Photophoretic Effects in the Stratosphere

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ABSTRACT

Photophoresis, the movement of small particles under the influence of light, may exert a significant effect on stratospheric processes. The photophoretic behavior of salt and metallic particles from 0.1 to 2.0 microns in radius under pressures of from 4 to 50 mm Hg with artificial light of known intensity was investigated. The velocities expected to be imparted to particles by sunlight at altitudes of from 22 to 40 km were then calculated from typical measured force values. It is concluded that, in the absence of wind and other effects, some particles may actually be caused to rise against the force of gravity while others are induced to fall considerably more rapidly than they would under gravity alone.

1. Introduction

Many airborne particles under reduced pressures experience a force when exposed to intense, unfocused, visible light which causes them to migrate directly toward or away from the light source. The phenomenon was termed photophoresis by its discoverer (Ehrenhaft, 1910 and 1918). In focused light beams particles move along the light rays, follow circular, elliptical, and even figure-eight orbits (Ehrenhaft, 1951; Preining, 1955), as well as bounce along the light boundary (Keng and Orr, 1963a). Explanations for all the various forms of motion have not been offered. The cause of even the simple, linear motion is open to some question, but most investigators (Balkenhol, 1954; Rohatschek, 1955) agree that it arises predominantly from a radiometer effect.

Particle motion is thus most likely due to uneven heating. When the hotter side of a particle is toward the source, as it might logically be expected to be, the more energetic bombardment from and rebound of ambient gas molecules on that side results in particle motion away from the source. This is considered to be positive photophoretic reaction. A negative photophoretic reaction, or movement toward the source of light, probably arises in the same way, and must be due to the focusing of energy in some manner through the particle onto its opposite side. Whether this latter results from a lens effect, the crystal make-up of the particle resulting in different absorption and reflection characteristics on its different faces, or anisotropic thermal conductivity within the crystal has not been established. The purpose of this communication is not to delve into the causes of photophoretic phenomena, however. Instead, it is to present measured photophoretic velocities for selected compounds and to suggest that the photophoretic force may be of some significance in stratospheric exchange (Junge, Chagnon and Manson, 1960) and other processes.

There are, first of all, several upper atmospheric observations for which unqualified explanations are lacking and for which photophoresis may provide new insight. The presence of sodium is one (Massey and Boyd, 1958). An obvious source is the sodium chloride nuclei coming from the oceans and distributed world-wide throughout the atmosphere. As shown subsequently, some salt crystals exhibit negative photophoresis (i.e., they move toward a light source) in air at pressures equivalent to 22 and 27 km altitude. Conceivably then, photophoresis induced by sunlight may play a part in causing these nuclei to rise to high altitudes where they can be decomposed by the intense incoming radiation. Another observation concerns the particle layers in the upper atmosphere at altitudes of 16 to 24 km (Chagnon and Junge, 1961). These may be maintained in part by the photophoretic effect. Noctilucent clouds at altitudes of 80 km or so and the behavior of the tails of comets may be other phenomena involving photophoresis to some degree.

2. Experimental

The main features of the experimental technique and the calculation procedures have been presented earlier (Rosen and Orr, 1964). Basically, the former involves following visually the motion of a particle in a chamber containing air at reduced pressure into which is directed vertically a beam of light. With light positive particles, i.e., those that move away from the light, the beam is directed upward. The particle falls, of course, under the influence of gravity when the light is interrupted. Thus, by regulating the timing of the periods when the light is and is not permitted to enter the chamber, the travel of

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a particle up and down can be adjusted to a repeatable path. Observation of the time to fall one path's length under gravity permits calculation of the particle radius when the particle density is known [through application of the Stoke's law equation, suitably corrected for slip because submicron sizes are involved (Davies, 1945)]. This results in the expression for particle radius "r":

$$r=\sqrt{\frac{9V_s\mu}{2Sg\rho_p}}. \tag{1}$$

Here V_s is the measured particle settling velocity (equal to L_s/t, where L_s is the length of the path the particle settled in the time t), μ is the air viscosity at the pressure and temperature inside the test chamber, g is gravity, ρ_p is the particle density. S is a slip correction factor (Knudsen and Weber, 1911) defined by the expression

$$S=1+\lambda/r[A+B\exp(-Cr/\lambda)], \tag{2}$$

where A, B, and C have values of 1.257, 0.400, and 1.10 (Davies, 1945), respectively. λ is the mean free path length of the gas molecules, given by

$$\lambda=\frac{\mu}{0.499P}\sqrt{\frac{\pi RT}{8M}} \tag{3}$$

where P is the gas pressure, R is the gas constant, T is the absolute temperature, and M is the molecular weight of the gas.

