In 1861 the young chemist William Crookes discovered the new element thallium. This discovery was one of the first triumphs of the spectral analysis which had been developed shortly before by Robert Bunsen and Gustav Kirchhoff. Only in the previous year had these investigators noted the characteristic blue line of cesium, the first element so to be discovered; the second element, rubidium (from its red line), was found by them in 1861. Crookes followed the new tradition in naming his element for its telltale green line (thallos — "green twig").

During the ensuing decade Crookes spent much of his spare time performing "very laborious researches" to determine the atomic weight of thallium. The element is a heavy one, which made it difficult to obtain a precise value for its atomic weight, since the difference between the weight of a given amount of the element and of a compound formed with it and known elements would generally be relatively small. Crookes hoped to attain an accuracy sufficient to check the validity of William Prout's hypothesis of integral atomic weights. His success in this undertaking proved to be illusory, for the weight he determined—203.642, which he did not doubt was accurate enough to add to the researches of Jean Stas demonstrating the existence of nonintegral atomic weights— is farther off than he realized, the currently accepted value being 204.39.

In order to determine the absolute weights of his samples, Crookes weighed them at atmospheric pressure and in a rough vacuum. In the vacuum it happened that thermal equilibrium—which was disturbed not only by slight differences in the original temperatures of the samples but also by the process of exhaustion—required a fair amount of time (of the order of hours) to be reestablished before the weighings could be made. At this stage of the research Crookes noticed a phenomenon for which he could not account:

In particularly describing the vacuum-balance, I have one peculiarity to note in relation to the effect of heat in diminishing the weight of bodies.

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* Yeshiva University. Much of this work was done while the author was on an NSF Science Faculty Fellowship at Yale University during the academic year 1962-1963. He wishes to express his gratitude for the support of the National Science Foundation and the hospitality of the Department of the History of Science and Medicine at Yale.

1 Philosophical Magazine, 1861, Ser. 4, 21: 301-305.

That a hot body should appear to be lighter than a cold one has been con-
sidered as arising from the film of air or aqueous vapour condensed upon
or adhering to the surface of the colder body, or from the upward currents
of air caused by the expansion of the atmosphere in the vicinity of the heated
body. But neither hypothesis can be held when the variation of the force
of gravitation occurs in a vacuum as perfect as the mercurial gauge will
register, and under other conditions which I am now supplying, and which
I purpose embodying in a paper to be submitted to The Royal Society during
a subsequent session.8

A year later, in 1874, in the first of a series of long papers on "Repul-
sion Resulting from Radiation" appearing in the Philosophical Transac-
tions,4 Crookes presented his preliminary investigations of the new phe-
nomenon. At the beginning he suspected a direct influence of heat on
gravitation. He constructed a device in which one end of a balanced rod
in an evacuated chamber could be heated by a current of warm water
flowing through a tube alongside it (Fig. 1). However, the behavior of the

rod was irregular, and Crookes constructed a more sensitive device with
a smaller evacuated volume containing a pair of pith balls at the ends of
a rod suspended on a horizontal needle which crossed the evacuated tube
(Fig. 2). Holding warm water beneath one of the pith balls, he found that
it rose, but as he pumped out the air the effect became smaller, until at

\[ \text{Figure 1. Crookes' first apparatus for investigating the radiometer effect} \]
\[ \text{(from Phil. Trans., 1874, 164:506).} \]
7 mm of mercury it disappeared altogether. "The inference was almost irresistible that when the last trace of air had been removed from the tube . . . the pith ball would remain motionless." Yet he continued exhausting. As the pressure dropped further the pith ball rose again when heated from beneath. The effect at moderate pressures was attributed to convection of the air in the tube, and occurred in the same direction when the heat was applied from above, but below the neutral point in pressure the pith ball was repelled downward. This reversed motion eliminated the idea of a direct effect of heat on the weight of the body. Whereas hot bodies had the power to repel the ball, ice attracted it. The existence of a neutral pressure at which no effect was noted, and the low density of the air below this point, seemed to rule out convection as the explanation at the low pressures. Though Crookes was careful not to commit himself prematurely to hypotheses in this field, the increase in the effect the further he exhausted (for he had not yet been able to attain the pressure at which the effect is maximum), and its apparent dependence on the surface area rather than on the mass of the object affected, could be explained by "assuming that the movement is due to a repulsive action of radiation." Moreover, he
felt it possible that the new force could be the "key of some as yet unsolved problems in celestial mechanics," mentioning comets' tails and solar flares; and he even went so far as to point out that there should be a repulsion of a planet by the sun "unless we fill space with a body acting like air," in which case there would be an attraction. He concluded:

Although the force of which I have spoken is clearly not gravity solely as we know it, it is attraction developed from chemical activity, and connecting that greatest and most mysterious of all natural forces, action at a distance, with the more intelligible acts of matter. In the radiant molecular energy of solar masses may at last be found that "agent acting constantly according to certain laws" which Newton held to be the cause of gravity. 5

It seems that Crookes could not yet relinquish his initial idea of a relation between heat and gravitation, even though the apparent direct connection which had suggested this had proven to be spurious. At low pressures bodies are repelled, not lightened, by sources of heat in their neighborhood.

