

On the Thermal-Diffusion Effect in the Thermosphere

Marcel Nicolet

Summary

Fifty years ago Chapman (1917) found in the course of his work on the general kinetic theory of gases the phenomenon of thermal diffusion (earlier discovered in a special case by Enskog 1911); this is the relative motion of the components of a mixture arising from a temperature gradient. There has been much experimental study of thermal diffusion since the first experimental confirmation (Chapman & Dootson 1917). In the terrestrial atmosphere where the principal constituents of air are molecular nitrogen and oxygen the thermal-diffusion flux is practically negligible compared with the diffusive flux due to the pressure gradient. Thermal diffusion is, however, important in the thermosphere where helium and hydrogen diffuse through a region with high temperature gradients.

For simplicity, consider a neutral gas of mass m_2 with another neutral constituent of mass m_1 . The formula for molecular diffusion in this case (Chapman & Cowling 1939),

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

in which $w_1 - w_2$ is the velocity of diffusion of constituent of mass m_1 and concentration n_1 relative to constituent of mass m_2 and concentration n_2 , D_{12} is the coefficient of diffusion and α_T is the thermal-diffusion factor. The properties of the gas are taken to vary in only one direction namely the Earth's radius r . Here p denotes the pressure $p = nkT$ where $n = n_1 + n_2$, k is the Boltzmann constant, and T the temperature.

If the gas is at rest

$$n_1 w_1 + n_2 w_2 = 0, \quad (2)$$

and, in this instance, equation (1) may be replaced by

$$w_1 \equiv w_D = -D_{12} \left[\frac{1}{n_1} \frac{\partial n_1}{\partial r} - \frac{1}{n} \frac{\partial n}{\partial r} + \frac{(m_2 - m_1)n_2}{nm} \frac{1}{p} \frac{\partial p}{\partial r} + \alpha_T \frac{n_2}{n} \frac{1}{T} \frac{\partial T}{\partial r} \right], \quad (3)$$

which gives the vertical diffusive speed w_D of constituent of mass m_1 relative to the general mass.

Differentiations of the gas law in the form $p = nkT$ leads to

$$\frac{dp}{p} = \frac{dn}{n} + \frac{dT}{T} = -\frac{dr}{H} \quad (4)$$

if the statical law $dp = -g n m dr$ is used. H is the scale height defined by

$$H = kT/mg, \quad (5)$$

where g denotes the gravitational acceleration.

Substitution of n and p in equation (3) from equation (4) simplifies the velocity expression to the form

$$w_D = -D_{12} \left[\frac{1}{n_1} \frac{\partial n_1}{\partial r} + \frac{m_1}{mH} + \frac{1}{T} \frac{\partial T}{\partial r} \left(1 + \alpha_T \frac{n_2}{n} \right) \right]. \quad (6)$$

It is helpful to use a scale height \mathcal{H}_1 for the constituent of mass m_1 defined by

$$\frac{1}{n_1} \frac{\partial n_1}{\partial r} + \frac{1}{T} \frac{\partial T}{\partial r} = -\frac{1}{\mathcal{H}_1}. \quad (7)$$

This particular transformation permits one to write the formula (6) for molecular diffusion as follows:

$$w_D = \frac{D_{12}}{H} \left[\frac{H}{\mathcal{H}_1} - \left(\frac{m_1}{m} + \alpha_T \frac{n_2}{n} \frac{H}{T} \frac{\partial T}{\partial r} \right) \right]. \quad (8)$$

The corresponding isothermal expression, $\partial T/\partial r = 0$, is

$$w_D = \frac{D_{12}}{H} \left[\frac{H}{\mathcal{H}_1} - \frac{m_1}{m} \right]. \quad (8a)$$

Thermal diffusion is usually unimportant since α_T the thermal diffusion factor and dT/dr are simultaneously small. But, from equation (8), it is clear that the inclusion of the term involving thermal diffusion has an appreciable effect when m_1/m is small, i.e. when the minor diffusing constituent in the thermosphere is helium or hydrogen (Mange 1955).

The vertical distribution of the constituent of mass m_1 under mixing equilibrium conditions leads to $\mathcal{H}_1 = H$, and equation (8) becomes

$$w_D (\text{mixing}) = \frac{D_{12}}{H} \left[1 - \left(\frac{m_1}{m} + \alpha_T \frac{n_2}{n} \frac{H}{T} \frac{\partial T}{\partial r} \right) \right], \quad (9)$$

and the corresponding isothermal expression is

$$w_D (\text{mixing}) = \frac{D_{12}}{H} \left[1 - \frac{m_1}{m} \right]. \quad (9a)$$

The mass ratio m_1/m plays the essential role in determining the transport, upward if $m_1 < m$ and downward if $m_1 > m$, since the term in α_T is usually small.

