A handbook of chemical manipulation

Williams, Charles Greville

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Section VI. Heat Measurers

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SECTION VI.

HEAT MEASURERS.

Thermometers. Pyrometers.

63. In chemical research there are few things of more importance than the accurate measurement of temperatures; in fact, when we consider that the theories of chemistry, as now received, more especially the organic part, are, to a great extent, founded on the relations of substances to heat, we shall see that one of the most important things to a chemist is the unimpeachable accuracy of his thermometers. The laws of expansion of gases, by which we calculate the results of experiments on the specific gravity of vapours, the theory of the rise of boiling-point in liquids as the carbon atoms increase, and lowering of the same by the addition of hydrogen, facts which promise to have the most important bearings upon all the ramifications of chemical philosophy, are entirely dependent for their experimental verification on the correctness of our means of measuring minute variations of temperature. Moreover, the actual practice of ordinary chemistry shows frequent instances of the importance of an intimate acquaintance with the manipulations connected with heat-measurers. Fractional distillation is sometimes the only means we have of separating substances from each other; and it is also possible, in some instances, to effect a more or less perfect disjunction of bodies having different points of volatility, by keeping the mixture at a steady temperature, by which means we may expel the more volatile, and thus obtain both in a state of comparative purity. In the section on Distillation, we shall notice some points of this kind.

64. To construct a thermometer of even moderate approximation to accuracy, is a matter of far more difficulty than would be supposed from the directions to be found in some works on this subject. The difficulties alluded to are almost entirely of a practical description, and relate to peculiarities in the details of the

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process which would not suggest themselves to many persons. It is therefore strongly advised that the student should not attempt the construction of these instruments, even if he has obtained considerable proficiency in glass-blowing, it being quite unnecessary in an economical point of view, as it is possible to obtain excellent instruments at comparatively moderate prices. Nevertheless, as in a work on Manipulation it would be improper to omit a short description of the method adopted in the construction of these useful adjuncts to the student's labours, the following brief outline will be found to give an idea of the nature of the process.

65. In the first place, we must decide whether to select a tube of perfect equality, or to content ourselves with an imperfect tube, making allowance for the variations in the calibre in a subsequent stage of the proceedings. It has been said by an eminent philosophical instrument maker, that a perfect tube is never to be found; such, however, is not the case, and those whose chief occupation is the construction of thermometers, and who, consequently, have always at hand a very large stock of tubes to select from, are frequently able to cut from a long tube, a portion sufficient for the construction of an instrument so nearly perfect, that no error can be made evident even by the most carefully applied tests.

66. The best method of ascertaining the fitness of a tube for the construction of a thermometer according to the first method, is to draw a small quantity of mercury, say 1 inch, into it and measure it at different intervals; this is easily effected by moving the tube in such a manner as to cause the mercury to pass slowly down; if it measures exactly the same at several points, both at the ends and middle, it is, of course, evident that the bore is equal. The operation of calibrating the tube may be facilitated by the use of the thermometer-gauge; it consists of a syringe, the piston-rod of which is formed from a fine screw, so that by turning the milled head at the top, it may be made to descend, or ascend, in the cylinder, which is filled with mercury. On connecting the instrument by a caoutchouc joint with the

thermometer-tube, so as to be quite air-tight, we have it in our power to inject a small or large portion of mercury at will; and, by a very little management, it may be separated into a column of any length, and be moved with facility to every part of the tube. It is scarcely necessary to caution the operator against handling the tube during this operation in such a manner as to cause the mercury to expand from the warmth communicated by the contact of the fingers.