In the course of writing his paper Crookes searched the literature for earlier discoveries of the effect. In 1792, Reverend Bennet had reported the negative result of an experiment in which he caused light to shine onto a paper vane at the end of a wire suspended horizontally from a spider thread in a vacuum, and he was unable to "perceive any motion distinguishable from the effects of heat." 6 This had been cited as evidence in favor of the wave theory of light as opposed to the corpuscular theory by Bennet, Thomas Young, 7 and as late as 1866 by Balfour Stewart. 8 Crookes commented:

Bearing in mind the overwhelming proofs we now possess that the undulatory theory more nearly expresses the truth than does the emissive theory, it is not likely that the very different results I have succeeded in obtaining . . ., by the employment of instruments of a delicacy unattainable eighty years ago, will have any weight in modifying the accepted theories of light and heat. 9

Although he was then most inclined to attribute the effect to a direct repulsion caused by radiation, Crookes was unaware of Maxwell's prediction of light pressure, which appeared in the Treatise on Electricity and Magnetism (1873), accompanied by a proposal for an experiment of the type Crookes was performing. 10 Maxwell had suggested that if intense light were allowed to fall on a thin metal disc suspended in a vacuum, the radiation pressure might be noticed.

The only clear-cut anticipation which Crookes could find was that of Fresnel, 11 who in 1825 had discovered a repulsion between two foil vanes when sunlight was focused on them, the vanes being suspended in a con-

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5 Phil. Trans., 1874, 164:527.
6 Phil. Trans., 1792, 82:81–98.
7 Phil. Trans., 1802, 92:12–48, p. 46.
9 Phil. Trans., 1874, 164:503.
10 § 793.
tainer exhausted to a pressure of 1 or 2 mm of mercury. He concluded, as Crookes did nearly fifty years later, that the observed repulsion was not caused by the convection of heated air or the evaporation of vapor from the surfaces, for when he admitted fifteen to twenty times as much air, the effect was hardly changed and certainly not increased. Fresnel, who was thirty-seven years old in 1825, had died of tuberculosis two years later, and for half a century his observations had lain neglected.

Some of the most cogent criticisms of Crookes' interpretation of his experiments came from Osborne Reynolds, whose name is associated with the Reynolds number of fluid dynamics. A chance observation suggested to Reynolds that the new force did not act directly between the radiant source and the body repelled.12 At a soirée of the Royal Society, Crookes had exhibited the phenomenon by means of a rod carrying a pith ball at its end suspended horizontally from a fiber in a rough vacuum. When a candle was brought close, the rod oscillated, as might be expected from a force impinging on the pith ball. But the oscillations, Reynolds noted, were not damped; they increased in amplitude. This could not occur if the force were constant, or if it only depended on the distance from the flame; instead this suggested a delayed effect, such as might depend on the heating of the pith. Reynolds initially attempted an account in terms of recoil of the pith caused by evaporation of vapor from the heated surface, but as a postscript to his paper he appended the first suggestion of a kinetic-theory explanation in terms of the gas remaining in the container. Correlated to the temperature of the gas is a mean molecular speed, related as follows:

\[ \frac{1}{2}mv^2 \propto T, \]

where \( m \) is the mass of a molecule of the gas, \( v \) its (root-mean-square) speed, and \( T \) the absolute temperature of the gas. The gas molecules impinging upon the warmer surface of the vane rebound from it with an increased speed, presumed to be that corresponding to the higher temperature of this surface compared with the surroundings. The pressure on the vane is proportional to the momentum or velocity change of the molecules striking it, and one easily obtains for small differences in temperature:

\[ \frac{dp}{p} = \frac{1}{4} \frac{dT}{T}, \]

giving the excess pressure on the warmer side in terms of its excess temperature.

