[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

The Development of the Air-Driven Spinning Top as Transparent Ultracentrifuge

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An ultracentrifuge is any centrifuge of low or high power in which convection does not occur, and in which it is possible to measure any redistribution of the contents.[1] Up to last year, Svedberg alone had developed such convectionless ultracentrifuges. Further, the contents could be submitted to optical observation while in motion. Svedberg and his collaborators have extended their application from the largest respiratory proteins down to the smallest molecules in aqueous solution. To observe sedimentation equilibrium with the former, a very low power is obligatory since sedimentation outward must be exactly balanced by diffusion inward. For sedimentation equilibrium of ordinary molecules, powers ranging from 100,000 to 1,000,000 times gravity are essential. Still higher powers will be required for observing their sedimentation velocity.[2]

The remarkable results obtained at the Upsala laboratories in the last few years have made abundantly evident the important place the ultracentrifuge now occupies in chemical research. Unfortunately, the enormous cost of these elaborate high-powered machines has, up to now, necessarily confined them to one laboratory. The urgent need of a far less expensive type of ultracentrifuge, which would yet completely duplicate the achievements of those of Svedberg, impelled us to attempt during the past four years the task of developing the air-driven spinning top of Henriot and Huguenard[3] as a quantitative ultracentrifuge. One of us has elsewhere called attention to the almost unlimited possibilities in applying their original top to the study of systems which are inherently convectionless, such as jellies, curds and liquid crystals.

The essential features of the air-driven spinning top itself have already been sufficiently described in the literature.[3,4,5,6] The modifications that we have introduced in order to convert it into an ultracentrifuge and the auxiliary apparatus that we have used in the problem can all be discussed under seven heads: Stability, Speed, Transparent Rotor and Stator, Cell, Temperature Control, Light Source and Optical System.

Stability

Any form of vibration in an ultracentrifuge will tend to cause convection currents in the liquid under examination and make sedimentation difficult or impossible, according to the magnitude of the convection in relation to the strength of the restoring field. We found that the instability of the spinning top is of three kinds: precession, vertical vibration and horizontal wobble.

Precession is caused by an unlevel stator or by uneven propulsion (*e. g.*, a plugged air-port or nozzle), and is easily avoided by keeping the stator carefully leveled and by building into the manifold of the stator a very fine mesh strainer. For a stator with air-ports made with a number 73 drill (0.024″), we found a 100 mesh strainer works very well.

Vertical vibration has been treated fully by Girard and Chukri.[5] At high speeds the vacuum under the rotor becomes great enough to overcome the supporting effect of the exhausting air and cause the rotor momentarily to touch the stator. The phenomenon is periodic and produces a loud note of rather low frequency. It is eliminated by simply admitting a little atmospheric air to the space between the rotor and the stator through a valve connected to the apex of the cone of the stator. The method of adjustment is to open the valve rather too much at first, then, when the rotor has attained the desired speed, to close it slowly until the vibration just begins to be heard (or felt in the stator with the hand), at which point the valve is opened again very slightly. This adjustable arrangement is preferable to the uncontrolled opening lately adopted by Beams and his co-workers[4] because the admission of more air than is actually needed slightly reduces the speed and noticeably increases the horizontal wobble.

We have found it impossible to attach to the central air inlet a long tube of any description or a

(1) The term is due to T. Svedberg who has carefully discussed its definition [*Ber.*, **67A**, 117 (1934)]. It has been used loosely by others.

(2) Only one such measurement has ever been recorded: J. W. McBain and C. M. O'Sullivan, THIS JOURNAL, **57**, 780 (1935), with mercuric chloride.

(3) Henriot and Huguenard, *Compt. rend.*, **180**, 1389 (1925); *J. Phys. Radium*, **8**, 433 (1927).

(4) Beams, *Rev. Sci. Inst.*, **1**, 667 (1930); Beams and Weed, *Science*, **74**, 44 (1931); Beams, *Phys. Rev.*, **A39**, 858 (1932); Beams, Weed and Pickels, *Science*, **78**, 2024 (1933); Pickels and Beams, *ibid.*, **81**, 342 (1935); *Rev. Sci. Instr.*, **6**, 299 (1935).

(5) Girard and Chukri, *Compt. rend.*, [5] **196** (1933).

(6) Garman, *Rev. Sci. Inst.*, **4**, 450 (1933).

short tube of soft rubber without causing excessive wobble. As will be described later, we have taken the air for the central air inlet out of the guard. The connecting tube is of glass, about 15 cm. long, and attached to the inlet by the shortest possible section of rubber tubing. The adjustment is made with a screw clamp on the tubing.

Horizontal wobble is the name we have given to that form of instability in which, while the axis of rotation remains perfectly vertical, the whole rotor moves horizontally in spasmodic jerks. The phenomenon is not periodic. It has two causes. The first results from the fact that the rotor, like any spinning top, rotates not on its center of figure but on its center of gravity. Since these centers do not, in general, coincide, the periphery of the rotor necessarily revolves eccentrically. If the stator is rigidly mounted, this eccentricity becomes cumulative, causing the rotor finally to touch the stator and leap out. If the stator is flexibly mounted it is able to follow the eccentric running of the rotor and the danger of the rotor's jumping out is eliminated. However, the customary slightly flexible stator mounting still leaves another horizontal wobble of smaller amplitude and higher frequency. We found that greatly increasing the flexibility of the stator mounting and reducing the mass of the stator and manifold as much as possible reduced the wobble to about 0.02 or 0.04 mm. (as measured with a low power microscope) a few times a second. The second cause of the horizontal wobble is turbulence in the exhausting air, which becomes quite noticeable when higher pressures and greater volumes of air are used. The turbulence may be eliminated by mounting on the stator (not on the guard) three vertical and radial metal strips which we have called the "baffle strips." Nearly filling the space between the walls of the guard and the sides of the rotor, they are adjusted to clear the sides of the rotor by about 1 mm. As long as they do not extend within the "boundary layer" of air carried by the rotor, which is a little less than 1 mm. thick, their effect on the speed of the rotor is negligible. For a rotor 37 mm. in diameter running in a stator having 12 air-ports made with a number 73 drill, the effect of the baffle strips on the stability was to make the horizontal wobble wholly imperceptible under the microscope at 50 lb. air pressure, and about 0.01 mm. in amplitude at 100 lb. pressure. At still higher pressures the wobble is proportionally greater.

