic Theory of Gases.

6. *The Law of Molecular Distribution in the Atmosphere of a Rotating Planet.*

The modification of "MAXWELL's Law" for the case of a gas in a field of external force has been discussed by several writers, the proofs given by WATSON being simple and neat.* The case of a rotating gas was discussed by MAXWELL, but his treatment is hardly lucid. We now proceed to investigate the modifications which must be made in the BOLTZMANN-MAXWELL distribution in order to take account of axial rotation. We assume the field of force due to the planet's attraction to be symmetrical about the axis of rotation.

Let F_1, F_2 be the functions determining the frequencies of given distributions of co-ordinates and momenta of two molecules. These satisfy the following conditions :—

(i.) In the absence of encounters, F_1 and F_2 are constant.

(ii.) When an encounter occurs, the values before and after the encounter are connected by the relation

$$F_1 F_2 = F_1' F_2' \quad \ldots \ldots \ldots \quad (5).$$

Condition (i.) is satisfied if F_1 and F_2 are functions of any of the integrals of the

* 'Treatise on the Kinetic Theory of Gases,' § 11.

equations of motion of the molecules. In the case commonly considered the only known integral is the energy, and hence F_1 and F_2 are taken to be functions of the energies E_1 and E_2.

Condition (ii.), combined with the fact that the sum of the energies is unaltered by an encounter, then leads us to the well-known forms

$$F_1 \propto e^{-hE_1}, \qquad F_2 \propto e^{-hE_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6).$$

But if the field is symmetrical about the axis of z, and Γ_1, Γ_2 are the angular momenta of the molecules about this axis, we also know that—

(a) In the absence of an encounter Γ_1 and Γ_2 are constant ;

(b) The total angular momentum is unaltered by encounters, so that the values before and after an encounter satisfy the relation $\Gamma_1 + \Gamma_2 = \Gamma_1' + \Gamma_2'$.

We thus see that a more general solution satisfying conditions (i.) and (ii.) now exists, of the form

$$F_1 = n_1 e^{-hE_1 + k\Gamma_1}, \qquad F_2 = n_2 e^{-hE_2 + k\Gamma_2} \quad . \quad . \quad . \quad . \quad . \quad (7),$$

the frequency functions F_1 and F_2 now containing exponential functions of the angular momentum as well as of the total energy. Take the case in which the molecules are regarded as material points of mass m, and suppose in the first instance that x, y, z, and u, v, w represent co-ordinates and velocities referred to *fixed* axes, the axis of z coinciding with the axis of rotation. Also let V be the gravitation potential of the field of force, and suppose $k = h\Omega$. Then the above expressions for F_1 and F_2 show that a permanent distribution can exist, in which the number of molecules whose co-ordinates and velocities lie within the limits $dx\,dy\,dz$ and $du\,dv\,dw$ respectively, is of the form

$$n \exp - hm\{\tfrac{1}{2}(u^2 + v^2 + w^2) - \Omega(vx - uy) - V\}\,dx\,dy\,dz\,du\,dv\,dw \quad . \quad (8),$$

where h, Ω, may be any constants up to this point, and n is proportional to the total number of molecules.

Now take axes of ξ, η, ζ, rotating about the axis of z or ζ with angular velocity Ω and instantaneously coinciding with the axes of x, y, z. Then the velocities of a molecule *relative* to these axes are ξ', η', ζ' respectively, where

$$\xi' = \frac{d\xi}{dt} = u + \Omega y, \quad \eta' = \frac{d\eta}{dt} = v - \Omega x, \quad \zeta' = \frac{d\zeta}{dt} = w,$$

and the expression determining the frequency of distribution becomes

$$n \exp - hm\{\tfrac{1}{2}(\xi'^2 + \eta'^2 + \zeta'^2) - V - \tfrac{1}{2}\Omega^2(\xi^2 + \eta^2)\}\,d\xi\,d\eta\,d\zeta\,d\xi'd\eta'd\zeta' \quad (9).$$

The distribution of co-ordinates and relative velocities is thus the same as if the axes were fixed, and the potential of the field of force had the term $-\tfrac{1}{2}\Omega(\xi^2 + \eta^2)$ added to it. This term represents the potential of centrifugal force due to rotation with angular velocity Ω.

The above distribution, if it exist at any instant, will be permanent in the absence of encounters, and will be unaffected by encounters between the molecules; moreover, if the molecules form the atmosphere of a planet or other body rotating with angular velocity Ω, the distribution will clearly be unaffected by the molecules colliding with obstacles on the surface of the planet, while this could not be said of other distributions that might be assumed.

7. *Conditions for the above Law of Distribution.*

Let us now examine how far the conditions necessary for establishing this distribution are fulfilled in the atmosphere of a planet.

In the denser regions of the atmosphere where collisions are frequent, the effect of these collisions must be to distribute the velocities of the molecules, occurring per unit volume in the neighbourhood of a point, according to MAXWELL's law, the rate of progress towards the stationary state being calculable by the methods of BOLTZMANN, WATSON, BURBURY, and TAIT. The tendency to equalisation of the value of F in different regions of the atmosphere is determinable by the known methods of investigating diffusion, thermal conductivity, &c.

As we ascend in the planet's atmosphere, collisions between the molecules will become more and more infrequent, and at last we shall reach a region where practically all the molecules are describing free paths. These molecules will be those which are projected from the lower regions, and those which do not escape will frequently return to these lower regions. And since the proposed law of distribution remains permanent in the absence of intermolecular encounters, it follows that the molecules in question will remain distributed according to the same law, and this distribution will be brought about by the collisions which these molecules undergo in the less rarefied portions of the atmosphere.