67. In the next place, we must consider that if it is intended to construct an instrument with a very open scale, or, in other words, one which is to be greatly affected by comparatively small variations of temperature, a different proportion between the dimensions of the tube and the bulb will be necessary, than if the reverse is required. In the first case, we have a very large bulb and an exceedingly small bore, and, in the other, the bulb is made smaller, and a tube is selected of larger calibre. It is advisable to form the bulb into a cylinder instead of a globe, if it be intended to introduce it into retorts. To insert the mercury, the bulb is to be moderately heated to expand the air, and the open end of the tube is plunged under the surface of the metal; as the air cools and contracts, a portion enters the tube and bulb, and is then to be boiled rapidly, the tube being kept hot, and this is continued until the bulb and tube are filled with vapour; upon again plunging the open end into the metal and letting the whole cool, the vapour is condensed, and the instrument becomes filled with the fluid. It must now be considered upon which portion of the tube it is wished that any given point of the scale should fall: supposing, for instance, that it is desired the freezing-point should be about 1 inch from the bulb, and the boiling-point about the same distance from the other end, the instrument is plunged first into melting ice, and if, after it has attained the temperature of the medium, the mercury is found to occupy too high a point upon the scale, a portion is expelled by warming, but if it falls too low, some more is introduced by the same process as before; the operation is then repeated, substituting boiling water for the ice, and the point where the mercury rises to is observed; when

this is done, the flame of the lamp is directed about an inch above the spot to which the mercury rose at 212°; the glass is then drawn out until capillary, and the next point is to expel the air in the tube, that in the bulb having been already got rid of in the first part of the operation. The bulb is to be warmed until the mercurial column ascends, passing through the capillary into the piece of thermometer drawn out; by this procedure the mercury is made to fill the place previously occupied by the air; at this step of the proceedings the flame is directed upon the capillary tube, which is closed and removed.

Before fashioning the end into the knob or ring which is always seen upon the instruments (according as it is to be fixed in a wooden scale, or be graduated upon the stem), it is necessary to examine it carefully to ascertain the entire absence of air from the bulb and tube, which may be done as follows:—invert the instrument so that the bulb is uppermost; if the mercury descends with ease quite to the end we may be sure that air is absent, but it may nevertheless be in the bulb; to ascertain this, we must observe whether the vacuum bubble, which enters the bulb when the instrument is inverted, entirely vanishes from it upon restoring the tube to its proper position; if it does so, we may conclude that, in that respect, the instrument is perfect; if not, the fine point left upon drawing off the capillary-tube must be broken, and the operations previously described repeated, until the result required be obtained.

68. Sometimes a thermometer, when inverted, does not allow the mercury to descend, and inexperienced persons are liable to imagine that air must necessarily be present; but the effect alluded to is frequently caused by the adhesion between the mercury and the glass; if, however, we warm the bulb so as to cause the mercury to ascend in the tube and then invert the instrument, the metal should descend; and if no moderate tapping or swinging will make it do so, we may safely conclude that air forms the impediment. Supposing, however, all these trials to have yielded satisfactory results, we may proceed to lay off the scale, which is usually effected by plunging the instrument first into melting ice,

and then, after the temperature of the bath is attained, marking the position of the mercury upon the tube; we now place it an inch from the bottom of a deep metallic vessel nearly filled with water, and heat until rapid ebullition ensues, care being taken that the barometer is at, or very near, the standard height, otherwise a correction must be made; in this manner another point upon the stem is formed, and from these two points all the others are obtained. Fahrenheit's scale being, if not the most philosophical, at all events the standard generally adopted in England, it is usual to divide the space between the two points mentioned into 180 equal parts or degrees, and, if the calibre of the tube be perfect, the gradations may be continued upwards and downwards as far as may be desired. For all purposes of ordinary research, it may be assumed that the expansion of mercury is equal for equal increments of temperature; we need not therefore make the degrees above 212° of a different value to the others*.

69. The directions given for the construction of a thermometer will also enable the student to examine the accuracy of any that he may purchase; it must be remembered, therefore, that the examination resolves itself into the following operations, viz. measuring a column of mercury at different intervals along the tube to ascertain the equality of the bore, ascertaining that the degrees on the scale are equal in value by measurement of the number of degrees included between any given distance with a pair of compasses, and taking the freezing- and boiling-points,—not forgetting that a difference of 1 inch of mercury in the height of the barometer raises or lowers the ebullition point by almost exactly two degrees Fahr.†,—and, finally, testing the instrument as to the presence of air by the methods already given.