Speed

Measuring the Speed.—Our method of measuring the speed of the rotors is to adjust the note made by a calibrated beat-frequency oscillator to zero-beat with the note made by the running rotor. In order to prove that the note made by the running rotor is quantitatively the same as its number of revolutions per second, and also as an auxiliary method for doubtful cases, we employ the following procedure. The top surface of the rotor is painted black half way around; light from outdoors or from a direct current lamp (flash light) is reflected from the rotor into a photoelectric cell; the resulting pulsating electric current is amplified to audible proportions, the output being connected to the same head-phones to which is connected the output of the beat-frequency oscillator. The amplitudes of both notes can be adjusted to equality, making it easy to bring the two notes to coincidence to within 0.1 beat per second. If the black paint on the top of the rotor is blended out at its edges so that there is really one point of maximum blackness and one point of maximum brightness with regions of gradual change between, the current in the photoelectric cell approximates a sine wave more closely, harmonics are suppressed and it is comparatively easy to select the correct octave of the note of the beat-frequency oscillator. If the correct octave is still doubtful, a mechanical stroboscope used once will settle the doubt permanently, especially if the rotor is marked in one spot only.

Increasing the Speed.—Contrary to first expectations, one cannot achieve unlimited rotational speed with an air-driven spinning top of given diameter by indefinitely increasing the air pressure, because the velocity of air flowing through an orifice quickly approaches a limiting value. For a compressible fluid flowing through a frictionless orifice of ideal design, the relation between the downstream velocity and the upstream and downstream pressures is given by the equation[7,8,9,10,11]

$$u_2 = \sqrt{2gp_1v_1\ [1 - (p_2/p_1)^{k-1/k}]\ k/k - 1}$$

(7) Wm. Ripper, "Steam Engine Theory and Practice," Longmans, Green and Company, New York City, 1922.

(8) Walker, Lewis and McAdams, "Principles of Chemical Engineering," Chap. III, McGraw-Hill Book Co., Inc., New York City, 1927.

(9) Stodola, "Steam and Gas Turbines," McGraw-Hill Book Co., Inc., 1927.

(10) Ewald, Pöschl and Prandtl, "Physics of Solids and Fluids," Blackie and Son, London, 1930.

(11) Kearton, "Steam Turbine Theory and Design," Sir I. Pitman and Sons, 1931.

where u_2 = downstream velocity (upstream velocity is considered negligible), g = acceleration of gravity, k = ratio C_p/C_v for the gas in question, p_1 = the upstream pressure, p_2 = the downstream pressure and v_1 = the specific volume of the gas at the pressure p_1.

For dry air at 20° this equation reduces to

$$u_2 = 764 \sqrt{1 - (p_2/p_1)^{0.288}} \text{ meters per second}$$

If we take p_2 = 0.967 atm. (1 kg./sq. cm.) this equation gives the curve of Fig. 1. The curve shows that it is scarcely economical to use more than 14 kg./sq. cm. (200 lb. per sq. in.). As a matter of fact, we seldom use more than 100 lb. per sq. in. because of the increase in wobble at higher pressures.

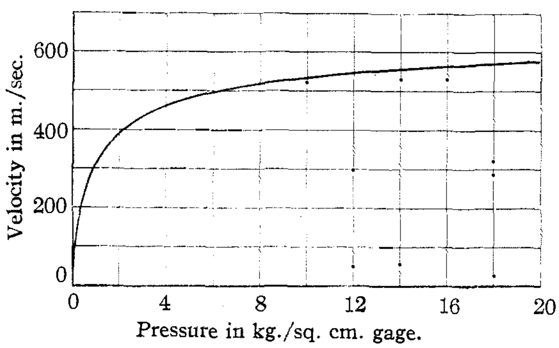

Fig. 1.—Theoretical velocity of air flowing through an ideal orifice as a function of the upstream pressure.

It will be noted from the above equations that the velocity of the air increases not only with increasing p_1 but also with decreasing p_2. We made one attempt to utilize this fact. An ordinary paper pill-box, larger in diameter than the rotor by about 4 mm., and having a hole cut in its bottom over which a glass disk was cemented to serve as a window, was inverted over a rotor while it was running and lightly fastened so that it could not turn. The box was pulled down to the top surface of the stator with great force by the escaping air until it was only a small fraction of a millimeter from it, indicating the establishment of a partial vacuum inside the box. Very low rotors ran about 8% faster inside the pill-box and with no observable instability under the microscope even at 100 lb. pressure. Higher rotors, even those only just high enough to take the lowest of our ultracentrifuge cells, refused to run at all. This, together with the fact that with all rotors there was a noticeable heating of the pill-box due to air friction, induced us temporarily to discontinue experimentation along this line.

The pressure, p_2, between the stator and the rotor can also be reduced and the velocity of the air through the air-ports correspondingly increased by increasing the ratio between the angle of the stator cone and the angle of the rotor cone. Unfortunately, this results in an increase in vertical vibration which can only be eliminated by permitting more air to enter through the central air inlet valve, which in turn increases horizontal wobble. We found the best values for these angles to be 100 to 102° for the rotor cone and 90° for the stator cone.

Since for a given pressure the velocity of the air through the air-ports is constant, it follows that the angular velocity of different rotors will be in inverse proportion to their diameters. For ease of experimentation we chose the comparatively large diameter of 37 mm.

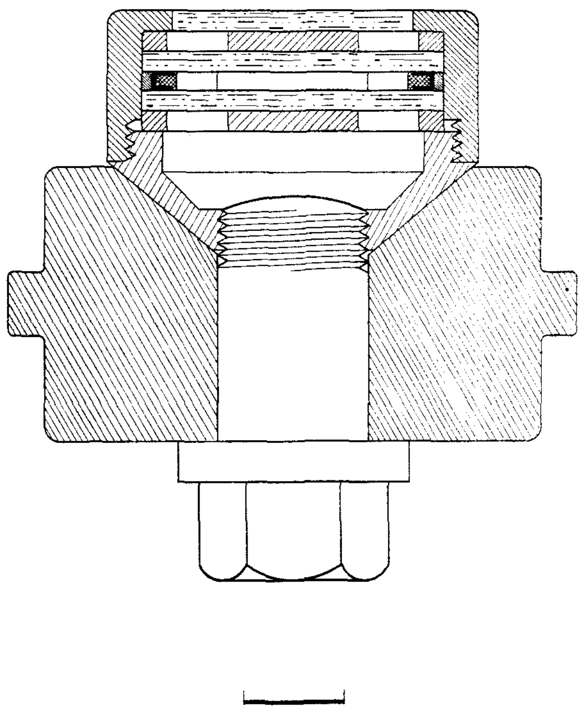

Fig. 2.—The first type of rotor described in the text (shown with the jig which is used to hold the cone of the rotor while the rotor is being assembled—a plumber's strap-wrench is used on the upper part).