At still greater distances from the planet we may have to deal with cases in which instead of there being a large number of molecules in a unit volume, the presence of a single molecule in, say, a cubic kilom., is an event of rare occurrence, owing to the smallness of e^{+hmV}. But as the BOLTZMANN-MAXWELL distribution is generally accepted to be a theorem in probability, we may still apply the present distribution to determine the probability that a molecule may reach these regions. It has been objected that the error law cannot be applied to calculate the probability of events of exceptional occurrence; but it appears to be the generally accepted view that such cases should, if anything, be excluded. Practically, it is immaterial which course we take. If theory proves that the escape of a molecule is of such exceptional occurrence as will be found in some of the subsequent calculations, it will make no difference to the permanence of the atmosphere whether we assume the escaping molecule to exist or not.

The chief objection to the distribution is that it is an isothermal one, whereas in

the lower regions of our atmosphere, in consequence of convection currents and winds, the adiabatic law more nearly represents the true distribution of density. The calculation of numerical data showing the effect of this correction must be deferred for future investigation, but a general discussion of the effects which may be expected to arise from this cause will be given later.

8. *Rate at which the Molecules are escaping across a Concentric Spherical Surface.*

Assuming the distribution given by (7) and supposing the planet to be spherical, so that the potential at distance r from the centre is M/r, let us calculate the number of molecules per unit time which are crossing a concentric spherical shell of radius r with sufficient velocity to carry them to infinity if they do not encounter other molecules in their subsequent paths.

For this purpose refer to polar co-ordinates, then the frequency of distribution (7) assumes the form

$$n \exp\left[-hm\left\{\tfrac{1}{2}(u_1^2 + u_2^2 + u_3^2) - \Omega u_3\, r \sin\theta - M/r\right\}\right]$$
$$r^2 \sin\theta\, dr\, d\theta\, d\phi\, du_1\, du_2\, du_3 \quad . \quad . \quad . \quad . \quad (10),$$

where u_1, u_2, u_3 are the velocity components relative to axes fixed in space coinciding with the directions of the line elements dr, $rd\theta$ and $r \sin r\theta\phi$ at the point (r, θ, ϕ). Thus u_1, u_2, u_3 are the velocities resolved along the vertical, the meridian and the parallel of latitude at the point.

To find the number of molecules crossing the spherical surface-element $r^2 \sin\theta\, d\theta\, d\phi$ with velocities within the limits of the multiple differential du_1, du_2, du_3, we write $u_1\, dt$ for dr in the above expression, and if the number is required per unit time we divide by dt.

Of the molecules crossing the surface *outwards*, those which will escape from the planet's attraction if they do not encounter other molecules, have their resultant velocity greater than Q where $Q^2 = 2M/r$. Calling these the "escaping molecules," the number of escaping molecules across the element $r^2 \sin\theta\, d\theta\, d\phi$ per unit time is

$$r^2 \sin\theta\, d\theta\, d\phi \iiint n \exp\left[-hm\left\{\tfrac{1}{2}(u_1^2 + u_2^2 + u_3^2) - \Omega u_3\, r \sin\theta - M/r\right\}\right] u_1\, du_1\, du_2\, du_3$$
$$. \quad . \quad . \quad . \quad . \quad (11),$$

the limits of integration being defined by the relation $u_1^2 + u_2^2 + u_3^2 > Q^2$

Now transform the integral by putting

$$u_1 = q \sin\alpha \sin\beta, \quad u_2 = q \cos\alpha, \quad u_3 = q \sin\alpha \cos\beta,$$

and at the same time integrate with respect to θ and ϕ.

Then we obtain for the total number of escaping molecules the expression

$$\int_{Q}^{\infty} dq \int_{0}^{\pi} d\theta \int_{0}^{2\pi} d\phi \int_{0}^{\pi} d\alpha \int_{0}^{\pi} d\beta \, . \, n \, \exp\left[- hm \left\{ \tfrac{1}{2}q^2 - \Omega rq \sin \alpha \cos \beta \sin \theta - \mathrm{M}/r \right\} \right]$$
$$q \sin \alpha \sin \beta \, . \, q^2 \sin \alpha \, . \, r^2 \sin \theta \quad . \quad . \quad . \quad . \quad . \quad . \quad (12).$$

Integrate first with respect to β and ϕ. We obtain

$$2\pi n \int_{Q}^{x} dq \int_{0}^{\pi} d\theta \int_{0}^{\pi} d\alpha \, e^{- hm \left\{ \frac{1}{2}q^2 - \mathrm{M}/r \right\}} \left\{ e^{hm\Omega rq \sin \alpha \sin \theta} - e^{- hm\Omega rq \sin \alpha \sin \theta} \right\} \frac{rq^2 \sin \alpha}{hm\Omega}.$$

This expression cannot be integrated very simply with respect to α alone or θ alone, as we should obtain integrals of the forms $\int_{0}^{\pi} e^{k \sin x} \, dx$ and $\int_{0}^{\pi} e^{k \sin x} \sin x \, dx$.

It is therefore not possible to express the number of "escaping molecules" in the neighbourhood of a given parallel of latitude except by integrals of these forms.

But the double integration can be effected very simply by regarding α, θ as polar co-ordinates of a point on a sphere, and changing the axis of polar co-ordinates to one at right angles to the former axis.

