

Radiative and Photochemical Processes in Mesospheric Dynamics : Part I, Models for Radiative and Photochemical Processes

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ABSTRACT

The equations for the photochemistry of ozone and radiative heating in the mesosphere are, for certain regions, reduced from differential-integral equations to much simpler differential-algebraic equations which are more readily incorporated into hydrodynamic models. The simplified equations are first solved for joint radiative-photochemical equilibrium; the distributions obtained are in fair agreement with the more detailed calculations of Leovy (1964). The equations for temperature and ozone, with advection included, are linearized in terms of perturbations on the equilibrium fields, and a brief discussion of the effect of photochemistry, radiative transfer and their interaction on the thermal response to a field of motion is presented. Finally, the problem of the joint photochemical-radiative relaxation of perturbations in the absence of motion is investigated. It is found that the coupling sharply accelerates thermal relaxation above 35 km, and appreciably accelerates photochemical relaxation and decelerates thermal relaxation in a region in the neighborhood of 26 km. The coupling also leads to oscillating relaxation in the neighborhood of 30 km.

1. Introduction

The total behavior of a planetary atmosphere involves many interdependent processes. The velocity field can in principle be calculated from the equations of motion, given the differential heating; but the temperature field is also a solution of the equations, and the differential radiative heating is, in turn, a functional of the temperatures. Radiative effects are also dependent upon the chemical composition, which is itself dependent upon transport terms and upon the temperature. Finally there is a direct connection between composition and heating through latent heat and heat of reaction.

Despite these couplings, most dynamical studies have treated the hydrodynamics in isolation. In some cases this may be justified because of the time scales or space scales under consideration. For example, short period weather forecasts are usually on a time scale which is less than that of radiative processes, and over large space scales condensation has a small net effect. Thus successful numerical prediction techniques have been developed which take account neither of radiation nor of condensation (Thompson, 1961).

In the mesosphere, however, such conditions no longer obtain. The radiative time scale is of the order of two to three weeks (Murgatroyd and Goody, 1958), while photochemical time constants vary from minutes at 55 km to years at 20 km (Dütsch, 1961); such time constants are obviously significant when considering such phenomena as the "26-month" oscillation in the equatorial stratosphere (Reed and Rodgers, 1962). Also, unlike the troposphere, the stratosphere has a large

static stability, and baroclinic disturbances will therefore develop more slowly, offering more opportunity for radiative and photochemical effects to be felt. It is not, therefore, particularly surprising to find that adiabatic explanations of phenomena such as the "sudden warming" have little success (Murray, 1960).

The inclusion of radiation and photochemistry in mesospheric hydrodynamic models is, therefore, a matter of importance. Unfortunately, it is also a matter of considerable complexity. There is, to begin with, the complexity of the individual processes of photochemistry (see for example, Craig, 1950) and radiative transfer (Murgatroyd and Goody, 1958). The radiative heating of the mesosphere depends on the ozone concentration, while the ozone photochemistry is temperature-dependent. Consequently, these processes must be considered jointly (Leovy, 1964), and also, of course, in combination with the advection of ozone and heat by the fluid.

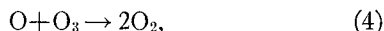
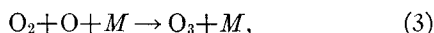
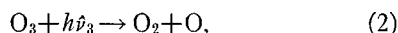
We have made no attempt to consider the problem in its full, realistic complexity. Instead, in the various parts of this paper we examine the simplest model problems which still retain important interactions. Even for these model problems to be tractable it proves essential to simplify the differential-integral equations for the radiation and photochemistry. It will be shown in Part I that situations exist under which these equations may be reduced to simple differential-algebraic equations, and these equations will be used to discuss the relaxation of perturbations away from equilibrium. Parts II, III, and IV will deal, respectively, with the vertical propagation of long period waves at the equator, the stability of baroclinic zonal flow at mid-latitudes to axially symmetric disturbances, and the stability of

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baroclinic zonal flow at mid-latitudes to baroclinic waves.

2. Photochemistry of ozone

Descriptions of the reactions involved in the photochemistry of ozone are available in the literature. Below 70 km the most important of these reactions are (Paetzold and Regener, 1961; Craig, 1950; Leovy, 1964),



where M is any third body, and $h\nu_3$ and $h\nu_2$ are quanta of radiation with frequencies in the absorption bands of ozone and molecular oxygen, respectively.

Ozone and atomic oxygen are produced at the following rates

$$r_1 = 2Q_2 + Q_3 - k_{12}n_1n_2n_m - k_{13}n_1n_3, \quad (5)$$

$$r_3 = k_{12}n_1n_2n_m - Q_3 - k_{13}n_1n_3, \quad (6)$$

where k_{12} and k_{13} are the temperature dependent coefficients for reactions (3) and (4); n_i is the number density of O_i (n_2 is assumed to be relatively unaffected by reactions); n_m is the molecular number density; and Q_2 and Q_3 are, respectively, the number of $h\nu_2$ and $h\nu_3$ quanta absorbed per unit time per unit volume by O_2 and O_3 .

