ART. XXVI.—*Calorimetric Investigations;* by R. BUNSEN.*

1. *The Ice Calorimeter.*

THE calorimetric methods hitherto in use are attended with the disadvantage that proportionately large quantities of the calorimetric fluid, as well as of the substance under investigation, must be employed, in order that the loss of heat which unavoidably attends the measurements may be so reduced that all corrections therefor may be small in comparison with the amount of heat to be measured. In the determination of specific heat, especially when the more exact of the methods previously in use are employed, satisfactory results can hardly be anticipated when the amount of material used in the experiments is less than from 10 to 40 grams. The preparation of the rarer substances, in a state of absolute purity, in such quantities often presents almost unsurmountable difficulties, and it is perhaps only on this account conceivable that we are not acquainted with the specific heats even of all the elements which have been isolated in a state of purity, although these determinations are of fundamental importance for the establishment of the atomic weights.

The instrument described in the following pages is designed to aid in overcoming this disadvantage. It is based on the principle of measuring the amount of ice melted by the communicated heat by means of the diminution in volume which this ice undergoes on melting.

The instrument, fig. 1, which was made at the glass blower's lamp, consists of an inner glass vessel, *a*, having the form of an ordinary test tube and melted into the cylindrical glass case *b*. From this case *b* issues the glass tube *c*, to whose upper extremity the iron head-piece *d* is cemented. The inner vessel *a* is filled from α to μ, the outer case *b* from β to λ, with previously boiled water; the remainder of the case *b* together with the tube *c*, is filled up to the height γ with previously boiled mercury. In order to arrange the apparatus for use, a cylinder of ice enclosing the entire vessel *a* is produced in the case *b*, the whole apparatus is then surrounded with snow in a large vessel, and the calibrated scale tube *s*, which has been cemented into the cork with fine sealing-wax, is screwed down through the mercury of the head-piece *d* very tight into the opening of the tube *c*, whereby the scale tube fills itself with mercury. In order that the pressing in of the stopper may be unattended with danger for the rather fragile apparatus, the instrument is

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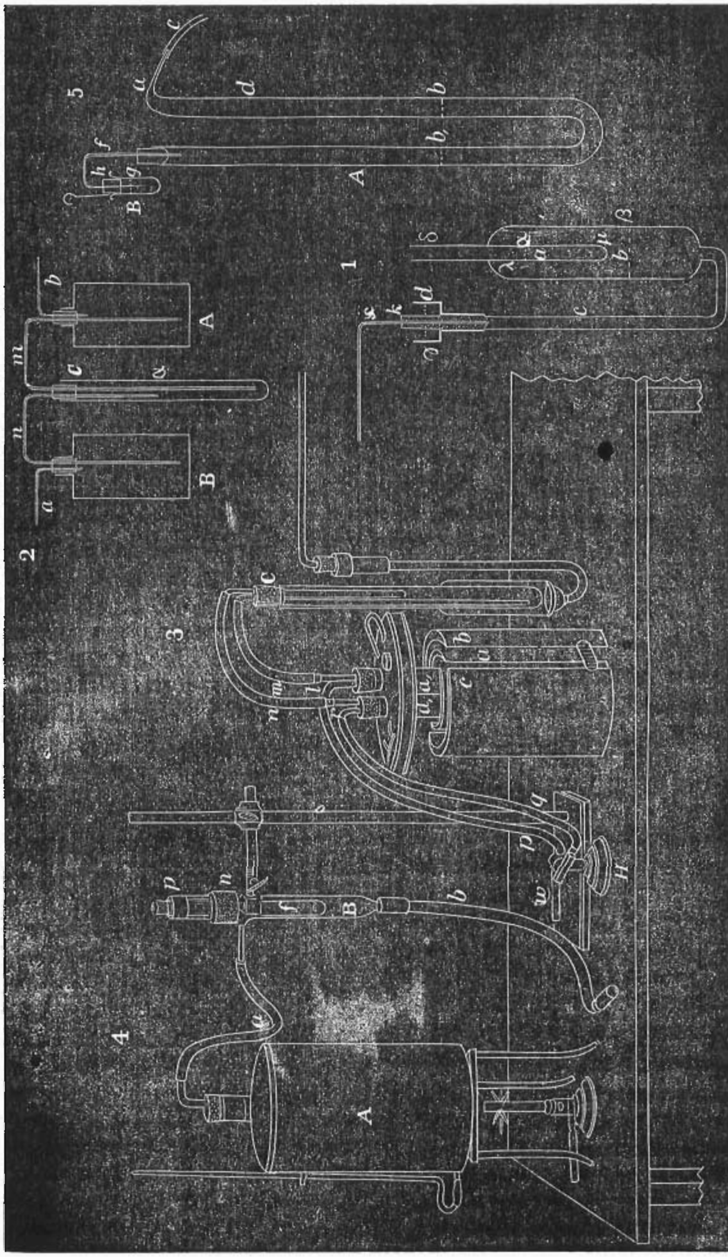

