Radiative equilibrium in the ionosphere

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The equations of radiative equilibrium in the earth’s atmosphere are examined with special reference to high temperatures in the ionosphere arising out of a radiation balance between heavy ultra-violet absorption in the ultra-violet and relatively weak infra-red emission. It is suggested that while molecular oxygen is the principal ultra-violet absorption agent at heights below 250 km., at greater heights the absorption is mainly due to atomic oxygen. Similarly, it is suggested that while water vapour is the principal infra-red radiator at a height of 100 km., at much greater heights water vapour is absent and the temperature is effectively controlled by negative ions at a height of 250 km. and perhaps by dust at much greater heights.

The gravitational equilibrium of a dissociating oxygen atmosphere is discussed, reference being made to the effects of collisions and of absorption of the dissociating radiation.

1. The generally accepted theory that the upper layers of the earth’s atmosphere are in radiative equilibrium was put forward by Gold (1909). Gold’s theory was discussed by Milne (1922) in a paper to which detailed reference will be made later. In the same year Lindemann & Dobson (1922) produced observational evidence to show that the temperature increased considerably above the stratosphere. Gowan (1928) worked out a heat balance between absorption of ultra-violet sunlight by ozone and emission of temperature radiation by water vapour, and showed that temperatures of order 300° C were to be expected. In a later paper, Gowan (1930) gave temperatures between 250 and 500° C at a height of 80 km., depending on the relative amounts of these two constituents of the atmosphere. A few years later it was suggested by various authors that at greater heights the temperature attained much greater values. Thus Angenheister (1932) studied the heights of polar aurorae in summer and winter and concluded that if the winter temperature from 100 to 200 km. was 300° C, the summer temperature was 1200° C. Appleton & Naismith (1935) made a similar deduction from seasonal variations in the critical frequency of the $F_2$ region. Martyn & Pulley (1936) found that relative collision frequencies in the $E$ and $F_2$ regions could only be explained by a temperature of order 1000° C in the atmosphere between these regions, and put forward the hypothesis that this high
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temperature persisted all the year round. Shortly afterwards Godfrey & Price (1937) found theoretical temperatures of order 1000° C by working out a heat balance between infra-red water vapour emission and ultra-violet absorption by molecular oxygen (as well as ozone). These authors followed Gowan’s method, which considers a single layer, without working out the temperature, as a function of height from the equations of transfer of radiation, as was done by Milne.

The present paper develops equations for the temperature as a function of the height in a form suitable for distinguishing between the various molecular processes of re-emission of light following upon absorption. It is pointed out that dissociation of oxygen affects the heat balance profoundly, and expressions for the dissociation of molecular oxygen as a function of height are worked out. The paper is concerned with heights above the ozone layer and a discussion of the formation of ozone is explicitly avoided.

2. In any atmosphere, let \( I_r(\theta) \frac{dv d\omega}{4\pi} \) be the flow of radiation per sq.cm./sec. in frequencies between \( v \) and \( v + dv \) in directions falling within a cone of solid angle \( d\omega \) inclined at an angle \( \theta \) to the vertical, which is the axis of \( x \) taken positive upwards. Consider the passage of this radiation through a cylinder of unit cross-section and of length \( ds = dx \sec \theta \). The radiation will lose by absorption the amount

\[
k_r I_r(\theta) \rho ds d\omega / 4\pi,
\]

where \( k_r \) is the coefficient of absorption per unit mass of the atmosphere. The energy which is removed in this way may be merely scattered, or it may be converted into kinetic energy of the particles of the gas, or it may be emitted in frequencies outside the range from \( v \) to \( v + dv \) by fluorescence. Let the fraction \( \xi_r \), of the energy absorbed be scattered, the fraction \( \eta_r \) be converted into kinetic energy, and let the fraction \( \zeta_r \) be transferred to other frequencies, where \( \xi_r + \eta_r + \zeta_r = 1 \).

Now examine the emission with the cone \( d\omega \) in frequencies within the range \( v \) to \( v + dv \) by the cylinder. If the scattered radiation is isotropic, the amount scattered into \( d\omega \) is

\[
\xi_r k_r \rho ds d\omega / 4\pi \times J_r,
\]

where \( J_r \) is the average value of \( I_r(\theta) \) over a sphere, or \( 4\pi J_r = \int I_r(\theta) d\omega \). The absorption \( k_r \eta_r \) is balanced by thermal emission. The balance is exact in thermodynamical equilibrium, and the amount emitted depends only on the kinetic energy of the molecules of the gas. If the molecules have a Maxwellian velocity distribution appropriate to some temperature \( T \), then the emission is

\[
\eta_r k_r \rho ds d\omega / 4\pi \times B(v, T),
\]

where \( B(v, T) \) is the intensity of equilibrium (black-body) radiation,

\[
= 8\pi hv^3 e^{-2(ehv/kT) - 1}^{-1}.
\]

The symbols \( h \), \( R \) stand for Planck’s constant and Boltzmann’s constant.
Finally, there will be some emission into the frequency range \( \nu \) to \( \nu + d\nu \) by fluorescent transfer of energy from other frequencies. Let this be

\[
\xi_\nu k_\nu \rho ds d\nu d\omega /4\pi \times E_\nu.
\]

Summing up the gains and losses to the flow \( I_\nu(\theta) d\nu d\omega /4\pi \) on account of its passage through the cylinder, then

\[
\cos \theta \frac{dI_\nu(\theta)}{k_\nu \rho dx} = -I_\nu(\theta) + \xi_\nu J_\nu + \eta_\nu B(\nu, T) + \xi_\nu E_\nu.
\] (2.1)

Now define two further quantities \( H_\nu \) and \( K_\nu \) by

\[
4\pi H_\nu = \int I_\nu(\theta) \cos \theta d\omega, \quad 4\pi K_\nu = \int I_\nu(\theta) \cos^2 \theta d\omega,
\]

both integrals being taken over a sphere. \( H_\nu \) is the flux of radiation in the direction \( \nu \) and \( K_\nu \) may be thought of as the potential of this flux. Then averaging equation (2.1) over a sphere,

\[
\frac{dH_\nu}{k_\nu \rho dx} = -J_\nu(1 - \xi_\nu) + \eta_\nu B(\nu, T) + \xi_\nu E_\nu.
\] (2.2)

Multiplying equation (2.2) by \( k_\nu d\nu \) and integrating, then

\[
\frac{dH}{\rho dx} = -\int (1 - \xi_\nu) k_\nu J_\nu d\nu + \int \eta_\nu k_\nu B(\nu, T) d\nu + \int \xi_\nu k_\nu E_\nu d\nu,
\]

writing \( H \) for \( \int H_\nu d\nu \). If there are no sources or sinks of energy in the atmosphere, the net flux is constant (although \( H_\nu \) is not so), and hence

\[
\int (1 - \xi_\nu) k_\nu J_\nu d\nu = \int \eta_\nu k_\nu B(\nu, T) d\nu + \int \xi_\nu k_\nu E_\nu d\nu.
\]

Since fluorescence only transfers energy from one frequency to another

\[
\int \xi_\nu k_\nu E_\nu d\nu = \int \xi_\nu k_\nu J_\nu d\nu.
\]

Hence, when there are no sources or sinks,

\[
\int \eta_\nu k_\nu J_\nu d\nu = \int \eta_\nu k_\nu B(\nu, T) d\nu.
\] (2.3)

This is the equation of radiative equilibrium which determines the temperature \( T \) of the atmosphere as judged by the kinetic energy of the particles. In the remainder of this paper it will be assumed that the velocities of the particles are distributed according to Maxwell’s law, and the parameter \( T \) in that law will be referred to as the temperature of the atmosphere.
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Multiplying equation (2·1) by \( \cos \theta \) and integrating over a sphere, then

\[
\frac{dK_v}{k_v \rho \, dx} = -H_v. \tag{2·4}
\]

(It may throw some light on the nature and importance of the quantity \( K = \int K_v \, dv \) to remark that \( \nabla^2 K = -k_v \rho \div H + \int \rho \frac{dK_v}{dv} \div H \, dv \), so that if there are no sources or sinks of energy and \( \div H = 0 \), then \( \nabla^2 K = 0 \). In most applications, however, there is either plane or spherical symmetry and the equation reduces to simpler forms.)