That this explanation of the force on the vane, which is quite popular

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13 The pressure is proportional to the change in momentum of the molecules, which for a molecule rebounding perpendicularly from a surface at temperature \( T \) is \( 2mv \), and from the surface at the slightly higher temperature \( T + dT \) is \( mv + m(v + dv) = 2mv + mdv \). Thus \( dp/p = dv/2v \). On the other hand, the proportionality of kinetic energy to \( T \) yields \( 2dv/v = dT/T \). Combining the equations gives \( dp/p = \frac{1}{2} dT/T \).
today, could not be fully correct, and that the mean free path of the gas molecules plays an essential role in the phenomenon, was first noted by P. G. Tait and James Dewar in 1875. The fullest description of the talk appears in *Nature*, and contains the following statement:

> When [the particles of the gas] impinge on the heated disc their velocity is increased, they go off with a greater velocity than those which go off from the colder side, and hence there is a recoil of the disc. When the gas is at all dense the particles get a very short way before they are met by another and sent back, and so the velocity gets a common velocity before any visible action takes place. When the gas is rare the particles may get a long way off before they meet others, and so the action becomes perceptible.

Dewar, who had presented the paper, did not have adequate opportunity to emend this rather unclear report. But it does demonstrate an awareness of the importance of the mean path between the mutual molecular collisions, as compared with the dimensions of the apparatus, in understanding the new force. The mean free path varies inversely with gas density or, equivalently, with pressure, becoming longer the more rarefied the gas.

At about this time, the radiometer in the form familiar to us, with its alternately black and light faces, was invented by Crookes while he was investigating the effects of different rays of the spectrum and of different vane surfaces (Fig. 3). In order to compare the forces on different surfaces, Crookes developed a device in which a suspended horizontal rod had pith discs fastened to both ends, one of the discs being blackened. Crookes found that a strong enough light would spin the bar completely around, the black disc receding; so he blackened alternate faces and mounted it to rotate freely, creating his "radiometer" or "light mill." The observed rotation of the vanes is the opposite of what would be expected if the effect were caused by radiation pressure rather than by the residual gas. The change in momentum of the radiation incident on the reflecting surface, and the consequent force exerted on this surface, would be twice that of the radiation incident on the blackened, absorbing surface.

Crookes, who rejected the kinetic-molecular theory explanation at this time, had a rather crude idea of radiation pressure. According to him the white surface reflected the force of the ray incident on it, while at the black

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*Figure 3. The radiometer (from Phil. Trans., 1876, 166:339).*

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15 *Phil. Trans.*, 1876, 166:338–341.
surface the force was absorbed and changed into motion, driving the black surface back. But Reynolds pointed out that if the new force were a direct action between the heat source and the body—a direct pressure of radiant heat—a contradiction of the fundamental laws of mechanics would ensue. Since hot bodies repel cold ones, while cold ones attract warmer ones—as demonstrated by Crookes' early experiments in which he used ice as well as hot objects—Newton's third law would be violated and a hot and a cold body would move off together at an increasing speed, the hot body chasing the cold. According to Reynolds, the observed rapid attainment of a terminal speed by the fly, or moving part, of the radiometer, and its equally rapid cessation of motion when the light or heat source was removed, indicated that the residual gas in the container played an important role in limiting the speed of the fly, and so might equally well be the source of the motion.

The crucial experiment distinguishing between a direct and a gas-moderated force was performed by Arthur Schuster in 1876. The radiometer case was suspended by two parallel fibers and light was directed onto the vanes. If Crookes was right and the force was a direct repulsion due to radiation, the fly would turn, and because of the small friction at the support and in the residual gas, the case should be twisted slightly in the same direction as the rotation of the fly. On the other hand, if the radiometer phenomenon was caused by an interaction between the heated side of the vane and the gas, then the gas, and hence the case, should be pushed in the opposite direction according to Newton's third law. The latter effect was much more reasonably to be expected on the basis of existing theories, and it was in fact observed. "I can still remember the excitement and the anxiety with which I waited for the verdict," wrote J. J. Thomson much later, "and the relief on hearing that the case had rotated in the opposite direction to the vanes." In his report Schuster mentioned the radiation pressure expected on the basis of Maxwell's theory, but he explained that this force would be too small to affect the experiment. He suggested that if an intense light beam were used, the method of his experiment could distinguish between internal (gas) forces and radiation pressure.