Other factors in the design of the stator which affect the speed of the rotors are the total area of the cross sections of the air-ports (regulating the volume of air used), their shape and their orientation. Increasing beyond a certain point the volume of air used increases the horizontal wobble. We found that 12 air-ports 0.024″ in di-

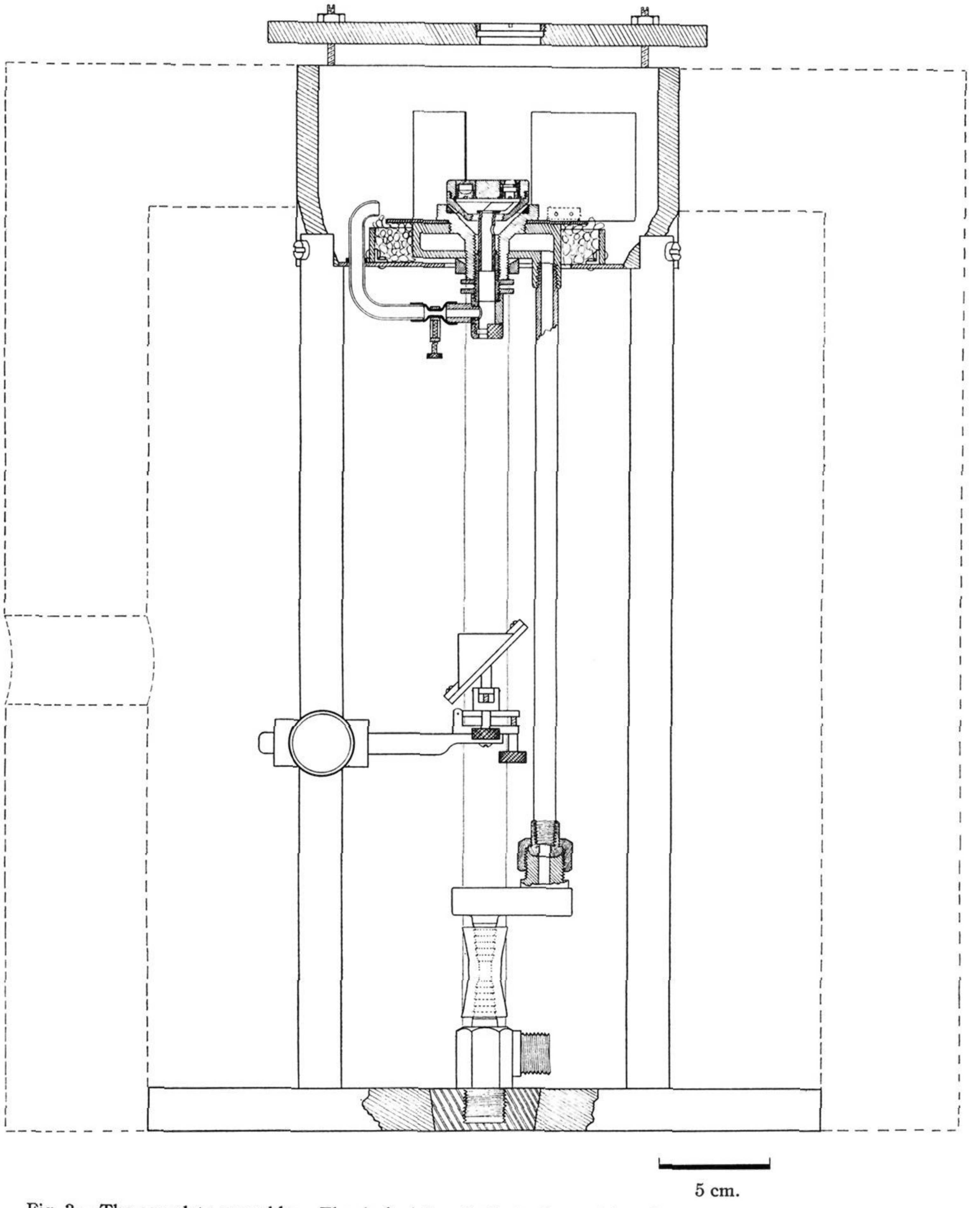

Fig. 3.—The complete assembly. The dashed lines indicate the position of the wool-filled insulating cover.

ameter (No. 73 drill) worked best for a 37-mm. stator.

Theoretically, the air-ports should be shaped like de Laval nozzles, their converging and diverging angles being calculated exactly for the actual conditions of operation. In practice we found that straight drill-hole nozzles, slightly beveled on the upstream side, gave the highest efficiency as far as speed was concerned. Assuming that the mean circle of impact on a 37-mm. rotor is 30 mm. in diameter and that the ratio of the peripheral velocity of the mean circle of impact

