

Atomic Oxygen in the Polar Winter Mesosphere^{1,2}

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ABSTRACT

Kellogg's hypothesis that the winter warmth of the polar mesosphere is due to the chemical energy released by the formation of molecular oxygen from atomic oxygen is examined. Reactions involving O, O₂, and O₃ are considered. Computations reveal that slow rates of subsidence (~ 0.2 cm sec⁻¹) are clearly sufficient to provide the required energy at the proper heights, when considered in association with published infrared cooling rates due to CO₂. The possibility that the released energy is lost to the atmospheric region of concern due to radiation in the Kaplan-Meinel or infrared atmospheric bands of O₂ is considered. If collisional deactivation by an atom-atom interchange is the predominant deactivating mechanism at the level of maximum energy release, then most of the energy released will appear as sensible heat.

1. Introduction

That portion of the atmosphere between about 65 and 100 km and north of about 55N exhibits an anomalous temperature behavior during the winter months. During the winter months, from about November to February, this layer either receives no illumination from the sun, or else the sun's rays strike at such an oblique angle that very little energy is received. Yet rocket soundings show that temperatures in the layer from 75 to 95 km are up to 70K warmer in winter than in summer. Fig. 1, taken from data of Stroud *et al.* (1960), clearly shows this warming. It is unfortunate that the only lengthy series of rocket soundings are from Fort Churchill, situated near 59N at the southern boundary of the polar region defined above.

By contrast, Murgatroyd and Goody (1958) have shown that in winter a heat sink exists at the heights under consideration from about 50N to the pole. They attribute the heat losses to infrared radiation from the carbon dioxide molecule and estimate cooling rates of from 15 to 20K per day.

Kellogg (1961) sought to account for this warming by assuming that a meridional circulation transports atomic oxygen at heights of 110 to 120 km from southerly latitudes towards the pole. Gentle subsidence would then occur at high latitudes and sensible heat will be realized through adiabatic compression, and through chemical energy release due to atomic oxygen combining to form molecular oxygen.

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Recently Murgatroyd and Singleton (1961) have constructed a model for the meridional circulation in the stratosphere and mesosphere using the distribution of heat sources and sinks obtained by Murgatroyd and Goody (1958). Their computations indicate a poleward mesospheric flow in winter with subsidence extending to below 50 km over polar regions. Haurwitz (1961) has developed a model mesospheric circulation based on frictional effects; his computations indicate a northerly flow at heights greater than 100 km with subsidence extending down to only about 90 km. Thus there is

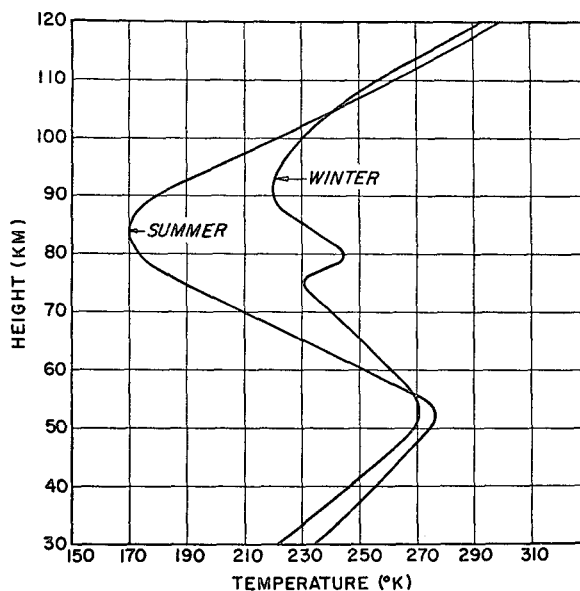


FIG. 1. Typical vertical temperature profiles in summer and winter at Churchill, based on data of Stroud *et al.* (1960).

some agreement on the existence of a circulation such as is required for Kellogg's hypothesis to be valid.

In his original paper, Kellogg estimated the contribution to the heating of the mesosphere by the recombination mechanism by assuming a steady profile of concentration of O. While this may be valid as a first approximation, it leaves much to be desired as a definitive evaluation of this effect. We have sought to improve the qualitative evaluation of the energy release through the recombination of atomic oxygen by adopting a Lagrangian point of view and following a parcel of air as it subsides.

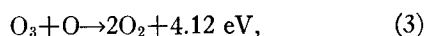
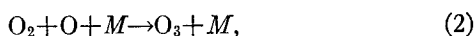
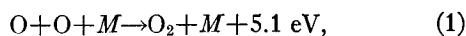
The chemical reactions which we have considered and the associated rate equations and coefficients are discussed in the following section. In Section 3, our numerical methods are presented; the results of the computation are described in Section 4.

The basic computations yield directly the amounts of chemical energy which are released by the recombination of atomic oxygen, but give no information as to whether this energy will appear as molecular kinetic energy (heat) or as radiant energy. The possibility that an appreciable amount of the energy released may appear in some of the band systems associated with the excited oxygen molecule (viz. Herzberg, Kaplan-Meinel and infrared atmospheric band systems) is examined in Section 5.

As stated in the conclusion, Section 6, the Kellogg mechanism for producing the observed high temperatures of the polar winter mesosphere is entirely verified by our results, and only a small part of the released energy is likely to appear as radiation.