In diffusive equilibrium, since $w_D = 0$,

$$\frac{H}{\mathcal{H}_1} = \frac{m_1}{m} + \alpha_T \frac{n_2}{n} \frac{H}{T} \frac{\partial T}{\partial r}, \quad (10)$$

and the corresponding isothermal expression is

$$\frac{H}{\mathcal{H}_1} = \frac{m_1}{m}, \quad (10a)$$

i.e.

$$\mathcal{H}_1 = H_1 = kT/m_1 g. \quad (11)$$

If the constituent of mass m_1 and number density n_1 is a minor constituent we require that

$$n_1 + n_2 \simeq n_2 \quad (12)$$

and

$$n_1 m_1 + n_2 m_2 \simeq n_2 m_2. \quad (13)$$

With these approximations, in the present special instance, equation (8) may be replaced by

$$w_D = \frac{D_{12}}{H_2} \left[\frac{H_2}{\mathcal{H}_1} - \left(\frac{m_1}{m_2} + \alpha_T \frac{H_2}{T} \frac{\partial T}{\partial r} \right) \right], \quad (14)$$

and, for isothermal conditions,

$$w_D = \frac{D_{12}}{H_2} \left[\frac{H_2}{\mathcal{H}_1} - \frac{m_1}{m_2} \right]. \quad (15)$$

It is also of some interest to indicate another form of the vertical diffusive speed w_D of constituent of mass m_1 when $H_1 = kT/m_1g$ and its gradient $\beta_1 = dH/dr$ are used in equation (14). Clearly equation (14) becomes

$$w_D = \frac{D_{12}}{H_2} \left\{ \frac{H_2}{\mathcal{H}_1} - \frac{m_1}{m_2} [1 + \alpha_T(\beta_1 - 2H_1/r)] \right\}. \quad (16)$$

The isothermal conditions are given by

$$\beta_1 = 2H_1/r, \quad (17)$$

and equation (16) leads, therefore, to equation (15).

Another form worthy of mention is the formula using only H_1 , i.e.

$$w_D = \frac{D_{12}}{H_1} \left\{ \frac{H_1}{\mathcal{H}_1} - [1 + \alpha_T(\beta_1 - 2H_1/r)] \right\}. \quad (18)$$

The isothermal expression (15) shows that the Daltonian state (diffusive equilibrium) is reached when $H/\mathcal{H}_1 = m_1/m_2$ or $H_1/\mathcal{H}_1 = 1$, i.e. when each gas distributes itself according to its own scale height. But diffusive equilibrium conditions in a region with a temperature gradient require that, equations (16) and (18),

$$\frac{m_2 H_2}{m_1 \mathcal{H}_1} = 1 + \alpha_T(\beta_1 - 2H_1/r) = \frac{H_1}{\mathcal{H}_1} \equiv \frac{m_1^*}{m_1}. \quad (19)$$

Thus it is not sufficient, except for illustration, to consider an isothermal atmosphere passing from a state of complete mixing to the state of diffusive equilibrium. Nevertheless, considering the simplicity of the isothermal case and formula (19) we use the following form

$$w_D = \frac{D_{12}}{H_2} \left\{ \frac{H_2}{\mathcal{H}_1} - \frac{m_1^*}{m_2} \right\}, \quad (20)$$

in which m_1^* denotes an effective mass different from mass m_1 by a certain factor depending on the product of the thermal-diffusion factor and the scale height gradient due to the temperature, i.e.

$$m_1^*/m_1 = 1 + \alpha_T(\beta_1 - 2H_1/r). \quad (21)$$

In the presence of eddy diffusion equation (20) must be modified. A simple way is to add to the right-hand side another term, and the vertical speed $w_{D,\mathcal{D}}$ of constituent of mass m_1 , which is due to molecular and eddy diffusion is written

$$w_{D,\mathcal{D}} = \frac{D_{12}}{H_2} \left\{ \left[\frac{H_2}{\mathcal{H}_1} - \frac{m_1^*}{m_2} \right] + \Lambda \left[\frac{H_2}{\mathcal{H}_1} - 1 \right] \right\}, \quad (22)$$

where Λ is the ratio of the coefficients of molecular diffusion D_{12} and of eddy diffusion \mathcal{D} .