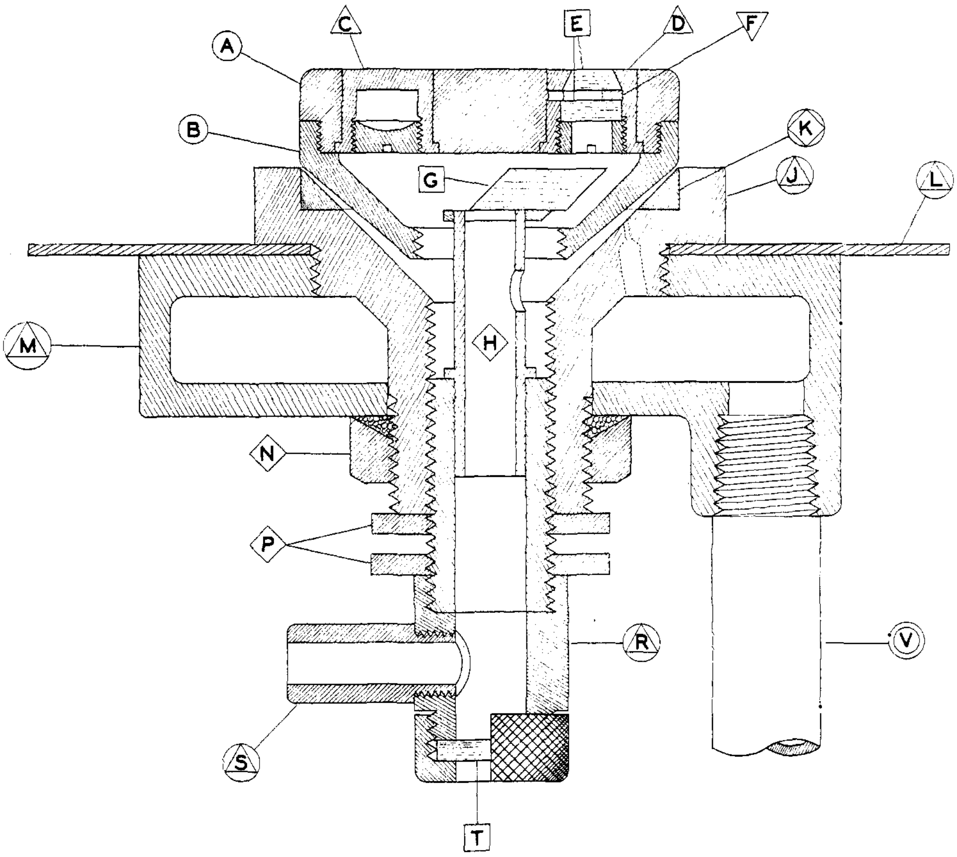

Fig. 4.—Details of rotor (second type described in text), stator, and periscope: A, cell-holder; B. rotor cone; C, dummy cell; D, cell; E, quartz disks; F, hard rubber separator, G, periscope prism; H, periscope tube; J, stator; K, bronze insert; L, disk to which baffle strips are fastened; M, manifold; N, packing nut; P, lock-nuts; R, holder for central air inlet and window; S, connection to central air inlet; T, window; V. high pressure supply tube. The symbols indicate the materials of construction: ○, Republic Steel Corporation's UMA 4, hardened and ground; △, Monel Metal; □, quartz; ▽, hard rubber; ◇, brass; ○△. duralumin (17ST); ⊙◇. bronze; ◎, aluminum.

to the velocity of the air is 1 to 2, the ratio of maximum energy transfer (this neglects the angle the air-jets make with the tangent plane), then a stator with straight drill-hole nozzles has an efficiency of 85%, whereas a stator with nozzles having a divergence of 3° beyond the throat had an efficiency of 71% and a stator with nozzles having a divergence of 6° had an efficiency of only 54%.

The optimum orientation of the air-ports was studied by Garman.[6] Their orientation can be described by two angles, the angle with the horizontal and the angle with a vertical plane through the center of the outlet of the air-port and the axis of the stator. In conformity with our experience, the first should be 35°. For the second we have adopted Garman's value of 65°.

A final and rather obvious factor influencing the speed of the rotors is their skin resistance. To reduce this to a minimum, the rotors must be made as low as possible, be free from anything like eccentric open holes or radial slots and must be highly polished. These features will be noted in the rotors to be described later.

The best material for the construction of the rotors is a high tensile strength alloy tool steel. We have finally adopted Republic Steel Corporation's UMA 4, a chrome–manganese alloy steel. If oil-quenched from 1525°F. and drawn at 600° F., it attains an ultimate tensile strength of 250,000 lb./sq. in. and a yield point of nearly 220,000 lb./sq. in. As the highest speed we have ever attained with a rotor as large as 37 mm. is 3000 r. p. s., and as the stress in a thin steel ring (the shape experiencing maximum stress under rotation) rotating at that speed is only about 130,000

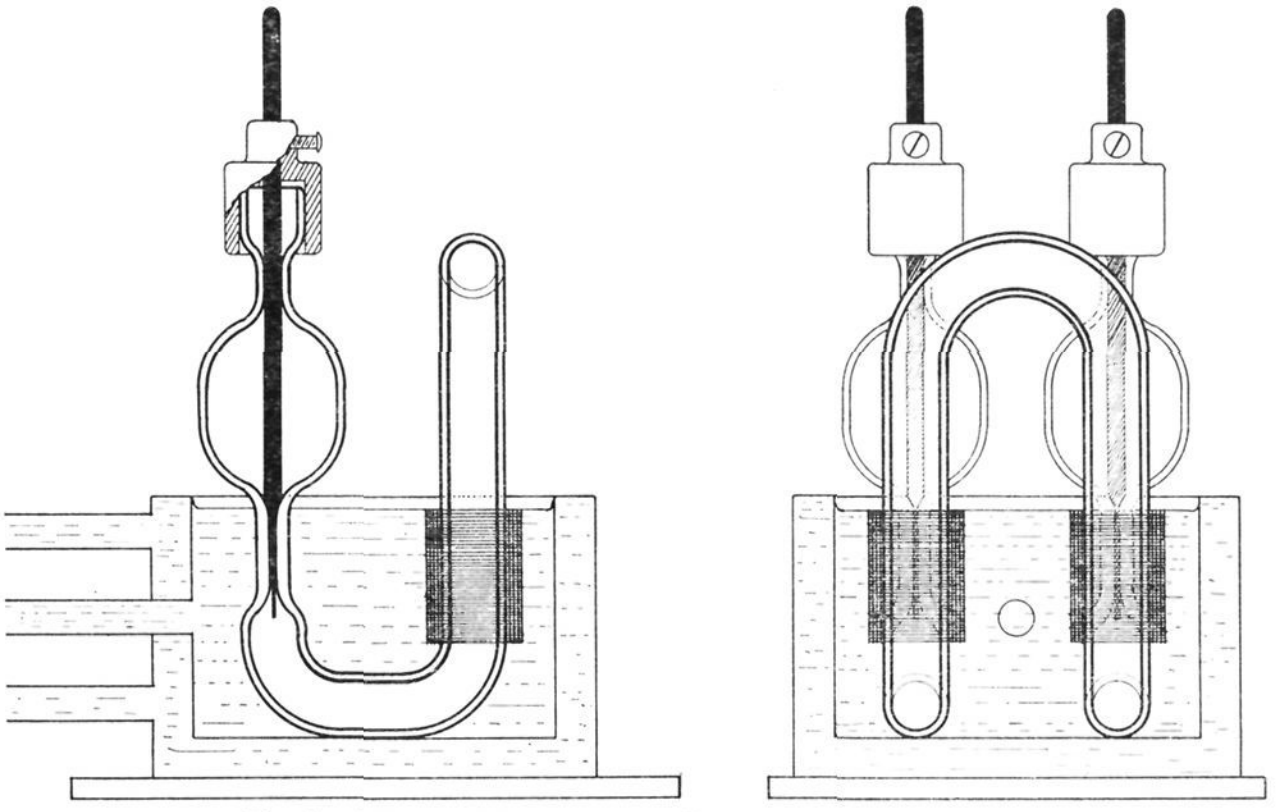

Fig. 5.—Modified Forbes quartz high pressure mercury arc.

lb./sq. in., it is better to draw the steel at 850°F. This gives a tensile strength of about 200,000 and a yield point of about 175,000 lb./sq. in. and an increased resistance to shock. Duralumin, despite the fact that it is nearly three times lighter than steel, compares unfavorably with the alloy steels. The strongest of the wrought Duralumin alloys is 17ST, with an ultimate tensile strength of 58,000 and a yield point of 35,000 lb./sq. in. Its density is 2.79 which is about 0.354 the density of steel. Thus its *effective* tensile strength in the centrifuge in terms of steel is 58,000/0.354 = 163,500 lb./sq. in.

