

reaction with the metal of the tube, say 1 min, and then pumped out. After purging the tube with inert gas and filling with some suitable counting gas, such as methane, the amount of deposited nonvolatile radioactive product left in the tube is determined by the counting rate.

The radioactive gas may then be readmitted for another exposure period, and the amount of increase in deposit subsequently determined. In this way, one may measure the rate of reaction, and the variation of the rate, with different parameters.

It is obvious, of course, that any of the radioactive gas left in the tube at the time of counting, whether chemically reacted with the metal surfaces or physically adsorbed thereon, contributes to the total radioactive count. This constitutes a disadvantage in that care must be exercised to outgas thoroughly the adsorbed gas before determination of the reaction extent. This constitutes an advantage also, however, in that knowledge of physical adsorption and factors like temperature governing the adsorption, often highly desired, is easily obtained. That is, it is often of great assistance in interpreting a reaction to know how the deposited film may be removed, or how it behaves in other ways, as well as the rate at which the reaction originally proceeded. In this way the effects on deposited radioactive films of extended evacuation, high temperatures, treatment with hydrogen, fluorine, etc., have been studied.

Method 2. The second method to be described has not been used as extensively as the first. It is, in fact, still in the developmental-calibration stage, but it seems to offer certain advantages for the study of particular reactions.

The metal involved in the gas-metal reaction to be studied is made into the form of a fine wire, say 0.005 in. in diam. The wire is wound into a loose coil and mounted inside a chamber, where exposure to the radioactive gas can occur under the chosen conditions. One end of the wire extends from the chamber into a suitably arranged "withdrawal alley," through which, at chosen intervals, short lengths of the wire may be removed as samples. The wire samples, removed at successive intervals after the start of the exposure, contain on their surfaces increasing amounts of radioactive deposit, proportional to the extent of reaction occurring before their removal from the exposure chamber.

The wire samples are mounted in succession along the axis of a suitably designed Geiger-Müller or proportional radioactivity counting tube, where they serve both as the source of radioactivity being measured and the ion-collecting electrode of the tube. By measuring the activity of similar samples receiving increasingly long exposures to the corrosive gas, a history of the reaction may be obtained.

Each of the methods described has certain advantages and disadvantages. With the metal of interest in the form of a counter tube, the same metal surface is intermittently exposed to the corrosive gas, with periods of evacuation and exposure to inert counting gas between corrosive gas exposure. Presumably, the intermittency of

exposure and the effect of inert gas would have little influence on the gas-metal reaction being studied, but this would have to be established. The chief advantages of the method are: (a) the system, in contrast to the usual "weight gain" technique, does not have to be broken, with attendant likelihood of moisture contamination, etc., to permit periodic observations of the extent of the reaction; (b) once the system is set up, periodic observations of the extent of the reaction are quickly, easily, and reliably made; and (c) the exposure and counting system is easily set up, and with simple gas manifold and counter switching arrangement can handle many samples as easily as one.

With the metal of interest in the form of wire, individual samples are removed from the exposure chamber and not reused. The chief advantage is that the removal of a sample in wire form is easy to achieve without interrupting the course of the reaction on other samples left in the exposure chamber. Samples in the shape of disks, for example, would be extremely difficult to remove from an exposure chamber without interrupting the reaction, or opening the exposure chamber to ambient atmosphere; etc. Placing the wire sample in a clean, well-designed counter tube is rapidly accomplished, and gives suitable counting results.

Either of these methods, by adequate care in calibration, may be arranged to give absolute values of reaction rates. It is considerably easier to use the technique for obtaining relative values of the reaction rates between different metals and a given corrosive gas.

The most troublesome item to be encountered in the use of the methods described is the condition of the metal surfaces involved in the reaction. Extreme care in preparation of smooth, clean, uniform surfaces is necessary if reproducible data are desired.

Instrumental Methods of Studying Some Properties of Aerosols¹

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The general properties of aerosols were recently described elsewhere by the author (3). These colloidal dispersions of liquid or solid particles in a gas are the most ephemeral and elusive of colloidal systems. Hence they have received less study than liquid-dispersed systems, although they comprise clouds and smokes, dusts and bacterial spores of great economic and practical, as well as theoretical, importance. Recent developments of instrumental methods allow rapid investigation of the mass

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concentration, number, and size of the dispersed particles, which will be outlined in this paper.