2. Chemical reactions

The reactions considered are:



where M is a third body, either O_2 or N_2 . Reaction (2) is slightly exothermic. However, the energy released has been neglected in the ensuing computations so that the heating rates arrived at will be conservative values. Part of the energy released through reaction (1) may be bound initially in an excited oxygen molecule, and could subsequently be lost by radiation. The final dispensation of the energy will be considered later. Initially we shall be concerned only with the total amount of energy released.

Reactions (2) and (3) involving ozone are introduced since any ozone formed will be destroyed only by collisions and not, in the absence of sunlight, by the more normal effects of radiation ($\lambda \leq 11,000\text{\AA}$). Reaction (3), which accounts for the destruction of ozone, is of course another mechanism for destroying atomic

oxygen. Because of the lack of atomic oxygen at low levels, any ozone that is not destroyed by about 75 km will be transported downward to lower levels. Given sufficient subsidence this might account for the observed increase in ozone in polar regions with the approach of spring. Equation (1) is the dominant reaction in the layer under consideration.

Considering the above reactions the rate equations are

$$\frac{dn(\text{O})}{dt} = -k_{12}n(\text{O})n(\text{O}_2)n(M) - k_{13}n(\text{O})n(\text{O}_3) - 2k_{11}[n(\text{O})]^2n(M), \quad (4)$$

$$\frac{dn(\text{O}_2)}{dt} = -k_{12}n(\text{O})n(\text{O}_2)n(M) + 2k_{13}n(\text{O})n(\text{O}_3) + k_{11}[n(\text{O})]^2n(M), \quad (5)$$

$$\frac{dn(\text{O}_3)}{dt} = k_{12}n(\text{O})n(\text{O}_2)n(M) - k_{13}n(\text{O})n(\text{O}_3), \quad (6)$$

where $n(\text{O})$, $n(\text{O}_2)$ and $n(\text{O}_3)$ are the concentrations (particles per unit volume) of atomic oxygen, molecular oxygen and ozone, respectively. For the concentration of the third body in reactions (1) and (2) we choose

$$n(M) = n(\text{O}_2) + 0.6n(\text{N}_2), \quad (7)$$

where $n(\text{N}_2)$ and $n(M)$ are the nitrogen and third body concentrations, respectively. The factor 0.6 appearing in (7) is in line with the suggestion of Paetzold and Regener (1957) that nitrogen is not as effective a third body as oxygen. The rate coefficients k_{11} , k_{12} , and k_{13} appearing in (4), (5) and (6) correspond to reactions (1), (2) and (3), respectively. Two different sets of values for k_{11} and k_{12} were used in the computations. These are given in Table 1.

TABLE 1. Values for the rate coefficients k_{11} and k_{12} .

	Set A	Set B
k_{11}	$5 \times 10^{-34} T^{1/2} \text{ cm}^6 \text{ sec}^{-1}$ (1)	$2.7 \times 10^{-33} \text{ cm}^6 \text{ sec}^{-1}$ (3)
k_{12}	$8 \times 10^{-35} \text{ cm}^6 \text{ sec}^{-1}$ (2)	$6.0 \times 10^{-34} \text{ cm}^6 \text{ sec}^{-1}$ (3)

(1) Nicolet, 1961.

(2) Paetzold and Regener, 1957.

(3) Reeves, Manella and Harteck, 1960.

The third coefficient, k_{13} , is taken to be $\exp(4.493 \times 10^{-2} \times T - 43.88) \text{ cm}^3 \text{ sec}^{-1}$ where T is the absolute temperature. For the temperatures of interest this expression yields values reasonably close to those of Benson and Axworthy (1957).

Other values for k_{11} , k_{12} and k_{13} have appeared in the literature (Harteck and Reeves, 1961), but the difference between these values and the ones used in this study would not have a significant effect on our results,

since their values lie fairly close to those given in Set B of Table 1.

3. Computational procedures

To simplify the notation, let n_1, n_2, n_3 and n_4 denote the number of oxygen atoms, oxygen molecules, ozone molecules and nitrogen molecules, respectively, in a unit volume. The pressure p is given by

$$p = nkT, \tag{8}$$

where $n = \sum_{i=1}^4 n_i$, k is Boltzmann's constant and T the initial absolute temperature. The change in pressure, Δp , corresponding to a height change, Δz , is obtained from the hydrostatic equation,

$$\Delta p = gm\Delta z, \tag{9}$$

where g is the acceleration of gravity. m is given by $\sum m_i = \sum n_i M_i$, where the m_i are the masses of the oxygen atoms, oxygen molecules, ozone molecules and nitrogen molecules, respectively, ($i=1, \dots, 4$) contained in a unit volume, and the M_i are the masses of the individual molecules. The acceleration of gravity is computed as

$$g = 980 \left[\frac{R}{R+h} \right]^2 \text{ cm sec}^{-2},$$

where R is the earth's radius and h the height at which g is desired. From (8) and (9) we have

$$p' = p + \Delta p = kT \sum n_i + g \Delta z \sum n_i M_i,$$

where p' is the pressure following subsidence through a distance Δz . Adiabatic compression will release energy equivalent to a temperature rise ΔT_{ad} given by

$$\Delta T_{ad} = \Delta p / \sum (c_{pi} m_i),$$

where the c_{pi} are the specific heats of the appropriate gases.