An application of the preceding formula to the lower thermosphere, where $\mathcal{H}_1 = H_2$ corresponds to perfect mixing, shows that an increase of the total helium content is impossible. At the mesopause level the time necessary to increase the

He content by a factor of two would require about 3 months. But at 100 km the time taken decreases to less than one week, and this is a clear indication that there is a possibility of a departure from mixing equilibrium conditions for helium. For example, in the 100–105 km region where the molecular diffusion coefficient D (He, N₂) is between 1 and $2 \times 10^6 \text{ cm}^2 \text{ s}^{-1}$ (Kockarts 1966), an equivalent value of the eddy diffusion coefficient \mathcal{D} leads to a scale height $\mathcal{H}(\text{He}) = 2H(\text{N}_2)$. In the 115–120 km region, the same conditions $\mathcal{H}(\text{He}) = 2H(\text{N}_2)$ are obtained with $\mathcal{D} = D_{12}(\text{He}, \text{N}_2) \simeq 2 \times 10^7 \text{ cm}^2 \text{ s}^{-1}$. Diffusive equilibrium for helium requires a value of the eddy diffusion coefficient which is ten times less than the molecular diffusion coefficient, namely $\leq 2 \times 10^6 \text{ cm}^2 \text{ s}^{-1}$ at 120 km.

Thus it is clear from the helium behaviour that the whole region from 100 km to 120 km must be considered as a transition region, where a turbopause level may be found, i.e. an equivalent level where it is possible to apply diffusive equilibrium conditions in order to determine an exact concentration of helium above the thermopause. It is not easy to obtain a precise estimate of the situation since one can only predict the presence of a diffusive state by comparing it with some other possible equilibrium state. In fact, if there is at 100 km a variation of the eddy diffusion coefficient between $10^6 \text{ cm}^2 \text{ s}^{-1}$ and $10^5 \text{ cm}^2 \text{ s}^{-1}$ the scale height of helium may increase from $\mathcal{H}(\text{He}) = 2H(\text{N}_2)$ to $\mathcal{H}(\text{He}) = 6H(\text{N}_2)$, i.e. almost to diffusive equilibrium. At and above 115 km, the same increase of He may occur if \mathcal{D} varies from $10^7 \text{ cm}^2 \text{ s}^{-1}$ to $10^6 \text{ cm}^2 \text{ s}^{-1}$. There is, therefore, a gradual departure from mixing equilibrium conditions before reaching diffusive equilibrium conditions. However, since it is not possible to predict an exact variation of the eddy diffusion coefficient which is subject to seasonal and latitudinal and perhaps daily variations, it is clear that all discussions are limited by arbitrarily fixed conditions. For a reasonable atmospheric distribution, it can be said that a change of about 5 km in the equivalent level of the turbopause corresponds to a variation of $n(\text{He})$ by a factor of 2. Thus, the structure of the upper thermosphere is very sensitive to the lower boundary conditions which are chosen in the 100–120 km region.

In equation (21) the thermal diffusion factor for He is $\alpha_T = -0.38$. Such a value is obtained (Kockarts 1963) from the Chapman–Cowling formula applied to rigid elastic spheres. The Kimura first approximation discussed by Mason (1957) leads to an almost identical value $\alpha_T = -0.35$. A value of $\alpha_T = -0.4$ has been used (Kockarts & Nicolet 1962, 1963) for atomic hydrogen diffusing in the thermosphere. Such relatively high values of α_T indicate that an important thermal-diffusion effect occurs at the turbopause levels where the scale height gradient is between 0.2 and 0.3. Thus, according to equation (21), the effective mass m_1^* for helium is reduced to $0.3m$ for $\beta = 0.3$ and $0.5m$ for $\beta = 0.2$.

The vertical diffusive speed of helium and hydrogen atoms at the 100 km level are about 1 cm s^{-1} and 2 cm s^{-1} , respectively. Detailed calculations on the helium distribution (Kockarts 1963) show that the introduction of thermal diffusion leads to an increase of atmospheric densities above the thermopause level by a factor of 1.5 to 2.5, depending on the thermopause temperatures.

This treatment is an example of the way thermal-diffusion theory can be of use in analysing aeronomic processes. These theoretical conclusions, which are not without observational support, show how thermal diffusion is of importance in aeronomy fifty years after its theoretical and experimental discovery by Chapman.

*Institut d'Aéronomie Spatiale de Belgique,
3 Avenue Circulaire,
Bruxelles 18.*

References

- Chapman, S., 1917. *Phil. Mag.*, **34**, 146.
Chapman, S. & Cowling, T. G., 1939. *The Mathematical Theory of Non-Uniform Gases*, University Press, Cambridge.
Chapman, S. & Dootson, F. W. 1917. *Phil. Mag.*, **33**, 248.
Enskog, D., 1911. *Phys. Z.*, **12**, 56 and 533.
Kockarts, G., 1963. *Bull. Acad. r. Belg. Cl. Sci.*, **49**, 1135.
Kockarts, G., 1966. *Annl. Géophys.*, **22**, 161.
Kockarts, G. & Nicolet, M., 1962. *Annl. Géophys.*, **18**, 269.
Kockarts, G. & Nicolet, M., 1963. *Annl. Géophys.*, **19**, 370.
Mason, E. A., 1957. *J. chem. Phys.*, **27**, 782.
Mange, P., 1955. *Annl. Géophys.*, **11**, 153.