Advance has been made in the treatment of radiative equilibrium in the solar atmosphere by assuming a relation between \( K_v \) and \( J_v \) based on some simple assumption about the distribution of \( I_v(\theta) \) with \( \theta \). For example, if \( I_v(\theta) = I_1 \) when \( 0 < \theta < \frac{\pi}{2} \), and if \( I_v(\theta) = I_2 \) when \( \frac{\pi}{2} < \theta < \pi \), then \( K_v = \frac{1}{3} J_v \). Again, if \( I_v(\theta) = a + b \cos \theta \), once more \( K_v = \frac{1}{3} J_v \). The solution of the simplest astrophysical problem is as follows. Consider an atmosphere in which there are no absorption lines, so that \( \xi_v = 0 \) and ignore fluorescence, so that \( \zeta_v = 0 \). Then \( \eta = 1 \). Further, suppose that \( k_v \) is independent of \( v \) and equal to \( k \) and \( d\tau = -k \rho \, dx \). Then using \( K = \frac{1}{3} J \) it follows that

\[
J = 3H\tau + \text{constant,}
\]

the boundary condition being no inflow of radiation at the surface of the star or

\[
\int I_v(\theta) \, d\omega = 0 \quad \text{over a hemisphere equal to zero where} \quad \tau = 0.
\]

This gives \( J = 2H \) at \( \tau = 0 \) according to one approximation \((I_v(\theta)\) constant over a hemisphere\)) and \( J = \frac{3}{2} H \) according to the other \((I_v(\theta) = a + b \cos \theta \). Adopting the former, then

\[
J = H(2 + 3\tau).
\]

This gives the temperature, since \( J = B(T) = acT^4 \) and

\[
T^4 = T_0^4(1 + \frac{3}{2}\tau).
\]

This equation is due to Milne. It receives support from the observed darkening of the solar limb.

The approximation \( K_v = \frac{1}{3} J_v \) has had further successes in accounting for the main features of absorption lines, and further mathematical approximation has shown that in some cases at any rate the errors involved in assuming that \( K_v = \frac{1}{3} J_v \) are small.

3. It may be asked whether this approximation is of any value in dealing with the earth’s atmosphere. In this case it is convenient to assume that the flow of radiation has the intensity \( I_v'(\theta) \) in all directions except in a cone of solid angle \( 4\pi \omega \) (the cone subtended by the sun’s disk) in which the intensity is \( I_v'(\pi - z) + S_v \) where \( z \) is the sun’s zenith distance. Write

\[
4\pi J_v' = \int I_v'(\theta) \, d\omega, \quad 4\pi H_v' = \int I_v'(\theta) \cos \theta \, d\omega, \quad 4\pi K_v' = \int I_v'(\theta) \cos^2 \theta \, d\omega,
\]
all the integrals being taken over a sphere. Then

\[ J_\nu = J'_\nu + \omega S_\nu, \quad H_\nu = H'_\nu - \omega S_\nu \cos z, \quad K_\nu = K'_\nu + \omega S_\nu \cos^2 z. \]

The radiation outside the special cone may be supposed evenly distributed according to some simple law such as \( I'_\nu(\theta) = a + b \cos \theta \), so that it may be supposed that \( K'_\nu = \frac{1}{3} J'_\nu \). It is at once clear that in the special case \( \sec^2 z = 3 \), \( K_\nu = \frac{1}{3} J_\nu \) also. It is also clear that \( K_\nu = \cos^2 z J'_\nu \) will be a better approximation than \( K_\nu = \frac{1}{3} J_\nu \) if direct sunlight preponderates over a scattered sunlight.

In what follows the intensity \( I_\nu(\theta) \) will be used, defined by

\[
I_\nu(\theta) = I'_\nu(\theta) \quad \text{outside the special cone} \quad 4\pi \omega,
I_\nu(\theta) = I'_\nu(\pi - z) + S_\nu \quad \text{inside the special cone} \quad 4\pi \omega.
\]

A distinction of this kind was made by Milne (1922).

By definition, \( 4\pi \omega \) is the solid angle subtended by the solar disk. According to Auwers the mean solar diameter is \( 31'59'' \), which gives \( \omega = 5.410 \times 10^{-6} \). Let \( \rho \) be the radius of the sun, and let \( R \) be the radius of the earth’s orbit. Let \( \Sigma_\nu \) be the emission per sec./sq.cm. of the sun’s surface. The total emission from the sun is then \( 4\pi \rho^2 \Sigma_\nu \). Since all this radiation passes through a sphere of radius \( R \) the amount which passes through 1 sq.cm. normal to the sun at the earth’s mean distance per sec. is \( \rho^2/R^2 \Sigma_\nu \). But this is \( 4\pi \omega S_\nu^0 \), where \( S_\nu^0 \) is the value of \( S_\nu \) at the top of the earth’s atmosphere. Again \( 4\pi \omega = \pi \rho^2/R^2 \), so that

\[ \pi S_\nu^0 = \Sigma_\nu. \]

The value of \( \Sigma_\nu \) is not known in the far ultra-violet regions of the spectrum in which present interest lies. In the visible spectrum and in the infra-red, however, it is known that the distribution in frequency of solar radiation is close to that of a black body at 6850° (Plaskett), while the effective temperature is known, more reliably, to be 5740°. If a colour temperature of 6825° be assumed (\( = 5740° \times 24 \)), then

\[ \Sigma_\nu = \frac{\pi \hbar \nu^2}{e^2} (e^{\hbar \nu RT'} - 1)^{-1}, \]

where \( T' = 6825° \). This gives

\[ \int \Sigma_\nu \, d\nu = \frac{3}{8} \alpha c T'^4 = \frac{1}{4} \alpha c T_\epsilon^4 \]

with \( T_\epsilon = 5740 \). Now

\[ S_\nu^0 = \hbar \nu^2 c^{-2} (e^{\hbar \nu RT'} - 1)^{-1}, \]

and since for ultra-violet radiation \( e^{\hbar \nu RT'} \) is much greater than 1, then

\[ S_\nu^0 = \hbar \nu^2 c^{-2} e^{-\beta \nu}, \quad (3·1) \]

where \( \beta = 6.991 \times 10^{-15} \) and \( \log \beta = 15.8446 \). This value of \( \beta \) is applicable to the visible spectrum. As it is likely that the solar absorption coefficient increases with increasing frequency, it is probable that in the far ultra-violet the solar radiation is less than is given by (3·1) with \( T' = 6825° \). In particular, it is very likely that there is a drop in the continuous spectrum at the head of the Lyman series at 912 A.
4. In this section an atmosphere is considered in which there is neither scattering nor fluorescence, that is to say, $\xi = \zeta = 0$ and $\eta = 1$. The case in which $k_\nu$ is independent of $\nu$ was treated by Milne. It has no application to the earth’s upper atmosphere in which $k_\nu$ has large values in the infra-red and ultra-violet and is practically zero in the visible spectrum. Now pass on to a mathematical case which, though far too crude to give an accurate representation of the actual atmosphere, illustrates several points, and in particular the reversal of the temperature gradient. Let $k_\nu = k_1$ from $\nu_1$ to $\nu_1 + \Delta \nu_1$ (infra-red frequencies), and let $k_\nu = k_2$ from $\nu_2$ to $\nu_2 + \Delta \nu_2$ (ultra-violet frequencies), and let $k_\nu$ be zero for all other frequencies. Then from (2·1)

$$\cos \theta \frac{dI_1(\theta)}{\rho dx} = -k_1 I_1(\theta) + k_1 B(\nu_1, T),$$

$$\cos \theta \frac{dI_2(\theta)}{\rho dx} = -k_2 I_2(\theta) + k_2 B(\nu_2, T).$$

In the earth’s atmosphere $T$ will be so small that $B(\nu_2, T)$ may be neglected in comparison with $\omega S^0_{\nu_2}$ (in the ultra-violet frequencies). In this case

$$\frac{dH_2}{\rho dx} = -k_2 J_2, \quad \frac{dK_2}{\rho dx} = -k_2 H_2.$$ 

The ultra-violet light is almost entirely direct sunlight so that $K_2 = \cos^2 z J_2$, and the equations give $\cos^2 z \frac{d^2 J_2}{\rho^2 dx^2} = k_2^2 J_2$, or

$$J_2 = J_2^0 \exp \left( k_2 \sec z \int^\infty_x \rho dx \right),$$

which is ordinary exponential absorption. Now in radiative equilibrium with no sources or sinks of energy it follows from (2·3) that

$$k_1 \Delta \nu_1 (J_1 - B(\nu_1, T)) + k_2 \Delta \nu_2 J_2 = 0.$$ 

Write $\Delta \nu_2 = \lambda \Delta \nu_1$ and $k_2 = \alpha k_1$ and let $d\tau = -k_1 \rho dx$. Then

$$\frac{dH_1}{d\tau} = J_1 - B(\nu_1, T) = -\alpha \lambda J_2^0 e^{-\alpha \sec z},$$

$$H_1 = A + \lambda \cos z J_2^0 e^{-\alpha \sec z}.$$ 

Notice that $H = H_1 \Delta \nu_1 + H_2 \Delta \nu_2$ is constant, as it must be if there are no sources or sinks.