Equations (4), (5) and (6) are used to arrive at the change in concentration of the atomic and molecular oxygen and ozone during an interval of time $\Delta t = \Delta z/w$, where w is the vertical velocity. The chemical energy release can then be computed using (1) and (3). Equations (4) and (5) are written in finite difference form as

$$\Delta n_1 = [-k_{12} n_1 n_2 n_5 - k_{13} n_1 n_3 - 2k_{11} n_1^2 n_5] \Delta t, \tag{10}$$

$$\Delta n_2 = [-k_{12} n_1 n_2 n_5 + 2k_{13} n_1 n_3 + k_{11} n_1^2 n_5] \Delta t, \tag{11}$$

where $n_5 = n_2 + 0.6n_4$.

The evaluation of the change of ozone concentration (Δn_3) requires some caution. If the initial conditions are far from equilibrium the relative change of n_3 is so large that a computational instability arises for the time steps contemplated. To resolve this difficulty it was assumed that within each time step n_1 and n_2 were

constant in (6). This assumption enables (6) to be integrated to give

$$n_3' = k_{12}^* n_2 n_5 - (k_{12}^* n_2 n_5 - n_3) \exp(-k_{13} n_1 \Delta t), \tag{12}$$

where $k_{12}^* = k_{12}/k_{13}$ and $n_3' = n_3 + \Delta n_3$ is the value of n_3 after a time Δt has elapsed. Equation (10) can be written

$$\Delta n_1 = \delta_1 + \delta_2 + \delta_3, \tag{13}$$

where

$$\delta_1 = (-k_{12} n_1 n_2 n_5) \Delta t,$$

$$\delta_2 = (-k_{13} n_1 n_3) \Delta t,$$

$$\delta_3 = (-2k_{11} n_1^2 n_5) \Delta t.$$

The chemical energy released in the reactions (1) and (3), expressed as a temperature rise in a time interval Δt , is then given by

$$\frac{\Delta T_{ch}}{\Delta t} = -[6.6 \times 10^{-12} \times \delta_2 + 4.057 \times 10^{-12} \times \delta_3] / \sum m_i c_{pi}. \tag{14}$$

Furthermore, using forward time differences

$$n_1' = n_1 + \Delta n_1,$$

and

$$n_2' = n_2 + \Delta n_2.$$

It is to be noted that n_1', n_2' and n_3' are the numbers of particles of the appropriate gases after an elapsed time Δt , but due to compressive effects the volume they occupy after moving down a distance Δz is decreased. In order to repeat the above procedure and move down another Δz it is convenient to normalize the n_i' to a unit volume. This can be accomplished by dividing each concentration by V where

$$V = \frac{n' k T'}{p'}, \quad n' = \sum_{i=1}^4 n_i'. \tag{15}$$

T' is the absolute temperature corresponding to the new height.

The above process is then repeated using the new gas concentrations. Profiles of gas concentration and energy release have been computed, in this way, by iterating the procedure 500 times. The initial height is 115 km, the final height 65 km, and the time steps are chosen to correspond to 0.1 km vertical displacement. The computations were performed on an IBM 709.

As can be seen from the above discussion it is necessary to assume a temperature profile in order to apply (8) and (15). Fig. 1 shows the two temperature profiles which were used. They are composites of those given by Stroud *et al.* (1960) and represent approximate average conditions for summer and winter over Fort Churchill.

A wide range of values was chosen for the initial concentrations of O, O₂, and N₂ at 115 km to bracket

most of the estimates for the gas concentrations at that level. [See, e.g., Miller (1957), Chamberlain (1961).]

4. Results

Initial calculations were made to examine the effects of using the summer and winter temperature profiles of Fig. 1 and the two sets of rate coefficients of Table 1. Fig. 2 shows the atomic oxygen distribution using two

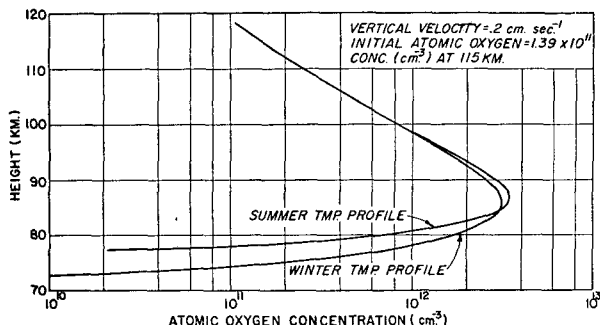


FIG. 2. Computed profiles of atomic oxygen concentration for summer and winter temperature distributions.

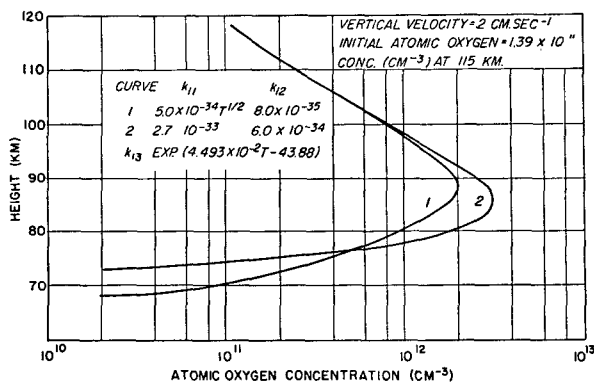


FIG. 3. Computed profiles of atomic oxygen concentration based on different sets of rate coefficients.