The photophoretic force is calculated from the path length, the time the light is permitted to act on a particle to cause it to move one path length upward, and the particle density by balancing this force against the sum of the gravitational and the drag forces exerted by the gas. This force balance is written

$$F_p=\frac{6\pi V_r\mu r}{S}+\frac{4\pi r^3 g\rho_p}{3}, \tag{4}$$

where F_p is the photophoretic force, V_r the rising velocity under the light's influence (equal to L_r/t, where L_r is the length of the path the particle rose in the time t), and other terms are as employed before.

Light-negative particle forces are similarly measured except that the light is now directed downward. Particle motion, as before, is upward in the light and downward in the dark. The calculations are basically identical.

Particles above a few microns in radius fall too rapidly through air at the reduced pressures for their up and down paths to be established readily. Particles with radii of less than about 0.1 μ are too difficult to observe to be critically evaluted as to photophoretic response. For these reasons, the above limits establish the range of sizes for which reliable measurements have been made.

Some few tests have utilized sunlight to establish definitely that photophoretic reactions were produced with it. Quantitative measures, however, were made with light from a high-pressure mercury arc lamp that was as intense and as nearly parallel as could be achieved with a lens system. The intensity was measured with a thermopile. In estimating from these measures the behavior of particles in sunlight, the relative intensities of the test beam (0.91 watts cm^{-2}) and sunlight (0.108 watts cm^{-2}) were taken into account. Wavelength was investigated only to the extent that photophoretic reactions still existed when a series of filters having absorptions up to about 6000 Å were interposed in the beam (Keng and Orr, 1963b). Small particles were obtained simply by mechanically grinding dried powders of the parent substances. A small quantity of the preparation was placed in the testing chamber; the chamber was sealed; and then evacuated to the desired pressure. Particles were subsequently suspended by shaking the whole chamber. After allowing a few moments for most of the particle pieces to settle, the light was admitted and a particle showing a photophoretic response was selected for examination.

Only a portion of the particles in any powder show photophoretic responses, and, generally, those revealing positive photophoresis appear to be more numerous than those showing negative action. No quantitative measure of the proportion of active particles has been made, however.

3. Results

Tables 1 and 2 present photophoretic force values for sodium chloride and zinc particles, the former being of most interest meteorologically and the latter being somewhat representative of fallout and meteoric debris. Iron and nickel particles, which would be expected to behave most like particles of meteoric origin, were found indeed to exhibit both positive and negative photophoresis. Their response, however, was often both lateral and vertical, so accurate measurements were not obtained with them. In general, the response of iron and nickel particles was as great as was the reaction of zinc particles. Discrete particle sizes in regular increments were not actually measured as the data in the tables might suggest. The results from a number of measurements were found to plot as a straight line on a log-log graph of the photophoretic force against particle radius. These plots were employed in selecting the values for the tables. Intermediate values can be obtained by interpolation; some extrapolation of the values to lesser and greater size particles may be justified.

Tables 3 and 4 give calculated values for the velocities of particles under gravity and under the influence of sunlight.

4. Conclusions

Small particles may be very significantly influenced by the action of light. In the stratosphere, some salt

Table 1. Photophoretic force values for sodium chloride particles in air at reduced pressures and exposed to light[a] from a mercury arc lamp.

Particle radius (micron)	Photophoretic force at pressures of			
	Positive		Negative	
	30 mm Hg[b] (dyne)×10^8	50 mm Hg[c] (dyne)×10^8	30 mm Hg (dyne)×10^8	50 mm Hg (dyne)×10^8
0.1	0.017	0.016	0.15	0.016
0.2	0.081	0.095	0.40	0.095
0.5	0.8	1.2	2.0	1.2
1.0	4.6	7.2	6.4	7.2
2.0	24	48	20	48

[a] Average intensity, 0.91 watts cm^{-2}.
[b] Equivalent to about 27 km altitude.
[c] Equivalent to about 22 km altitude.