fastened on a heavy iron stand by means of a vice, whose jaws surround tightly the lower part of the iron head-piece *d.*

The amount of heat which a body evolves in cooling from a given temperature to 0° C., is determined by dropping it into the water in the vessel *a* and thereupon closing the vessel at δ with a cork, to prevent any circulation of air. If the problem be the relative measurements of quantities of heat, as in the determination of specific heats, then the standard of comparison is directly afforded by the number of scale-divisions which the mercury thread has passed on its retreat. If the readings are rendered in an absolute measure, as for instance, in grams of melted ice, or in units of heat, as the unit in the following pages, (always that quantity of heat being understood which one gram of water at 0° C. absorbs in order to raise its temperature to 1° C.), then it is only necessary to multiply the readings on the scale with a constant which results from the following consideration.

A mercury thread measured in the scale tube, which has the temperature $t°$ and occupies T divisions of the tube after being corrected by the calibration table, weighs g grams. Let further the specific gravity of mercury at 0° C. be S_q, its coefficient of expansion α, then is the volume v of a corrected division on the scale, measured in cubic centimeters,

$$v = \frac{g\,(1+\alpha t)}{S_q T}.$$

For the instrument which I used, the values were:

$g = 0{\cdot}5326$ $\quad\alpha = 0{\cdot}0001815$ $\quad t = 9°$ C.
$S_q = 13{\cdot}596$ $\quad T = 507{\cdot}4$

and therefore

$$v = 0{\cdot}00007733 \text{ c.c.} \qquad (1)$$

If the specific gravity of ice at 0° C. be denoted by S_e, the specific gravity of water at the same temperature by S_w, the weight of melted ice expressed in grams, which corresponds to the volume v, that is, to one scale division with p, then is

$$\frac{1}{\frac{1}{S_e} - \frac{1}{S_w}} = \frac{p}{v}$$

or

$$\frac{v\,S_w\,S_e}{S_w - S_e} = p \qquad (2)$$

With regard to the specific gravity of ice we have many observations. The following comparison shows how little they agree among themselves. For S_e

Thomson found	0·920	Plücker and Geissler,	0·920
Heinrich,	0·905	Kopp,	0·908
Osan,	0·927	Dufour,	0·922 (max.)
Royer and Dumas,	0·950	Dufour,	0·914 (min.)
Brunner,	0·918		

