W. H. Slabaugh
Oregon State University
Corvallis

Determination of Avogadro's Number by Perrin's Law

An experimental verification of the kinetic theory of matter and the universality of the gas laws is afforded by the Perrin method of determining Avogadro's number. Assuming that a colloidal particle behaves like a gas molecule, J. B. Perrin[1] described the distribution of "colloidal molecules" as a function of height in a gravitational field:

$$2.3 \log \frac{n_1}{n_2} = \frac{N}{RT} mg (h_2 - h_1) \left(1 - \frac{d}{D}\right)$$

Thus, at two different heights in a colloidal dispersion, h_2 and h_1, the number of particles per unit volume, n_2 and n_1, settle as a function of their mass m and density D, the gravitational constant g and the density of the medium d.

The experimental procedure for determining Avogadro's number by the Perrin method includes preparing a monodisperse colloid, ascertaining the mass of the particles, and making an accurate count of the number of particles at two points in the equilibrated colloid. Perrin prepared a colloid of gum gamboge, and, after months of elaborate fractional centrifuging, obtained a few tenths of a gram of dispersed gamboge from an original sample of 1 kg. Furthermore, he counted more than 17,000 particles. By sacrificing the accuracy of this experiment and making certain assumptions, we have reduced this experiment to the level of the general chemistry laboratory where it can be performed within a period of about 2 weeks.

[1] PERRIN, J. B., *Compt. Rend.*, **147**, 475 (1908); **149**, 549 (1909); PERRIN, J. B., "Atoms," D. Van Nostrand Co., New York, **1917**; REILLY, J., "Physico-Chemical Methods," D. Van Nostrand Co., New York, **1926**, p. 704.

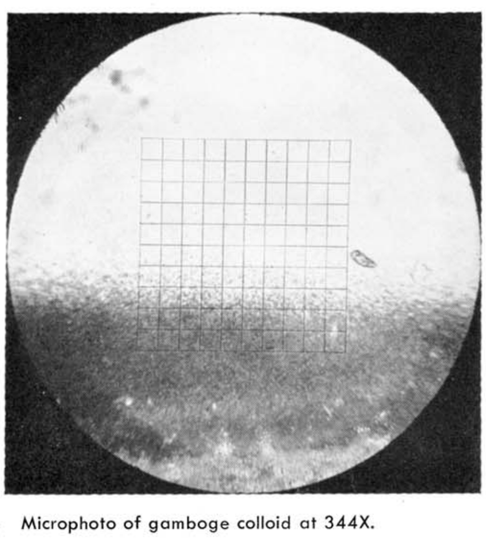

Figure 1. Microphoto of gamboge colloid at 344X.

Preparation of Colloid

A 1% solution of gum gamboge in ethanol is mixed rapidly with an equal volume of distilled water, and the resulting colloidal dispersion is left standing overnight. It is then subjected to fractional centrifuging in order to obtain a nearly monodisperse system. It is possible to obtain a fairly suitable colloid by two steps: short rapid centrifuging and discarding the residue, then moderate centrifuging for a half hour and discarding the supernatant liquid. The residue from this second centrifuging is dispersed in water and this colloid may suffice.

A more nearly monodisperse system, shown in Figure 1, was prepared by a student in a series of centrifuging steps at about 1500 rpm as follows:

Duration of centrifuging	*Recovery procedure*
4 min	Residue, redisperse in water
3 min	Residue, redisperse in water
1 min	Supernatant (discard residue)
3 min	Residue, redisperse in water
1 1/2 min	Supernatant (discard residue)
3 min	Residue, redisperse in water
1 1/2 min	Supernatant (discard residue)
3 min	Supernatant (discard residue)
3 min	Supernatant (discard residue)
10 min	Residue, redisperse in water

Counting the Particles

The dispersion from the last centrifuging step was placed in a concavity microscope slide, covered and sealed with wax, and placed on its edge for 3 days (Fig. 2). The slide was then observed on the stage of a microscope adjusted to a horizontal position in order to maintain the slide in a vertical position. A 4-mm objective (43X) and an 8X eyepiece containing a grid reticle was calibrated with a scale of known length. This grid, as noted in Figure 1, is made of 100 squares, the edge of each one equal to 16 microns at the focal plane of the objective. The grid, superimposed on the field of view, served to identify the heights at which

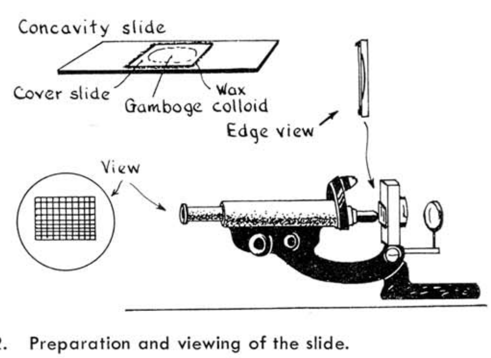

Figure 2. Preparation and viewing of the slide.

the particles were counted and to estimate the actual size of the particles.

Students prefer to count the particles from a photograph, such as Figure 1, but a major outcome of this experiment is the opportunity to observe directly the Brownian movement of the dispersed particles. Once a routine counting system is established, students can count a sufficient number of particles in about 30 min. The following data are from a student's report and represent the average number of particles observed in several squares at each height.

Height (microns)	*No. of particles (average)*
112	0.20
96	0.50
80	1.20
64	2.50
48	7.60
32	14.2
16	26.0
0	37.0

A plot of the log of the number of particles versus height was made and from the best linear relationship of these data, two values for n and for h were selected in making the final calculation. Linearity of the log n versus h plot is assurance of the validity of the counting data.

Calculations

For the conventional terms in the Perrin equation, the following values were used: $R = 8.3 \times 10^7$ erg deg^{-1} mole^{-1}, $T = 297$°K, $d = 0.992$ g cm^{-3}, $D = 1.194$ g cm^{-3}, and $g = 980.6$ cm sec^{-2}. The radius of the colloidal particles was estimated by counting the number of particles required to fit along the edge of one of the squares near the bottom of the dispersed region. This is probably the chief source of error in this experiment. A measurement of $r = 4.8 \times 10^{-5}$ cm was obtained by the same student who reported the particle counts above, and from these data obtained a value of 2×10^{23} for N. Other students, observing the same slide, obtained values for N ranging from 1.5×10^{23} to 5×10^{23}.