Following this experiment, Crookes came to accept a simple quantitative kinetic-theory explanation proposed by Johnstone Stoney in 1876, apparently independently of Tait and Dewar. Crookes expressed his version of Stoney's ideas in the following fashion:

When the mean length of path between successive collisions of the molecules is small compared with the dimensions of the vessel, the molecules rebounding from the heated surface, and therefore moving with an extra velocity, help to keep back the more slowly moving molecules which are ad-

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16 Ibid., p. 350.  
17 Phil. Trans., 1876, 166:725-735.  
18 Phil. Trans., 1876, 166:715-724.  
20 Phil. Mag., 1876, Ser. 5, 1:177-181, 305-313. A more detailed theory was given by R. Finkener, Annalen der Physik u. Chemie, 1876, 158:572-595.
vancing towards the heated surface; it thus happens that though the individual kicks against the heated surface are increased in strength in consequence of heating, yet the number of molecules struck is diminished in the same proportion, so that there is equilibrium on the two sides of the disk, even though the temperatures of the faces are unequal. But when the exhaustion is carried to so high a point that the molecules are sufficiently few and the mean length of path between their successive collisions is comparable with the dimensions of the vessel, the swiftly moving, rebounding molecules spend their force, in part or in whole, on the sides of the vessel, and the onward crowding, more slowly moving molecules are not kept back as before, so that the number which strike the warmer face approaches to, and in the limit equals, the number which strike the back, cooler face; and as the individual impacts are stronger on the warmer than on the cooler face, pressure is produced, causing the warmer face to retreat.21

The difficulty with this explanation, as was pointed out by Johann Zöllner 22 and by S. Tolver Preston 23 in 1877, is that at a typical pressure of 1/10 mm of mercury the mean free molecular path in air is about 6/10 mm, which is small compared to the typical distance between the vane and the neighboring wall. Furthermore, Crookes had already noted radiometric forces at a pressure of 35 mm of mercury, corresponding to a mean free path of 1/500 mm. Stoney himself had recognized that the transition layer in which equilibration occurs next to the vane could be a good deal thicker than a mean free path, but it is difficult to understand why it should be so much greater, since it is after all the molecular collisions which bring about the equilibration. Stoney's numerical estimate of this thickness was misleading, since it was based on an incorrect relation between the mean free path and the pressure, which yielded too large values for the former at low pressures. However, the theory gave a good qualitative account of the numerous experiments performed by Crookes during the decade, and neither theory nor experiment was advanced enough to make accurate quantitative tests. Crookes represented the phenomena in his later papers by imagining rays of increased molecular pressure extending perpendicularly from the warm side of the vane, causing the vane to recoil when they were long enough to reach the case.

In 1879, Reynolds gave a detailed discussion of the role of the mean free path in radiometer phenomena.24 He had come to appreciate that, as Tait and Dewar had noted, his earlier kinetic-theory explanation of the radiometer effect must be incorrect. Indeed, if viewed naively, it was open to the same sort of objection that he had raised against Crookes' early hypothesis. If we consider two infinite parallel plates, the inner surface of one being at an elevated temperature, the increased pressure on the warm surface would cause the two plates, if attached together, to accelerate perpendicularly to their planes; the one with the hot surface would lead, and the gas between would be carried along with them. This is absurd, and when the

21 Phil. Trans., 1876, 166:375–376 (added in January 1877).
distance between the surfaces is much greater than the mean free path, there should be no excess pressure over the extent of the warm surface. Nonetheless the radiometer vane moves. The solution to the apparent paradox, according to the sophisticated theoretical analyses given almost simultaneously by Reynolds and by Maxwell,\textsuperscript{25} is that an unbalanced force exists near the edge of the heated side of the vane, where the heat flow in the gas is nonuniform. Reynolds emphasized that the radiometer effect provided the first real demonstration of the dimensional (that is, heterogeneous) structure of gases; the effect would vanish in the limit of vanishing mean free path.

In the meanwhile, Crookes, with his extraordinary capacity for perceiving the significance of the unusual, had discovered a new form of the radiometer.\textsuperscript{26} He had tried using vanes of gold leaf, lampblackened on alternate sides, but one of these radiometers turned the wrong way, the blackened sides leading. On close examination, one of the vanes was found to be somewhat crumpled. From this observation Crookes developed the cup radiometer, which consists of polished metal cups mounted at the ends of arms spinning with their edges forward, in the opposite sense to an anemometer. Crookes viewed the phenomenon in terms of his lines of molecular pressure. Some of the recoiling molecules from the outside of the cup would hit the wall rather than colliding with and holding back incoming gas molecules, and there would be a net repulsion between the cup and the wall causing the cups to spin in the observed direction (Fig. 4).