With so slight an agreement between these different observers, it appeared to me indispensable to determine, with greater exactitude than has hitherto been possible, the value of S_e necessary for the calculation of the constant p. I employed for this purpose the following method, in which the sources of error which have made the previous determinations uncertain have been entirely avoided: Fig. 5 is a thick walled U-shaped tube, of difficultly fusible glass, which has been drawn out at *a* to a thick walled point. This is filled with mercury to *b b*, and both limbs are well boiled out, as is done with barometers. The point *a* is provided with a small rubber tube through which, by means of alternate warming and cooling of the air in the limb *a b*, distilled water, free from air, is allowed to enter above the mercury by *b*. If this water be boiled for half an hour and the rubber tube *c* be kept under the surface of water, which has likewise been kept in continual ebullition in a beaker glass, the space *a b* will, as soon as the boiling by *b* is discontinued, fill itself completely with perfectly airless water. The rubber tube *c* is now closed under water by means of a small glass stopper and the point by *a* melted off, which may be easily and safely done with the ordinary non-luminous gas flame, without the aid of the blowpipe, when the part of the tube where it begins to narrow out into the point is so strongly heated that it is filled with steam instead of water. If the apparatus has been weighed before filling with water, and after the filling be weighed again together with the dry point, the weight of the water contained in the instrument will be obtained. The open limb is now completely filled with boiled-out mercury and especially, in order to prevent the adhesion of air bubbles to the glass walls, through a long capillary glass tube. If the apparatus be exposed in the open air to a temperature below 0° C., an ice tube, corresponding to the glass tube, will be formed which at last closes in different places, and still contains water surrounded with ice. By the freezing of these last portions of water the ice already formed is exposed to a very high pressure, which may very considerably alter its specific gravity, may in fact even burst the glass tube eighty-atmosphere strong. In order to remove this disadvantage and permit the ice formation to take place, during its entire duration, under the same pressure, it is simply necessary to sink the whole instrument in sawdust and to expose only the upper part by *a* to air of a temperature below 0° C., after you have previously, in order to prevent the effects of abnormal lowering of the freezing point (Ueber-schruelzung), produced an ice mass by *a*, which is allowed to dwindle by melting to a small granule. The freezing then goes on very regularly from *a* downward to *b* and can be very conveniently regulated by letting the limb containing the water project, according to requirement, more and more above the sawdust. The ice cylinder shows on its basis a very regular hemispherical cavity, which progresses unaltered until its edges touch the mercury by *b*, and the last portions of water have been frozen from above downward. After the formation of ice is at an end, the instrument is still exposed some time to a temperature below 0° C. in order to freeze the last traces of water which exist by *b* between the mercury and the glass walls. The ice cylinder thus formed is perfectly free from air bubbles, and equals in clearness and transparency the finest crystal glass. The piece of apparatus designated in the figure with the letter B is now combined, by means of the cork *e* forcibly pressed in, with the open limb of the apparatus A in such a manner that not a trace of air is included between the cork and mercury, whereby the displaced mercury flows through the capillary tube *f* into the glass vessel, which is filled with mercury to *g*. The capillary tube is cemented with the finest sealing-wax into the smooth and perfectly poreless cork. To cement the cork likewise on the wider tube in which it sits, would be wholly superfluous, as a displacement is as little to be feared as an elastic effect afterward, as I have convinced myself by direct experiment. The instrument thus arranged is placed in a room having the greatest possible constancy of temperature, and is surrounded on all sides with a thick envelope of snow which has, at a temperature above 0° C., become completely coherent without at the same time becoming saturated with water. When, after 6 to 12 hours, the entire instrument has attained 0° C., the mercury vessel is removed from the cork *h*, weighed with the mercury it contains, and, after any mercury which may still adhere to the capillary tube, has been carefully removed, returned to its place. The apparatus is then removed from its envelope of snow, the ice it contains is melted by radiation from a non-luminous gas flame brought in its neighborhood, and it is permitted to attain as before in an envelope of snow, the temperature of 0° C. The mercury vessel is now removed and reweighed. The loss in weight, compared with the first weighing, is the weight of the mercury, whose volume calculated for 0° C. expresses the diminution in volume which the ice cylinder at 0° C. has suffered in melting to water at the same temperature.

Let G_w be the weight of the water frozen,
G_q the weight of mercury which entered the instrument during the melting of the ice,
S_w the specific gravity of water at 0° C.,
S_q the specific gravity of mercury at 0° C.,
S_e the specific gravity of ice at 0° C.,

then is
$$\frac{G_q}{S_q} + \frac{G_w}{S^w} = \frac{G_w}{S_e}$$

and therefore:
$$\frac{S_w G_w}{G_w + \frac{S_w}{S_q} G_q} = S_e.$$

On account of the great accuracy which the method just described permits, it appeared to me superfluous to make more than three experiments. In the first of these the water froze between −3° C. and −5° C., in the second between −1° C. and −3° C., in the third between 0° C. and −2° C. The following weights, reduced to vacuo, were obtained:

	G_w	= 14·1580 grams.
1st expt.	G_q	= 17·4400 "
2d "	G_q	= 17·4624 "
3d "	G_q	= 17·4757 "

If we make further
$$S_w = 0{\cdot}99988 \qquad S_q = 13{\cdot}59600,$$
then the resulting specific gravity of ice S_e will be:

