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W. G. Palmer

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Introduction

NOTES ON WEIGHING, CALIBRATION, AND THE USE OF GRAPHICAL METHODS

(1) Weighing

To weigh 0.5 g. of precipitate to 1 mg., or 1 in 500, when it is contained in a crucible weighing 20 g., demands an accuracy of 1 in 20,000 in the balance, which should therefore be treated with the care and attention due to delicate apparatus. The sensitiveness of a balance, measured by the displacement of the beam by 1 mg. difference in load, depends principally on the inertia, i.e. size, of the beam, and, less markedly, on the total load. A micro-balance, used for weighing minute masses, is therefore literally a small balance.

If a balance of the enclosed type is of good quality, kept in a suitable room at even temperature and not exposed to direct sunlight, it may be assumed that mechanical defects, such as unequal length of beam, are absent. It may, however, be remarked that weighing by difference, which is almost always the method of chemistry, does not of itself eliminate the effect of such a fault, unless the nature of the determination in hand implies that the weighings will be used in ratio; thus the error is eliminated in a cryoscopic determination of molecular weight when the solvent and the solute are both weighed on the same pan of the same balance, but not when the solvent is measured by volume. In the latter case, however, the error will usually be merged in the probably greater errors in volume measurement. It is hardly worth while to calibrate good-quality modern weights; if this is attempted, it is probably better regarded as a test of the operator's skill in exact weighing than as a test of the accuracy of the weights.

It is advisable to acquire the habit of regarding the scale

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over which the pointer swings as graduated thus (or in the opposite sense):

0	5	10	15	20
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and not to place the zero graduation in the centre. On the plan advocated the resting-point is found simply by dividing the sum of the readings of the extremities of the swing by two, and confusing differences of sign will not arise. Thus if the swings give 6.5, 15.1 and 7.0, the resting-point is

$$\frac{1}{2} (6.75 + 15.1) = 10.9.$$

With a little practice this calculation can be correctly made without the aid of pencil and paper.

Before proceeding to an accurate weighing, the resting-point of the unloaded balance should always be checked; only if this point does not lie within the limits 7 to 13 does the balance need adjustment, by appropriate movement of one of the small screws at the ends of the beams. Much time is saved in the final adjustment of the rider if the sensitiveness (defined above) is approximately known. To determine this, set the rider at its zero position (where it should always be found at the beginning of a weighing, and when the balance is out of use), and then at the 1 or 2 mg. mark, observe the swings and calculate the resting-point for each position; the difference gives the required sensitiveness. It may be assumed that for moderate loads the sensitiveness is constant, but the variation can, of course, be tested if desired by carrying out the above operation with different equal loads on the pans.

Before starting an exact weighing, demanding considerable time, it is worth while to consider whether the accuracy attainable in other parts of the work merits such exactitude. A 'rough', i.e. open, balance weighing to 1 cg. should not be despised, and its employment in suitable instances may avoid much waste of time. Such a balance should always be used as a preliminary when it is desired, as in a freezing-point determination, to place in the weighing tube a pre-determined amount of substance, and for loads greater than 100 g.

It is perhaps unnecessary to stress the safeguard of double-checking the weights used, by adding on the pan, and subtracting in the box. Some boxes of weights are provided with only three compartments for the four pieces 500, 200 and two 100 mg. In this case mistakes are avoided by keeping the similarly shaped 100 mg. pieces separate, and the unlike 500 and 200 mg. in the same section. If necessary adopt the same arrangement for the 50, 20 and 10 mg. pieces.

(2) Calibration and standardization

Apparatus which may be expected to need calibration for use in work of even moderate accuracy comprises (a) volume-measuring apparatus, (b) temperature-measuring instruments.

(a) *Volume-measuring apparatus*

A distinction must be drawn between delivery apparatus, such as pipettes and burettes for liquids, and apparatus designed to contain a known volume. Calibration of pipettes is effected by weighing a charge of liquid delivered into a stoppered weighing bottle, the exact density of the liquid at the temperature concerned being ascertained from tables. Wherever possible the calibration should be made with the liquid to be subsequently used in the pipette, as differences of surface properties and viscosity lead to different drainage and shape of meniscus; mercury should never be used in standardizing pipettes for other liquids. A calibration is only strictly valid for the temperature at which it has been made, but no error appreciable in ordinary work is introduced by neglect of this point, if only small temperature variations are allowed. Volume-containing apparatus, such as graduated flasks, are calibrated by filling with liquid and weighing, on a suitable balance. Here drainage does not come in question, and difference in shape of meniscus is usually a very small fraction of the whole volume, so that water may always be used.