Thus considering the integral

$$\int_{0}^{\pi} \int_{0}^{\pi} e^{k \sin \alpha \sin \theta} \sin \alpha \, d\alpha \, d\theta,$$

we choose two new variables, χ, ψ, defined by the relations

$$\left. \begin{array}{r} \sin \alpha \sin \theta = \cos \chi, \\ \sin \alpha \cos \theta = \sin \chi \cos \psi, \\ \cos \alpha = \sin \chi \sin \psi, \end{array} \right\} \quad . \quad . \quad . \quad . \quad . \quad (13),$$

and by spherical geometry or otherwise

$$\sin \alpha \, d\alpha \, d\theta = \sin \chi \, d\chi \, d\psi$$

and the integral transforms into

$$\int_{0}^{2\pi} d\psi \int_{0}^{\frac{1}{2}\pi} d\chi \, e^{k \cos \chi} \sin \chi \, d\chi = 2\pi \, \frac{e^k - 1}{k} \quad . \quad . \quad . \quad . \quad (14).$$

Substituting $k = hm\Omega rq$ and $k = - hm\Omega rq$ in turn in (12), we obtain

$$4\pi^2 n e^{h\mathrm{M}m/r} \int_{Q}^{\infty} \frac{e^{-\frac{1}{2}hmq^2}(e^{hm\Omega rq} + e^{-hm\Omega rq} - 2)}{h^2 m^2 \Omega^2} \, q dq \quad . \quad . \quad . \quad . \quad (15).$$

The form most convenient for evaluating this integral must depend on the particular problem considered. If the effects of axial rotation on the rate of escape are small, then $2 \cosh hm\Omega rq$ may be expanded in powers of $hm\Omega rq$, and we thus obtain in the limiting case when $\Omega = 0$

$$4\pi^2 n e^{hMm/r} \int_Q^\infty e^{-\frac{1}{2}hmq^2} r^2 q^3 dq = 4\pi^2 n r^2 e^{hMm/r} \frac{hmQ^2 + 2}{h^2 m^2} e^{-\frac{1}{2}hmQ^2},$$

$$= 4\pi^2 n r^2 \frac{1 + hmM/r}{h^2 m^2} \quad . \quad . \quad . \quad \text{(since } Q^2 = 2M/r) \quad . \text{ (16)},$$

a result more easily obtainable independently of the present method. If, however, the expansion of $2\cosh hm\Omega rq$ in a series becomes inapplicable, we must express the integral by means of error functions. It becomes

$$\frac{4\pi^2 n e^{hMm/r}}{h^2 m^2 \Omega^2}\left\{ e^{\frac{1}{2}hm\Omega^2 r^2} \int_Q^\infty e^{-\frac{1}{2}hm(q-\Omega r)^2} q\,dq + e^{\frac{1}{2}hm\Omega^2 r^2} \int_Q^\infty e^{-\frac{1}{2}hm(q+\Omega r)^2} q\,dq - 2\int_Q^\infty e^{-\frac{1}{2}hmq^2} q\,dq \right\}.$$

Now
$$\int_Q^\infty e^{-\frac{1}{2}hmq^2} q\,dq = \frac{e^{-\frac{1}{2}hmQ^2}}{hm}$$

$$\int_Q^\infty e^{-\frac{1}{2}hm(q-\Omega r)^2}(q - \Omega r)dq = \frac{e^{-\frac{1}{2}hm(Q-\Omega r)^2}}{hm}$$

$$\int_Q^\infty e^{-\frac{1}{2}hm((q-\Omega r)^2}\Omega r\,dq = \frac{\Omega r}{\sqrt{(2hm)}} \text{Erfc}\left[(Q - \Omega r)\sqrt{(\tfrac{1}{2}hm)}\right],$$

and similarly for the reduction of the remaining integral. Hence we obtain finally

$$\frac{4\pi^2 n e^{hMm/r}}{h^3 m^3 \Omega^2}\left\{ e^{-\frac{1}{2}hmQ^2}\left(e^{hm\Omega rQ} + e^{-hm\Omega rQ} - 2\right)\right.$$

$$\left. + \Omega r \sqrt{(\tfrac{1}{2}hm)}\left(\text{Erfc}\left[(Q - \Omega r)\sqrt{(\tfrac{1}{2}hm)}\right] - \text{Erfc}\left[(Q + \Omega r)\sqrt{(\tfrac{1}{2}hm)}\right]\right)\right\} \quad . \quad . \quad . \text{ (17)},$$

and when the argument is large we may expand the error-function complements by means of the descending series referred to in § 3, equation (4). Remembering, too, that $Q^2 = 2M/r$, we obtain

$$\frac{4\pi^2 n}{h^3 m^3 \Omega}\left\{ e^{hm\Omega rQ}\left[1 + \frac{\Omega r}{4(Q - \Omega r)}\left\{1 - \frac{1}{hm(Q - \Omega r)^2} + \frac{1 \cdot 3}{h^2 m^2 (Q - \Omega r)^2} - \cdots\right\}\right]\right.$$

$$\left. + e^{-hm\Omega rQ}\left[1 - \frac{\Omega r}{4(Q + \Omega r)}\left\{1 - \frac{1}{hm(Q + \Omega r)^2} + \frac{1 \cdot 3}{h^2 m^2 (Q + \Omega r)^2} - \cdots\right\}\right] - 2\right\}$$

$$. \quad . \quad . \text{ (18)}.$$

This formula might be applied to form an estimate of the rate at which a planet is losing its atmosphere. We shall now, however, show that the law of distribution, and therefore the above formula, cease to hold good beyond a certain distance from the planet.

9. *Limit to the Height of a Planet's Atmosphere.*

It is obvious, on the *non*-kinetic view, that no matter could be retained in relative equilibrium beyond the distance at which a planet's attraction is just balanced by

centrifugal force. On the kinetic theory, this limitation finds its interpretation in the fact that the density of the atmosphere according to the above law of distribution is proportional to

$$\exp - hm\{V - \tfrac{1}{2}\Omega^2(\xi^2 + \eta^2)\} = \exp - hm\{V - \tfrac{1}{2}\Omega^2 r^2\} \text{ where } r^2 = \xi^2 + \eta^2 . \quad . (19).$$

If $dV/dr > \Omega^2 r$, the density decreases as we proceed outwards from the axis of the planet, it becomes a minimum when $dV/dr = \Omega^2 r$, and begins to increase again outwards when $dV/dr < \Omega^2 r$. Hence the point at which centrifugal force is just balanced by the planet's attraction is the point of minimum density in the atmosphere according to the above law of *permanent* distribution. And since the atmosphere does not extend to infinity, we conclude that it cannot be permanent unless the density at the point of minimum density is infinitesimal, and practically zero.