70. In chemical investigations, the most generally useful thermometer is one capable of being introduced into the tubulature of a retort, the bulb being, with this intent, made narrow and

* The increasing dilatation of the mercury, as the heat becomes greater, is nearly compensated for by the expansion of the bulb.

† For Table of boiling-points of water at different pressures, see end of the volume.

cylindrical, and the graduations directly engraved on the stem, as in fig. 57. The first thermometers made on this plan had, however, the disadvantage of preventing the position of the metal being observed by reflected light without considerable difficulty. It was usual, therefore, to keep a piece of paper behind it to facilitate the reading. Mr. Negretti has, however, entirely obviated the necessity for this, by having his tube made with a portion of white enamel down the back, so that the mercury is always distinctly seen. Those instruments which consist of two parts, being a thermometer with a paper scale placed inside a tube, are worse than useless; in the first place, although so bulky as to be impossible to be introduced into the tubulature of a small retort, they are infinitely more fragile than the far more slender ones engraved on the tube; in the next place, the paper scales contract by exposure of the instrument to even moderately high temperatures, causing, of course, considerable error from this alone; and when, as in some instruments I have seen, the scale is fixed in its place by sealing-wax, it is of course impossible to use it with any degree of safety.

Fig. 57.

Thermometers attached to wooden or ivory scales are equally inconvenient with those last described; in most chemical experiments, especially where accuracy is indispensable, even if the wood is jointed near the bottom, and has a hinge so placed as to permit it to be folded back to enable the bulb and part of the stem to be immersed in fluids, still the wood is liable to contract and warp, owing to its being exposed to considerable changes of temperature and variations in moisture.

71. No mercurial thermometer should be used for temperatures higher than 580° Fahr., above that point there being danger of the mercury boiling in the tube, as, from being *in vacuo*, the point of ebullition is lowered considerably.

Care must be taken, where the temperature of a fluid is to be observed, that sufficient time is allowed for the bulb and the mercury contained in it to acquire the same degree of heat as the medium. And this is especially necessary with gases, where, from their small conducting power, the time required is much greater.

72. In all experiments upon the volume of gases the accurate determination of temperature is of the last importance, from the great degree in which their bulk is influenced by the expansion, the coefficient of expansion of air for each degree Centigrade being 0·00367*.

73. All laboratories where chemical researches are undertaken, should be provided with several thermometers; one or two should have a range from zero to about 580° Fahr.; a very small one should also be at hand, capable of being introduced into a specific gravity bottle, to indicate the temperature of the fluid under examination. The same thermometer, if very accurate, may be used for gas experiments; but it is better to have one with a very large bulb and an exceedingly fine tube, so as to show readily minute differences.

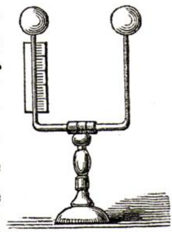
74. It will be quite unnecessary to describe all the varieties of thermometers in use in the various departments of science, the more especially as the investigations in which they are used are more of a physical than chemical nature; there are, however, some, which, from the fact that the chemical characters of substances are sometimes dependent upon their indications, fall to a certain extent within the plan of this work; in the list are found the Differential Thermometer, the Thermo-electric Multiplier, the Self-registering Thermometer, the Air-thermometer, and the Pyrometer.