Calibration of burettes for liquid delivery. Burettes for delivery of liquid may be standardized (for aqueous liquids) by the

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following method. An auxiliary pipette of the form shown in fig. 1 is prepared. The bulb should have a capacity somewhat less than the volume steps in which it is desired to calibrate the burette; steps of 5 ml. are not too large for a burette of good quality. The delivery tube of the pipette is closed by inserting a small glass bead *B* in the rubber connexion *c* (a spring-clip should *not* be used). The pipette is firmly attached to the delivery tip of the burette by a stout rubber union (in which it is desirable that the ends of the glass should touch), and held upright by the wire *w*.

Water is flushed from the burette through the connexions to remove all air-bubbles. The bulb *A* is emptied by squeezing the rubber round the bead *B* and thus opening a small channel; no air-bubble must remain in either connexion. An arbitrary level is marked below the bulb *A* at *d* by surrounding the tube with a narrow band of gummed paper. The burette is now filled, the water level

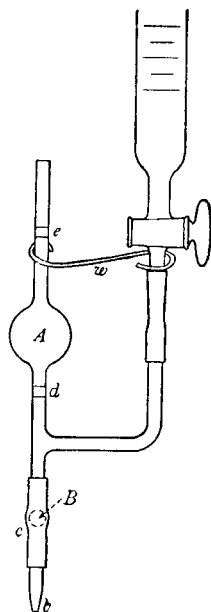


Fig. 1

brought as exactly as possible to the zero mark, and the burette tap then shut. Water is then run from the pipette (by opening the bead closure) exactly to the mark *d*, time being allowed for the full drainage of the bulb. The pipette is now refilled from the burette by allowing the water to descend slowly to the 5 ml. mark; the setting on the burette (which need not be exactly at 5 ml.) is read, and the upper level of the water in the pipette marked on the stem at *e* by the use of gummed paper as before. The contents of the pipette are now discharged to the mark *d* into a previously weighed stoppered bottle. Another portion of water is now allowed to flow from the burette exactly to the upper mark *e*, the burette setting noted, and the pipette then discharged as before into the bottle.

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Proceed in this way until the whole content of the burette has been run out in equal portions. The total weight of the water collected in the bottle being ascertained by a second weighing, its total volume is found by taking its temperature and using the density obtained from tables. The capacity between the marks on the pipette is now exactly known, and hence the true volume corresponding to the burette readings. A graph is made on squared paper relating readings to true volume, and the points joined by straight lines. Corrections for intermediate readings can then be read from the graph.

Example

Total weight of ten pipette charges = 50.440 g.

Temperature = 18.0°.

$$\begin{aligned} \text{Pipette capacity} &= \frac{5.044}{0.99878} = \frac{5.044}{1 - 0.00122} \\ &= 5.044 (1 + 0.00122)^* \\ &= 5.049 \text{ ml.} \end{aligned}$$

Burette reading	True volume ($n \times 5.049$)	Correction
5.00	5.05	+ 0.05
10.05	10.10	+ 0.05
15.10	15.15	+ 0.05
20.20	20.20	0.00
25.21	25.25	+ 0.04
etc.	etc.	etc.

Density of water (g./ml.)		Density of water (g./ml.)	
°C.		°C.	
15	0.99929	19	0.99859
16	0.99913	20	0.99839
17	0.99897	21	0.99818
18	0.99878	22	0.99796

Calibration of gas-holding apparatus. The capacity of glass apparatus intended to contain gas should be calibrated with

* When x is small, $(1 - x)^{-1} = 1 + x$.