This may be made clearer by drawing the meridian sections of the surfaces of equal density, and thus reproducing the results first obtained by EDOUARD ROCHE, of
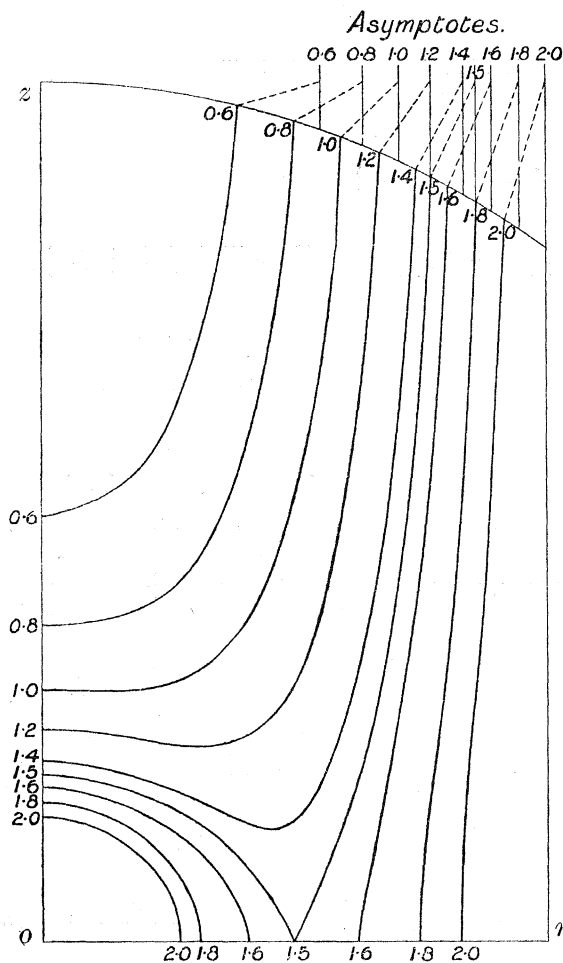
Montpellier. In the case of a spherical planet of mass M (astronomical units), these curves are given in cylindrical co-ordinates by the equation

$$\frac{M}{\sqrt{z^2 + r^2}} + \tfrac{1}{2}\Omega^2 r^2 = \text{const.}$$

This equation may be written

$$\left(\frac{r^2 + z^2}{a^2}\right)^{-\frac{1}{2}} + \tfrac{1}{2}\left(\frac{r}{a}\right)^2 = C \text{ (a constant)} \quad . \quad . \quad . \quad . \quad (20),$$

where

$$a^3 = \frac{M}{\Omega^2}.$$

At the point of minimum density in the equatorial plane, $z = 0$, $r = a$, and the curve of equal density through this point is the one for which $C = 1\cdot5$. This curve has a double point at the point in question.

The curves for which $C > 1\cdot5$, and for which the density is therefore greater than the equatorial minimum, each consist of a closed oval and an infinite branch having the line $\tfrac{1}{2}(r/a)^2 = C$ as asymptote, while the curves for which $C < 1\cdot5$ consist of infinite branches only. It is clear then that if any gas of appreciable density were to pass by diffusion beyond the closed portion of the surface $C = 1\cdot5$, it would diffuse itself indefinitely over the unclosed surfaces of equal density, and its molecules would not be able, by their collisions, to maintain the equilibrium of the distribution of molecules within the surface.

Calling the surface $C = 1\cdot5$ the critical surface, one condition for permanence is that the molecules which reach this surface must be so few and far between, that collisions rarely take place between them.

Such molecules will then describe free trajectories under the planet's attraction. If their velocity be greater than that required to carry them to infinity, they will leave the planet, describing parabolic or hyperbolic orbits. If the velocity be less than that amount, they will describe ellipses, and return to the planet's atmosphere.

Now at the singular point of the critical surface, the velocity due to axial rotation is just sufficient to make a particle, if projected with it, describe a circular orbit. For a parabolic orbit the velocity is $\sqrt{2}$ times as great. Hence a molecule at the singular point moving tangentially in the direction of rotation, will just leave the planet if its relative translatory velocity, due to the temperature of the atmosphere which it has left, be $\sqrt{2} - 1$ times the velocity due to rotation. If it be moving in any other direction, or it be situated at any other point of the critical surface, its velocity will have to be correspondingly greater.

10. *The Critical Density-ratio.*

It thus becomes important before proceeding further to calculate and tabulate, for different gases at different temperatures, the ratio of their densities at the surfaces of different members of the Solar System to their densities at the corresponding

critical surfaces, assuming the law of permanent distribution of § 6. This can easily be done from the formula, according to which the density at any point is proportional to

$$e^{-hm(V - \frac{1}{2}\Omega^2 r^2)}.$$

Calling the ratio in question the *critical density-ratio*, the condition for a permanent atmosphere requires this ratio to be very large. It must in fact be the ratio of a density of molecular distribution at the surface of the planet comparable with that of the gases in our atmosphere to one at the critical surface in which the molecules are very few and far between. For most purposes it will be sufficient to know the value of this ratio correct to the nearest power of 10, and this is shown quite as clearly by tabulating the logarithm of the ratio to base 10, for which purpose it is only necessary to multiply the difference of the potentials of gravitation and centrifugal force at the planet's surface and at the critical surface by $hm\mu$, where μ is the modulus of common logarithms. The tables are thus easy enough to calculate, but it is necessary to have them before one in order to arrive at any definite conclusions.

The logarithm to base 10 of the critical density-ratio, as thus defined, is equal to

$$\mu hm \left(V_0 + \tfrac{1}{2}u^2 - V_1\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21),$$

where V_0 is the gravitation potential at the planet's surface,

u is the velocity at the planet's equator due to axial rotation,

V_1 is the combined potential of gravitation and centrifugal force at the critical surface. Since this is constant over the critical surface, we may take V_1 to be the potential, due to gravitation alone, at the extremity of the polar radius of the critical surface. This polar radius is $\tfrac{2}{3}$ of the equatorial radius, and the latter is obtained by equating the planet's attraction to centrifugal force.

hm is equal to $3/Q^2$, where Q^2 is the mean of the squares of the velocities of the molecules. This quantity is proportional to the molecular weight and inversely proportional to the absolute temperature.