75. It sometimes happens in physical investigations that it is wished to ascertain whether a given phenomenon is capable of producing heat or cold under circumstances in which the ordinary thermometer is inadmissible; when it is merely desired to know whether a difference of temperature exists or is occasioned by the

* For Table of expansion of gases by heat, see end of volume.

phenomenon under examination, the instrument figured in the margin, and first used by Leslie in his experiments on heat, may be used. It consists of two balls (fig. 58) containing air and sufficient coloured oil of vitriol to fill two of the three limbs of the tube; when in the normal state, the liquid stands at the same height in both of the upright limbs, but when *one* of the bulbs is placed in a position where it is expected to find a disturbance of the thermal equilibrium, any change is instantly indicated by the motion of the fluid; if the temperature falls, the air in the bulb contracts its volume and the liquid rises in the tube; but if, on the other hand, heat is developed, an expansion takes place and the fluid recedes. An arbitrary scale is usually attached to the limb, but the amount of disturbance generally gives a sufficient idea of the degree of heat or cold developed; when, however, a scale is used, it may, if necessary, be converted into one of known value by comparison with a mercurial thermometer.

Fig. 58.



76. The Thermo-electric Multiplier of Melloni is an instrument intended to measure excessively small thermal differences by the amount of electricity developed in a number of bars of antimony and bismuth arranged in a series; the degree of excitement being indicated by the degree of angular motion of the astatic needle of a galvanometer.

77. The Self-registering Thermometer of Negretti and Zambra is an ingenious contrivance intended to facilitate the working out of meteorological observations, and is also used in techno-chemical processes for ascertaining the maximum temperature to which drying closets, &c. have arrived during the night, or any time when actual inspection of an ordinary thermometer placed inside is impossible. It is well known that the old instruments for this purpose contained in the tube, which was bent at right angles at a short distance from the bulb, small rods of steel or enamel, which being propelled forwards, as the mercury or spirit advanced, were left behind as it receded, and consequently indicated the maximum

temperature; but in the instrument now under consideration, the tube, which is bent as in the old ones, has a small piece of glass inserted a short distance from the bulb, which allows the mercury to pass it while expanding; but when contraction takes place, the metal is prevented by the impediment from returning to its normal position. When it is required to return the mercury to the bulb for the purpose of making a fresh observation, the end furthest from the bend is to be elevated, and the instrument is slightly agitated; by this means the metal repasses the obstruction and indicates the temperature at that time.

78. The Pyrometer of Daniell is an ingenious but comparatively seldom-used instrument, intended to effect the measurement of high temperatures, such as that of furnaces, by the expansion of a bar of platinum; the old plan of Wedgwood, which endeavoured to effect the same object by measuring the contraction that wedge-shaped pieces of clay underwent by exposure to heat, was liable to so many objections, that it became absolutely necessary to devise some plan by which high temperatures could be ascertained with precision; but, while the instrument of Daniell effects the object with greater accuracy than perhaps any other, its use is very limited, it being seldom necessary, in the present state of chemical investigation, to require for guidance anything more than is contained in the expressions dull red, bright red, yellow and white heats. It is undoubtedly true, that, as the science advances, more attention to the regulation of temperature will be required, as even now there are many instances known to chemists, where the same substances acting on each other at different temperatures produce very different compounds by their mutual reaction; and it is more than probable, that by greater attention to the modulation of temperature, the intensely interesting but highly complex groups of substances produced during the destructive distillation of animal and vegetable matters might be much better understood. As a general rule, it may be asserted that the higher the temperature the simpler the constitution of the substances formed, the more complex groups breaking up under the influence of strong heat into substances whose formulas contain a less number of

atoms, and those arranged in a manner which enables their relation to each other to be more clearly seen.

79. It fortunately happens that those methods of investigation in which the exact measure of temperature is necessary, seldom require a heat sufficiently intense to soften glass; when, therefore, the limits of the mercurial thermometer are passed, it is possible to have recourse to the air-thermometer, in which the values sought are obtained by the expansion of a known volume of air: this method is used chiefly in ascertaining the specific gravities of the vapours of the less volatile substances, and from the nature of the operation and the corrections required (the result of the air-thermometer being influenced not only by temperature, but also by the variations in the atmospheric pressure), the process is one requiring a little care in manipulation.

80. For the more modern and accurate data and researches upon this subject, chemists are chiefly indebted to the labours of M. Regnault; and as the process is every day becoming more indispensable, we shall quote the following description of the apparatus and method of procedure*.