In the infra-red, temperature radiation is more important than direct sunlight and $K_1 = \frac{1}{3} J_1$. Then

$$dJ_1/d\tau = 3H_1 = 3A + 3\lambda \cos z J_2^0 e^{-\alpha \sec z},$$

which gives

$$J_1 = J_1^0 + 3A \tau + 3x^{-1} \lambda \cos^2 z J_2^0 e^{-\alpha \sec z} + J_2^0 e^{-\alpha \sec z} (\alpha \lambda - 3x^{-1} \lambda \cos^2 z).$$

But

$$B(\nu_1, T) = J_1 + \alpha \lambda J_2.$$ 

Hence

$$\frac{dB(\nu_1, T)}{d\tau} = 3A + \lambda \sec z J_2^0 e^{-\alpha \sec z} (3 \cos^2 z - \alpha^2).$$
Now at the lower boundary of the radiative region (the tropopause), which is taken as \( \tau = \tau_1 \), infra-red radiation is given out by the earth so that \( H_1 \) has a positive value, say \( \mathcal{H} \). Then

\[
\mathcal{H} = A + \lambda \cos z J_0^\theta e^{-\alpha_1 \sec z},
\]

it may be supposed that no ultra-violet radiation reaches the lower boundary and \( J_0^\theta e^{-\alpha_1 \sec z} \) may be neglected. This gives \( A = \mathcal{H} \), and accordingly

\[
\frac{dB(v_1, T)}{dT} = 3 \mathcal{H} - \lambda \sec z J_0^\theta (\alpha^2 - 3 \cos^2 z) e^{-\alpha \sec z}.
\]

If \( \alpha \) is large \( 3 \cos^2 z \) may be neglected compared with \( \alpha^2 \). Then the temperature gradient changes sign at \( \tau = \tau' \), where

\[
\mathcal{H} = \frac{1}{3} \lambda \alpha^2 J_0^\theta \sec z e^{-\alpha \sec z}.
\]

The boundary condition at the top of the atmosphere is no inflow of infra-red radiation, or \( J_1 = 2H_1 \). (The solar infra-red radiation has in intensity of order \( \omega T'/T \) compared with the earth’s radiation.) Then \( J_1^\theta = 2(\mathcal{H} + \lambda \cos z J_0^\theta) \). But

\[ B(v_1, T) = J_1 + \alpha \lambda J_2 \] so that if \( T = T_0 \) at \( \tau = 0 \)

\[ B(v_1, T_0) = 2\mathcal{H} + \lambda J_0^\theta (\alpha + 2 \cos z). \]

The temperature at the point where the gradient is reversed \( \tau = \tau' \) is \( T_{\text{min}} \), where

\[ B(v_1, T_{\text{min}}) = 2\mathcal{H}(1 + \frac{3}{2} \tau' + 3 \alpha^{-1} \sec z) + \lambda J_0^\theta (2 \cos z + 3 \alpha^{-1} \cos^2 z). \]

For \( \alpha \) large these expressions become

\[
B(v_1, T_0) = 2\mathcal{H} + \alpha \lambda J_2^\theta,
\]

\[
B(v_1, T_{\text{min}}) = 2\mathcal{H}(1 + \frac{3}{2} \tau') + 2\lambda \cos^2 z J_2^\theta,
\]

giving the temperature at the top of the atmosphere \( T_0 \) and the minimum temperature \( T_{\text{min}} \). \( \mathcal{H} \) is supposed known and \( J_0^\theta = \omega S_2^\theta \). Equation (4·1) is very similar to Milne’s equation (28"), from which it differs slightly because Milne’s approximation is not quite the same as \( K = \frac{1}{3} J \), and also because an internal boundary has been used in deriving (4·1). The use of this internal boundary shows that a minimum temperature can occur in an atmosphere in radiative equilibrium. It should be noticed that Milne’s statement that \( \cos \alpha > \frac{1}{2} \pi \) (in our notation \( \cos z > \sqrt{3} \alpha \)), in most applications, is correct if one is comparing heavy infra-red absorption with an almost transparent visible spectrum; but the introduction of still heavier absorption in the far ultra-violet leads to \( \alpha \) large with, of course, very different consequences. Milne’s use of exponential absorption for direct sunlight and his use of (24) and (25) for earth radiation correspond to our approximation \( K_2 = \cos^2 z J_2 \) and \( K_1 = \frac{1}{3} J_1 \).

5. One cannot proceed from (4·1) to an evaluation of the actual temperatures which will be encountered in the atmosphere because \( k_\nu \) is not even roughly independent of \( \nu \) in the far ultra-violet. Consider first the ultra-violet absorption due to molecular oxygen \( O_2 \). The absorption is in the Schumann-Runge continuum and is
Absorbed by the ground state \( x^3\Sigma \). It results in dissociation of the molecule into two atoms, one in the ground state \( ^3\text{P} \) and one in a metastable state \( ^1\text{D} \), thus

\[
\text{O}_2(x^3\Sigma) + h\nu \rightarrow \text{O}(^3\text{P}) + \text{O}(^1\text{D}).
\]

The dissociation potential of \( \text{O}_2 \) is 5.09 V and the excitation potential of \( \text{O}(^1\text{D}) \) is 1.96 V. Hence the excess of energy over 7.05 V (corresponding to \( \nu = 5.7 \times 10^4 \text{ cm}^{-1} \)) absorbed in the Schumann-Runge continuum is converted into kinetic energy. Turning to the potential energy, the most likely transitions for the \( \text{O}(^1\text{D}) \) atom are:

I. Ordinary recombination \( \text{O}(^1\text{D}) + \text{O}(^3\text{P}) \rightarrow \text{O}_2 + h\nu \), contributing to \( \xi \).

II. (a) Super-elastic collision \( \text{O}(^1\text{D}) + X \rightarrow \text{O}(^3\text{P}) + X + \frac{1}{2}m\nu^2 \), contributing to \( \eta \).

(b) Super-elastic collision \( \text{O}(^1\text{D}) + X \rightarrow \text{O}(^3\text{P}) + X' \), contributing to \( \eta \).

\[
X' \rightarrow X + h\nu
\]

III. Forbidden transition \( \text{O}(^1\text{D}) \rightarrow \text{O}(^3\text{P}) + h\nu \), contributing to \( \zeta \).

Of these the forbidden transition is by far the most likely when the number of particles per c.c. is \( 10^{14} \) or less, as the mean life of the metastable state is only 0.5 sec. Accordingly, scattering is negligible: most of the energy absorbed is transferred to other frequencies by fluorescence and hence

\[
\xi = 0, \quad \eta = (\nu - \nu_0)/\nu, \quad \zeta = \nu_0/\nu.
\]

(5.1)

Now work out the temperature distribution in an atmosphere in which absorption is performed by molecular oxygen, leaving atomic oxygen out of account for the moment. Define a mean absorption coefficient for infra-red frequencies by

\[
\bar{k}B(T) = \int k_\nu B(\nu, T) \, d\nu,
\]

the integral being taken over the infra-red, and \( T \) being that of some representative level in the atmosphere. Strictly speaking \( \int \eta_\nu k_\nu J_\nu d\nu \) over the infra-red frequencies is not necessarily equal to \( \bar{k}J_1 \), but it will be supposed that this is so: then the equation of radiative equilibrium (2.3) gives

\[
\bar{k}(J_1 - B_1) + \int_{\nu_0}^{\infty} \eta_\nu k_\nu J_\nu d\nu = 0,
\]

(5.2)

where \( \nu_0 \) is the low-frequency limit of the ultra-violet absorption.