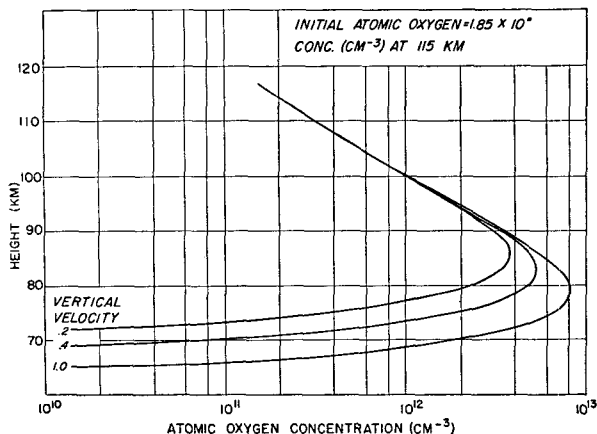


FIG. 4. Computed profiles of atomic oxygen concentration for vertical velocities of 0.2, 0.4 and 1.0 cm sec⁻¹.

different temperature profiles. The results show very little difference in the atomic oxygen concentration from 115 km to the height of maximum atomic oxygen concentration, but below this value the two curves diverge considerably. The differences in the height of maximum n_1 , and the amount and height of maximum energy release, are not great. Unless stated otherwise, in the results to follow the winter temperature profile was used.

The results obtained using the two sets of rate coefficients are shown in Fig. 3. In this case there is quite a difference between the two curves even at the atomic oxygen maximum. The recent experimental values of Reeves, Manella and Harteck (1960) were used in all subsequent calculations.

The effects of changing the vertical velocity and initial atomic oxygen concentration were also studied. Fig. 4 shows the atomic oxygen profiles obtained for different vertical velocities with fixed initial concentrations. The height of the atomic oxygen maximum is lowered as the vertical velocity is increased and the atomic oxygen concentration at the maximum is increased with the increased vertical velocity. This can be explained by noting that the reactions which destroy atomic oxygen are time dependent and thus increased subsidence will allow more atomic oxygen to reach lower levels where normal compressive effects will give an increased atomic oxygen concentration at the maximum.

As might have been expected the value chosen for the density at 115 km is the major determinant of the height of the maximum atomic oxygen concentration (which is also very nearly the height of the maximum energy release). This is illustrated in Fig. 5; curve 2 corresponds to an initial density of 2.62×10^{-11} gm cm⁻³, which is very close to the ARDC value for 115 km. It would be desirable to have accurate density measurements at heights above 100 km over polar regions since the initial density has such an influence on the height of the atomic oxygen maximum and hence the height of the maximum energy release.

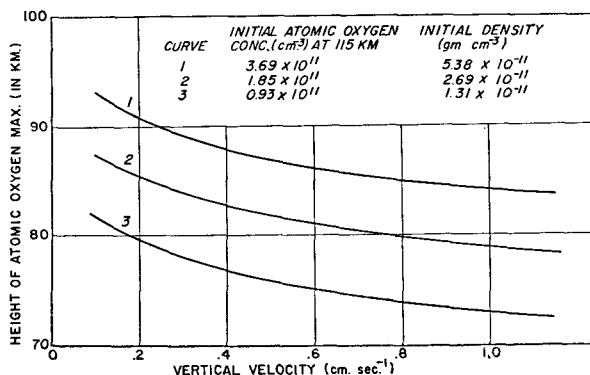


FIG. 5. Height of maximum atomic oxygen concentration as function of vertical velocity for several initial densities at 115 km.

We have chosen to represent the energy released as a rate of temperature change (as though all energy appears as kinetic molecular energy and kinetic equilibrium is established). Fig. 6 shows the computed temperature increase per day versus height for various vertical velocities and initial atomic oxygen concentrations. The greater the vertical velocity and initial atomic oxygen concentration the more energy is released. For example, with a vertical velocity of 0.5 cm sec⁻¹ and an initial atomic oxygen concentration of 2.25×10¹¹ cm⁻³ the maximum energy released corre-

sponds to a temperature rise of about 100K per day; with a vertical velocity of 0.2 cm sec⁻¹ and atomic oxygen concentrations from 0.93×10¹¹ to 1.85×10¹¹ cm⁻³ maximum heating rates from about 18 to 35K per day were obtained. These latter values appear more reasonable since they are of the order of Murgatroyd and Goody's (1958) cooling rates. The possibility that some of the energy released will appear as radiation is discussed below.

Some of the results obtained for various initial molecular concentrations are summarized in Tables 2

TABLE 2. Maximum atomic oxygen concentrations and rates of energy release as functions of vertical velocity and initial density. Initial concentrations of O, O₂, N₂ are in ratio 9:1:22.