If n_3/n_m , and n_1/n_m are both $\ll 1$, as is observed to be the case in the altitude range 20–70 km, then we have as our approximate equation of continuity

$$\frac{dn_m}{dt} + n_m \nabla \cdot \mathbf{v} = 0, \quad (7)$$

where \mathbf{v} is the velocity and d/dt is the substantive derivative; our continuity equations for atomic oxygen and ozone concentrations are then

$$\frac{\partial n_i}{\partial t} + \nabla \cdot (n_i \mathbf{v}) = r_i, \quad i = 1, 3, \quad (8)$$

which become, upon substituting for $\nabla \cdot \mathbf{v}$ from (7)

$$\frac{d}{dt} \left(\frac{n_i}{n_m} \right) = \frac{r_i}{n_m}, \quad i = 1, 3. \quad (9)$$

The adjustment of ozone to equilibrium with atomic oxygen proceeds at a rate associated with a time scale of from 10 seconds to 15 minutes Leovy (1964). This is greater than that rate at which total odd molecules adjust to equilibrium and that associated with advections and drives. As a result, it is approximately correct to take n_1 to be in photochemical equilibrium with n_3 ,

and we obtain

$$\left(1 + \frac{k_{13}n_3}{k_{12}n_2n_m} \right) \frac{d}{dt} \left(\frac{n_3}{n_m} \right) = 2 \frac{Q_2}{n_m} \left(1 - \frac{k_{13}n_3}{k_{12}n_2n_m} \right) - 2 \frac{Q_3}{n_m} \frac{k_{13}n_3}{k_{12}n_2n_m}. \quad (10)$$

One may use the data of Craig (1950) to show that for reasonable distributions of ozone the quantity $k_{13}n_3/k_{12}n_2n_m$ is $\ll 1$ below 70 km, varying from about 2×10^{-2} to 10^{-4} as we go from 70 to 20 km. Thus, (10) may be approximated by the following

$$\frac{d\phi}{dt} = 2q_2 \frac{n_2}{n_m} - 2q_3 \frac{k_{13}}{k_{12}n_2} \phi^2, \quad (11)$$

where $\phi = n_3/n_m$, $Q_2 = q_2n_2$ and $Q_3 = q_3n_3$. Although the approximations involved in obtaining (11) are for the most part good below 70 km, their cumulative effect probably limits its accuracy to still lower altitudes. Dutsch (1961) considers it to be accurate below 55 km.

3. Heating and cooling

In this section we will concern ourselves with the heating due to the absorption of radiation by O_2 and O_3 [Eqs. (1) and (2)]; the energy associated with the reaction heats, $D(\text{O}_2)$ and $D(\text{O}_3)$ for the dissociation of O_2 into 2O , and O_3 into O_2 and O , respectively; and the cooling due to thermal emission. The first is responsible for the radiative heating in the stratosphere. The second effect has generally been neglected in the literature,² because the net effect of reaction heats is zero in equilibrium and most calculations to date have concerned themselves with equilibrium situations. In nonequilibrium situations their net effect is finite but, as will be seen, negligible when compared to other thermal process—at least below 70 km.

Associated with reactions (1)–(4) are the following energy changes:

$$\epsilon_1 = h\nu_2 - D(\text{O}_2), \quad (12)$$

$$\epsilon_2 = h\nu_3 - D(\text{O}_3), \quad (13)$$

$$\epsilon_3 = D(\text{O}_3), \quad (14)$$

$$\epsilon_4 = D(\text{O}_2) - D(\text{O}_3), \quad (15)$$

where h = Planck's constant, and ν_2 and ν_3 are the frequencies of quanta absorbed by O_2 and O_3 .

The contributions of reactions (3) and (4) to the heating rate are equal to ϵ_3 and ϵ_4 times the respective reaction rates. For reactions (1) and (2) the situation is a little more complicated due to the fact that while the

² Leovy (1964) does, in fact, consider reaction heats in discussing the radiative-photochemical response to diurnal variations in radiation. In agreement with the results obtained here, he finds the effects small below 70 km.