The absorption coefficient of \( \text{O}_2 \) in the Schumann-Runge continuum has been measured by Ladenburg & van Voorhis (1933), according to whom it increases almost linearly from \( \nu = 5.9 \times 10^4 \text{ cm}^{-1} \) to \( \nu = 6.9 \times 10^4 \text{ cm}^{-1} \), decreasing sharply thereafter. For present purposes take \( k_\nu = a(\nu - \nu_0) \). A rather cumbrous calculation allowing for the decrease in \( k_\nu \) beyond \( 6.9 \times 10^4 \text{ cm}^{-1} \) shows that little error is introduced by this simple assumption: the physical justification is that the solar energy curve weakens very rapidly with increasing frequency.
Now the energy from sunlight in the Schumann-Runge continuum once absorbed is re-emitted in other wave-lengths so that no radiation field is built up comparable in intensity with direct sunlight. Hence $K_v = \sec z J_v$, and thus

$$J_v = \omega S^0_v \exp \{-k_v \sec z/k \tau\}.$$  

Then

$$\int_{\nu_v}^{\infty} \eta_v k_v J_v dv = \omega h c^{-2} \int_{\nu_v}^{\infty} a(v - \nu_0)^2 v^2 \exp \{-\beta v - a \sec z/k \tau\} dv, \quad (5.3)$$

or with sufficient accuracy

$$\int_{\nu_v}^{\infty} \eta_v k_v J_v dv = a\omega \nu_0^{-1} S^0_v \int_0^{\infty} x^2 \exp \{-\beta(1+\mu \tau)\} dx$$

$$= 2a\omega S^0_v / (\nu_0 \beta^3 (1+\mu \tau)^3). \quad (5.31)$$

Here $\mu = a \sec z / (k \beta)$. Then from (5.2) and (5.31) it follows that

$$B_1 = J_1 + C(1+\mu \tau)^{-3},$$

where $C = 2a\omega S^0_v / (k \nu_0 \beta^3)$.

If an analysis similar to that in § 4 is carried out, assuming again that no ultra-violet light reaches the lower boundary $\tau = \tau_1$, then

$$B(T) = \mathcal{H}(2+3\tau) + \frac{3C}{2\mu^2} \left( \frac{2\mu}{3} + 1 - (1+\mu \tau)^{-1} + \frac{2\mu^2}{3} (1+\mu \tau)^{-3} \right),$$

$$B(0) = 2\mathcal{H} + C. \quad (5.4)$$

Or since $\mu$ is large

$$B(0) = 2\mathcal{H} + C. \quad (5.41)$$

It may be remarked that, if the approximation from (5.3) to (5.31) is not made, a more elaborate series (going up to inverse fifth powers) is obtained in place of (5.4) and, with $\beta \nu_0 = 12.4$, in place of (5.41) one obtains

$$B(0) = 2\mathcal{H} + 1.56C. \quad (5.42)$$

It is convenient to express the constant $C$ in terms of $k'$, the absorption coefficient when $\beta(v - \nu_0) = 1$. Then $\beta k' = a$ and hence

$$C = \frac{k' 2\omega S^0_v}{k \beta^2 \nu_0}. \quad (5.5)$$

To evaluate $\mathcal{H}$, let $r$ be the radius of the earth, $\rho$ the radius of the sun and $R$ the mean radius of the earth's orbit. Let the total emission from the sun be $4\pi \rho^2 \Sigma$ ergs/sec. Of all the radiation which leaves the sun, the fraction $\pi r^2/4\pi R^2$ is intercepted by the earth. Of this, the fraction 0.37 is reflected as visible light (according to Abbott), while the remainder is converted into longer wave-lengths and distributed over the day and night hemispheres. Hence the average infra-red emission per sq.cm. is

$$\mathcal{H} = 0.63 \Sigma \times \rho^2/4R^2 = 0.63 \times \omega \Sigma.$$  

Now $\Sigma = \frac{1}{4}acT_e^4$, where $a$ is the coefficient in Stefan's law and $T_e$ is the effective temperature of the sun or $5740^\circ$. Hence

$$\mathcal{H} = 0.63 \omega \times \frac{1}{4}acT_e^4. \quad (5.6)$$
Radiative equilibrium in the ionosphere

But \( B(T) = acT^4 \), so that if \( B(T) = 2\mathcal{H} \times f \), where \( f \) is some factor,

\[
T = T_e \times (0.315w_0 f)\, \frac{1}{4}
= 207^\circ.5 \times f^4. 
\] (5·7)

Again, from (3·1), (5·5) and (5·6),

\[
\frac{C}{2\mathcal{H}} = \frac{k'}{k} \times \frac{4R\nu_a^3 e^{-\beta\nu_0}}{0.315 \beta a c^3 T''^3} 
\]

since \( T''^4 = 2T_e^4 \) has been assumed. Inserting numerical values and using (5·42), it is found that

\[
T = 207^\circ.5 \times \{1 + 7.9 \times 10^{-5} k'/k\}^4. 
\] (5·8)

If \( k'/k \) is of order \( 10^8 \), \( T \) is of order 2000\(^\circ\).

The infra-red absorption due to water vapour has been measured by Hettner and also by Weber and Randall. The results do not agree, and as Hettner’s observations are far more extensive they must be used. The coefficient varies irregularly with the wave-length, and Hettner’s results do not extend far enough into the infra-red to give reliable results for temperatures as low as 300\(^\circ\). A rough estimate from Hettner’s results as reproduced in Brunt’s Physical and dynamical meteorology gives \( \bar{k} = 15w \) at 2000\(^\circ\) and \( \bar{k} = 30w \) at 1000\(^\circ\), where \( w \) is the proportion of water vapour by weight in the atmosphere. (A very rough estimate suggests \( \bar{k} = 100w \) at 300\(^\circ\).) The value of \( k' \) as measured by Ladenburg & van Voorhis (1933) is \( 1.65 \times 10^8w' \), where \( w' \) is the proportion of molecular oxygen by weight in the atmosphere.

While the value of \( w' \) presents no difficulty apart from dissociation, the value of \( w \) is most uncertain. On the earth’s surface the water-vapour pressure is about 10 mb., but at the minimum temperature in the stratosphere (about 220\(^\circ\)) the saturation pressure is only about 0·025 mb. This occurs at about 20 km., where the pressure of oxygen is about 27 mb., so that at this level there is about one molecule of water vapour to every thousand oxygen molecules and the ratio by mass is one to two thousand. If this ratio persists upwards the boundary temperature given by (5·8) is about 1000\(^\circ\) C.

If, however, water molecules can pass the barrier at 20 km., possibly in the form of ice crystals, the water-vapour population may build up above this rather low limit. It does not appear impossible to ascertain the total water-vapour content above the stratosphere by actual experiment in the near future, by exposing a spectrogram in an aircraft flying at a great height.* If the above estimate of the water-vapour population is too low by a factor of 10, the boundary temperature drops from 1000\(^\circ\) C to about 500\(^\circ\) C. (As the temperature lowers, the value of \( \bar{k} \) becomes less certain.)

By (5·4), near \( \tau = 0, \ T \propto (1 + \mu \tau)^{-\frac{1}{2}} \). Roughly speaking the temperature at a given level is inversely proportional to the mass of molecular oxygen above that level if the ratio of number of water-vapour molecules to number of oxygen molecules is constant. The temperature drops to one-half the boundary value below \( 2 \times 10^{17} \)

* (Note added in 1946.) Or released from a high altitude rocket.
molecules, when the sun is in the zenith. The results of later sections may be anticipated by saying that the results of this section are thought to apply roughly to heights from 100 to 200 km.

6. At very great heights the oxygen will be dissociated to atomic O which will absorb ultra-violet radiation capable of ionizing the atom in its ground state, that is to say of wave-length below 912 \( \lambda \), thus

\[
O + h\nu \rightarrow O^+ + e.
\]

The excess energy over 13.54 \( V \) (the ionization potential) appears as kinetic energy of the electrons. These will rapidly distribute their velocities according to a Maxwellian law, and the recombination spectrum will be distributed in frequency according to the molecular-velocity temperature of the (earth's) atmosphere.

It may be inquired what equilibrium would result if the atmosphere consisted entirely of one element, moreover, one which exhibited only one continuous spectrum. From each quantum \( h\nu \) absorbed, the excess over the ionization energy \( h(\nu - \nu_0) \) is imparted to the electrons as kinetic energy. The electrons will by collisions distribute their kinetic energy according to a Maxwellian distribution characterized by some parameter \( T \). The emission spectrum arising from the capture of electrons with this velocity distribution will have the same frequency distribution as temperature emission for \( T \), so that the emission per gram of the neutral element will be \( \lambda k_v B(\nu, T) \) \( d\nu \), where \( \lambda \) is some constant.