Starting with the case of the Earth and hydrogen, I have used the data given in Dr. JOHNSTONE STONEY's paper, pp. 310, 312, viz.,

Earth's equatorial radius = 6378 kiloms.

Value of g at equator due to Earth's attraction at equator = 981·5 centims./sec.²

u the equatorial velocity due to rotation = 464 metre/sec.

$Q^2 = (11140)^2 T$, in C.G.S. units at absolute temperature T.

It will be convenient to assume a temperature of 100° absolute (−173° C.) in the first calculations, since the values for other temperatures can be more easily calculated by taking a round number to start with.

We thus obtain the following values for the various terms :—

$\mu hm V_0$ the term due to the gravitation potential at the Earth's surface = 65·718
Call this term A.

$\mu hm \cdot \frac{1}{2}u^2$ the term due to centrifugal force at the Earth's surface $= \cdot 1130$. Call this term B.

$\mu hm \mathrm{V}_1$ the term due to the total potential at the critical surface $= 14\cdot880$. Call this term C.

The logarithm of the critical density ratio is equal to $\mathrm{A} + \mathrm{B} - \mathrm{C}$.

Hence we obtain the following results :—

TABLE of Logarithms of the Critical Density-ratio for Hydrogen relative to the Earth.

Absolute temp.	Centigrade temp.	Log. crit. dens. ratio.
100°	− 173°	50·951
200	− 73	25·475
300	+ 27	16·987

To make the meaning of these figures perfectly clear we notice, as remarked by Dr. STONEY, that at the bottom of our atmosphere the number of molecules in each cub. centim. of air is about 10^{21}. Supposing now that the earth was invested with an atmosphere of hydrogen containing 10^{21} molecules per cub. centim. at the surface of the earth. Then at a temperature of 27° C. there would be $10^{21-16\cdot987}$, or roughly 10^4 or 10,000 molecules in every cub. centim. at the critical surface; at −73° C. there would be on an average one molecule to every $10^{25\cdot175-21}$, or roughly $10^{4\cdot475}$ or 30,000 cub. centims. at the critical surface; at −173° there would only be one molecule per $10^{50\cdot951-21}$ or 10^{30} cub. centims. at the critical surface.

In the first case a considerable escape of gas would take place through molecules passing beyond the critical surface. In the second case it will be noticed that there would be about 33 molecules per cubic metre up at the critical surface, so that molecules would escape fairly frequently, though the rate of loss of the atmosphere would of course be very slow. In interpreting the third case it will be convenient to observe that the equatorial radius of the critical surface is about $4\cdot225 \times 10^9$ centims., and the volume of a sphere having this radius, and therefore enclosing the whole of the Earth's atmosphere, is about $3\cdot162 \times 10^{29}$ cub. centims. The calculated result for the frequency of distribution at the critical surface represents an average of about one-third of a molecule per volume equal to this vast enclosing sphere.

11. *Calculation for other Planets.*

In performing the calculations of the logarithm of the critical density-ratio for other planets, the data for the Earth may be taken as a starting-point, it being observed (as may be easily proved) that

(i.) The term A representing the gravitation potential at the planet's surface,

$$\propto \frac{\text{mass of planet}}{\text{radius}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22).$$

(ii.) The term B representing the potential of centrifugal force at the surface of the equator,

$$\propto \left(\frac{\text{radius of planet}}{\text{time of axial rotation}} \right)^2 \quad . \quad . \quad . \quad . \quad . \quad (23).$$

(iii.) The term C representing the combined potential of gravitation and centrifugal force over the critical surface,

$$\propto \left(\frac{\text{mass of planet}}{\text{time of rotation}} \right)^{\frac{2}{3}} \quad . \quad . \quad . \quad . \quad . \quad (24).$$

(iv.) It will also be convenient to notice that the equatorial radius of the closed part of the critical surface (which we have denoted by a)

$$\propto (\text{mass})^{\frac{1}{3}} \times (\text{time of rotation})^{\frac{2}{3}}. \quad . \quad . \quad . \quad . \quad . \quad (25).$$

Employing the values for the radii, masses and times of rotation given in Dr. STONEY's paper, taking the Earth's as unity, I obtain the following results :—

TABLE of Logarithms of the Critical Density-ratio for Hydrogen for various Planets.

	100° absolute.	200° absolute.	300° absolute.
Venus . .	40·6360	20·3180	13·5453
Earth . .	50·951	25·475	16·987
Mars . .	10·4690	5·2345	3·4896
Jupiter. .	711·94	355·97	237·31
Saturn . .	165·98	82·99	55·33

The logarithm of the critical density-ratio being inversely proportional to the absolute temperature and directly proportional to the molecular weight of the gas, it becomes unnecessary to perform the calculations for other gases or other temperatures, as this is a mere matter of simple arithmetic.

The high values for the logarithm of the critical density-ratio on Jupiter and Saturn leave little doubt as to the possibility of the lightest gases, such as hydrogen, remaining practically permanent in the atmospheres of these planets. When we apply the methods to helium (assuming its molecular weight twice that of hydrogen) on the Earth and watery vapour (molecular weight nine times that of hydrogen) on Mars, we have the following results :—

	100° absolute.	200° absolute.	300° absolute.
Terrestrial helium . .	101·90	50·95	33·97
Water on Mars . . .	94·22	47·11	31·41

The values of the logarithm of the critical density-ratio at 200° absolute—a point sufficiently near the temperature −66° C. assumed in Dr. JOHNSTONE STONEY's paper—appear far too great to be consistent with any appreciable loss taking place from the planets at those temperatures. Even at 300° absolute or 27° C., the figures represent averages of 100 and 30,000 molecules per cub. kilom. at the critical surface for every 10^{21} molecules per cub. centim. at the surface of the planet. While the figures show that the conditions for water on Mars are less favourable than for terrestrial helium, they appear distinctly favourable to both these elements at the temperatures ordinarily assumed for planetary atmospheres. To examine this point more fully it is important to calculate limits for the rate at which a planet would lose its atmosphere for the supposed values of the critical density-ratio, and for the time in which this loss would become appreciable.