Many properties of aerosols may be studied by measuring the light which they scatter. Lord Rayleigh (11) in 1871 developed the theory of light scattering by very small particles, showing that it varies with the sixth power of the radius of the particle and inversely with the fourth power of the wavelength of the light, thus explaining the blue color of the sky and the red color of the sun near the horizon as resulting from selective scattering of the shorter wavelengths of sunlight by clouds, dust, and even the molecules of the atmosphere. In 1908 Gustav Mie (10) extended the theory to particles comparable with the wavelength of light and larger, showing that the scattering from these particles was chiefly in the forward direction, with a number of other maxima which increased with the size of the particle. This causes a series of spectra when white light passes through a *homogeneous* aerosol, as shown by V. K. LaMer and D. Sinclair (9), who counted the number of red bands between 0 and 180° to determine the size of the particles, since the number of spectra is practically equal to the radius in tenths of a micron. Particles too fine to show spectral orders show a regular change in polarization of light they scatter sideways, as the radius increases. LaMer and Sinclair developed a simple method of determining the size of homogeneous aerosols, based upon this fact.

Most liquid-dispersed systems are stable over long periods of time, while all but the most dilute aerosols change rather rapidly by settling and coagulation. Mass concentrations of the order of 100 $\mu\text{g/l}$, containing ten million particles or less, do not change appreciably in a few minutes, but their systematic study requires a continuous generator which can be controlled to put out a uniform concentration. In our laboratory, A. H. Peterson has developed such a mass concentration control, applicable to any aerosol of uniform particle size or constant particle size distribution. An aliquot of the aerosol is passed through a cell where it is subjected to strong dark field illumination. The scattered light is focused upon a photomultiplier tube and compared with a beam of the direct light from the lamp, attenuated by suitable filters to about the same level of intensity. This arrangement eliminates the effect of changing light intensity. The two beams, falling alternately upon the same part of the photomultiplier surface to insure uniform response, may be compared in rapid succession, or the direct signal may be used at longer intervals to standardize the gain of the photomultiplier, the output of which is amplified to control the diluting air and hence the mass concentration of the aerosol. The same system can be used to measure, as well as control, the mass concentration. In either case, to avoid recalibration of the apparatus when a new lamp is inserted and the optical system is cleaned, we find that the light scattered by an organic vapor such as ether is sufficient to serve as an internal standard.

An earlier apparatus for measuring aerosol concentrations, developed in our laboratory by H. B. Pickard and C. T. O'Konski (2, 4) collects the light scattered at right angles by the aerosol and focuses it upon a vacuum pho-

totube. The photocurrent, passing through a very high resistance, gives a voltage drop which is measured potentiometrically, using a single vacuum tube amplifier with a balanced plate circuit and galvanometer as a null indicator. This instrument, sensitive to $5 \cdot 10^{-9}$ lumen or 10^{-3} $\mu\text{g/l}$ of dioctyl phthalate aerosol of 0.3 μ diam, was used as a direct-reading penetration meter, capable of testing the best respirator filters.

Photoelectronic methods of counting individual aerosol particles and thus determining particulate concentrations were developed in our laboratory by C. T. O'Konski, H. B. Pickard, and J. N. Pitts, Jr. (7), and have been evaluated by R. N. Ferry, L. E. Farr, Jr., and Mary G. Hartman (1). The aerosol flows through a cell under intense dark field illumination, the pulses of light scattered in the forward direction are collected upon a thalofide or photomultiplier cell, the resulting electrical pulses are amplified, and those above any desired value actuate a thyratron trigger tube and a mechanical counter. This allows the counting of spherical particles down to about 0.5 μ diam, or of spores of *Bacillus globigii*, which are ellipsoidal, averaging $0.8 \times 0.8 \times 1.2$ microns, at rates up to about 1000 per minute. Later work by C. T. O'Konski (6) in this laboratory, using an improved optical system, reduced the background light to the point where three-quarters of it came from the scattering of the air molecules in the 7-mm³ illuminated space viewed by the phototube. This apparatus, now being tested by D. G. Rose, should be capable of counting at considerably higher rates, using an electronic counter or rate meter. It also has a differential pulse amplitude selector, designed to count the pulses within a predetermined voltage range and thus allow the rapid determination of particle size distribution. If the light field is sufficiently stable and uniform, the apparatus should classify particles 1 μ in diam or larger into 1- μ -size range groups with a resolution of 5 or 10%.

An electrostatic method of counting particles 2.5 μ or more in diam and of determining their size distribution was developed by A. C. Guyton (8). The aerosol is sucked through a hole 0.8 mm in diam to impinge upon a charged collecting plate or wire. The individual particles produce electrical pulses, the voltages of which are proportional to the squares of the particle diameters. With a suitable electrical discriminator, this apparatus provides a convenient and rapid method of determining particle size distribution in the range over which it is applicable. A discussion of the theory of this counter and a comparison with the photoelectronic type has been given by C. T. O'Konski and the author (5).