Density (gm cm ⁻³)	Vertical velocity (cm sec ⁻¹)	Max concentration of O		Max energy release		Height (km)
		Amount (cm ⁻³)	Height (km)	Rate (K day ⁻¹)	Rate (ergs gm ⁻¹ day ⁻¹)	
5.38×10 ⁻¹¹	0.2	3.73×10 ¹²	91.0	35.8	3.76×10 ⁸	89.5
	0.3	4.58×10 ¹²	89.0	53.6	5.63×10 ⁸	88.0
	0.4	5.29×10 ¹²	88.0	71.4	7.50×10 ⁸	87.0
	0.5	5.91×10 ¹²	87.0	89.4	9.39×10 ⁸	86.0
	1.0	8.32×10 ¹²	84.5	178.6	1.88×10 ⁹	83.5
2.69×10 ⁻¹¹	0.2	3.73×10 ¹²	85.5	34.9	3.66×10 ⁸	84.5
	0.3	4.55×10 ¹²	84.0	52.3	5.49×10 ⁸	82.5
	0.4	5.22×10 ¹²	83.0	69.7	7.32×10 ⁸	81.5
	0.5	5.82×10 ¹²	82.0	87.3	9.17×10 ⁸	80.5
	1.0	8.12×10 ¹²	79.0	167.9	1.83×10 ⁹	77.5
1.35×10 ⁻¹¹	0.2	3.65×10 ¹²	80.0	33.6	3.53×10 ⁸	78.5
	0.3	4.44×10 ¹²	78.0	50.2	5.27×10 ⁸	77.0
	0.4	5.12×10 ¹²	77.0	66.9	7.02×10 ⁸	75.5
	0.5	5.74×10 ¹²	76.0	83.8	8.80×10 ⁸	74.5
	1.0	8.18×10 ¹²	73.0	167.4	1.76×10 ⁹	72.0

TABLE 3. Maximum atomic oxygen concentrations and rates of energy release as functions of vertical velocity and initial composition. Initial density at 115 km is 2.69×10⁻¹¹ gm cm⁻³.

Ratio of n ₁ :n ₂ :n ₄	Vertical velocity (cm sec ⁻¹)	Max concentration of O		Max energy release		Height (km)
		Amount (cm ⁻³)	Height (km)	Rate (K day ⁻¹)	Rate (ergs gm ⁻¹ day ⁻¹)	
225:1:450	0.2	4.25×10 ¹²	85.5	43.0	4.51×10 ⁸	84.0
	0.3	5.19×10 ¹²	83.5	63.5	6.74×10 ⁸	82.5
	0.4	5.96×10 ¹²	82.5	83.8	8.89×10 ⁸	81.5
	0.5	6.63×10 ¹²	81.5	103.7	1.10×10 ⁹	80.5
	1.0	9.25×10 ¹²	78.5	203.9	2.14×10 ⁹	77.0
9:1:22	0.2	3.73×10 ¹²	85.5	34.9	3.66×10 ⁸	84.5
	0.3	4.55×10 ¹²	84.0	52.3	5.49×10 ⁸	82.5
	0.4	5.22×10 ¹²	83.0	69.7	7.32×10 ⁸	81.5
	0.5	5.82×10 ¹²	82.0	87.3	9.17×10 ⁸	80.5
	1.0	8.12×10 ¹²	79.0	167.9	1.83×10 ⁹	77.5
3.2:1:10.2	0.2	3.09×10 ¹²	85.5	26.8	2.78×10 ⁸	84.5
	0.3	3.76×10 ¹²	84.0	39.7	4.12×10 ⁸	83.0
	0.4	4.32×10 ¹²	83.0	52.4	5.44×10 ⁸	82.0
	0.5	4.81×10 ¹²	82.0	64.8	6.73×10 ⁸	81.0
	1.0	6.71×10 ¹²	79.5	126.8	1.30×10 ⁹	78.0
1.5:1:6.6	0.2	2.35×10 ¹²	85.5	18.1	1.88×10 ⁸	84.5
	0.3	2.86×10 ¹²	84.0	26.8	2.78×10 ⁸	83.0
	0.4	3.29×10 ¹²	83.0	35.4	3.67×10 ⁸	82.0
	0.5	3.66×10 ¹²	82.0	43.8	4.55×10 ⁸	81.0
	1.0	5.11×10 ¹²	79.5	85.6	8.89×10 ⁸	78.0