Table 2. Photophoretic force values for zinc particles in air at reduced pressures and exposed to light[a] from a mercury arc lamp.

Particle radius (micron)	Photophoretic force at pressures of			
	Positive		Negative	
	4 mm Hg[b] (dyne)×10^8	10 mm Hg[c] (dyne)×10^8	4 mm Hg (dyne)×10^8	10 mm Hg (dyne)×10^8
0.1	0.008	0.013	0.028	0.0042
0.2	0.060	0.079	0.12	0.034
0.5	1.0	1.0	0.88	0.58
1.0	8.5	6.3	3.8	4.3
2.0	63	41	16	35

[a] Average intensity, 0.91 watts cm^{-2}.
[b] Equivalent to about 40 km altitude.
[c] Equivalent to about 32 km altitude.

Table 3. Calculated movement of sodium chloride crystals in the stratosphere.[a]

Particle radius (micron)	Velocity due to gravity only (cm sec^{-1})×10^2	Velocity due to photophoresis only		Net velocity[b]	
		Positive (downward) reaction (cm sec^{-1})×10^2	Negative (upward) reaction (cm sec^{-1})×10^2	Particle showing positive photophoresis (cm sec^{-1})×10^2	Particle showing negative photophoresis (cm sec^{-1})×10^2
(Pressure of 30 mm Hg)					
0.1	0.65	1.70	14.05	+ 2.35	−13.4
0.2	1.34	1.97	9.69	+ 3.31	− 8.35
0.5	3.60	3.34	8.29	+ 6.94	− 4.69
1.0	8.24	5.56	7.63	+13.8	+ 0.61
2.0	21.2	9.30	7.70	+30.5	+13.5
(Pressure of 50 mm Hg)					
0.1	0.41	0.93	0.95	+ 1.34	− 0.54
0.2	0.86	1.45	1.48	+ 2.31	− 0.62
0.5	2.46	3.34	3.42	+ 5.80	− 0.96
1.0	5.98	6.12	6.24	+12.1	− 0.26
2.0	17.0	14.30	14.78	+31.3	+ 2.22

[a] Under sunlight of intensity 0.108 watts cm^{-2}.
[b] A positive sign means that the direction of motion is the same as that induced by gravity; a negative sign indicates opposition to gravity.

Table 4. Calculated movement of zinc particles in the stratosphere.[a]

Particle radius (micron)	Velocity due to gravity only (cm sec^{-1})×10^2	Velocity due to photophoresis only		Net velocity[b]	
		Positive (downward) reaction (cm sec^{-1})×10^2	Negative (upward) reaction (cm sec^{-1})×10^2	Particle showing positive photophoresis (cm sec^{-1})×10^2	Particle showing negative photophoresis (cm sec^{-1})×10^2
(Pressure of 4 mm Hg)					
0.1	0.15	0.06	0.20	+0.21	−0.05
0.2	0.39	0.11	0.21	+0.50	+0.18
0.5	0.95	0.30	0.25	+1.25	+0.70
1.0	1.72	0.64	0.28	+2.36	+1.44
2.0	3.55	1.25	0.32	+4.80	+3.23
(Pressure of 10 mm Hg)					
0.1	0.065	0.035	0.012	+0.10	+0.053
0.2	0.14	0.06	0.05	+0.20	+0.09
0.5	0.36	0.12	0.08	+0.48	+0.28
1.0	0.74	0.19	0.15	+0.93	+0.59
2.0	1.60	0.34	0.32	+1.94	+1.28

[a] Under sunlight of intensity 0.108 watts cm^{-2}.
[b] A positive sign means that the direction of motion is the same as that induced by gravity; a negative sign indicates opposition to gravity.

nuclei may very well have upward velocities imparted to them while others are given downward velocities exceeding considerably those due to gravity. Heavy metallic particles are likely to be accelerated upward only when very small. They can be given a downward push, however, that increases their velocity of fall quite considerably.

Since particles could be observed only over a few inches of movement in the test chamber, it must be noted that it has not been definitely established that motion would continue in one direction long enough for significant shifts in altitude to occur. Some particles of all materials have occasionally been observed to change their photophoretic response from positive to negative and *vice versa*. In a few cases with zinc and sodium chloride, however, particles have also been observed to respond in one fashion for as long as two hours, giving every indication of so behaving indefinitely. More research is needed.

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