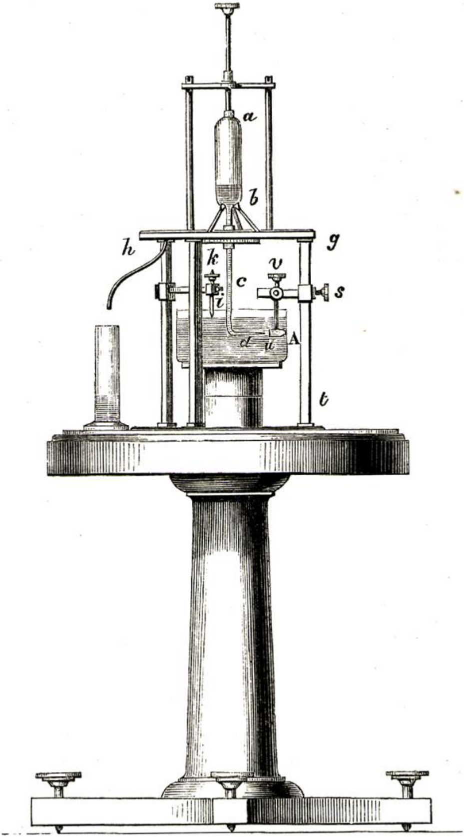
81. "The air-thermometer used in these experiments consists of a simple cylindrical glass reservoir of about 2 centimetres in diameter and 12 or 15 centimetres in length, and terminating by a capillary tube, of which the calibre is 1 or 2 millimetres, and which is bent to a right angle and drawn out at its end. The reservoir, *a b*, is kept in the bath alongside of the balloon in which the vapour is to be generated. The first step is to perfectly dry the reservoir, *a b*, by creating a vacuum in it several times, and allowing air to enter which has been dried by passing through a tube filled with pumice-stone soaked in concentrated sulphuric acid; after which the bath is heated, and when the temperature

* Regnault, Cours Élémentaire de Chimie, tome quatrième, p. 63. I have, however, taken the engraving from the plates in the Mémoires de l'Académie Royale des Sciences de l'Institut de France, tome xxi., merely altering the lettering to suit the text. I have also, in a note, given the co-efficients of expansion of glass from a different part of the same work, and inserted the meaning of the letters used in the formulæ, in order to make the quotation intelligible. The degrees apply to the centigrade thermometer.

becomes stationary at the point at which the experiment is to be terminated, the point of the balloon and that of the air-thermometer are closed simultaneously by means of a lamp.

82. "The air-reservoir is then placed on the metallic support represented in fig. 59, the stem passing through a cork which

Fig. 59.



closes a tubulure made in the centre of the disk g h, while the curved point, *c d*, enters a small mercurial bath. The extremity of the point being broken by pincers, the mercury rises in the tube and partly fills the reservoir *a b*, which is surrounded with pounded ice, in order to reduce the temperature of the air it contains to 0°, when the open point is closed with a ball of soft wax. In order to perform this operation easily, without changing the level of the mercury in the vessel A, a small iron spoon, *u*, is used, soldered to an iron rod, *u v*, which slides along a horizontal bar *v s*, itself moveable along the vertical foot *s t*; the moveable rod, *v s*, being fixed at such a height that the bowl of the spoon, filled with soft wax, is exactly at the height and in the direction of the point *d*. It is therefore sufficient, in order to close the point, to slide the end, *u v*, along the horizontal rod, *v s*. The mercury in the vessel, A, is then exactly levelled to the point, *i*, of a double-pointed screw, *k i*; the ice which surrounded the reservoir, *a b*, is removed, and, when the mercurial column attains the temperature of the surrounding air, the difference of height between the mercury in the reservoir, *a b*, and the upper point, *k*, is exactly measured by means of a cathetometer; and by adding to this difference the length of the screw, *k i*, the height, *h*, of the column of mercury elevated in the air-thermometer is obtained. Let h_0 be this height at 0°, H_0 the height of the barometer also at 0°, when the point, *d*, is closed with wax; then will $(H_0 - h_0)$ represent the elastic force of the air in the reservoir, *a b*, at the temperature of 0°. The support is then inverted, the air-thermometer removed, after having detached the spoon, *u*, and it is weighed with the mercury contained: let this weight be represented by Q. The thermometer is then filled with mercury, which is boiled to drive off the last bubbles of air, the point, *c d*, being kept during this time in a small capsule filled with mercury.