Controlling the Speed.—For any given set of experimental conditions the speed of the rotor is a function only of the air pressure. Hence the attainment of the speed constancy so important in an ultracentrifuge is merely a matter of achieving constant air pressure.[12] Our method is to employ two tanks with a reducing valve between them. A General Electric Co. pressure control switch starts the compressor (a Rix two-stage water-cooled compressor) when the pressure in the first tank falls to 500 lb. and stops it when the pressure reaches 550 lb. The reducing valve, a Fisher Pressure Governor,[13] pilot operated, keeps the second tank at 400 lb. The accuracy of the Fisher valve varies with the load. Under the usual load, the variation of the second tank is ± 0.5 lb., the "hunting" having a period of about five minutes. Under some loads the variation may be as much as ±2 lb., or as little as ±0.05 lb. As a usual operating pressure is 100 lb., the variation of the second tank is reduced to one-fourth at the throttle valve. Furthermore, the pressure–speed curve is already rather flat at 100 lb. so that the final effect on the rotor speed is slight. By setting the beat-frequency oscillator to zero beat with the rotor's note, listening to it for some time and measuring the frequency of the beat note that gradually appears, one can measure exactly the constancy of the rotor speed. The variation is generally much less than 0.1%.

Transparent Rotor and Stator

Two types of transparent rotors were developed. Each consists of two parts, the upper, cylindrical part, containing the cell for the liquid, and the lower, conical part which is the air-turbine proper. In both types the lower part is truncated and hollow and has a 13-mm. threaded hole through the truncated bottom. When the rotor is running, a stationary periscope projects up through the hole into the hollow rotating cone. The head of the periscope is a single quartz prism[14] whose cross section at right angles to the light

(12) W. R. Hewlett of the Electrical Engineering Department at Stanford University has found definite indication that even with varying air pressure the speed may be held constant by means of synchronous impulses applied to a magnet or probably to laminations carried in the rotor.

(13) Supplied by the Fisher Governor Company, Los Angeles.

(14) We are indebted to the Fred C. Henson Company, Pasadena, Calif., for the care and precision with which crystalline quartz of best optical quality cut so as to be singly refracting has been supplied for all our optical equipment.

beam is a square 4 mm. on a side, and whose cross section parallel to the light beam is a 45° rhomboid with an over-all length of 13.5 mm. The purpose of the periscope is to offset a distance of 9.5 mm. the light beam which comes up through the center of the stator, 9.5 mm. being the distance from the center of the rotor to the average radius of the liquid column in the cell. The head of the periscope has a minimum clearance of 2 mm. inside the hollow cone of the rotor. The presence or absence of the periscope has only a very minute effect on the speed and temperature of the rotor, provided the under side of the upper half of the rotor is smooth. This is insured by inserting a disk of celluloid between the halves (or a disk of cellophane when light of $\lambda < 3000$ Å. is used). An additional advantage of this disk will be described later.

The stator extends entirely through the manifold, being made pressure tight below with a packing nut. This part of the stator is cylindrical and is threaded inside as well as outside. Into it screws a short brass tube, furnished with a lock nut, into which tube, in turn, drops the periscope tube from above with a smooth sliding fit. The periscope tube has a shoulder part way down its side which rests on the top of the other tube, and a key-way which engages a pin near the top of the other tube. The pin determines the orientation of the periscope. The orientation and the height of the periscope can be adjusted by loosening the lock nut on the other tube. The periscope tube has a hole in its side just under the quartz prism to permit the entrance of air to the space between the rotor and stator from the central air inlet valve, as described before. To the other end of the tube into which the periscope tube drops is screwed a Duralumin tube having the central air inlet valve in its side and a small quartz window at the bottom.

The hole in the bottom of the rotor is large enough to permit the passage of the head of the periscope when the periscope is lifted a little and the rotor is tipped slightly to one side.

Below the window in the bottom of the stator a right-angled reflecting quartz prism is attached to one of the legs of the guard by means of an adjustable mounting. The high pressure supply to the manifold is offset, so as to clear the reflecting prism. A high degree of flexibility in the high pressure supply is achieved by making the metal tube attached to the manifold very long, bringing it back to the center line below the reflecting prism, and attaching it to the pressure supply nipple at the base by a very short section of $^1/_4''$ high pressure hose (Linde). The hose is made very short to reduce to a negligible amount the contraction of the hose due to increase in pressure. The manifold is kept centered by the rubber sponge which surrounds it to damp out vibrations.

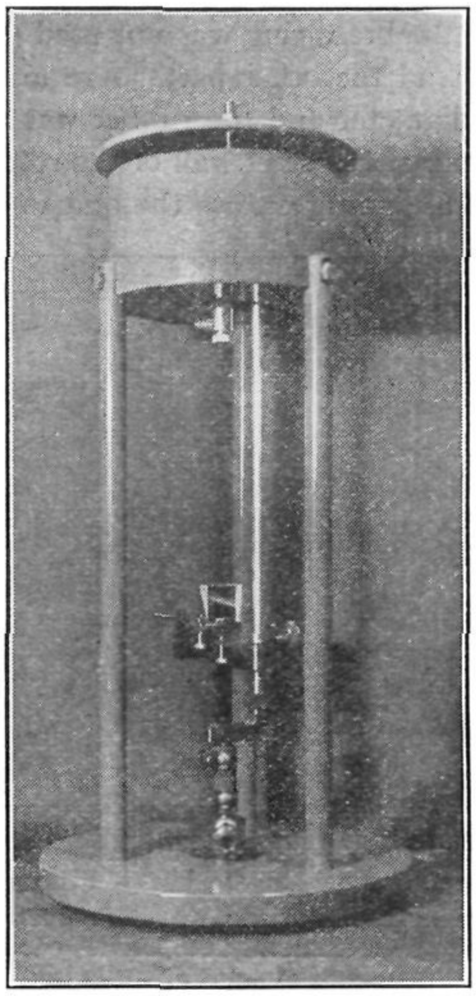

Fig. 6.—The assembly shown in Fig. 3.