12. *Rate of Flow across Critical Surface.*

The total rate of effusion across the closed portion of the critical surface may be calculated from the formula

$$\tfrac{1}{4} q \rho \, \mathrm{S} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (26),$$

where q is the mean translational speed of the molecules, ρ the density, and S the area of the critical surface.

Without entering into the mathematical problem of the quadrature of the surface in question by actual integration, its area can be found sufficiently closely for our purpose by noticing that the closed portion in question consists of two caps cutting their common base at 60°, and whose heights are $\tfrac{2}{3}$ of the radius of the base. Now, if we take two *spherical* caps the radius of whose common base is a, and whose heights are each $\tfrac{2}{3}a$, the area of the closed surface formed by them $= \tfrac{26}{9}\pi a^2$; while if we take two spherical caps on the same base and cutting that base at an angle of 60° the area $= \tfrac{24}{9}\pi a^2$. As the closed part of the critical surface lies between the first and second pair of spherical caps, we know that its superficial area is $\tfrac{25}{9}\pi a^2$, correct to within $\pm$ 4 per cent., and this value we shall adopt.

For the Earth $a = 6\cdot625$ R, where R = Earth's radius;
$$\therefore a = 4\cdot225 \times 10^9 \text{ centims.}$$

If we imagine all the molecules which cross the surface in question to leave the planet's atmosphere, and leave out of count all those which return after describing

free trajectories, the formula gives a superior limit to the rate at which the planet is losing its atmosphere. To obtain an estimate of the time which must elapse before the loss in question would have an appreciable effect on the amount of the gas present in the atmosphere, let us calculate the time in which the loss would represent an amount of gas equivalent to the removal of a layer 1 centim. thick from the surface of the planet. If q be measured in centims. per sec., and if L represent the critical density-ratio, then the required time

$$= \frac{144}{25} \frac{a^2}{R^2} \frac{L}{q} .$$

Putting this equal to L/E years, we have

$$E = \frac{365 \cdot 25 \times 24 \times 60 \times 60 \times 25}{144} \frac{R^2 q}{a^2} \quad . \quad . \quad . \quad . \quad . \quad (27).$$

Calculating the value of log E from this formula for hydrogen at temperature 100° absolute, we have the following results :—

Hydrogen at −173° C. = 100° absolute.	Log E.
The Earth	14·40133
Venus.	14·35456
Mars	14·35149
Jupiter	13·47129
Saturn	13·27377

For other gases at other temperatures, the value of log E is easily deduced.

For E varies as q, which varies as the square root of the absolute temperature divided by the square root of the molecular weight. Thus for hydrogen at 200° absolute, the temperature is doubled, E is increased in the ratio $\sqrt{2} : 1$, and log E has to be increased by $\frac{1}{2} \log 2$. For oxygen, the molecular weight is 16 times as great as for hydrogen, E is decreased in the ratio of 4 : 1, and log E has to be decreased by log 4; similarly for other cases. It will be seen, however, that log E is, roughly, somewhere about 14 for the majority of gases at ordinary temperatures relative to the Earth, Venus, or Mars, and rather less (namely, about 13) for the larger planets.

It follows that *if the logarithm of the critical density-ratio for a given gas at a given temperature relative to a given planet is equal to about* 14, *the total rate of effusion of that gas across the critical surface would be equivalent to the removal of the amount of that gas present in a layer* 1 *centim. thick over the surface of the planet in a period of time comparable with a year.*

If the logarithm of the critical density-ratio is 20, *the corresponding period of time would be comparable with a million years; if* 26, *with a billion years, and so on,*

The rate of effusion is proportional to the quantity of gas present, so that in cases where a gas does not exist in appreciable quantities in the atmosphere of the planet, the figures enable us to calculate what *would* happen supposing the planet to be endowed with an atmosphere of any given gas at a given temperature.

We now obtain the results given in the following tables :—

NUMBER of Years in which the Efflux across the Critical Surface would equal the Removal of the Gas in a Superficial Layer 1 centim. thick.

I. EARTH'S ATMOSPHERE.

Hydrogen at absolute temp.	Helium at absolute temp.	Years.
100°	200°	$3 \cdot 54 \times 10^{36}$
150	300	$3 \cdot 06 \times 10^{19}$
200	400	$8 \cdot 40 \times 10^{10} = 84,000,000,000$
250	500	$6 \cdot 02 \times 10^{5} = 602,000$
300	600	$2 \cdot 22 \times 10^{2} = 222$

II. ATMOSPHERE OF MARS.

Vapour of water at absolute temperature.	Years.
200°	$1 \cdot 22 \times 10^{33}$
250	$3 \cdot 37 \times 10^{23}$
300	$1 \cdot 94 \times 10^{16}$
400	$2 \cdot 40 \times 10^{9} = 2,400,000,000$
500	$4 \cdot 28 \times 10^{4} = 42,800$
600	$1 \cdot 06 \times 10^{2} = 106$

The following table shows the corresponding absolute temperatures on the Earth and Mars at which the calculations for helium and water respectively would lead to approximately the same numerical results :—

Earth and helium . .	200°	300°	400°	500°	600°
Mars and water . . .	187	281	376	472	571

The removal of a layer of atmosphere 1 centim. thick from the surface of a planet would of course decrease the barometric pressures on that planet by an amount equal to the decrease for 1 centim. of altitude, and such a change would therefore be practically quite imperceptible. A secular diminution in atmospheric pressure would not make itself noticeable to any practical extent till it corresponded to an altitude comparable with, say, 100 metres. For such a change the numbers of years in the foregoing table would have to be multiplied by 10,000.

