A Method of measuring the Net Density of a Powdery Substance Which dissolves a Little in a Liquid

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Abstract

A method of measuring the net density of a powdery substance by immersing in a liquid which dissolves a small quantity of the substance, is described. The net density of picric acid is measured by this method by immersing it in water, and the values of 1.7642 was obtained for purified picric acid.

Some years ago Mr. Takei and one of the writers[1] devised a method of measuring the net density of a fibrous, powdery or porous substance which is liable to occlude gases and water. The essential part of that method is to evacuate off all the occluded gases and water from the specimen. With this method we must, of course, select a proper liquid which does not dissolve the solid specimen as is usually the case. But it occurs sometimes, with some specimens, that it is difficult to select such a liquid which does not dissolve the specimen entirely and that we are obliged to use a liquid into which dissolves a small part of the solid specimen. The present method consists of giving a proper correction in such occasion.

As the method is essentially the same as before an explanation of it will be repeated briefly in the following for the sake of convenience. Several grams of the specimen are put into a glass tube which is sealed at one end as is shown by A in Fig. 1. Then the tube is necked with a burner several centimetres from its sealed end as is shown by B in the same figure. Sufficient care is to be taken, in this case, not to heat the specimen contained in the sealed end. The tube is scraped with a file at a and b in B, Fig. 1, so as to be easily broken afterwards at these points. Then the tube is evacuated sufficiently down to a pressure of about 0.01 mm of mercury by proper heating. When thoroughly evacuated, the tube is sealed at its neck as shown in C, Fig. 1. Then it is weighed, and its volume is measured by immersing it in water contained in a measuring cylin-

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1. These Memoirs, 15, 1 (1932).

der. The volume of the sealed tube serves for the reduction of weighing in vacuo. The liquid is then introduced into the tube by breaking the neck of the tube at *b* in a certain liquid of known density in which the density is to be measured, as is shown by D in Fig. 1. Next the weight of the specimen in the liquid is measured. After the weight in the liquid of the glass tube containing the specimen,
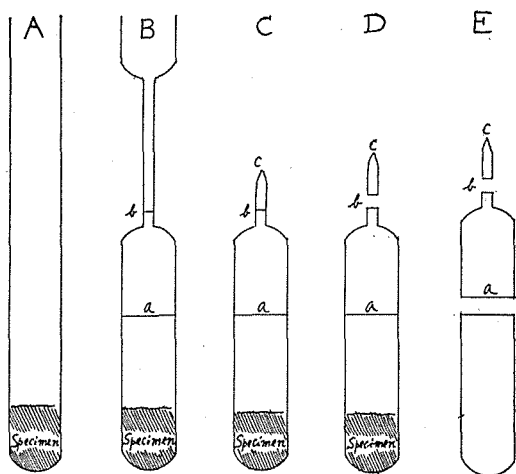

Fig. 1

and the broken neck, both of which are perfectly filled with the liquid, has been measured in the usual way, the glass tube is broken along the filed line *a*, and the specimen is taken out of the tube. Then the weight in the liquid of all the parts of the broken glass tube, as shown by E in Fig. 1, is measured in the same way, and the weight of the specimen only in the liquid is obtained immediately. Finally after all the parts of the broken glass tube have been freed from the liquid, rinsed well in distilled water and well dried, their total weight in air is measured. From this total weight and that of the evacuated sealed glass tube containing the specimen, we can obtain immediately the net weight of the specimen. From this net weight of the specimen and its weight in the liquid of known density, the net density of the specimen is calculated. In the procedure above stated, the reduction of weighings in vacuo and the correction due to the change of the density of the liquid with temperature are, of course, to be made always.

When, for a given solid specimen, it is impossible to find a liquid which does not dissolve the specimen entirely, and we are obliged to employ a liquid of known density which does not act chemically with the specimen but dissolves a small part of it, then we are to find, anyhow, its apparent density by assuming that the dissolved quantity of the specimen is negligible.

Let m', S, C, D, E_1 and E_2 have respectively the following meanings:

m' : the weight of the specimen contained in the evacuated sealed glass tube,

S : the density of the liquid into which the specimen is to be dipped,

C : the weight of the evacuated sealed glass tube which contains the specimen,

D : the weight of the specimen and the broken pieces of the glass tube when they are immersed together in the liquid,

E_1 : the weight of all the broken pieces of the glass tube when they are immersed together in the liquid,

E_2 : the weight of all the broken pieces of the glass tube when they are well washed and dried.