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mercury, when the connexions allow, and the size is small, but more usually it will be necessary to calibrate by ascertaining the pressure change when *dry* air, at atmospheric pressure, is expanded from a standard capacity into the highly exhausted apparatus. For maximum accuracy the standard volume should be nearly equal to the volume to be standardized. Gas burettes may be calibrated by a method analogous to that given above for burettes delivering liquid. A small glass pipette, of 2–5 ml. capacity, with capillary tubes (fig. 2), is first calibrated with mercury between marks on the tubes. The pipette is then connected with the gas burette as shown, and filled with mercury to the upper mark with the aid of the levelling funnel *F*. The gas burette is filled with dry air through the side-tube *t* and the mercury set to its lowest graduation and levelled. The side-tube being now closed, air is drawn from the burette into the pipette to the lower mark by lowering the funnel *F*. After again levelling the mercury in both pipette and burette, the reading on the latter is noted. The air is now expelled from the pipette through the opened side-tube and the above operation repeated until the whole of the air has been taken from the burette.

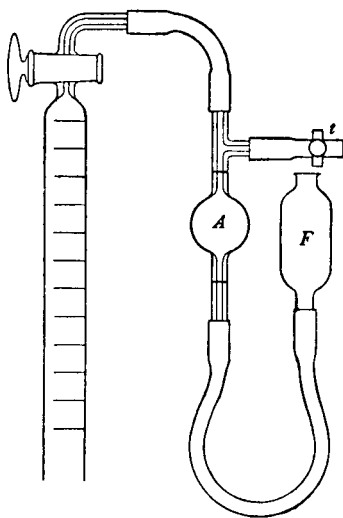


Fig. 2

(b) The calibration of thermometers, and thermo-couples

As fixed points the invariant systems provided by solid-liquid mixtures, under atmospheric pressure, are always to be preferred to boiling-points, on account of the insensitivity of the former to pressure change, and also because in

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general crystalline solids are far more easily purified than liquids.

Transition points of hydrated salts are eminently suitable as fixed points in the range near room temperature, as the required systems are very readily set up, and the temperature, once established, remains constant, even in simple apparatus, for an exceptionally long period, usually over 1 hr.:

0°. Ice-water. For procedure, see exp. *c* (i), p. 104.

32.383°. $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} \rightleftharpoons \text{Na}_2\text{SO}_4 + 10\text{H}_2\text{O}$. * Pure sodium sulphate (e.g. *Analar* brand) must be used. The method of exp. *b* (i), p. 73, should be followed.

48.45°. $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O} \rightleftharpoons \text{Na}_2\text{S}_2\text{O}_3 \cdot 2\text{H}_2\text{O} + 3\text{H}_2\text{O}$. †

50.674 ± 0.005°. $\text{NaBr} \cdot 2\text{H}_2\text{O} \rightleftharpoons \text{NaBr} + 2\text{H}_2\text{O}$. ‡

The solubility diagram for sodium bromide is very simple, § while that for the thiosulphate is exceptionally complex †. On this account the sodium bromide system would be preferred, were it not for the extreme difficulty of purifying the salt from chloride (Richards and Wells).

To use the thiosulphate system, proceed as follows. 50 g. of the pure pentahydrate (*Analar* brand) are placed in a boiling tube and kept at about 60° until an easily stirred mixture of solid and solution is produced. The tube is closed with a grooved cork carrying the thermometer, and is transferred to a larger tube serving as an air-jacket (see fig. 34), which may, for greater accuracy, be immersed in a water-bath regulated to 40°. The mixture is stirred regularly as the temperature falls to about 47°, when it is seeded with a small quantity of the pentahydrate. After inoculation the stirring is continued vigorously, when the temperature rises rather slowly to a maximum at 48.45°, where it remains constant for

* Redlich and Loeffler, *Z. Elektrochem.* **36**, 716 (1930).

† Picon, *Bull. Soc. chim. France*, **35**, 1097 (1924).

‡ Richards and Wells, *Z. physikal. Chem.* **56**, 348 (1906).

§ Abegg, *Handbuch*, **2**, Abt. 1 (Group I), p. 236; also Gmelin, *Handbuch*, Aufl. 8, Syst.-Nr. 21, Sodium, p. 420.

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over an hour, if the mixture is stirred occasionally to prevent it from clotting into a hard mass:

80.22°. The melting-point of naphthalene*. For method see p. 96.

100°. Use a steam-distillation method, as on p. 92.