Hence

\[
\cos \theta \frac{dI_\nu(\theta)}{\rho dr} = -k_v I_\nu(\theta) + \lambda k_v B(\nu, T),
\]

(6.11)

\[
\frac{dH_\nu}{\rho dx} = -k_v J_\nu + \lambda k_v B(\nu, T),
\]

(6.12)

and integrating (6.12) with respect to \( \nu \), then

\[
\frac{dH}{\rho dx} = -k_v J_\nu d\nu + \lambda k_v B(\nu, T) d\nu.
\]

(6.13)

But \( H \) is constant so that

\[
\int_{\nu_0}^{\infty} k_v J_\nu d\nu = \lambda \int_{\nu_0}^{\infty} k_v B(\nu, T) d\nu,
\]

(6.2)

the equation of radiative equilibrium in this case.

If the electron gas has no means of exchanging energy with the atmosphere except through transitions in this one continuous spectrum, one can equate the fraction of the energy absorbed which goes to electron velocities with the fraction of the capture spectrum which diminishes electron velocity energies, or

\[
\int_{\nu_0}^{\infty} \frac{\nu - \nu_0}{\nu} k_v J_\nu d\nu = \lambda \int_{\nu_0}^{\infty} \frac{\nu - \nu_0}{\nu} k_v B(\nu, T) d\nu.
\]

(6.3)
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If now $J_ρ$ is $ωS(ν, T')$, where $ω$ is some fraction and $S(ν, T')$ is a temperature distribution corresponding to a (solar) temperature $T'$, (6·2) and (6·3) can only be satisfied if $λ = ω$ and $T = T'$. The re-emission is exactly the same as if the process were true scattering in a bound-bound transition: but the electrons, if they have no means of exchanging energy with the atmosphere except in this one band, must take up a velocity distribution appropriate to the colour temperature of the sun.

There will, of course, in any real atom be more than one continuous spectrum. In the case of O where ground state is $^3P_{0,1,2}$, there are excited states $^1D_2$ and $^3S_0$ with energies of 1·96 and 4·17 V. At sufficiently low dilution factors $ω$ the forbidden transitions between these states and the ground state will become important, and the atom will transfer radiation from the ultra-violet band O($^3P$)$\rightarrow$O$(^4S)$ to the bands O($^3S$)$\rightarrow$O$(^4S)$ and O($^1D$)$\rightarrow$O$(^4S)$. The velocity distribution of the electrons will not be reduced unless high-velocity electrons show a greater tendency to fall with an excited state (rather than the ground state) than slow electrons.

If the temperature of the upper boundary of the earth's atmosphere falls much below 6000°, there must be some infra-red radiators, and if water vapour is dissociated at very great heights (see § 13) search must be made elsewhere for emission of low-temperature radiation. Two possibilities present themselves, which will be examined in succeeding sections. These are negative ions (§ 7) and dust (§ 8).

7. Although negative ions with their low dissociation potentials are very greatly dissociated into atoms and electrons in sunlight there will at all times be a small but finite negative-ion population. Since the continuous spectrum of the negative ion lies in the visible or infra-red, a very small negative-ion population may have a great effect on the temperature if there are no other low-frequency radiations available.

Let $n_ε$, $n^-_ε$ and $n$ be the numbers of electrons, negative ions and atoms per c.c. Then in dilute solar radiation the populations will be given by the modified Saha formula

$$\frac{n_εn^-_ε}{n} = 2(2πmR)^{1/2} \frac{σω}{8π^3h^3} e^{-\frac{1}{k_b}RT'} \times F(T, T'),$$

(7·1)

where $σ$ is the ratio of the statistical weights of the atom and negative ion, $λ$ is the dissociation potential, $T'$ the solar temperature, $T$ the temperature of the atmosphere, and $F(T, T')$ is a factor which depends upon the form of the absorption coefficient of the negative ion as a function of frequency. In particular, if $k_ε$ is proportional to $ν^{-2}$, $F(T, T') = T'^k$. The subject is discussed very fully by Pannekoek (1930).

For given values of $n_ε$ and $n$ we have $n^-_ε$ proportional to $e^{\frac{1}{k_b}RT'}$. The infra-red emission per c.c. of such ions is proportional to

$$e^{\frac{1}{k_b}RT'} \int_{ν_o}^{∞} k_ε B(ν, T) dν,$$
where $\hbar \nu = \chi'$ and the result of this integration will depend on the variation of $k_\nu$ with $\nu$, but the most important term will be proportional to $e^{-\chi'/RT'}$. Hence the emission per c.c. varies with

$$\exp\{\chi'/RT' - \chi/RT\},$$

and if $T'$ is considerably greater than $T$ the emission is greater for small values of $\chi$ than for large ones. Thus the ion $N^-$ whose dissociation potential is estimated at 0.04 V is more important than $O^-$ whose potential is between 2 and 3 V.

As $n_e$ decreases with increasing height, the ratio $n^-/n$ decreases with increasing height, according to (7.1), so that in the limit where interstellar space is approached the influence of the negative ions disappears. However, at heights of 200 to 300 km. the negative ions will have a profound effect.

It is not possible to work out the radiation balance accurately because the proportion of nitrogen to oxygen, and the state of the nitrogen (whether molecular or atomic), is uncertain at great heights, and also because the absorption coefficient of negative nitrogen ions $N^-$ and $N_2^-$ are unknown. If $N_2^-$ has a very low dissociation potential and an absorption coefficient nearly equal to that of $N^-$, it will make no difference to the calculation whether the nitrogen is in the molecular or atomic state, given the ratio of nitrogen particles to oxygen atoms. It will be supposed that negative ions showing a very low dissociation potential and exhibiting an absorption coefficient independent of frequency and equal to $4.5 \times 10^{-18}$ cm$^2$ (the absorption coefficient of O) have to be dealt with. (It is known that the absorption coefficient of $O^-$ is of order $10^{-18}$ cm$^2$.)

Now if $k_\nu$ is independent of $\nu$ and if $\chi$ is small, the function $F(T', T')$ in (7.1) becomes $(T'/T)^3$. Assuming a solar temperature of 6825° (for the visible spectrum) and an atmospheric temperature of 1000° for nitrogen it is found that

$$\frac{n_e n^-}{n} = 4.7 \times 10^{15}.$$  \hspace{1cm} (7.11)

Now assume that the atomic oxygen population is equal to the nitrogen population, and assume values of $n$ and $n_e$. Then temperatures may be calculated from

$$n^- \cdot a \cdot T^4 = n \int_{\nu_0}^{\infty} \omega \hbar \nu^2 (\nu - \nu_0) e^{-2\nu - \hbar \nu/RT'} d\nu.$$  \hspace{1cm} (7.2)

Some results are shown in table 1. In computing this table $T'$ has been taken as 6000° for the spectrum beyond 912 A. This is very uncertain, and the values of $T$ are very sensitive to the adopted value of $T'$.

<table>
<thead>
<tr>
<th>Table 1. Temperatures by equilibrium between negative nitrogen ions and oxygen atoms</th>
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</thead>
<tbody>
<tr>
<td>log $n$ assumed</td>
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<tr>
<td>log $n_e$ assumed</td>
</tr>
<tr>
<td>log $n^-$ from (7.11)</td>
</tr>
<tr>
<td>$T'$ from (7.2)</td>
</tr>
</tbody>
</table>
Table 1 shows that the negative ions probably play a very important part in controlling the temperature. They are able, on the figures assumed, to radiate enough energy, compared with the intake of oxygen atoms, to pull the temperature down to 1000° or so. But as each oxygen molecule absorbs $4 \times 10^5$ times as much energy from full radiation at 6000° as an oxygen atom does, the negative ions would play no effective part in cooling a concentration of $10^{10}$ oxygen molecules per c.c. A discussion of the change-over from atomic to molecular oxygen with decreasing height in the atmosphere is given in § 14.

If it be supposed that the absorption coefficient of the negative ions is $4.5 \times 10^{-18}$ and the molecular velocity temperature 1000°, and that there are $10^{10}$ relevant neutral particles and $10^{87}$ electrons per c.c., each neutral particle will capture an electron once in about 18 days. Accordingly, since the neutral particles carry nearly all the kinetic energy, and can only lose it by capturing an electron and radiating a quantum, the atmosphere will not sensibly change its temperature from day to night. To obtain a day and night average, the temperatures shown in table 1 must be multiplied by $2^{-4}$, so that the value for $n = 10^{10}$ becomes 840°, etc.

It should be noticed that the absorption of ultra-violet energy is attributed to oxygen and not nitrogen. The nitrogen molecule does not appear to have a strong absorption continuum, and the nitrogen atom has an ionization potential of 14.40 V against 13.54 V for atomic oxygen, so that the nitrogen atom is the less efficient of the two in absorbing solar radiation.