Then the apparent density d of the specimen will be given by the following equation :

$$\frac{1}{d} = \frac{1}{m'S}\left\{(C-E_2)-(D-E_1)\right\}$$
$$= \frac{1}{S(C-E_2)}\left\{(C-E_2)-(D-E_1)\right\} \dots\dots\dots\dots\dots(1).$$

Next let m'', m_g, m_l, V and d_g have respectively the following meanings :

m'' : the mass of the specimen which still remained as the solid when it is immersed in the liquid,

m_g : the mass of the glass tube,

m_l : the mass of the liquid in the glass tube which dissolved a small part of the solid specimen,

V : sum of the volume of the solid specimen and the liquid contained in the glass tube,

d_g : the density of the glass.

Then

$$C = m' + m_g, \quad D = (m'' + m_g + m_l) - \left(V + \frac{m_g}{d_g}\right)S,$$

$$E_1 = m_g - \frac{m_g}{d_g}S, \quad E_2 = m_g.$$

And the equation (1) becomes

$$\frac{1}{d} = \frac{1}{Sm'}\left[m' - \left\{(m'' + m_g + m_l) - \left(V + \frac{m_g}{d_g}\right)S\right\} + m_g - \frac{m_g}{d_g}S\right]$$

$$= \frac{1}{Sm'}\left\{(m' - m'') + (VS - m_l)\right\} \dots\dots\dots\dots\dots\dots(2).$$

If we represent the dissolved part of the solid specimen by $\varDelta m$, then equation (2) becomes

$$\frac{1}{d}=\frac{1}{Sm'}\left\{\Delta m+(VS-m_l)\right\} \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3).$$

When the real density of the specimen is D, and the volume of the liquid contained in the glass tube is V_s, then:

$$V=V_s+\frac{m''}{D}=V_s+\frac{m'}{D}-\frac{\Delta m}{D},$$

and the equation (3) becomes

$$\frac{1}{d}=\frac{1}{Sm'}\left\{\Delta m+V_s\cdot S+\frac{m'}{D}S-\frac{\Delta m}{D}S-m_l\right\}$$

$$=\frac{1}{D}+\left\{\frac{\Delta m}{m'}\left(\frac{1}{S}-\frac{1}{D}\right)+\frac{1}{Sm'}(V_s S-m_l)\right\} \quad\ldots\ldots\ldots(4).$$

When the solid specimen does not dissolve, $\Delta m=0$, and $V_s S=m_l$; and consequently d itself becomes to be the same as D from equation (4), as ought to be.

Now we must consider closely the mass m_l of the liquid part contained in the glass tube, in which the specimen is dissolved a little. Let S be the density of the pure liquid, and V_s be the volume of the solution when a small quantity m of the solid specimen is dissolved uniformly in the pure liquid of volume V', then the concentration of the solute in the solution will be m/V_s. We must enquire, before every thing, about the relation between the concentration and the corresponding density of the solution. Though it is a little different from the actual case usually, it is convenient to consider the ideal case that the volume of the solute and the solvent is additive in forming the solution. In this case the density of the solution D_s is calculated as follows :

$$D_s=\frac{SV'+m}{V'+\frac{m}{D}}=\frac{S\left(1+\frac{m}{SV'}\right)}{1+\frac{m}{DV'}}\doteqdot S\left\{1+\frac{m}{V'}\left(\frac{1}{S}-\frac{1}{D}\right)\right\}$$

$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5).$$

When m is very small we can regard V' and D approximately equal respectively to V_s and d in the above equation. Then (5) becomes

$$D_s=S\left\{1+\frac{m}{V_s}\left(\frac{1}{S}-\frac{1}{d}\right)\right\} \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(6),$$

where m/V_s is the concentration of the solute in the solution. If we represent D_s in the form

$$D_s=S(1+\Delta x),$$

then from equation (6) we obtain

$$\varDelta x = \frac{m}{V_s}\left(\frac{1}{S} - \frac{1}{d}\right) \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(7),$$