rates at which reactions (1) and (2) proceed are, to a close approximation, proportional to the density of absorbable quanta, the energy of the quanta is proportional to their frequency. Thus, the heating rate per unit volume due to reactions (1)–(4) may be written

$$\mathcal{E} = Q_2 \bar{\epsilon}_1 + Q_3 \bar{\epsilon}_2 + k_{12} n_1 n_2 n_m \epsilon_3 + k_{13} n_1 n_3 \epsilon_4, \quad (16)$$

where

$$Q_i = n_i \int \alpha_i I_{0\nu} \exp(-\alpha_2 x_2 - \alpha_3 x_3) d\nu, \quad i = 2, 3; \quad (16a)$$

$$\bar{\epsilon}_1 = h\bar{\nu}_2 - D(O_2), \quad (16b)$$

$$\bar{\epsilon}_2 = h\bar{\nu}_3 - D(O_3), \quad (16c)$$

$$\bar{\nu}_i = Q_i^{-1} n_i \int \alpha_i I_{0\nu} \nu \exp(-\alpha_2 x_2 - \alpha_3 x_3) d\nu, \quad i = 2, 3, \quad (16d)$$

and where $\alpha_i(\nu)$ is the absorption cross section of O_i in cm^2 , $I_{0\nu}$ is the photon flux outside the atmosphere, and x_i is the total number of O_i molecules between the point in question and the sun. Eq. (16) may be rewritten using (5) and (6) as

$$\mathcal{E} = Q_2 h\bar{\nu}_2 + Q_3 h\bar{\nu}_3 + r_3 (D(O_3) - \frac{1}{2} D(O_2)) - \frac{1}{2} r_1 D(O_3). \quad (17)$$

In Fig. 1 we see Q_2 and Q_3 as functions of altitude using the data of Craig (1950). Note that $Q_3 \gg Q_2$. Since $h\nu_3/h\nu_2$ varies from about 0.75 at 70 km to 0.4 at 20 km, we see that $Q_3 h\nu_3 \gg Q_2 h\nu_2$ and consequently $Q_2 h\nu_2$ may be neglected in (17).

It is appropriate at this point to consider our heating processes in terms of the heat equation of hydrodynamics (Goldstein, 1960):

$$\rho c_v \frac{dT}{dt} = S + p \nabla \cdot \mathbf{v}, \quad (18)$$

where ρ = density, c_v = heat capacity at constant volume, T = temperature, p = pressure and

$$S = \mathcal{E} + C,$$

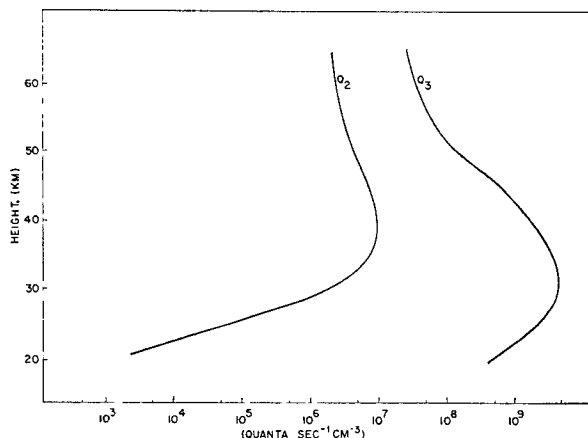


FIG. 1. Absorption of quanta by ozone and oxygen. Based on calculations of Craig (1950).

where C = is the heat exchange due to thermal radiation. We will, in this paper, neglect turbulent diffusion, though some discussion will be included in Part II.

It is shown by Jeffreys (1930) that for low Mach number flows in a gravitational field where fractional changes in density are small, the effect of the $p \nabla \cdot \mathbf{v}$ term in (18) may be taken into account by changing c_v to c_p , the heat capacity at constant pressure, and by changing

$$\frac{\partial T}{\partial z} \text{ in } \frac{dT}{dt} \text{ to } \left(\frac{\partial T}{\partial z} + \frac{g}{c_p} \right).$$

Thus (18) becomes

$$\frac{\partial T}{\partial t} + u \frac{\partial T}{\partial x} + v \frac{\partial T}{\partial y} + w \left(\frac{\partial T}{\partial z} + \frac{g}{c_p} \right) = \frac{1}{\rho c_p} S, \quad (19)$$

where x will be taken to be in the west–east direction, y in the south–north direction, and z vertically upward; u, v, w are, respectively, the velocity components in these directions.

Now let

$$\bar{\mathcal{E}} = \mathcal{E} / \rho c_p, \quad (20)$$

and let

$$\frac{Q_3 h\nu_3}{\rho c_p} = \eta \phi, \quad (21)$$

where

$$\eta \equiv \frac{q_3 n_m}{\rho c_p} h\bar{\nu}_3, \quad (22)$$

$$\bar{\mathcal{E}} \doteq \eta \phi + \frac{1}{\rho c_p} \{ r_3 [D(O_3) - \frac{1}{2} D(O_2)] - \frac{1}{2} r_1 D(O_3) \}. \quad (23)$$

As pointed out in §1, n_1 and n_3 are approximately in equilibrium with each other. Hence, from (6) we have

$$n_1 \doteq \frac{q_3}{k_{12} n_2 n_m - k_{13} n_3} n_3,$$

and

$$r_1 \doteq \frac{q_3}{k_{12} n_2 n_m - k_{13} n_3} r_3.$$

From (9) and (11) we have

$$r_3 = 2q_2 n_2 - 2q_3 \frac{k_{13} n_m}{k_{12} n_2} \phi^2.$$

As a result, the second term on the right of Eq. (23) may be rewritten

$$R = \frac{1}{\rho c_p} \left\{ D(O_3) - \frac{1}{2} D(O_2) - \frac{q_3 D(O_3)}{2 k_{12} n_2 n_m - k_{13} n_3} \right\} \times \left\{ 2q_2 n_2 - 2q_3 \frac{k_{13} n_m}{k_{12} n_2} \phi^2 \right\}.$$