13. *Effect of Air Currents in the Lower Regions.*

As previously indicated, one effect of convection currents, or winds, is to produce a temperature-gradient in the lower regions of a planet's atmosphere, rendering the adiabatic law of distribution a closer approximation than the isothermal. While a discussion of the numerical results obtained with that law must be left for future investigation, there appear to be many reasons on general grounds why such a distribution should not lead to results differing widely from ours, and why these results should certainly not be more favourable to the escape of the lighter gases from the atmospheres of planets.

The correction required to take account of the temperature-gradient may be roughly estimated in various ways :—

(1) We may calculate the values of the critical density-ratio for the highest and lowest temperatures known to exist in the atmosphere, the actual state of affairs being intermediate between these extreme cases.

(2) We may apply a correction to the results above calculated by comparing the actual gradient of density in the strata of the atmosphere which have been explored with the gradient which would exist if the distribution were isothermal. To make this correction sufficient, it would be necessary to carry the investigation up to the height at which the temperature becomes sensibly constant.

Now if the density of the atmosphere at the assumed upper limit be appreciable, the factor by which the critical density-ratio must be multiplied in order to apply the correction will be finite. Such a correction, then, cannot possibly affect the permanence, for example, of helium in the Earth's atmosphere at ordinary temperatures, where, if the rate of escape were multiplied, say, a millionfold, it would still be inappreciable.

But the existence of these air currents has a further influence on the distribution of the atmosphere. For, according to the isothermal distribution of the kinetic theory, the density of the heavier constituents falls off much more rapidly with the altitude than that of the lighter ones, and we therefore believe that the lighter gases extend to altitudes at which the heavier ones have practically ceased to exist. The effect of air currents is to equalise the percentage composition of the atmosphere in the upper and lower regions; in this way a greater percentage of the lighter constituents will be retained in the lower regions than would be the case if equilibrium were attained by diffusion. The conditions will be more favourable to the escape of the heavier constituents, or less favourable to the escape of the lighter ones, or both.

14. *Conclusions.*

Without entering into the debatable question of the "Age of the Earth," we may take Lord KELVIN's estimate of 10^8 years as affording some indication of the order of

magnitude of the times which have to be taken into account in tracing the past history of our planet under conditions more or less similar to those prevailing in present or geological times.

The times calculated in the previous paragraph range up to far higher orders of magnitude.

We may therefore safely draw the following conclusions :—

1. The Earth's attraction is capable, according to the kinetic theory, of retaining a gas of twice the weight of hydrogen in the form of a (practically) permanent atmosphere of uniform temperature, as high as any temperatures commonly existing in its present atmosphere.

2. The vapour of water is similarly capable, according to the kinetic theory, of existing on Mars in the form of a (practically) permanent atmosphere of uniform temperature, at any ordinary temperature. Hence it follows that *either*

(*a*) Helium does not escape from our atmosphere and water does not escape from that of Mars ;

Or (*b*) The escape takes place under far more favourable conditions, such as far higher temperatures than those assumed in previous investigations, or than we should be naturally led to assume from our knowledge of the conditions prevailing in those regions of our atmosphere that have been explored ;

Or (*c*) The escape is due to translational movements of molecules other than those investigated by the methods of the kinetic theory of gases.

[*Postscript added August*, 1900 ; *revised October*, 1900.

Since the above paper was read, Dr. JOHNSTONE STONEY has written several papers in which he maintains that helium does escape from our atmosphere. If this view be adopted, the present investigation must be regarded as a proof that the escape, instead of being attributable to the motions which the kinetic theory assigns to the molecules of a gas under ordinary conditions as to temperature, &c., must be due either (1) to the existence of other causes or conditions, or (2) to a divergence between the law of distribution which forms the basis of our commonly accepted kinetic theory and that occurring in an actual atmosphere.

Owing to the vastness of the subject, it appears only desirable for me in the present note to touch briefly on a few of the main points.

In connection with (1) Dr. STONEY points out that the actual distribution of molecules of a gas in any particular problem is dependent on two functions, π and δ, of which he supposes the first to determine the normal distribution, while the second represents the deviations due to disturbing causes. He is of opinion that the effect of the δ function is to increase the probability of a molecule acquiring a velocity considerably in excess of the mean velocity. In that case it must also correspondingly decrease the probability of the molecule possessing a velocity not considerably in

excess of the mean. The mean itself may be increased, but as the present calculations are based on the hypothesis that the mean translational energy is proportional to the temperature, such an increase would be equivalent to an assumed increase of the temperature.

Now if the molecular distribution in the upper regions of the atmosphere were dependent entirely on encounters between the molecules taking place in those regions, the rare occurrence of such encounters would no doubt practically prevent their having any appreciable effect in bringing about the normal or "π" distribution; and the distribution, if it followed any law at all, would be determined by any disturbances whose aggregate effect was sufficiently marked to give rise to a "δ" function.

But it is my contention that the molecules in the upper regions in describing free paths frequently descend to the denser portions of the atmosphere where they collide with other molecules, and their place is supplied by molecules shot up from these lower regions. The causes tending to bring about the law of distribution investigated in this paper are therefore not of infrequent occurrence, and we are justified in assuming the effects of the "π" function to be considerable even in the higher strata of the atmosphere.

Going now to the disturbing causes, the following include the principal ones suggested by Dr. STONEY, viz. :—

(a) Tides in the atmosphere.
(b) Convection currents.
(c) Solar radiation.
(d) Atmospheric storms and the transferences of energy associated with them.
(e) Electrical disturbances giving rise to " prominences."