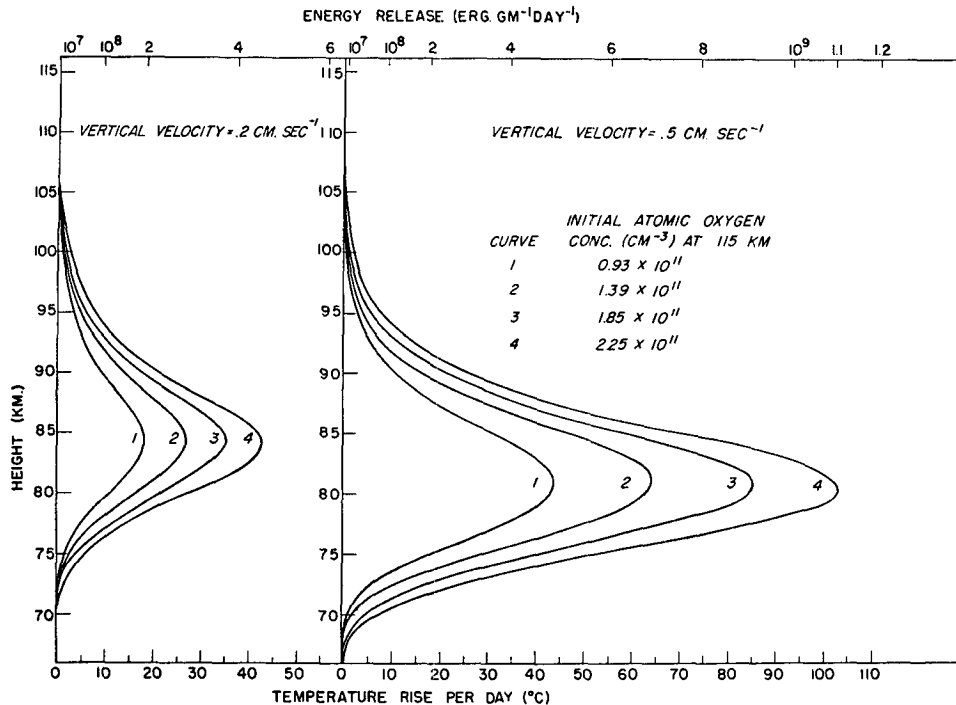


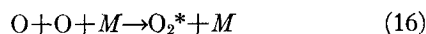
FIG. 6. Heating rates as function of height for various vertical velocities and initial concentrations of atomic oxygen.

and 3. Table 2 shows results obtained using a constant initial ratio, $n_1:n_2:n_4$, but varying the density, while Table 3 shows those using a constant density but varying the molecular composition. It is evident that by suitable choice of the relevant parameters (i.e., initial density, initial atomic oxygen concentration and vertical velocity) the high temperatures near 80 km can be quantitatively explained. For example, a vertical velocity of 0.2 cm sec⁻¹, initial density of 2.62×10^{-11} gm cm⁻³ and initial atomic oxygen concentration of 1.39×10^{11} cm⁻³ gives a maximum heating rate of 27K per day at 84 km. Fluctuations in density and vertical velocity will change both the rate of release of energy and also the height of the maximum energy release.

The energy released by adiabatic compression is generally small by comparison, amounting to about 0.9K per 0.1 km step. This corresponds to a temperature rise of 1.6K per day for a vertical velocity of 0.2 cm sec⁻¹.

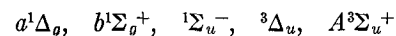
5. Radiation by molecular oxygen

The reaction



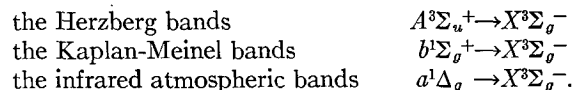
is the most important of the atomic oxygen destroying mechanisms. The question arises as to the manner in which the excited oxygen molecules lose their energy. How much energy appears as thermal energy and how much takes the form of radiation?

In reaction (16) the oxygen molecules may be excited to one of the higher energy levels



or remain in the ground state $X^3\Sigma_g^-$. A molecule excited to higher levels can drop spontaneously to the ground state with the excess energy appearing as radiation, or it may lose its excess energy as the result of a collision with another particle. Whichever is more likely depends on such factors as the Einstein coefficient for the particular state and the frequency and efficiency of collisions.

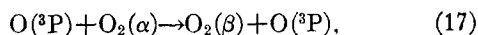
Only three band systems have so far been observed in the spectrum of the night airglow:



Chamberlain (1961) gives 5×10^8 R as the intensity for the 0-1 band of the infrared atmospheric system with about 5×10^3 R for the emission from the Herzberg system. With regard to the Kaplan-Meinel system, only the 0-1 band (8645A) is observed, its intensity being about 1.5×10^3 R; the 0-0 band (7619A) of this system, which should be much stronger, is not observed at the ground.

According to Bates (1955), direct conversion of excitation to kinetic energy by superelastic collisions between heavy particles is very inefficient. He proposes

atom-atom interchange as a more important deactivation mechanism:



where the α state has a higher energy than the β state. This process is essentially a chemical one and the rate coefficient should thus be high: Bates estimates it to be the order of $10^{-10} \text{ cm}^3 \text{ sec}^{-1}$.

The $^1\Sigma_u^-$, $^3\Delta_u$ and $A^3\Sigma_u^+$ states of the excited oxygen molecule have small binding energies so that Bates' atom-atom interchange mechanism would easily deactivate them. Indeed, no evidence of radiation corresponding to the first two have been observed. The $A^3\Sigma_u^+ \rightarrow X^3\Sigma_g^-$ transition produces the Herzberg bands, but these bands are much weaker than the infrared atmospheric and the Kaplan-Meinel bands. The 0-0 bands of the infrared atmospheric and Kaplan-Meinel systems, are not observed even though the 0-0 band of the Kaplan-Meinel system should be about 21 times stronger than the 0-1 band and the 0-0 band of the infrared atmospheric system about 10 times stronger than the 0-1 band. Molecular oxygen will absorb the 0-0 bands of both of these systems below the level of emission, but it remains to be seen where this radiation is absorbed, how much is reemitted, and how much appears as kinetic energy.