Clearly, $R=0$ for equilibrium. Therefore, let us write $\phi = \phi_0 + \phi_1$ where ϕ_0 is the equilibrium value of ϕ . Then $R = \hat{R}\phi_1$, where

$$\hat{R} = -\frac{2n_m q_3 k_{13}}{\rho c_p k_{12} n_2} \times \left\{ D(O_3) - \frac{1}{2} D(O_2) - \frac{1}{2} \frac{q_3 D(O_3)}{k_{12} n_2 n_m - k_{13} n_3} \right\} (2\phi_0 + \phi_1).$$

Assuming $D(O_2) \sim h\nu_2$ and $D(O_3) \sim h\nu_3$, and using Craig's (1950) values for other quantities, we find $\hat{R}/\eta \lesssim 3 \cdot 10^{-2}$ for almost all reasonable choices of ϕ_1 and temperature below 70 km—even for the observed values of ϕ in the lower stratosphere where $\phi_1 \gg \phi_0$; at higher altitudes it is unlikely that ϕ will differ greatly from ϕ_0 . Hence, it proves possible to neglect R even in non-equilibrium situations. Thus our expression for \tilde{g} reduces to

$$\tilde{g} = \eta\phi. \quad (24)$$

There remains the cooling term, C . It would be very difficult to include this form in all its complexity, even for a grey absorbing atmosphere. Fortunately, because of the tenuous nature of the atmosphere at the levels under consideration, a very simple approximation is available. Much of the cooling is caused by direct escape of photons to space, and is directly proportional to the Planck function. Murgatroyd and Goody (1958) demonstrate the validity of this approximation for carbon dioxide (the 15μ band) and use it to estimate the cooling caused by the 9.6μ band of ozone. The possibility of some cooling by water vapor cannot be overlooked in the light of recent results for the lower mesosphere, but we still expect the 15μ carbon dioxide band to be the primary source of mesospheric cooling.

Writing

$$C \doteq aT - b, \quad (25)$$

we may estimate a and b from Murgatroyd and Goody's work on carbon dioxide, and we find as a best fit to widely scattered data:

below 40 km,

$$\begin{aligned} a &\doteq 5 \times 10^{-7} \text{ sec}^{-1}, \\ b &= 9 \times 10^{-5} \text{ K sec}^{-1}; \end{aligned} \quad (26)$$

above 40 km,

$$\begin{aligned} a &\doteq 7 \times 10^{-7} \text{ sec}^{-1}, \\ b &= 9 \times 10^{-5} \text{ K sec}^{-1}. \end{aligned}$$

From (24), (25) and (19) we now have

$$\frac{\partial T}{\partial t} + u \frac{\partial T}{\partial x} + v \frac{\partial T}{\partial y} + w \left(\frac{\partial T}{\partial z} + \frac{g}{c_p} \right) = \eta\phi - aT + b. \quad (27)$$

The apparent simplicity of (27) is somewhat deceptive insofar as η , q_3 and a_2 are still functionals of the ozone

distribution (viz. (16) and (22)). But these features are, in certain situations, also amenable to marked simplifications.

Below 70 km, the overlap between the absorption bands of O_2 and O_3 is small as concerns its effect in the integrals for Q_i and $\bar{\nu}_i$. As a result

$$Q_i \doteq n_i \int \alpha_i I_{0,\nu} \exp(-\alpha_i x_i) d\nu, \quad i=2, 3; \quad (28a)$$

and

$$\bar{\nu}_i = Q_i^{-1} n_i \int \alpha_i I_{0,\nu} \nu \exp(-\alpha_i x_i) d\nu, \quad i=2, 3. \quad (28b)$$

Thus, since n_2/n_m is assumed constant, Q_2 may be specified as a known function of position (and time).

Next, it may be seen in Fig. 2 that above 43 km and below 33 km η and q_3 are approximately constant. Thus, if we wish to study the interactions of photochemistry and radiative transfer with hydrodynamics in these regions our problem is appreciably simplified.

Constancy of η and q_3 is associated with absorption in an optically thin atmosphere. Above 43 km absorption is by the intense Hartley bands, but below 33 km these bands are strongly absorbed and no longer contribute to q_3 . Below 33 km absorption is by the visible Chappuis bands, which remain optically thin down to ground level. They are however important because of their great width, and their position in the most intense part of the solar spectrum.