Another method of determining particle size distribution under investigation in our laboratory by George J. Doyle involves a measurement of the amplitude of vibration of individual particles of a moderately dilute aerosol in an intense sonic field. Very light particles vibrate with the full amplitude of the air molecules, while very heavy particles are not affected by the sound. For any particular frequency there is a range of particle size over which the amplitudes are spread out enough to allow a determination of the size distribution, at least for spherical

particles which obey the Stokes-Cunningham law. Intense dark field illumination of the particles allows photography of a number of vibrating particles in a small fraction of a second. Our present apparatus employs standing waves of 5-kc frequency, generated by the type of oscillator described by H. F. St. Clair (12), and is applicable to particles from 1 to 5 μ in diam, while a 40-kc frequency will cover the range from 0.1 to 1 μ .

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A Contact Modulated Amplifier and Some of Its Laboratory Uses

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Developed to measure d-c signals on the order of a few hundredths of a microvolt, this amplifier employs motor-driven contacts to modulate the input signal (2). It features ruggedness, portability, stability, low noise level, and insensitivity to vibration.

Direct-current input signals are converted to a-c (80 cycles) by means of a mechanical breaker, stepped up in

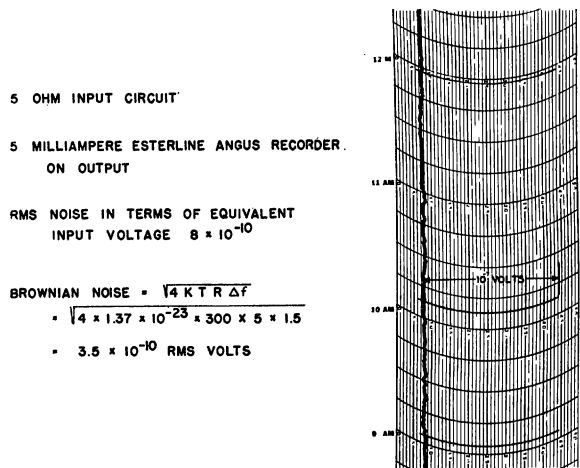


FIG. 1. Amplifier noise level and drift over a 3-hr period.

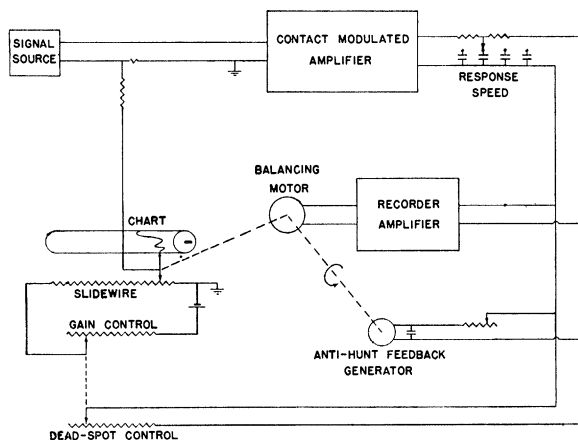


FIG. 2. Infrared spectrograph recording circuit.

voltage by a transformer, amplified with several vacuum tube stages, and finally rectified by another breaker driven synchronously with the input breaker. This arrangement reduces the effect of random variations in the amplifier and favors the wanted signals introduced at the input.

Drift due to small temperature differences between components in the input circuit has been minimized by careful construction and selection of materials. Thermoelectric coefficients of the copper components in this part of the amplifier are matched and junctions are soldered with a special solder (70% Cd, 30% Sn) having a low thermo emf with respect to copper. The input transformer is magnetically shielded with multiple, concentric layers of Mumetal and soft iron.

Fig. 1 shows a performance record of the amplifier. A test signal of 10^{-7} v applied to the 5-ohm input circuit provides calibration from which the random noise level can be measured. An interesting comparison is made in Fig. 1 between the observed noise of 8×10^{-10} rms v and the Brownian noise due to thermal agitation in the input circuit. In the expression for Brownian noise:

K = Boltzman constant

T = Temperature in degrees Kelvin

R = Resistance of input circuit

Δf = Over-all band width (cycles) of amplifier and recorder.

The observed noise is only a little more than twice the theoretical minimum.

This amplifier has found one of its most important applications in the field of infrared spectroscopy. It is

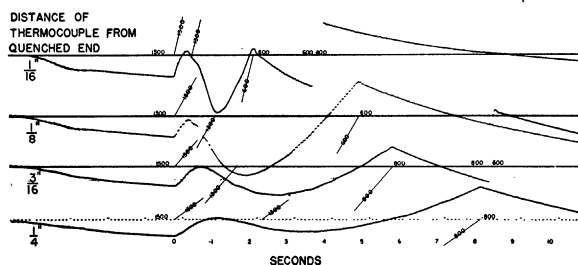


FIG. 3. Record obtained from end-quenched 1020 steel bar.