8. Dust particles, if present in sufficient numbers, can cool the gases in the upper atmosphere. Suppose that there are $N$ spherical dust particles per c.c. each of radius $r$ and let $nr^2N = \sigma$. Then if there are $n$ gas molecules per c.c. each of mass $M$ the total number of molecules which strike dust particles per c.c./sec. is

$$2\sigma n \left( \frac{2RT}{\pi M} \right)^{\frac{1}{2}},$$

the average kinetic energy being $2RT$ (swifter particles striking more often than slower ones). As usual $T$ is the parameter which characterizes the Maxwellian velocity distribution of the gas. If the dust particles are maintained by their radiation balance at some temperature $T''$, the gas molecules will rebound from the dust with an average kinetic energy $2RT''$, where

$$T - T'' = \alpha(T - T'),$$

and $\alpha$ is called the accommodation coefficient. Hence the net interchange of energy per c.c./sec. from the gas to the dust is

$$2\sigma n \left( \frac{2RT}{\pi M} \right)^{\frac{1}{2}} 2\alpha R(T - T'),$$

and if $E$ is the energy absorbed per c.c./sec. by each molecule from the radiation field, and if the dust is the principal cooler, then

$$E = 4\alpha\sigma R \left( \frac{2RT}{\pi M} \right)^{\frac{1}{2}} (T - T').$$

(8.1)
The value of $\sigma$ may be estimated from the brightness of the zodiacal light. According to Elvey & Roach (1937) the brightness of one square degree of the zodiacal light at a point on the ecliptic 90° from the sun is equal to 200 stars of the tenth magnitude. Let the albedo of the dust be $\epsilon$. Then

$$\epsilon\sigma = 5 \times 10^{-17} \times \phi,$$

where $\phi$ is a factor depending on the law of distribution of $\sigma$ as a function of the distance from the sun, having the value of 0.67 if $\sigma$ is inversely proportional to the distance of 1.25 if it is proportional to the inverse fourth power, so that one may assume $\phi = 1$. The value of the albedo may be estimated from that of the moon (0.07) and of Ceres (0.06) rather than from the albedos of planets which have atmospheres. Taking $\epsilon = 0.07$ and $\phi = 1$, then $\sigma = 7 \times 10^{-16}$. Now it is easily seen that in the upper atmosphere the intake of solar energy by oxygen atoms is unable to heat the dust materially so that $T' = 233°$ (by day). If it be supposed that oxygen atoms constitute the fraction $f$ of the total population which conveys energy from gas to dust and differences of mass in the gas particles be ignored, then

$$\frac{Ef}{\sigma \alpha} = 4 R^2 \left( \frac{2}{\pi M} \right) T^1 (T - 233), \quad \text{(8-2)}$$

and $E$ can be calculated from the absorption coefficient for oxygen.

The resultant values of $T$ are highly dependent on the assumed temperature of the sun in the ultra-violet, and on the values of $f$, $\alpha$ and $\sigma$. With $f = \frac{1}{2}$, $\alpha = \frac{1}{2}$, $\sigma = 7 \times 10^{-16}$ and a solar temperature of 6000° we get $T = 4000°$. With these figures the dust is less efficient as a cooler than negative nitrogen ions at a level in the atmosphere when $n = 10^8$ atoms per c.c., according to the preceding section.

It should, however, be emphasized that both calculations may be substantially revised when relevant coefficients and conditions become better known. In default of other infra-red radiators, however, one or other of these types of particle, or possibly both acting at different heights, must determine the molecular velocity temperature at great heights in the earth’s atmosphere.

9. It is not possible to proceed further without examining the dissociation of the molecules in the atmosphere into their constituent atoms as a function of height. In full equilibrium at a temperature $T$ the dissociation of a homonuclear diatomic molecule is given by

$$\left( \frac{n_1^2}{n_2} \right)_T = \frac{G}{2 hr_0^2 \left( \frac{MRT}{\pi} \right)^{\frac{1}{2}}} e^{-\chi/RT}, \quad \text{(9-1)}$$

where $n_1$, $n_2$ are the numbers of atoms and molecules per c.c., $M$ the mass of each atom and $G$, $r_0$ and $\chi$ are constants, the latter being the dissociation potential. This expression is derived, for example, in Rosseland’s *Theoretical Astrophysics*, where values of the constants for various molecules are given. For oxygen, $G = 27$, $r_0 = 1.20 \times 10^{-8}$ cm., and $\chi = 5.09$ V. Then from (9-1) with $T = 1000°$, $n_1^2/n_2 = 0.319$ and for $T = 300°$ the value is $3 \times 10^{-41}$. Just as Saha’s equation leads to Milne’s well-known relation (1924a) between the continuous absorption coefficient of an
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atom and the probability that an ion will capture an electron, so equation (9.1) (which is called the isochore) leads to a relation between the absorption coefficient of the molecule and the probability of recombination between two atoms, which is mentioned here because the oxygen absorption coefficient already quoted in earlier sections leads to a mean life of the oxygen atoms of the order of 25 days with \( n_1 = 10^{12} \), showing that dissociation may safely be averaged over day and night.

The effect of departures from thermodynamical equilibrium on ionization (which is very similar in this respect to dissociation) was first examined by Woltjer and applied to stellar atmospheres by Pannekoek (1926, 1930). The same ideas have been applied specifically to dissociation by Majumdar (1938). The form of the result will depend on the variation of \( k_\nu \) with \( \nu \). If one supposes, for example, that \( k_\nu \) is proportional to \( \nu^{-2} (\nu - \nu_0) \) (where \( h\nu_0 = \chi \)) for all \( \nu > \nu_0 \) and zero for \( \nu < \nu_0 \), then (9.1) becomes

\[
\frac{n_1^2}{n_2} = \frac{G \omega (MRT)'^3}{16\pi^4 h^3 \nu_0^6} \left( \frac{T'}{T} \right)^2 e^{-\chi R T'},
\]

where \( T' \) is as before the solar temperature. With \( T' = 6825^\circ \) and \( \omega = 5.41 \times 10^{-6} \), then for oxygen, with \( T = 1000^\circ \), \( n_1^2/n_2 = 2.73 \times 10^{46} \) and with \( T = 300^\circ \), \( n_1^2/n_2 = 1.66 \times 10^{17} \), in great contrast to the values given by (9.1). Except at the top of the atmosphere, the radiation is not simply dilute temperature radiation, but is weakened by absorption by day and is absent at night. Since the life of the dissociated atom is large compared with 24 hr., the dissociation may be calculated by taking an average over day and night, and as regards absorption, the value of \( n_1^2/n_2 \) must be multiplied by an appropriate factor before this average is taken.

Ozone will be ignored and attention confined to heights above the ozone layer. Besides radiative recombination and dissociation consideration will be given to the effects of three-body collisions of type

\[ O_2 + X \rightleftharpoons O + O + X. \]

If \( n_x \) is the number of \( X \) particles per c.c. the number of dissociations per c.c./sec. due to collisions is proportional to \( n_2 n_x \), and the number of recombinations is proportional to \( n_1^2 n_x \). Then if the day and night variation of dissociation is small secular equilibrium follows, or

\[
n_2(q + \Sigma b_x n_x) = n_1^2(a + \Sigma \lambda_x n_x),
\]

the summation being over all possible types of third body \( X \). \( q \) is the number of dissociating quanta absorbed per second by the molecule. In thermodynamic equilibrium the collision processes balance, or

\[
(n_2 \Sigma b_x n_x)_T = (n_1^2 \Sigma \lambda_x n_x)_T,
\]

so that if dilute radiation greatly increases the value of \( n_1^2/n_2 \) over \( (n_1^2/n_2)_T \), then \( n_1^2 \Sigma \lambda_x n_x \) is much greater than \( n_2 \Sigma b_x n_x \). Under such circumstances the dissociation equilibrium equation is

\[
n_2 q = n_1^2(a + \Sigma \lambda_x n_x).
\]
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This may be compared with a formula used by Wulf & Deming (1936) in calculating the dissociation of oxygen in the atmosphere. Their equation (8) in the present notation is

\[ n_2q = n_2^2 \sum \lambda_x n_x, \]

(9.4)

which is clearly applicable in regions where the recombination through collisions is more important than radiative recombination. It is clear, however, that (9.4) will give too small a molecular concentration when \( n_x \) becomes small—that is, at great heights.