We will show, in the next section, that the approxi-

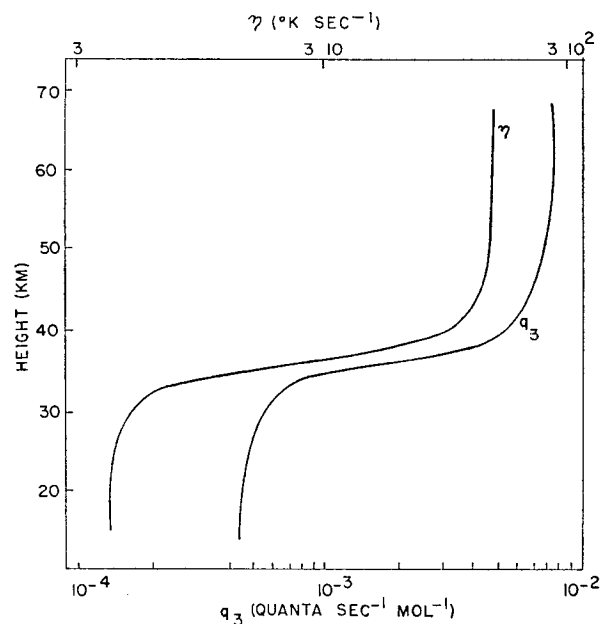


FIG. 2. η and q_3 as functions of altitude. The calculation of η and q_3 was based on Craig's (1950) theoretical ozone distribution; however, their dependence on the details of the ozone distribution is small.

mate equations we have developed are still capable of predicting equilibrium distributions of temperature and ozone in fair agreement with the more detailed calculations of others—differing little more from these other calculations than these other calculations differ from each other and from observations. It therefore appears that the physics of the photochemical and radiative processes is retained, while the equations have been sufficiently simplified to make tractable the coupled equations with hydrodynamics.

4. Radiative-photochemical equilibrium

If we set the left sides of Eqs. (11) and (27) equal to zero, we are left (within the context of the approximations involved in obtaining these equations) with the equations for photochemical and radiative equilibrium:

$$Q_2 \frac{n_2}{n_m} - q_3 \frac{k_{13}}{k_{12}} \phi^2 = 0, \tag{29}$$

$$\eta\phi - aT + b = 0. \tag{30}$$

The quantity k_{13}/k_{12} has a temperature dependence of the form

$$K \equiv \frac{k_{13}}{k_{12}} = Ee^{-D/T}, \tag{31}$$

where E and D are constants. Experimental determinations of E and D vary considerably. We have used the following values from Craig (1950):

$$E = 3.55 \times 10^{27} \text{ molecules cm}^{-3},$$

$$D = 3.3 \times 10^3 \text{ K.} \tag{32}$$

Since K is temperature dependent, the equations for photochemical and radiative equilibrium are coupled, and must be solved simultaneously.

We have computed the joint photochemical-radiative equilibrium distributions of temperature and ozone using Eqs. (20) and (30) and the results are exhibited

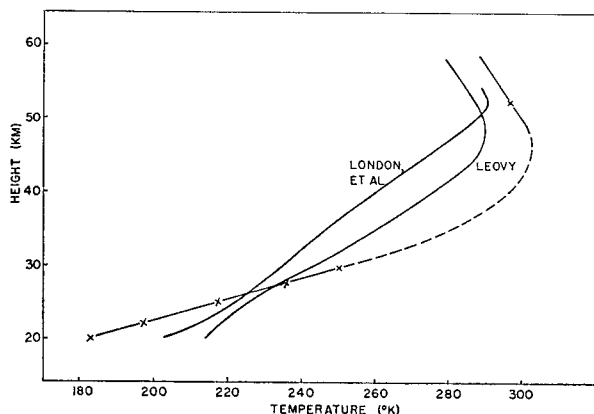


FIG. 3. Temperature vs. height at the equator (northern hemisphere spring). Crosses mark the calculated points. The slopes at 30 km and at 52.5 km have also been calculated. Also shown are Leovy's (1964) calculations based on the same ozone distribution and the observed temperatures reported by London *et al.* (unpublished report).

in Figs. 3, 4, 5, and 6. Accuracy may be assessed by a comparison with the more precise computations by Leovy who used much the same data, although his values of K and $I_{0,\nu}$ differ somewhat from Craig's.

The agreement with Leovy's data is fair, particularly above 25 km. Reasonable adjustments of a and b in Eq. (25) would give much better agreement, but in view of the many other difficulties encountered in atmospheric dynamics, particularly with non-linear terms, the agreement is considered to be adequate for the purposes of this paper.

