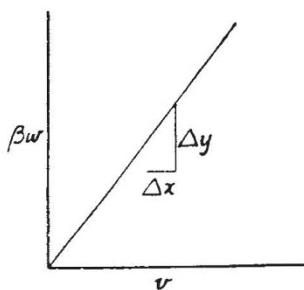the respective mean values as zero. If the pairs of measured values are plotted on new scales : $y = \beta w$, $x = v$, where $\beta = \sigma_v/\sigma_w$, deviations in x and y are of equal weight.

Let $\triangle x$, $\triangle y$ represent deviations of a measured point from a point on a line representing the true relation. Now, by the principle of least squares, the best estimate of the true relation is obtained by minimizing the sum of values of $(\triangle x^2 + \triangle y^2)$, that is, by the principal axis of smaller second moment.

When transformed back to the original scales, this curve is the line through the origin and of slope

$$\rho = \frac{\left\{\left(\frac{1}{k\beta} - k\beta\right)^2 + 4r^2\right\}^{1/2} - \left(\frac{1}{k\beta} - k\beta\right)}{2r\beta} \quad . \quad (1)$$

where $\beta = \dfrac{\sigma_v}{\sigma_w}$, $k = \sqrt{\dfrac{\Sigma w^2}{\Sigma v^2}}$, $r = \dfrac{\Sigma wv}{\sqrt{\Sigma w^2 \Sigma v^2}}$

It may be noted that when variables are subject to error, the equations of the regression lines will vary systematically with the range and distribution of true values, whereas that of the curve of best fit given by (1) will not. The appropriate regression line, however, for example, of w on v, gives the most probable measured value of w corresponding to a measured value v, provided this value has been drawn from a population with a distribution of true values similar to that of the sample. If there is no information as to range, or the range is different and, in particular, if it is desired to extrapolate, then the curve of best fit is to be preferred.

When, as sometimes occurs, the relative uncertainty of the two sets of measurements is not known, but there is reason to ascribe some error to each set of values, it is convenient to make the assumption $\sigma_w = \rho\sigma_v$, for the expression for the slope then becomes :

$$\rho = \sqrt{\frac{\Sigma w^2}{\Sigma v^2}} \quad . \quad . \quad . \quad . \quad (2)$$

which does not involve Σwv, which need not therefore be calculated.

Since making this analysis we have noticed that a similar problem has been considered by Seares[1]. His solution, in our nomenclature,

$$\rho = \left(\frac{\overline{w^2} - \sigma_w{}^2}{\overline{v^2} - \sigma_v{}^2}\right)^{1/2} \quad . \quad . \quad . \quad (3)$$

tends to our expression (1) as the size of sample increases. We believe, however, that our treatment gives the better estimate when the difference is appreciable, as may happen with small samples.

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[1] Seares, F. H., *Astrophys. J.*, **100**, 255 (1944).

Flow of Gases through Fine Powders and the Measurement of Specific Surface

RIGDEN[1] has given a modified form of Kozeny's equation, corrected for the 'slip' which becomes appreciable when the voids of the powder are not incomparably greater in width than the molecular mean free path of the gas. If the voids are much narrower than the mean free path, however, so that intermolecular collisions are very rare, the flow ceases to be governed by the viscosity of the gas and becomes a process of diffusion.

It can be shown that the diffusion coefficient is given by Meyer's uncorrected formula for self-diffusion, that is :

$$D = \frac{\lambda \bar{c}}{3},$$

where λ, the mean free path, is determined by the dimensions of the voids. By geometry the free path is found to be :

$$\lambda = \frac{4\varepsilon}{S(1-\varepsilon)\rho}$$

using Rigden's notation.

It follows from these relations that the mass-flow per unit area per unit time is given by :

$$Q = -\frac{8}{3} \sqrt{\frac{2M}{\pi RT}} \cdot \frac{\varepsilon^2}{S(1-\varepsilon)\rho} \cdot \frac{dp}{dx}$$

where x is measured in the direction of flow.

This equation enables the specific surface of a powder of any degree of fineness to be calculated from permeability measurements made at a suitable gas pressure. It has the advantage of involving no empirical constants. The accuracy of the method is being investigated here.

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[1] Rigden, P. J., *Nature*, **157**, 268 (1946).

I AM interested to note that an attempt is being made to use a 'molecular flow' formula for the air permeability method instead of a corrected Poiseuille formula. I have been aware of this possibility and have found an equation, based on the law of molecular flow through a tube at very low pressure, with a porosity function of the same form as that given by Holmes, namely,

$$\frac{\varepsilon^2 \Delta p}{(1-\varepsilon)\rho Sl}.$$

This method has not been examined experimentally here, as the powders we are normally concerned with are not fine enough.

This formula is only valid if the diameter of all pores in the bed of powder is considerably less than the mean free path, a condition which will only obtain if a sufficiently fine powder is used or if the working pressure is sufficiently low. I would suggest that, at atmospheric pressure, only powder as fine as carbon blacks would meet this requirement (say, 50 m.²/gm.).

Any formula, whatever its theoretical basis, for relating specific surface of a powder to its permeability when compacted into a bed, must contain an empirical constant which has to be determined experimentally. It will be interesting to see whether surface areas deduced by Holmes' formula agree with those found by other methods, for example, the nitrogen adsorption method.

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Optical Stability of Diphenyl Derivatives

ON the assumption that the racemization of a 2 : 2′ : 6-trisubstituted diphenyl (I) involves the rotation of the two benzene rings relative to one another about the bond joining them as axis, the rate of racemization must depend on the ease with which the substituents A and D or B and D (depending on whether A or B is the smaller) can pass one another.

Adams and Hale[1] have made a study of the isomerides II, III and IV and have found that their rates of racemization decrease in this order. These authors point out that since the relative sizes of the substituents are $NO_2 > Me > CO_2H$, the racemization of II and IV should involve the methyl group passing the carboxyl group, and that of III, the nitro group passing the carboxyl group ; consequently, the rates of racemization should be II = IV > III. Similarly[2], the rates of racemization of V, VI and VII decrease in this order, whereas the relative sizes of substituents, $NO_2 > CO_2H > OMe$, would be compatible with rates V = VII > VI.