10. Now consider the gravitational equilibrium of an isothermal dissociating atmosphere in which there is no mixing by vertical transport. Choosing the axis of \( x \) vertical and positive upwards, the equation of hydrostatic equilibrium is

\[ dp = -g \rho dx, \]

(10.1)

where \( p \) is the total pressure and \( \rho \) the total density. Consider an atmosphere consisting only of O and \( \text{O}_2 \) reacting with one another. Let \( M \) be the mass of the oxygen atom and let there be \( n_1 \) oxygen atoms and \( n_2 \) oxygen molecules per c.c. Then

\[ p = (n_1 + n_2)RT, \quad \rho = M(n_1 + 2n_2). \]

If there is no absorption of the dissociating radiation and if collisions may be neglected, then

\[ q n_2 = a n_1^2, \]

(10.2)

where \( q \) and \( a \) are constant. These conditions apply to the top of the atmosphere. Equation (10.1) becomes

\[ (dn_1 + dn_2)RT = -Mgdx(n_1 + 2n_2). \]

But from (10.2) \( qdn_2 = 2an_1dn_1 \). Accordingly

\[ dn_1(q + 2an_1)RT = -Mgdx(q + 2an_1), \]

\[ \frac{dn_1}{n_1} = -\frac{Mg}{RT} dx, \]

and writing \( \frac{RT}{Mg} = H \), then

\[ n_1 = Ae^{-x/H}, \quad n_2 = Be^{-2x/H}. \]

(10.3)

The constants \( A \) and \( B \) are related by \( qB = aA^2 \). Each constituent is distributed vertically with height exactly as if the reaction did not take place. This result applies to any number of reacting constituents. It may be proved in the case of full equilibrium from a general theorem due to Willard Gibbs (1875), and the result was applied to gravitational equilibrium in a reaction of type (10.2) with \( q/a \) constant by Milne (1924b). The result, of course, does not hold if \( n_1 \) and \( n_2 \) are connected by the more general relation

\[ n_2(q + \Sigma b_x n_x) = n_1^2(a + \Sigma \lambda_x n_x), \]
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unless (1) there is full equilibrium or (2) collisions are much less important than radiation (equation (10·2) above) or (3) collisions are much more important than radiation. In the earth's atmosphere case (2) applies to great heights and case (3) to levels near the ground. The transition is examined in the next section.

11. The term \( q \) is weakened by absorption as one goes downwards in the atmosphere, but to obtain a solution it will be supposed that \( q \) is constant until the transition from atomic to molecular oxygen has been passed. With \( q \) constant a simple solution of (10·1) and (10·2) is obtained if the third bodies \( X \) are the oxygen molecules and atoms themselves, and if they are equally efficient in three-body collisions, for then (10·2) becomes (9·3), in this case

\[
qn_2 = n_2^a(a + \lambda(n_1 + n_2)).
\]  

(11·1)

The solution of (10·1) and (11·1) is

\[
n_1(1 - \lambda q^{-1} n_2^a)^{-1} = C e^{-x/H}, \quad qn_2 = (a + \lambda n_1) C^a e^{-2x/H}.
\]  

(11·2)

For \( n_1 \) small, then \( n_1 = C e^{-x/H} \) and \( qn_2 = a C^a e^{-2x/H} \), as in (10·3). As \( x \) decreases, \( n_1 \) increases until it approaches the value \( q^a \lambda^{-1} \) asymptotically. At low levels \( n_2 \) is approximately equal to

\[
\left[ \frac{a}{q} + \left( \frac{\lambda}{q} \right)^i \right] C^a e^{-2x/H}.
\]

Now \( q/a \) is equal to the value of \( n_1^a/n_2 \) in (9·2), and \( q \) is known separately from the absorption coefficient. Further, \[ \left[ \frac{a}{q} + \left( \frac{\lambda}{q} \right)^i \right] C^a \] is the number of oxygen molecules per c.c. at ground level. Hence the distribution of oxygen molecules and atoms in the atmosphere is known if \( \lambda \) is known. The number of oxygen atoms per c.c. at ground level is not given correctly by these equations, as absorption will weaken \( q \) and finally reduce it to the level where the collision term \( n_2 \Sigma b_x n_x \) (omitted from (11·1)) is important. Thus the ground value of \( n_1 \) is given by (9·1) with the ground temperature of the atmosphere. If the absorption of the ultra-violet radiation only becomes important below the level where collisions have reduced the oxygen to the molecular state, the values of \( n_2 \) will be correct throughout the atmosphere and those of \( n_1 \) correct in and above the transition layer. It is, however, wrong to suppose that atoms are as efficient as molecules in absorbing energy in three-body collisions. The molecule with its vibrational and rotational degrees of freedom offers far greater possibilities of absorbing energy through resonance. Two cases arise: (a) where the molecules of the substance itself are the most important contributors to \( \Sigma \lambda_x n_x \) or \( \Sigma \lambda_x n_x = \lambda n_a \), and (b) where the molecules of another gas are the most important contributors, or

\[
\Sigma \lambda_x n_x = \lambda n'_e^{-2x/H}.
\]

In case (a), which presumably applies to nitrogen, the equation (9·3) becomes

\[
qn_2 = n_2^a(a + \lambda n_2),
\]
which, together with (10.1), has the solution

\[
\begin{align*}
1 + 2x_n^2 - \mu n_1^2 & \left( \sqrt{\alpha^2 + \mu} + \alpha - \mu n_1 \right)^{2/3} = D e^{-x/H}, \\
1 - \mu n_1^2 & \left( \sqrt{\alpha^2 + \mu} - \alpha + \mu n_1 \right)^{2/3} = n_2,
\end{align*}
\]

(11.3)

where \(a/q = \alpha, \mu = \alpha \lambda\) and \(D\) is a constant of integration.

Case (b) applies to oxygen with nitrogen molecules as the third bodies. Strictly speaking the value of \(H\) is not the same for the two molecules, but recognition of this produces analytical complications in expressions which are already cumbersome. Ignoring this point (9.3) becomes

\[
qn_2 = n_1^2 (a + be^{-2x/H}),
\]

(11.4)

It is convenient to write \(2an_1/q = y\). Then the solution of (11.4) and (10.1) is

\[
ay^2 = 2(E - \ln (1 + y) + y - \frac{1}{2}y^2) e^{-2x/H},
\]

(11.5)

\(n_2\) being derived from \(y\) by (11.4), and \(E\) being the constant of integration. It is not obvious that (11.4) and (11.5) are essentially similar to (11.2), but in (11.5) as one goes downwards \(y\) approaches the value \(y = y_1\), where

\[
\ln (1 + y_1) - y_1 + \frac{1}{2}y_1^2 = E.
\]

At the top of the atmosphere where \(y\) is small

\[
y = (2\lambda E)^{1/4} e^{-x/H},
\]

and at the bottom of the atmosphere

\[
n_2 = \frac{qby_1^2}{4a^2} e^{-2x/H}.
\]

Although the actual atmosphere is not isothermal, calculations for an isothermal atmosphere at \(T = 300^\circ\) probably represent the first 150 km. of the atmosphere well. From Wulf & Deming’s estimate (1938) of the collision factor \(b\) may be taken in (11.4) at 10^{-12}. If the solar temperature applicable to 2000 A be estimated at 6300^\circ, then \(q = 6 \times 10^{-5}\) quanta per sec. per molecule for oxygen. With \(T' = 6300\) and \(T = 300\) then \(q/a = n_1^2/n_2 = 4.9 \times 10^{18}\) from (9.2). Hence \(a = 1.26 \times 10^{-21}\). Values of log \(n_1\) and log \(n_2\) computed from (11.4) and (11.5) are shown in table 2. These values are plotted in figure 1 and joined by full lines. The pecked lines show the distribution of \(O\) and \(O_2\) at great heights if the temperature is 1000^\circ at those heights and if the value of \(n_1\) for \(O\) is \(2 \times 10^{10}\) (§14) and the dotted line shows values obtained in §12 (table 3). In §5 it was seen that the Schumann-Runge absorption is reduced to one-half below \(2 \times 10^{17}\) molecules. With the conditions assumed, this will occur rather above 100 km., and the assumption that \(q\) can be taken constant requires modification. This would result in greater molecular and smaller atomic populations than those shown in table 2. This effect will be increased by temperatures higher than 300^\circ.
Radiative equilibrium in the ionosphere

It is less easy to estimate the dissociation of nitrogen as the spectrum of $N_2$ is not so well known as the spectrum of $O_2$. On account of its greater dissociation potential (9 V) $N_2$ is much less dissociated than $O_2$.