Cells

In the first type of transparent rotor the cell is composed of two quartz disks 30 mm. in diameter and 2 mm. thick, fitting into a steel shell which screws on the lower part of the rotor. The liquid is confined between the disks by a special rubber seal made as follows. A 5-mm. slice of a finger of a rubber glove is stretched over the edge of a hard rubber ring 27 mm. outside diameter and 15 mm. inside diameter and about 1.1 mm. thick. The hard rubber ring has four 12° radial slots 4 mm. long cut in it from the inner circumference toward the outer. Outside the hard rubber ring with the soft rubber gasket stretched over its edge is placed an annealed brass ring 30 mm. outside diameter, 28 mm. inside diameter and 1.8 mm. thick. Several brass rings differing in thickness from 1.4 to 1.9 mm. are kept on hand to accommodate different thicknesses of rubber glove. When this assembly is placed between the two quartz disks, (about) three drops of liquid added, and the whole spun in the centrifuge, the hydrostatic pressure of the liquid expands the soft rubber against the quartz above and below and against the brass on the outside, forming a seal that only improves with increasing speed.

At first the brass ring was not used outside the seal. Instead the other parts were made a little larger in diameter and the rubber was allowed to expand against the steel wall of the rotor. Blow-outs were frequent because the quartz disks were not perfectly round, because some disks did not fit the rotor exactly, and because the steel of the rotor, being under a stress nine times greater than the stress in the quartz, expanded more than the quartz. The brass ring eliminated these troubles.

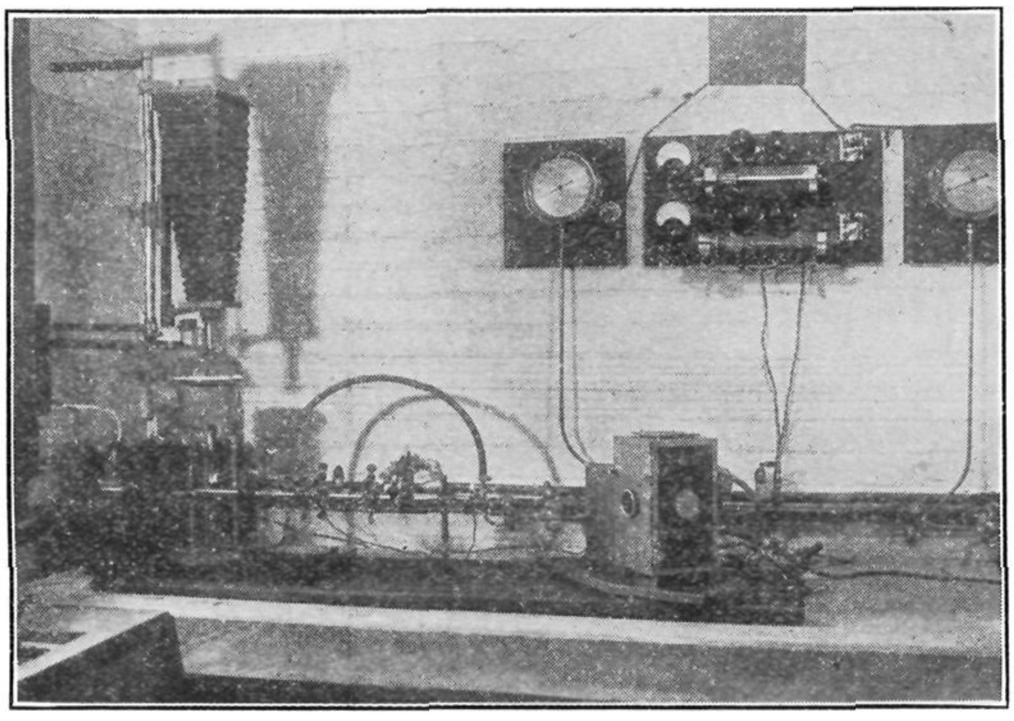

Fig. 7.—The complete centrifuge and optical system before the wool-filled cover and the thermostat for the driving air had been adopted.

To help the quartz disks bear the hydrostatic pressure of the liquid, two steel disks, 30 mm. in diameter and 2 mm. thick, and having four holes each, 6 mm. in diameter, 90° apart and 9.5 mm. from center of disk, are added, one above the upper quartz and one below the lower. The four holes in each disk are aligned with the four slots in the hard rubber ring. The lower steel disk has two pins which engage slots in the steel rotor cover and keep the assembly aligned while the rotor is being screwed together. To eliminate the air friction of the holes in the steel disk, the upper is covered with a 25-mm. disk of quartz and the lower with a 30-mm. disk of celluloid (or cellophane). The addition of these steel disks increases over 30% the speed at which the quartz disks break, giving over a 70% increase in centrifugal acceleration.

Various treatments were tried on the quartz and glass disks in an effort to increase their strength. By far the most successful was the following: besides the plane faces of the disks, their cylindrical sides were also optically polished and the edges formed by the plane faces and the cylindrical sides were slightly rounded and optically polished. Thus the disks were optically polished all over. This made an additional increase in the speed at which they broke of nearly 50%, or an increase in the acceleration of nearly 125%. Thirty-millimeter crystalline quartz disks so polished and supported against hydrostatic pressure by the two steel disks should spin 3000 r. p. s. without breaking (maximum 540,000 times gravity). Despite that fact, however, this type of cell cannot be safely used above 1500 r. p. s. No matter how carefully the quartz disks are handled, it seems impossible to avoid scratching them slightly, thus lowering their breaking speed enormously. Disks that have made many runs at 2500 r. p. s. will unexpectedly burst at 1700 r. p. s. Disk failures are costly because they generally cause the loss of the periscope also. Even at 1500 r. p. s. the factor of safety is low.