Of these causes, the effects of tide-generating forces still remain to be dealt with in a subsequent investigation. The same applies to convection currents, except so far as their general effects, introducing a temperature gradient, have been briefly mentioned. The effect of solar radiation is to increase the temperature of the gas on which it falls. But I freely admit that given a sufficiently high temperature helium will escape. Yet in his 1897 paper* Dr. STONEY assumes so low a temperature as $-66°$ C. or $207°$ absolute, while with considerably higher temperatures I find helium permanent. The question as to how the energy of solar radiation is absorbed by molecules and converted into kinetic energy of translation is one of great difficulty, and cannot be adequately discussed here, but if the view be accepted that the increase of translational kinetic energy takes place entirely at encounters, the effects of solar radiation in the upper layers of the atmosphere would seem to be small. Of the last two causes, if storms occasionally give rise to exceptionally high temperatures, it is clear again that our assumptions as to temperature conditions must be modified. Lastly, if the escape of gases be attributed to jets or prominences, the problem is

* 'Scientific Transactions of the Royal Dublin Society,' vol. 6, p. 13.

removed from the field of study of the kinetic theory, and the velocities necessary for the escape of gases are largely dependent on the velocities of the jets as a whole.

But if disturbing causes of any kind have to be invoked in order to account for the escape of gases, the BOLTZMANN-MAXWELL doctrine being abandoned as insufficient, I do not see how the arguments used by Dr. STONEY, in his 1897 paper, can be regarded as conclusive. In that paper the condition for escape is made to depend on the ratio of the velocity necessary for escape to the velocity of mean square. This implies that the velocities of the molecules of a gas are distributed about the mean according to some definite fixed law, such as "MAXWELL'S Law," so that (as stated on pp. 310, 314 of his paper) a velocity of say nine times the velocity of mean square is sufficiently frequent to give rise to a marked escape of gas, while a velocity of 20 times the velocity of mean square occurs so seldom as to have no appreciable effect on the progress of events. But directly external disturbing causes are brought to bear on the question, there is no longer any necessary fixed relation between the velocities these are capable of producing, and the velocities of mean square of the molecules on which they act.

For example, if the disturbing causes take the form of jets or prominences, they will have the effect of impressing on all the molecules affected the common velocity of the jet. If several different gases occur in the same jet, the changes of velocity will bear no fixed relation to the velocities of mean square, but will be independent of the latter. Again, consider the effects of tide generating force. If on two different planets, one with a satellite and one without, the conditions were equally favourable to the permanence of a certain gas, the tide-generating force due to the satellite might remove the gas from one planet while it was retained on the other. Or again, a certain gas on one planet might, owing to the smallness of the disturbing causes, so rarely attain a velocity of 10 times the velocity of mean square that such occurrences had no appreciable influence. On another planet the disturbing causes might become so great as to frequently give the molecules a velocity of 20 times the velocity of mean square.

In connection with (2), when reading Dr. STONEY's 1897 paper, I naturally imagined (as I believe others have done) that MAXWELL'S Law was tacitly assumed as the basis of his investigations, and my present calculations were undertaken in order to place the question on a statistical basis, in the expectation that the conclusions would confirm Dr. STONEY's. I assumed that the object of the *à posteriori* method was to overcome a difficulty I had long felt, of drawing a hard and fast line between gases which do escape, and those which do not. The nearness of the values of the critical velocity-ratios found by Dr. STONEY for helium in our atmosphere and water on Mars, interpreted in the light of the kinetic theory, naturally justified Dr. STONEY's inference that if the former gas escapes the latter will also escape. My calculations, however, show that on the assumed hypotheses neither gas escapes.

We are now told, however, that Dr. STONEY abandoned "MAXWELL'S Law"

about thirty years ago. The *special* objections which at that time might have been raised against the law being applied to planetary atmospheres, and which arise from the necessity of taking account of the effects of gravitation, axial rotation, &c., appear to be met by the modified form of the BOLTZMANN-MAXWELL distribution used as the basis of the present investigations (§ 6, equation 9), and the arguments in § 7. There remains the more *general* objection now raised by Dr. STONEY that MAXWELL's Law does not correctly represent the distribution in any actual gas, in support of which he remarks that the distribution according to MAXWELL's Law is a function of one variable, while he thinks that the distribution in an actual gas may be represented by a far less simple law.

Hitherto it has been generally supposed, however, that the deviations of an actual gas from MAXWELL's Law only become important in the case of dense gases, where the ratio of the volume of the molecules themselves to the total volume of the gas is no longer so small as to be negligible, where the time during which a molecule is encountering other molecules is not infinitely small compared with the time during which it is describing free paths, and where multiple encounters are not so exceptional that their effects may be neglected. So far as I am aware, the most successful attempt at dealing theoretically with such dense gases is Mr. BURBURY's method, in which the view is advanced that the velocities of neighbouring molecules become correlated, and the distribution function involves two constants. It is precisely in the more rarefied portions of a planet's atmosphere that the conditions seem to me to approach most nearly to those assumed in the ordinary proofs of the permanency of MAXWELL's Law, and of the generalised BOLTZMANN-MAXWELL distribution. Dr. STONEY's objection appears to require either (a) that the gases in the upper atmosphere do conform much more nearly to MAXWELL's Law than the denser gases near the Earth, and that the deviations in the latter are so great that experiments made with them lead to the velocity of mean square in the upper regions of the atmosphere being greatly under-estimated, or (b) that the Kinetic Theory of Gases must be abandoned in just those cases in which we have been accustomed to regard it as being least open to objection.

With regard to the contention that these deviations have been omitted from the present investigation, there do not as yet appear to be sufficient data available for including them in any calculation. The present methods may be utilised in the determination of such data. By calculations in which the unknown data are omitted, combined with experimental observations, it is possible to formulate an estimate of the extent to which the BOLTZMANN-MAXWELL distribution may fail to account for any experimentally observed phenomenon. The present investigation would then become an *à posteriori* determination indicating the extent to which the omitted causes must be invoked, and it would thus afford an estimate of their magnitude.]