Let n_2^* be the number of excited oxygen molecules per unit volume formed by (16) and k^* the rate coefficient for (17). The Einstein coefficient of spontaneous emission for



is denoted by A ; A will, of course, depend on the band system under consideration. Thus the rate equation

referring to the deactivation of excited molecular oxygen may be written

$$\frac{dn_2^*}{dt} = -An_2^* - k^*n_2^*n_1, \quad (19)$$

The ratio of molecules which are deactivated by atom-atom interchange to the total number being deactivated is given by

$$r = \frac{k^*n_2^*n_1}{An_2^* + k^*n_2^*n_1} = \frac{n_1}{A/k^* + n_1}. \quad (20)$$

It is apparent from (20) that A/k^* plays a most important role in determining the value of r . Values of r close to unity indicate that most of the energy of the excited molecules appears as kinetic energy, while for small values of r most of the energy will take the form of radiation. For the Kaplan-Meinel bands $A=0.18 \text{ sec}^{-1}$ (Chamberlain, 1954). Fig. 7 is a plot of r versus the atomic oxygen concentration for values of k^* ranging from 10^{-10} to $10^{-13} \text{ cm}^3 \text{ sec}^{-1}$.

The maximum concentrations of atomic oxygen, as shown in Tables 2 and 3, are in the range 3×10^{12} to $9 \times 10^{12} \text{ cm}^{-3}$. For values of k^* greater than $10^{-12} \text{ cm}^3 \text{ sec}^{-1}$, most of the energy of the excited oxygen molecules will be used to heat the region of maximum atomic oxygen concentration. Only if the efficiency of the atom-atom interchange is considerably less than postulated by Bates ($k^* \cong 10^{-13} \text{ cm}^3 \text{ sec}^{-1}$) and the atomic oxygen concentration is relatively small (less than 10^{12} cm^{-3}) will a large portion of the available energy appear at least initially as radiation. In considering the values of atomic oxygen concentration with which to enter Fig. 7, it must be borne in mind that the region

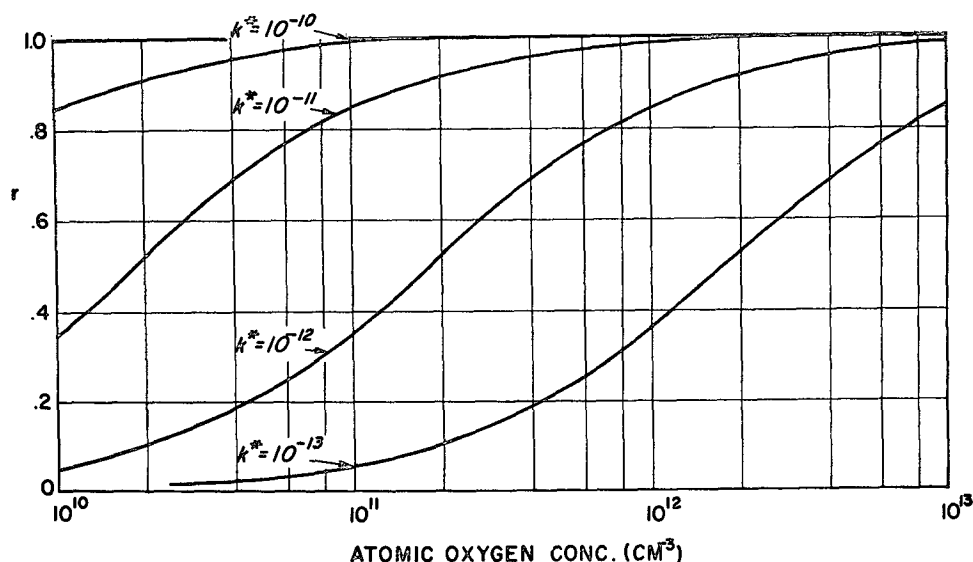


FIG. 7. Plot of r vs. n_1 for selected values of k^* .

of greatest release of chemical energy very nearly coincides with the level of maximum concentration of O. Since the concentration of O decreases rapidly both above and below the level of its maximum, so also does r . Thus the sharpness of the maximum of energy available as internal energy will be greater than suggested by the computations of the release of chemical energy. This is perhaps an explanation of the small peaks observed in most of the temperature profiles of Stroud *et al.* (1960).

It appears, then, that most of the chemical energy made available by the reactions considered will appear as heat. Only some rather indeterminate fraction of the oxygen molecules excited to either the $b^1\Sigma_g^+$ or $a^1\Delta_g$ levels will produce radiation capable of dissipating a significant portion of the energy. It is of interest to study the behavior of such radiation.

The appropriate equation for radiative transfer in a plane parallel atmosphere may be written

$$\cos\theta \frac{dI(\tau_\nu, \theta)}{d\tau_\nu} = -I(\tau_\nu, \theta) + \omega J(\tau_\nu). \quad (21)$$

Here $\tau_\nu = \int N_\nu \alpha_\nu dx$ is the optical depth corresponding to a geometric depth x (positive downward) and α_ν is the absorption coefficient per molecule. N_ν is the number of molecules per unit volume which are in the ground state and thus capable of absorbing the radiation in question (of frequency ν). The intensity of radiation in a direction which makes an angle θ with the nadir is $I(\tau_\nu, \theta)$ and, letting $\mu = \cos\theta$,

$$J(\tau) = \frac{1}{2} \int_{-1}^1 I(\tau, \mu) d\mu \quad (22)$$

is the intensity averaged over all directions. The coefficient ω is the fraction of the excited molecules which re-emit in the same wavelength. If p_0 is the probability that, if radiation occurs, it will be in the same band as that which was absorbed, then $\omega = p_0(1-r)$. For the 0-0 band of the Kaplan-Meinel system, $p_0 = 0.933$ (Fraser, Jarman and Nicholls, 1954). The absorption coefficient for the entire 0-0 band is $\alpha_0 = 1.30 \times 10^{-11} \text{ cm}^2 \text{ sec}^{-1}$ (van de Hulst, 1945) from which absorption coefficients for particular lines, α_ν , are readily obtained (cf. Chamberlain, 1954, 1961).