The second type of cell is somewhat similar to the cells in Svedberg's latest oil-turbine ultracentrifuges. The upper half of the rotor is a solid steel cylinder 37 mm. in diameter and 8.2 mm. high. Near the bottom it is reduced in diameter and threaded to screw into the rotor cone. The steel cylinder has two vertical holes on a diameter, each 8.6 mm. in diameter and 10 mm. from its center to the center of the cylinder. Into these are pushed from below two monel metal tubes, each of which has a flange 0.5 mm. wide which fits into a recess in the bottom of the large steel cylinder. When pushed all the way in, the tubes are flush with the upper and lower surfaces of the steel cylinder. One of the monel tubes (the dummy) is solid on the upper end and closed on the lower end with a brass screw whose weight is adjusted until the tubes balance. The other monel tube contains the cell, which is composed of seven parts: a slotted hard rubber separator, two thin soft rubber gaskets, two quartz disks, a brass washer and a hollow screw which keeps the assembly under pressure. The hard rubber separator is 6 mm. in diameter and 1 mm. thick. The 6° radial slot which forms the cell proper is 4 mm. long, cut in from the side toward the center of the rotor. The soft rubber gaskets which go between the separator and the quartz windows are cut from very thin sheet rubber to the shape and size of the separator, except that the slot must be a little larger to prevent the soft rubber from being pressed out into the slot in the hard rubber. The upper quartz disk is a truncated cone, 2 mm. thick, its upper diameter being 4 mm., its lower 6 mm. The top 2 mm. of the monel tube is tapered to fit the quartz cone so that the quartz, the monel and the steel are all quite flush on top. The lower quartz disk is a cylinder 2 mm. thick and 6 mm. in diameter. The brass washer is very thin and goes between the lower quartz disk and the hollow screw. In assembling the cell, pressure is applied to the parts by an external press. The office of the hollow screw is merely to maintain this pressure. The liquid is introduced into the cell through a small hole in the side of the monel tube opposite the end of the slot in the hard rubber separator. The liquid is covered with a small amount of pure paraffin oil to prevent evaporation. The cell is quickly taken apart for cleaning and reassembled. No trouble has ever been experienced from leaking, or from breaking of the quartz disk. This rotor, being lower than the previous type, runs 17% faster.

Temperature Control

In order to determine approximately the temperature of the two walls of the cell, three copper-constantan thermocouples are used. The cold junctions are kept at 0°. One hot junction is suspended directly over the center of the top surface of the spinning rotor, about 0.5 mm. above it. A second hot junction is mounted inside the hollow cone of the rotor, as close as possible to the center of the under side of the upper half of the rotor. Its leads enter through the wall of the stator inside a glass tube about 1 mm. in outside diameter. The glass tube then runs up alongside the periscope tube but without touching it. The third hot junction gives the temperature of the stator.

If the air used to spin the rotor is allowed to expand from room temperature, it will be found that when the rotor is being run at 100 lb. pressure the air in contact with the top of the rotor is about five degrees warmer than the air inside the hollow cone, and about seven degrees warmer than the stator. Such a temperature gradient between the two walls of the cell would cause convection currents and make sedimentation impossible. We eliminate the temperature gradient in the following way. To protect the top of the rotor from the slowly descending current of room air caused by the expanding exhaust, the guard is covered with an asbestos lined metal plate having a quartz window directly over the part of the rotor to be photographed. The plate rests on three screws which raise it about 10 mm. above the top edge of the guard. Less clearance causes instability in the rotor. The high pressure supply is thermally insulated from the stand and guard at the only point where they come in contact, *viz.*, at the base, by a large Bakelite bushing. The stand and guard are further insulated from the room air by a thick hood filled with lamb's wool which slips over the whole assembly, its top being flush with the top edge of the guard.

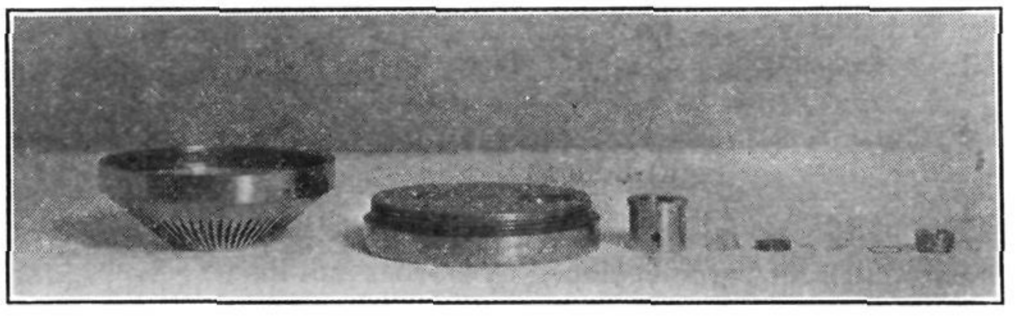

Fig. 8.—The second type rotor apart. From left to right the parts are: the rotor cone, the cell-holder, the shell of the cell, the upper (conical) quartz window, the hard rubber separator with the sectorial slot, the lower (cylindrical) quartz window, the brass washer and the hollow screw.

The driving air is heated by being passed through a large coil of 9.5 mm. copper tubing immersed in a water thermostat. By varying the room temperature, or the temperature of the water thermostat, or the driving pressure (and therefore the speed), it is possible to bring the temperatures above and below the cell to exact equality and to hold them thus indefinitely with a variation of less than ± 0.1°. With the room at 26°, the driving pressure at 100 lb./sq. in. we find that the water thermostat should be at 27°. Only about 70 watts are required to maintain the driving air at this temperature. The air for the central air inlet is taken out of the guard to ensure constancy of temperature.

From the standpoint of uniformity of temperature, the second type of rotor described above has two decided advantages over the first type. (1) In the second type, the cell is as entirely surrounded by metal as the exigencies of transparency will permit. This tends to short-circuit any temperature gradient existing between the top and bottom of the cell. (2) When the disk of celluloid or cellophane is inserted between the halves of the rotor, a dead air space 3 mm. high and 4 mm. in diameter is formed immediately below the lower quartz disk. This helps to insulate the quartz from temperature fluctuations in the cone of the rotor.

Light Source

The light source is a modified form of the high pressure mercury arc developed by Forbes and his collaborators.[15] The bridge placed by Forbes and Heidt between the mercury bulbs to permit the mercury transported to the cathode to flow back to the anode was found unnecessary.[16] If the bridge is omitted, the ionic transfer gradually raises the level of the cathode above the level of the water-bath until the mercury begins to boil. The boiling then compensates for the transfer and the arc reaches a steady state.

The opening used by the same authors for introducing the mercury into the quartz tube, a ground-in plug at the mid-point of the arc, was likewise found unnecessary.