5. Linearized equations

One of the most important difficulties remaining in Eqs. (11) and (27) is the presence of the non-linear advection terms. The solution of such non-linear equations is, in most cases, impossible without the aid of high speed computers. A common practice, therefore, is to assume that the fields of interest represent small perturbations on known mean fields. Under these conditions a non-linear term, $a \cdot b$, may be approximated by a sum of linear terms, $\bar{a} \cdot \bar{b} + \bar{a} \cdot b' + \bar{b} \cdot a'$ where \bar{a} and \bar{b} are the known mean fields, and a' and b' the perturbations; neglected is the "full" non-linear term, $a' \cdot b'$. It is, of course, true that for many motions of geophysical interest the "full" non-linear term is too large to be neglected. However, it is also true that many linearized theories yield results relevant to actual geophysical phenomena—viz. tidal theory and the theory of hydrodynamic instability. Consistent with our aim of investigating the simplest model problems wherein the interactions of radiative transfer, photochemistry and hydrodynamics are important, we will restrict ourselves, in this paper, to linearized theories.

We will, in general, take for our basic state axially symmetric, steady, radiative-photochemical equilibrium temperature and ozone fields. Our basic velocity field will be the geostrophic zonal wind consistent with the above temperature distribution; there will be no basic

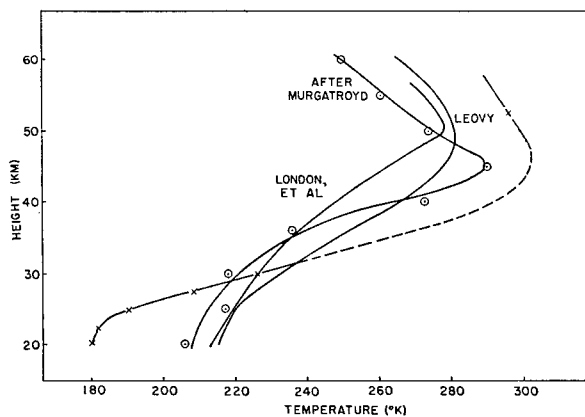


FIG. 4. Temperature vs. height for 45° latitude (spring). See caption of Fig. 3. Observations reported by Murgatroyd (1957), shown by encircled points, are also included.

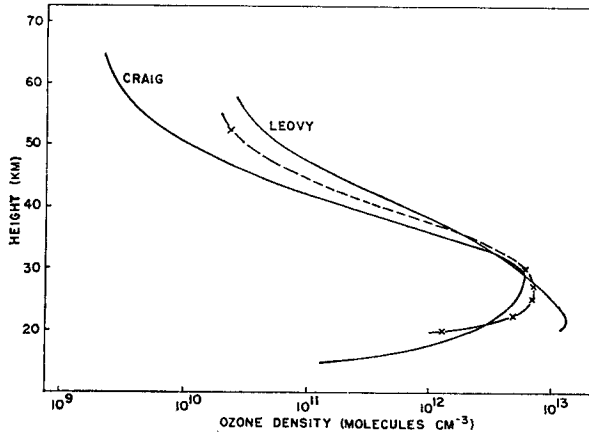


FIG. 5. Ozone density vs. height at the equator (spring). Crosses mark the calculated points. The slopes at 30 km and at 52.5 km have also been calculated. Also shown are the computations of Craig (1950) and Leovy (1964), based on the same temperature distribution.

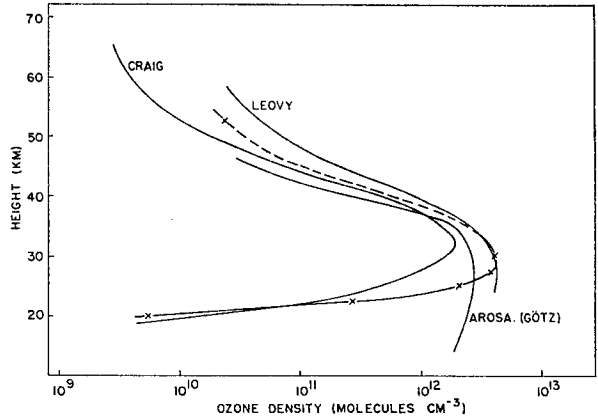


FIG. 6. Ozone density vs. height for 45° latitude (spring). See caption of Fig. 5. A distribution observed at Arosa (45N) by umkehr techniques (Götz, 1938) is also shown.

meridional circulation. Then, the x -derivatives of all mean fields are zero. Also, $v=w=0$.

Eq. (11) becomes

$$2q_2 \frac{n_2}{n_m} - 2q_3 K(\bar{T}) \frac{1}{\bar{n}} \bar{\phi}^2 = 0, \tag{33a}$$

$$\frac{\partial \phi'}{\partial t} + \bar{u} \frac{\partial \phi'}{\partial x} + v' \frac{\partial \bar{\phi}}{\partial y} + w' \frac{\partial \bar{\phi}}{\partial z} = -CT' - B\phi', \tag{33b}$$

and Eq. (27) becomes

$$\eta \bar{\phi} - a\bar{T} + b = 0, \tag{34a}$$

$$\frac{\partial T'}{\partial t} + \bar{u} \frac{\partial T'}{\partial x} + v' \frac{\partial \bar{T}}{\partial y} + w' \left(\frac{\partial \bar{T}}{\partial z} + \frac{g}{c_p} \right) = \eta \phi' - aT', \tag{34b}$$