"When the apparatus is cooled, it is surrounded with melting ice, and completely filled with mercury at 0°; when it is again weighed, giving now the weight Q′. The weight, *q*, of the envelope of glass alone being ascertained, after having emptied it of mercury, $(Q'-q)$ is therefore the weight of the mercury at 0°, and $(Q-q)$ is the weight of the mercury in the thermometer when it was on the support; $Q'-Q$ therefore represents the weight of the mercury at 0°, which occupies the same volume as the air remaining in the thermometer when it is at 0°, and under the pressure (H_0-h_0). If we designate by δ the density of the mercury at 0°, $\frac{Q'-q}{\delta}$ represents the capacity in cubic centimetres of the thermometer, and $\frac{Q'-Q}{\delta}$ the volume which the air occupies in this apparatus at the moment of closing the point, *d*, with wax.

Now the capacity of the thermometer, at the temperature T, being $\frac{Q'-q}{\delta}(1+kT)$*, the volume of air $\frac{Q'-Q}{\delta}$ at 0°, and under the pressure (H_0-h_0), therefore occupies, when it is raised to the temperature T and under the pressure H'_0, a volume $\frac{Q'-q}{\delta}(1+kT)$. The volume assumed by a volume of air $\frac{Q'-Q}{\delta}$ at 0° and under the pressure (H_0-h_0), when raised to the temperature T and under the pressure H'_0†, may be calculated, by the known laws of the expansion of air, under changes of temperature and pressure; and is thus found to be

$$\frac{Q'-Q}{\delta}(1+0{\cdot}00367.T)\frac{H_0-h_0}{H'_0},$$

which leads to the equation

$$\frac{Q'-Q}{\delta}(1+0{\cdot}00367.T\ \frac{H_0-h_0}{H'_0}=\frac{Q'-q}{\delta}(1+k\,T),$$

whence
$$\frac{1+k\,T}{1+0{\cdot}00367\,.\,T}=\frac{Q'-Q}{Q'-q}\cdot\frac{H_0-h_0}{H'_0}.$$

* k = coefficient of expansion of glass. The following are the values of k.

Between 0° and	100°	k = 0·0000276
„	150	0·0000284
„	200	0·0000291
„	250	0·0000298
„	300	0·0000306
„	350	0·0000313

The above values are for the ordinary glass of which the balloons used in Parisian laboratories are made.

† H'_0 = height of barometer at time of sealing.

T may be deduced from this equation, but there is no necessity of knowing its value in order to calculate the density of the vapour, which is in fact represented by the expression*.

$$\frac{P'-P+p}{0{\cdot}0012932\,.\,V\,.\,\frac{1+k\,T}{1+0{\cdot}00367\,.\,T}\,.\,\frac{H'_{\circ}}{760}}.$$

Substituting for $\frac{1+k\,T}{1+0.00367\,.\,T}$ the value first found, there results for the expression of the density of the vapour,

$$\frac{P'-P+p}{0{\cdot}0012932\,.\,V\,.\,\frac{Q'-Q}{Q'\quad q}\,.\,\frac{H_{\circ}-h_{\circ}}{760}}."$$

* P = Weight of balloon and air.
P′ = Weight of balloon and vapour.
p = Weight of V centimetres of air at *t*.
V = Capacity of balloon in centimetres cub.
T = Temperature of vapour.
t = Temperature of air.—C. G. W.