which shows that $\varDelta x$ is proportional to the concentration of the solute in the solution. This relation is represented by the dotted straight line I in Fig. 2. In actual case, this relation is somewhat different, but we may still assume with sufficient accuracy that $\varDelta x$ is
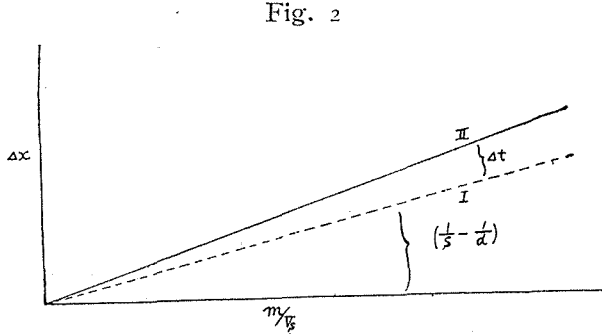
Fig. 2

proportional to m/V_s when the latter is small, as is shown by the straight line II in Fig. 2. Let the tangent value of the inclination of this straight line to the abscissa be t, and its excess to that of the straight line I be $\varDelta t$, then we get

$$1 + \varDelta x = 1 + \left(\frac{1}{S} - \frac{1}{d}\right)\frac{m}{V_s} + \varDelta t\frac{m}{V_s} \dots\dots\dots\dots\dots(8).$$

This relation is necessary in getting the correction to be added to the apparent density of the solid specimen, and a preliminary experiment is needed to get the value of $\varDelta t$ by measuring the densities of the solutions of various concentrations at a given temperature.

Next, in measuring the weight of the specimen and the broken pieces of the glass tube when they are immersed together in the liquid of density S, in the manner as shown by D in Fig. 1, the concentration of the dilute solution is different according to the position in the glass tube, and is generally smaller as we recede from the solid specimen. If we represent the coordinates of a point in the glass tube by (x, y, z), then the concentration c of the solution at that point will be represented as a certain function f of the coordinates of the point

$$c = f(x, y, z).$$

And the density of the solution at that point becomes from (8):

$$S + \left\{\left(\frac{1}{S} - \frac{1}{d}\right) + \varDelta t\right\}Sf(x, y, z) \dots\dots\dots\dots\dots\dots(9).$$

Thus if we represent by dV_s the volume element in the solution, then the total mass of the solution m_t which is contained in the glass tube is given by

$$m_t = \int \left[S + \left\{ \left(\frac{1}{S} - \frac{1}{d} \right) + \varDelta t \right\} Sf(x, y, z) \right] dV_s$$

$$= S \int dV_s + \left\{ S \left(\frac{1}{S} - \frac{1}{d} \right) + S\varDelta t \right\} \int f(x, y, z) dV_s \quad \ldots\ldots\ldots (10),$$

where the integral is to be extended to the whole portion occupied by the solution in the glass tube.   In the above equation the first integral is the volume occupied by the solution in the glass tube, and the second integral is nothing but the mass of the solute dissolved into the liquid contained in the glass tube, if we neglect the amount of the solute escaped through the narrow neck of the glass tube. Consequently equation (10) becomes

$$m_t = SV_s + \left\{ S \left(\frac{1}{S} - \frac{1}{d} \right) + S\varDelta t \right\} \varDelta m \quad \ldots\ldots\ldots\ldots (11).$$

By using this value of m_t, we get

$$V_s S - m_t = -S\varDelta m \left\{ \left(\frac{1}{S} - \frac{1}{d} \right) + \varDelta t \right\}.$$

And by inserting this relation into equation (4), we obtain

$$\frac{1}{d} = \frac{1}{D} + \left[\frac{\varDelta m}{m'} \left(\frac{1}{S} - \frac{1}{D} \right) - \frac{\varDelta m}{m'} \left\{ \left(\frac{1}{S} - \frac{1}{d} \right) + \varDelta t \right\} \right]$$

$$\doteqdot \frac{1}{D} - \frac{\varDelta m \varDelta t}{m'} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (12).$$

When the volume of the solute and the solvent is additive in forming the solution, $\varDelta t$ is nil as is stated, and the apparent density d becomes to be equal to the real density D, from the above equation, as is expected without any calculation.

When $\varDelta t$ is different from zero, as is actually the case, we get from (12)

$$D = d \left\{ 1 - d\varDelta t \frac{\varDelta m}{m'} \right\} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (13)$$

as the correction formula to obtain the real density D from the apparent density d.