$$\phi = \bar{\phi} + \phi'$$

$$T = \bar{T} + T',$$

$$n_2 \doteq \bar{n}_2 \left(1 - \frac{T'}{\bar{T}} \right)$$

$$K(T) \doteq K(\bar{T}) + \left(\frac{dK}{dT} \right)_{T=\bar{T}} T',$$

$$B = 4q_3 K(\bar{T}) \frac{1}{\bar{n}_2},$$

$$= 4q_3 E e^{-D/\bar{T}} \frac{1}{\bar{n}_2} \phi,$$

$$C = \frac{1}{2} B \bar{\phi} \left[\left(\frac{1}{K} \frac{dK}{dT} \right)_{T=\bar{T}} + \frac{1}{\bar{T}} \right],$$

$$= \frac{1}{2} B \frac{\bar{\phi}}{\bar{T}} \left(1 + \frac{D}{\bar{T}} \right).$$

Eqs. (33a) and (34a) describe the radiative-photochemical equilibrium fields discussed in §4; Eqs. (33b) and (34b) are the linearized equations for the perturbation fields. The presence of the term $-CT'$ and $\eta\phi'$ in (33b) and (34b) should be specially noted since they represent an important coupling between radiative and photochemical processes. If we take as given the temperature or ozone fields the relaxation of ozone or temperature is solely due to the terms $-B\phi'$ and $-aT'$, respectively. However, one cannot increase the ozone without increasing the heating rate, which in turn increases the temperature, thus decreasing the equilibrium value of the ozone to which the ozone is attempting to return. Similarly one cannot increase the temperature without causing the ozone to decrease, which in turn diminishes the heating rate. This joint problem will be treated in Section 6.

The remainder of this section will deal with some general implications of Eqs. (33b) and (34b) as regards the effect of photochemical and radiative processes in a field of motion. Let us replace the operator $[\partial/\partial t + u(\partial/\partial x)]$ by $\partial/\partial \tau$, a time derivative following the mean flow, and write

$$F_1 = - \left\{ v' \frac{\partial \bar{T}}{\partial y} + w' \left(\frac{\partial \bar{T}}{\partial z} + \frac{g}{c_p} \right) \right\},$$

$$F_2 = - \left\{ v' \frac{\partial \bar{\phi}}{\partial y} + w' \frac{\partial \bar{\phi}}{\partial z} \right\}.$$

F_1 is the advective heating, while F_2 is the advective increase of ozone. For adiabatic flow, the right hand side of (34b) is zero and

$$\frac{\partial T'}{\partial \tau} = F_1. \tag{35}$$

If the field of motion is oscillatory then, according to (35), temperature has a $\pi/2$ phase lag behind advective

heating. This phase relation is important for the dispersive and stability properties of a medium; it tells us, in part, whether motions resulting from a given temperature distribution give rise in turn to temperature changes which support, oppose or leave unaltered that motion. One of the most important effects arising from both photochemical and radiative effects is to alter this phase relation. Eliminating ϕ' between Eqs. (33b) and (34b) we get

$$\left\{ \frac{\partial^2}{\partial \tau^2} + (a+B) \frac{\partial}{\partial \tau} + (aB + \eta c) \right\} T' = \left(\frac{\partial}{\partial \tau} + B \right) F_1 + \eta F_2. \quad (36)$$

For time scales long compared with both the photochemical and radiative time scales (B^{-1} and a^{-1}) we have

$$(aB + \eta c) T' = B F_1 + \eta F_2. \quad (37)$$

Now we see the possibility that temperature will be in phase with advective heating rather than lagging behind it. Another interesting case arises when the characteristic time scale and a^{-1} are both much longer than B^{-1} . Then we have

$$\left\{ \frac{\partial}{\partial \tau} + \frac{(aB + \eta c)}{B} \right\} T' = F_1 + \frac{\eta}{B} F_2. \quad (38)$$

In such a situation $(\eta/B)F_2$ is usually small compared to F_1 , and as a result we have an uncoupled heat equation with additional Newtonian cooling, where, however, a is replaced by the larger quantity $(aB + \eta c)/B$.

Finally, we note that the relationship between a and B varies because of the strong variation of B with altitude. As will be seen in §6, B^{-1} varies from minutes at 55 km to years at 20 km.

6. Joint radiative-photochemical relaxation

Neglecting advection terms in (33b) and (34b) leads to the equations for the non-hydrodynamic relaxation of perturbations away from photochemical-radiative equilibrium:³

$$\frac{\partial \phi'}{\partial t} = -CT' - B\phi', \quad (39)$$

$$\frac{\partial T'}{\partial t} = \eta\phi' - aT'. \quad (40)$$

³ Note that thermal emission, as represented by $-aT'$, operates 24 hours a day, while the processes of absorption and photochemistry, as represented by $\eta\phi'$, $-CT'$ and $-B\phi'$ operate only during daylight hours. When dealing with time scales $\ll 12$ hours, the full values of η , B and C are used; for time scales $\gg 24$ hours their full values are multiplied by 1/2. Intermediate situations are interpolated.