For temperatures over 100° the following melting-points of metals are to be recommended; commercial pure tin and zinc are suitable, but a specially pure quality is required for lead:

183 ± 0.3°. The tin-lead eutectic.† The required mixture contains 61.9% by weight of tin.

231.9°. The melting-point of tin.‡

327.4°. The melting-point of lead.‡

419.5°. The melting-point of zinc.‡

For ordinary work the metals may be melted in deep crucibles under a layer of charcoal, and the temperature arrest on cooling registered; very little under-cooling is usually observed (see exp. (a), p. 97). The eutectic mixture should be occasionally stirred (with a thin carbon-arc pencil) during cooling. For very accurate standardization the metals must be manipulated in an inert atmosphere.

(3) The use of graphical methods

The portrayal of a series of experimental results in a graph is too well known a method to need description here, but the graph is too often drawn outside the laboratory after the experiment is completed, and possibility of modification or confirmation has passed. When an experiment involves the observation of a continuous change (e.g. cooling or heating curves, freezing-points in a molecular-weight determination, titration of samples in a reaction-velocity experiment), each successive reading should be plotted on squared paper directly it is taken.

* Timmermans, *Physico-chemical Constants of Pure Organic Compounds*, Elsevier, 1950, p. 178.

† Raynor, *Inst. Metals Ann. Diag.* No. 6, 1954.

‡ *Natl. Bur. Stand., Circular C 500* (1952).

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It is only from the evidence of a contemporaneous graphical record that the course of an experiment involving continuous variation can be intelligently followed, expected changes recognized, and, no less important, the source of novel effects explored in time to be either confirmed or rejected as spurious. When the magnitude of the probable error in the readings is known, this should be expressed in the graph by using lines, ellipses or circles instead of points.

A fundamental simplicity in natural law may legitimately encourage an expectation of discovering numerous linear relationships, but it is well to make sure in a particular case that the linear appearance of a graph is not due merely to an inappropriate choice of scale, or, for example, to the fact that $\log x$ varies more slowly than x .

In the author's opinion firm freehand drawing is superior to any form of flexible 'spline' in the production of justly drawn curvilinear graphs, but a length of 'composition' gas piping, $\frac{3}{16}$ or $\frac{1}{4}$ in. external diameter, which can be very easily bent to follow even high curvatures, forms a valuable guide if the graph is to be inked over. The best 'lie' of a suspected linear graph cannot be properly assessed by using an opaque ruler, and only indifferently by a transparent one. A better method consists in sliding the paper on which the points are marked under a length of thread stretched tightly between two drawing pins, until a satisfactory setting is reached; the correct ordinate and abscissa are noted and the line subsequently drawn through these points. A similar device can be recommended for 'tangenting' a curve (exp., p. 248).

Chapter I

THE DENSITIES OF GASES AND VAPOURS

The absolute density of a gas is defined as the mass in grams of 1 l. at N.T.P., and the relative density as the ratio of the density to that of hydrogen, under the same conditions, not necessarily N.T.P. Absolute density is thus to be expressed as a mass, and relative density as a pure number.

After the general acceptance, about the middle of last century, of Avogadro's theory, a rapidly increasing importance attached to the determination of gaseous and vapour densities as a means of establishing molecular and atomic weights. Methods of later date, especially those based on the principle of limiting densities, must be ranked among the most exact means at the chemist's disposal for the evaluation of atomic weights, at least of the lighter elements. In other directions it may be noted that even an approximate value of the density of a gaseous mixture may yield important information about its composition; and that we owe the discovery of the inert gases to an investigation of the density of atmospheric 'nitrogen'. The accounts by Lord Rayleigh of his researches on the densities of common gases should be consulted as still unsurpassed examples of exact work on this subject (refs. p. 12).

The following exercises illustrate the various ways of making for gases and vapours the two estimations of (1) weight, (2) volume, to which all determinations of the density of matter must reduce.

(1) The determination of molecular and atomic weights from gaseous density

(a) *The method of limiting density*

For gases of not too high molecular weight, and at pressures not greater than atmospheric, the van der Waals equation of state becomes practically exact:

$$(p + a/V^2)(V - b) = RT, \text{ or } pV = RT + bp - a/V + ab/V^2. \quad (1)$$