Actually the apparent density d can be obtained by equation (1) as is stated before, and $\varDelta t$ by plotting the relation between the density and the concentration of the solute in the solution in the manner as is shown by Fig. 2.   In order to get the dissolved amount $\varDelta m$ of the specimen, we collect in another proper vessel all the solution, excepting the solid part of the specimen, which is contained in the glass tube up to its broken neck, and measure its well mixed total volume V_s, and then its density by using a pyknometer.   From the value of the density of the solution, we get the concentration of

the solute in the solution from the curve in Fig. 2, which is plotted in the preliminary experiment; and consequently from this value of the concentration and the volume V_s of the solution we get immediately the dissolved amount $\varDelta m$ of the specimen. Thus the correction to be made to the apparent density is readily calculated by equation (13) by giving the values of d, $\varDelta t$ and $\varDelta m$ thus obtained.

As an example the writers measured the net densities of crude and purified picric acid by the above method by immersing the specimen in distilled water which dissolves picric acid a little. Densities of the solutions corresponding to various concentrations of crude picric acid in aqueous solution were measured at 17.°7 C by means of a pyk-

Fig. 3

Concentration of picric acid in g/cc at 17.7°c
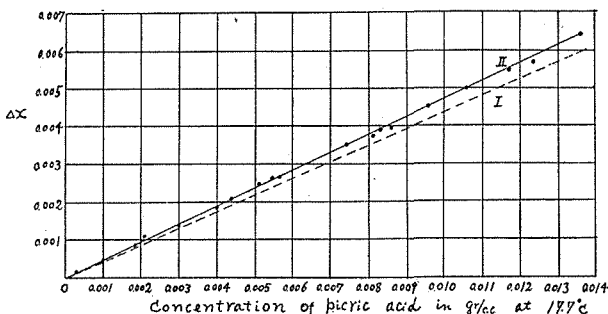
nometer, and the value of $\varDelta x$ was confirmed to be proportional to the concentration as is seen by the straight line drawn in full line in Fig. 3. The dotted straight line in the same figure represents the theoretical values calculated by assuming that the volumes of picric acid and the water is additive in forming the solution. The deviation of the observed values of $\varDelta x$ from those calculated is very small, and the value of $\varDelta t$ is found to be 0.0418 in this case. In the case of purified picric acid, the same experiment must be done, of course, with purified picric acid; but in addition to the smallness of the value of $\varDelta t$, the dissolved amount of picric acid was very small both in crude and purified specimens, and was of the order of about 1/100 of the specimen employed. These facts show that the correction is very small in both cases. Moreover, as the value of $\varDelta t$ seems not to be much different in both cases, the writers employed the value of $\varDelta t$ found thus with crude picric acid too in the case of the purified one. As to the correction due to the variation of the density of water with temperature, we had only to take the value of the density of water at the temperature at which the measurement was performed as the value of S, the density of the liquid in which the specimen and the broken glass tube are immersed. As the sample of the picric

acid was rather a porous one, it was ground into fine powder in a mortar before the measurement, so as to crush the enclosed vacant spaces as much as possible.

The results thus obtained are summarised in Table I and Table II. In every experiment the quantity of the picric acid employed was of the order of from 5 to 10 grams, and the probable error in the value of the density is estimated to be of the order of ± 0.001. For purified picric acid we get the mean value of 1.764^2 from six different measurements as its density; and this seems to be the most reliable value, though it is a little smaller than 1.767 given in Physikalisch-Chemische Tabellen of Landolt and Boernstein.

Table I.   Crude picric acid

No. of experiment	Apparent density d	Real density D
1	1.7718	1.7704
2	1.7731	1.7717
3	1.7737	1.7725
4	1.7737	1.7714
5	1.7713	1.7703
Mean value	1.772^7	1.771^3

Table II.   Purified picric acid

No. of experiment	Apparent density d	Real density D
1	1.7650	1.7632
2	1.7664	1.7651
3	1.7654	1.7642
4	1.7656	1.7645
5	1.7641	1.7630
6	1.7679	1.7652
Mean value	1.765^7	1.764^2

In conclusion the writers wish to express their hearty thanks to Professor Nozu for his kindness in preparing purified samples of picric acid for the present experiment.