Table 2. Dissociation of oxygen in an isothermal atmosphere

<table>
<thead>
<tr>
<th>$H$, km.</th>
<th>83</th>
<th>98</th>
<th>110</th>
<th>122</th>
<th>133</th>
<th>170</th>
<th>206</th>
<th>242</th>
<th>278</th>
</tr>
</thead>
<tbody>
<tr>
<td>log $n_2$</td>
<td>14.10</td>
<td>13.15</td>
<td>12.17</td>
<td>10.90</td>
<td>9.69</td>
<td>6.19</td>
<td>4.09</td>
<td>2.09</td>
<td>0.09</td>
</tr>
</tbody>
</table>

Figure 1. Distribution of O and $O_2$ with height. — Isothermal atmosphere at 300° C (table 2). —— temperature increasing from 300 to 1000° C (table 3). —— values based on collision frequencies (§ 14).

12. As has been seen in earlier sections, above 100 km. or so (the limit to which the Schumann-Runge radiation reaches) the temperature very probably increases, in a manner depending upon the distribution of the sources of ultra-violet absorption and infra-red emission. To examine the effect of the temperature gradient on the distribution of population with height, assume as a first approximation that the atmosphere consists of only one constituent and that the temperature gradient is proportional to the population at any level. Let there be $n$ particles per c.c., each of mass $M$. The $\rho = nM$ and $p = nRT$. Now it has been supposed that

$$RdT = \sigma \rho dx,$$

(12.1)

where $\sigma$ is some constant. In addition

$$dp = -g\rho dx.$$

(12.2)
These conditions are supposed to hold from \( x = x_1 \) to \( x = \infty \). Let \( T = T_1 \) and \( n = n_1 \), at \( x = x_1 \), and let \( RT_1/Mg = H_1 \). Then the solution of (12-1) and (12-2) is

\[
\frac{(\sigma n + 1)}{H} T = (\sigma n_1 + 1) T_1, \\
\frac{x-x_1}{H} + \left(\frac{T}{T_1} - 1\right) + (\sigma n_1 + 1) \ln \frac{nT}{n_1 T_1} = 0.
\]

Suppose, for example, that \( n_1 = 10^{13} \) and \( T_1 = 300^\circ \) at \( x_1 = 100 \text{ km} \), and that \( H_1 = 15 \text{ km} \). Let us choose the value of \( \sigma \) so as to make \( T \) tend to the limiting value \( 1000^\circ \). Then the temperature and population will be distributed with height as is shown in Table 3.

**Table 3. Temperature increasing uniformly with number of particles above 100 km.**

<table>
<thead>
<tr>
<th>log ( n )</th>
<th>13·0</th>
<th>12·48</th>
<th>12·0</th>
<th>11·48</th>
<th>11·0</th>
<th>10·48</th>
</tr>
</thead>
<tbody>
<tr>
<td>( H ), km.</td>
<td>100</td>
<td>112</td>
<td>140</td>
<td>187</td>
<td>222</td>
<td>282</td>
</tr>
<tr>
<td>( T )</td>
<td>300</td>
<td>589</td>
<td>810</td>
<td>935</td>
<td>977</td>
<td>993</td>
</tr>
</tbody>
</table>

13. On account of its importance as a source of infra-red radiation, water vapour requires special discussion. The equilibrium between \( N \) water-vapour molecules per c.c. on the one hand and \( n \) hydrogen atoms and \( n' \) oxygen atoms per c.c. on the other is given by a formula similar to (9-1), namely,

\[
N = n^2 n' K(T),
\]

and by the Willard Gibbs-Milne argument all the constituents are distributed vertically in an isothermal atmosphere in gravitational equilibrium just as if no dissociation took place or

\[
N = C e^{-x/H}, \tag{13-1}
\]

the value of \( H \) for water vapour being nearly equal to that of atomic (not molecular) oxygen. In full equilibrium, therefore, the water-vapour population would *gain* over the molecular oxygen population with increasing height. This argument, however, overlooks the escape of hydrogen from the earth’s atmosphere. The view was put forward by Chapman & Milne (1920) that there is no appreciable amount of free hydrogen in the atmosphere. This is generally accepted, and, if true, must have as a consequence the result that water vapour falls off with increasing height far more rapidly than is given by equation (13-1). If the temperatures at great heights were known one could calculate the rate at which hydrogen atoms escape from the atmosphere from a given population distribution; and at the same time work out the populations of hydrogen atoms and water-vapour molecules at all heights if a single constant were known—the rate at which water-vapour molecules are transported over unit area of the tropopause. This constant is related to the total number of water-vapour molecules in a column of unit cross-section above the tropopause. As has been suggested earlier, it appears to be within the reach of observation in
the near future. The importance of this constant to ionospheric theory can hardly be overestimated.

14. The physical arguments in §§ 6 to 13 are, from the point of view of the earlier sections, arguments about the absorption coefficient in the infra-red and ultra-violet as a function of height. The problem is complicated by the fact that one requires a knowledge of the temperature to determine the constituents of the atmosphere, so that even with the fullest knowledge of the atomic coefficients involved one would be compelled to proceed by successive approximation from an assumed temperature distribution. Since many quantities cannot at present be evaluated accurately, this will not be done. One may, however, inquire whether there are two substantially distinct regions heated by molecular oxygen and atomic oxygen and separated by a temperature minimum.

Possibly the soundest method of estimating the atomic population at great heights is an appeal to the observed collision frequency. According to Farmer & Ratcliffe (1935), an electron makes $1.3 \times 10^8$ collisions per second in the $F_2$ region. This experimental result is confirmed by Martyn & Pulley (1936). By comparison with the collision frequency in the $E$ region the latter authors deduce that the temperature in the $F$ region is of order $1000^\circ$. We may for definiteness suppose that at a height of $250$ km. the molecular population is $4 \times 10^{10}$, and that one-half of this is atomic oxygen (the result being either atomic or molecular nitrogen). Assuming that at this height one is well above the levels where Schumann-Runge radiation is substantially absorbed, then from (9-2) and making an allowance for day and night averaging, $n_2 = 5 \times 10^4$. Now at a temperature of $1000^\circ$ the value of $H$ for oxygen is $52.2$ km., so that if the atmosphere is isothermal above $250$ km. we have by $(10-3) 1.05 \times 10^{17}$ oxygen atoms and $3 \times 10^{11}$ oxygen molecules in a column of unit cross-section above this level. Since for O, $k = 4.5 \times 10^{-18}$, the atomic oxygen radiation is just becoming appreciably absorbed at this point, being reduced to $e^{-0.45}$ or 0.64 of its incident value.* With a solar-energy curve of $6000^\circ$ each oxygen molecule absorbs $4 \times 10^5$ times as much energy as an oxygen atom, and the two intakes of energy are roughly equal at $250$ km. with the figures which we have adopted.

Going upwards the temperature must increase, as the electron density decreases (the layer is the maximum electron density), so that atomic population gains over negative-ion concentrations with increasing height. Going downwards the electron population again decreases, so that the oxygen molecular population will gain over the negative-ion population. Hence unless water vapour is present in sufficient quantity to compete with the infra-red radiation from negative ions at the $250$ km. level, that level is, on the figures adopted, a minimum of the temperature. Going downwards from $250$ km. the temperature increases until water vapour is encountered. The fact that the recombination coefficient for the $F_1$ region (say $180$ km.) is much greater than that for the $F_2$ region (say $250$ km.) strongly suggests that there

* If the $F_1$ region is formed by the ionization of O to $O^+$ one would expect this radiation to be reduced to $e^{-1}$ of its initial value at the level of maximum ionization.
are many more negative (oxygen) ions in the lower region, and therefore that the temperature in the $F_1$ region is considerably lower than the temperature in the $F_2$ region.* This may well be due to an appreciable water-vapour population in the lower region.

The author acknowledges with pleasure the benefit he has derived from discussing ionospheric problems with Dr D. F. Martyn and Dr C. W. Allen.

REFERENCES

Chapman & Milne 1920 Quart. J. R. Met. Soc. 46, 357.
Ladenburg & van Voorhis 1933 Phys. Rev. 43, 315.
Majumdar 1938 Indian J. Phys. 21, 75.
Milne 1922 Phil. Mag. 44, 872.
Milne 1924a Phil. Mag. 47, 209.
Pannekoek 1930 Handbuch der Astrophysik, 3, 288.
Willard Gibbs 1875 Sci. Papers, 1, 144, 171.

* I owe this remark to Dr Martyn.