An approximate solution to (21) has been obtained using the Eddington approximation (semi-isotropy) for a stratified atmosphere.³ The boundary conditions chosen were

$$\begin{aligned} I^- &= I_0 & \text{at } \tau_\nu &= 0, \\ I^+ &= 0 & \text{at } \tau_\nu &= \tau_1, \end{aligned}$$

where I^+ and I^- are the upward and downward intensities, respectively. If one assumes that τ_1 is large (so

³ The authors wish to thank Mr. Richard Lindzen for suggesting this approximation.

that $e^{\tau_\nu - 2\tau_1}$ is small compared with $e^{-\tau_\nu}$, say the optical thickness at the earth's surface, then the net downward flux is given by

$$F = \frac{2\pi}{\gamma + 1} I_0 e^{-\tau_\nu [3(1-\omega)]^{1/2}}, \quad (23)$$

where

$$\gamma = \frac{1}{2} \left(\frac{3}{1-\omega} \right)^{1/2}.$$

Consider, for example, the situation when $k^* = 10^{-13} \text{ cm}^3 \text{ sec}^{-1}$ and $n_1 = 1.5 \times 10^{12} \text{ cm}^3$ so that $r \simeq 0.5$. This means that half the excited oxygen molecules lose their energy in the form of kinetic energy, with the rest of the energy appearing in the form of radiation. In this case $\omega = 0.47$ and (23) can be written as

$$F = .91\pi I_0 e^{-1.26\tau_\nu}. \quad (24)$$

If we assume that an average molecular oxygen concentration between 80 and 70 km is about $2 \times 10^{14} \text{ cm}^{-3}$ and consider one line of the band, say the line $J' = 6$ of the P-branch then $\tau_\nu \simeq 9 \times 10^{-2}$ for a path of 10 km. The exponential term in (24) then becomes $e^{-0.11} = 0.9$. This means that very little attenuation of the radiation will occur and most of any radiation emitted will escape out of the region of appreciable atomic oxygen concentration. It is obvious that as the molecular oxygen concentration increases the optical thickness will increase and so will the absorption. The absorbed energy will be re-emitted in the 0-0 band with a small fraction appearing in the 0-1 band. This is the fluorescence mechanism suggested by Chamberlain (1954). His solution of the transfer equation indicated that about 75 per cent of the observed intensity of the 0-1 emission could arise in this way and would originate primarily near 50 km, where the optical thickness of the molecular oxygen becomes substantial. Since Chamberlain considered only radiational deactivation and not Bates' suggestion of deactivation by an atom-atom interchange, the intensity of this emission may have to be adjusted and the level of its origin will be somewhat higher than 50 km. Nevertheless, the theoretical level of emission of the 0-1 radiation will still not be in agreement with the observational evidence. The rotational structure of this band indicates a temperature corresponding to an origin near 85 km (Meinel, 1950), and the rocket-borne photometer measurements discussed by Packer (1961) also indicate that the maximum emission occurs well above 50 km.

Similar discussions and conclusions can be applied in the case of the infrared atmospheric system. For the 0-0 band of this system the Einstein coefficient of spontaneous emission is about $1.9 \times 10^{-4} \text{ sec}^{-1}$, which gives a radiative lifetime of the order of 1 hr. In (20) A/k^* will be much smaller than n_1 for any reasonable values of n_1 and k^* , so that $r \simeq 1$. Thus the atom-atom

interchange deactivation mechanism will be very effective and no substantial radiative loss is to be expected at the level of maximum energy release.

The Herzberg bands have a smaller intensity than the other two systems. They arise from an excited state with a small binding energy so that atom-atom interchange would again be an effective deactivating mechanism. Thus most of the energy of the excited oxygen molecules produced by reaction (16) will appear as kinetic (heat) energy at the level of maximum energy release, and probably at other levels as well. Only a small fraction of the energy released will appear as the radiation in the 0–1 bands of the Kaplan-Meinel and infrared atmospheric systems which are observed at the ground.

6. Conclusions

It may be concluded from the foregoing that the observed conditions of the polar winter mesosphere can be explained in terms of Kellogg's oxygen recombination process. Regardless of one's choice of infrared cooling rates, one can find a set of values of vertical motion and high level density and oxygen mixing ratio which will provide precisely the proper amount of energy at just the right height. To actually do this at this time, however, would be merely an academic exercise of little value. In view of our very uncertain knowledge of the densities, mixing ratios, and cooling rates above 50 km, a complete quantitative analysis is not feasible.

It is quite clear that an extensive observational program of the polar mesosphere, presumably by rocket techniques, would be most valuable, especially if the standard meteorological measurements were supplemented to include measurements of the stratospheric composition at different heights.

Further, there are implicit in the analysis carried out in the previous section some interesting potentialities for the use of airglow observations in the study of the general circulation of the mesosphere and thermosphere. This would appear to be a fruitful meeting ground for aeronomy and meteorology.

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