![Figure 4. Cup radiometer, with lines of molecular pressure (from Phil. Trans., 1878, 169:293).](image-url)

Crookes became very much interested in charting the lines of molecular pressure in his radiometer, and in determining the thickness of the layer occupied by these lines—that is, in how far they extend from the vanes. He even hung tiny radiometer flies at various places near fixed vanes to chart the magnitude and direction of the excess pressure. These endeavors led Crookes straight into his famous researches on cathode rays. The last paper "On Repulsion Resulting from Radiation,"\textsuperscript{27} closing with paragraph 485, was read to the Royal Society on 21 November 1878; the Bakerian lecture\textsuperscript{28} inaugurating the cathode-ray work followed on 5 December. The latter is entitled "On the Illumination of Lines of Molecular Pressure, and the Trajectory of Molecules"; its first paragraph is numbered 486. Crookes was inspired by the idea that the dark space around the cathode in low-pressure electrical discharges was related to, if not identical with, the invisible gaseous transition layer of the radiometer, the layer of the lines of molecular pressure. "I have long been impressed," he wrote at the begin-

\textsuperscript{25} Phil. Trans., 1879, 170:231–256.  
\textsuperscript{26} Phil. Trans., 1878, 169:278–302.  
\textsuperscript{27} Phil. Trans., 1879, 170:87–134.  
\textsuperscript{28} Ibid., pp. 135–164.
WILLIAM CROOKES AND THE RADIOMETER

ning of the new series of papers,29 "with the idea that this dark space coating the pole was in some way related to the layer of molecular pressure causing movement in the radiometer, and the following experiments were instituted with the object of testing this hypothesis." Crookes was unable at first to succeed in using his tiny test flies to map out the motions of the rebounding charged gas molecules in the dark space, because the flies themselves became electrified and behaved erratically. So he constructed an electrical radiometer whose fly, with aluminum vanes blackened on alternate sides, just as in the ordinary radiometer, formed the cathode. The dark space of the discharge extended farther from the blackened side. When the dark space reached the wall of the casing, rotation of the fly began, the blackened side retreating. Results quite analogous to those obtained with ordinary cup radiometers were also obtained using an electrical cup radiometer. Indeed, referring retrospectively to Figure 4, which represents the hypothetical lines of increased pressure from the ordinary cup radiometer, Crookes wrote:

These figures were drawn long before the experiments just described were commenced, and it is a corroboration almost amounting to absolute proof that the theory was correct, to see how well those old drawings represent the actual lines of pressure as illuminated by the induction spark.

The experiment of the electrical radiometer justifies the theory that the induction spark actually illuminates the lines of molecular pressure caused by the electrical excitement of the negative pole. The thickness of the dark space is the measure of the length of the path between successive collisions of the molecules. The extra velocity with which the molecules rebound from the excited negative pole keeps back the more slowly-moving molecules which are advancing towards the pole. The conflict occurs at the boundary of the dark space, where the luminous margin bears witness to the energy of the discharge. When the exhaustion is sufficiently high for the length of path between successive collisions to be greater than the distance between the fly and the glass, the swiftly-moving rebounding molecules spend their energy, in part or in whole, on the side of the vessel, and a production of light accompanies this sudden arrest of velocity.30

As a result of his new researches, Crookes introduced his notion of a fourth or "ultra-gaseous" state of matter, in which the molecular mean free path is of the order of the size of the containing vessel.

The phenomena in these exhausted tubes reveal to physical science a new world—a world where matter may exist in a fourth state, where the corpuscular theory of light may be true, and where light does not always move in straight lines, but where we can never enter, and with which we must be content to observe and experiment from the outside.31

Crookes' conception of the cathode rays as ionized molecules was incorrect. In 1897, J. J. Thomson presented strong evidence that cathode rays were

29 Ibid., p. 135.
30 Ibid., p. 142.
31 Ibid., p. 164.
much less massive corpuscles (electrons), and it soon became clear that the rotation of the electrical radiometer was not a recoil effect but at least in part a thermal one. Handicapped by his lack of an advanced mathematical training, Crookes was unfortunate in his theoretical ideas, holding views in the radiometer research (radiation repulsion, then the lines of molecular pressure) which his most astute contemporaries knew to be incorrect. Nevertheless, these ideas enabled him to make a coherent picture of the new phenomena which his superb experimental intuition recognized in slight deviations from the expected. It was this latter ability in which he excelled, and it is most fitting to close with his own words on the subject:

One most significant conclusion which might be drawn, and which must surely suggest itself to every man of science who reads the history of the Radiometer, is the importance of residual phenomena. . . . If we carefully scrutinize the processes either of the laboratory or of nature, we may occasionally detect some slight anomaly, some excess or deficiency of action, some unanticipated phenomenon, which we cannot account for, and which, were received theories correct and sufficient, ought not to occur. Upon undrilled men these possibilities are simply thrown away. The untrained physicist or chemist fails to catch these suggestive glimpses.