Below each mercury bulb a short section of capillary tubing, about 1.6 mm. inside diameter, has been reintroduced. The electrodes are 3.2 mm. pure iron rods, slipping easily through the small tubing above the bulbs and turned down for part of their length to slip easily also through the capillary tubing below the bulbs. The shoulder on the iron rods where the two diameters meet is turned to a 45° angle and ground into the quartz with very fine carborundum. Across the face of the resulting valve is cut a single slot roughly 0.2 mm. wide and of the same depth. Heavy brass dust caps set-screwed to the top of the iron electrodes keep the valves seated during operation of the arc but permit them to open when the arc is started. The slots permit the pressure in the arc to remain atmospheric. The part of the iron electrodes having the smaller diameter must be long enough to extend entirely through the capillaries to prevent arcing therein.

The water-bath is double, a static bath of distilled water immediately surrounding the arc, and another of circulating tap water outside the first. The constancy of the level of the water-bath is extremely important in maintaining constant intensity. A constant drip and overflow device, situated at a distance from the lamp-house, proved most satisfactory. The water around the quartz tube tends to boil at the surface. It was found advantageous to surround each leg of the tube with several loose turns of copper gauze. This steadies the level of the water around the quartz by lowering the temperature at the surface.

A Weston photronic cell is mounted permanently in a water-cooled holder built into the transite lamp-house and protected from condensation from the water-bath by a Pyrex window. A 0 to 1.5 ma. milliammeter connected to the photronic cell gives a permanent check on the arc's intensity. With the above modifications the arc is as constant as the current source, a 550 volt d. c. motorgenerator whose variation is less than ±1%.

Optical System

The high intensity of the Forbes arc permits the use of a prism monochromator, a valuable asset for absorption photography. Starting from the arc, the optical system consists of a slit 0.3 mm. wide, a quartz collimating lens 5 cm. in diameter and 12 cm. focal length, a pair of 30° right-angled quartz prisms cut from the same crystal with the 60° angles in contact and 120° between the two hypotenuses, a focusing lens 5 cm. in diameter and 12 cm. focal length, a second slit (a hole 0.3 mm. in diameter), a second collimating lens 2 cm. in diameter and 4.8 cm. focal length, a right-angled reflecting quartz prism (directly under the center of the stator), the periscope, cell and camera lens. A fluorescent screen surrounding the second slit facilitates the selection of any line of the mercury arc.

(15) Forbes and Harrison, *J. Opt. Soc. Am.*, **10**, 1 (1925); *ibid.*, **11**, 99 (1925); THIS JOURNAL, **47**, 2449 (1925); Forbes and Leighton, *J. Phys. Chem.*, **30**, 1628 (1926); *J. Opt. Soc. Am.*, **12**, 58 (1926); Forbes and Heidt, THIS JOURNAL, **53**, 4349 (1931).

(16) Unpublished work of Dr. Philip A. Leighton and collaborators.

Stage of Development

An idea of the range of usefulness of the machine in the present state of its development can be gained from the following. Without heating the air or attempting in any way to control the natural temperature gradient existing in the rotor, the second type of rotor herein described sedimented at every trial such heavy molecules as the respiratory protein of the earthworm (5% solution; 1% in potassium chloride).[17] With the first crude air heating arrangement tried (manually adjusted electric heater inside the air supply tubing) which enabled us to keep the temperatures above and below the cell at the same value to within ± 0.3°, the same rotor easily sedimented molecules as small as the hemp seed protein edestin (molecular weight about 208,000). With the driving air arbitrarily thermostated to within ±0.02° and the room temperature controlled, the same rotor will sometimes sediment molecules as small as purified egg albumin (molecular weight about 35,000).

More remains to be done before the instrument is uniformly reliable for the smallest molecules. The authors are confident that once the exact relations between the temperatures recorded by the thermocouples and the temperatures of the cell walls have been determined, the problem will have been solved completely, for it is comparatively easy to maintain any desired temperature gradient between the air above and below the cell. Devices are contemplated which promise to make the temperature of the air above, within and below the rotor, wholly independent of the room temperature.[18]

(17) The best average value we have obtained for this protein (uncorrected for viscosity and density) is $s = 61.8 \times 10^{-13}$. The value of 72×10^{-13} published by us in THIS JOURNAL, **57**, 780 (1935), proved to be exceptionally high.

Summary

1. The air-driven spinning top has been developed as a transparent convectionless ultracentrifuge.

2. The three types of instability of the air-driven rotor are described, with their causes and remedies.

3. Means are given for measuring, increasing and controlling the speed of the top, with a discussion of the best materials of construction.

4. Spinning top centrifuges are described in which it is possible to photograph the cell by transmitted light of any monochromatic wave length, visible or ultraviolet.

5. Two different types of cells are described.

6. Means are discussed for measuring and controlling the temperature gradient existing between the top and bottom of the cell.

7. The present stage of the development of the instrument is described.

(18) Mr. H. J. Fouts in this Laboratory has since found that in order fully to equalize the temperature inside the rotor with the temperature of the slip stream from the driving air (on account of the friction caused by the periscope upon the air within the rotor) it is advisable to draw the air entering the periscope, as well as the air playing upon the top of the rotor, through a much colder thermostat, instead of taking it from the guard ring as described above.

STANFORD UNIVERSITY, CALIF. RECEIVED AUGUST 5, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Photochemical Decomposition of Nitric Oxide[1]

BY PAUL J. FLORY AND HERRICK L. JOHNSTON

Berthelot[2] observed that nitric oxide decomposed when irradiated with light from the quartz mercury arc and concluded that nitrogen and oxygen are the final products of the decomposition. Macdonald,[3] as part of his investigation of the nitrous oxide decomposition, made a brief study of the decomposition of nitric oxide under irradiation from the aluminum spark, between pressures of 50 and 650 mm. He observed that the rate seemed to depend entirely upon the amount of light absorbed and reported a quantum yield of 0.75. He interpreted his data in terms of a primary mechanism of activation. Noyes[4] found good evidence for the decomposition of nitric oxide through the agency of excited mercury atoms. Under the conditions of his experiments he observed no appreciable amount of direct photochemical reaction.

We have investigated the photochemical decomposition of nitric oxide both with the mercury arc and with sparks between various metal elec-

(1) Presented before the Division of Physical and Inorganic Chemistry at the Cleveland Meeting of the American Chemical Society, Sept., 1934.

(2) Berthelot, *Compt. rend.*, **150**, 1517 (1910).

(3) Macdonald, *J. Chem. Soc.*, 1 (1928).

(4) W. A. Noyes, Jr., THIS JOURNAL, **53**, 514 (1931).