This is the simplest system wherein the dynamic coupling between radiative and photochemical processes, as represented by the terms $-CT'$ and $\eta\phi'$, may be quantitatively investigated. If this coupling is omitted, solutions are obtained to (39) and (40) of the form

$$\phi' = \phi'_{t=0} e^{-Bt}, \quad (41)$$

and

$$T' = T'_{t=0} e^{-at}. \quad (42)$$

Eliminating either ϕ' or T' between (39) and (40) we obtain

$$\left[\frac{\partial^2}{\partial t^2} + (a+B) \frac{\partial}{\partial t} + (aB + \eta c) \right] \begin{Bmatrix} \phi' \\ T' \end{Bmatrix} = 0. \quad (43)$$

We now have a second order equation in time rather than a first order equation. This reflects the fact that it is now necessary to know the initial perturbation T' in order to determine the relaxation of an initial perturbation ϕ' , and vice-versa. For purposes of comparison with the solutions of the uncoupled equations we will consider two sets of initial conditions:

$$a) \quad \phi'(t=0) = \phi'_{t=0},$$

$$T'(t=0) = 0,$$

and

$$b) \quad T'(t=0) = T'_{t=0},$$

$$\phi'(t=0) = 0.$$

For case (a) the solution for the relaxation of $\phi'_{t=0}$ is

$$\phi' = \phi'_{t=0} \frac{(\sigma_2 + B)}{(\sigma_2 - \sigma_1)} \left\{ e^{\sigma_1 t} - \frac{(\sigma_1 + B)}{(\sigma_2 + B)} e^{\sigma_2 t} \right\}; \quad (44)$$

for case (b) our solution for the relaxation of $T'_{t=0}$ is

$$T' = T'_{t=0} \frac{(\sigma_2 + a)}{(\sigma_2 - \sigma_1)} \left\{ e^{\sigma_1 t} - \frac{(\sigma_1 + a)}{(\sigma_2 + a)} e^{\sigma_2 t} \right\}. \quad (45)$$

For both cases

$$\sigma_1 = \frac{1}{2} \{ -(a+B) - [(a-B)^2 - 4\eta c]^{1/2} \},$$

and

$$\sigma_2 = \frac{1}{2} \{ -(a+B) + [(a-B)^2 - 4\eta c]^{1/2} \}.$$

We see from (44) that $e^{\sigma_1 t}$ or $e^{\sigma_2 t}$ will dominate the relaxation of $\phi'_{t=0}$ according to whether σ_1 or σ_2 is closer to $-B$; similarly, from (45), the question is whether σ_1 or σ_2 is closer to $-a$. Thus, if coupling is to have a significant effect, both σ_1 and σ_2 must differ considerably from either $-a$ or $-B$.

In Fig. 7, a^{-1} , B^{-1} , $\tau_1 (= -[\text{Re}\sigma_1]^{-1})$, $\tau_2 (= -[\text{Re}\sigma_2]^{-1})$, and $\tau_{im} (= 2\pi[\text{Im}\sigma]^{-1})$, are shown as functions of altitude. (Craig's values are used for $\bar{\phi}$ and \bar{T} ; no important consequences result from this particular choice.) Several features should be noted. First, above 35 km both τ_1 and τ_2 are much less than a^{-1} and in consequence the coupling sharply accelerates cooling. Next, between

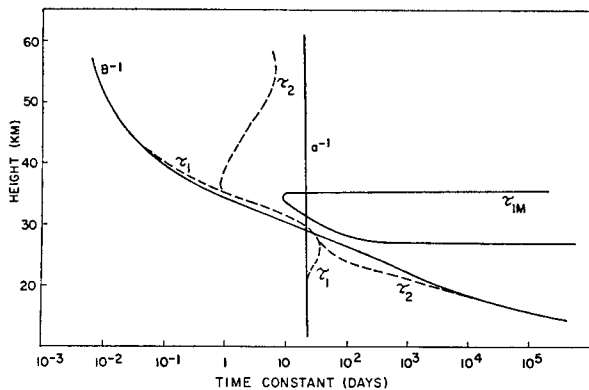


FIG. 7. Time scales for photochemical and thermal relaxation. See text for definitions. Craig's (1950) distribution of ozone was used in the calculation.

about 27 and 37 km coupling results in an oscillating decay of perturbations, and between 30 and 25 km both τ_1 and τ_2 are somewhat greater than a^{-1} and the coupling results in a reduced cooling rate. Finally, below 30 km, the coupling results in somewhat accelerated photochemical relaxation.

In subsequent parts of this paper we will return to (33b) and (34b) giving an equation for the thermal response to motion. Our hydrodynamic models, in turn, will yield equations relating the motion to the temperature field; and together they will form a closed system, which may be solved for motion, and ozone fields.

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