1st experiment,	0·91682
2d "	0·91673
3d "	0·91667
Mean of three expts.,	0·91674

We have therefore for the terms occurring in equation (2),
$$P = \frac{v\, S_e\, S_w}{S_w - S_e}$$
the values:
$$v = 0{\cdot}00007733 \qquad S_e = 0{\cdot}91674 \qquad S_w = 0{\cdot}99988$$
and thence
$$P = 0{\cdot}00085257.$$

The weight of melted ice e which corresponds to T corrected divisions on the scale is therefore:
$$e = 0{\cdot}00085257\ T \ldots\ldots. (3).$$

Let the latent heat of melting, for water, be l, then will one scale division correspond to $p\,l$ of the previously defined units of heat. For the amount of heat w, expressed in units of heat, which is indicated by T scale divisions, we have therefore,
$$w = p\,l\,T$$
or, if the value 80·025, hereafter to be determined, be substituted for l,
$$w = 0{\cdot}068227\ T \ldots\ldots. (4).$$

As the ice cylinder which surrounds the vessel *a* weighs forty to fifty grams, and it is necessary, on the average, to melt by each experiment only about 0·35 grams of ice, which corresponds to rather more than four hundred scale divisions, it is possible to make with the same ice cylinder as many as 100 different calorimetric determinations and to use the apparatus, arranged once for all, for weeks at a time, when care has been taken that the snow which surrounds the instrument be morning and evening renewed by refilling.

The ice cylinder may be easily produced by a contrivance which is rendered intelligible by fig. 2: A is a sheet tin vessel containing alcohol, B an empty one, both of which are cooled to about $-20°$ C. in a freezing mixture of salt and snow. C represents the inner vessel *a* fig. 1, around which the ice cylinder is to be produced. If suction be applied to the tube *a*, the cooled alcohol of the vessel A will be carried through the vessel C into the vessel B; if suction be then applied in the opposite direction by means of the tube *b*, the alcohol will return through the vessel C into the vessel A. By alternate suction at *a* and *b*, the vessel C may be kept to the height *α* as long as desired at a temperature of $-10°$ C. to $-15°$ C., by means of continually renewed cooled alcohol, and the required ice envelope will be produced in the water mass surrounding the vessel C which is denoted in fig. 1 by *b*. I have given this ice-producing apparatus the form, fig. 3. The *two* semi-cylindrical tin vessels *a* and *b*, which communicate with one another and with the tube *a* by means of tubes above and below, correspond to the *single* vessel A fig. 2, the precisely similar tin vessels opposite these, the outer one of which is denoted by *c*, correspond to the vessel B in fig. 2. These two vessels, each consisting of two concentric chambers, together with the tube *α*, possess, as may be seen, a very large cooling surface, and are sunk in one and the same freezing mixture. The arrangement of the system of tubes, fig. 3, by means of which the circulation of the cooled alcohol is effected, is rendered easy of comprehension, from the fact that the corresponding rubber tubes are designated by the same letters as in fig. 2. The alternate suction to and fro of the alcohol is regulated by the alternating cock H, which communicates with the water air-pump by means of the rubber tube *w*. When this cock is in the one position the rubber tube *q* communicates with the suction tube *w*, the tube *p* however with the atmosphere; in the other position the order is reversed, the suction tube *w* communicates with the rubber tube *p*, and *q* with the outer air. By means of this contrivance, the production of the ice cylinder becomes a very simple operation. The cooling apparatus with its attached rubber tubes is placed in the freezing mixture, *p* and *q* are connected with the alternating cock H, *w* with the water air-pump, the rubber stopper with its tubes *m* and *n* is sunk by C in the inner vessel of the instrument, and finally the tubes *m* and *n* are placed on the corresponding glass tubes of the cooling apparatus. If now, after the cock of the water air-pump has been opened, the alternating cock be turned alternately back and forth, the cooled alcohol stream may be allowed to operate as long as you please in producing the ice cylinder. The formation of the latter in the apparatus, which stands quite free in the room, may be beautifully observed with the naked eye or through the telescope, and presents not uninteresting peculiarities. The temperature of the perfectly airless water in the outer vessel *b*, fig. 1, sinks gradually, without freezing taking place, until far below 0° C., while the vessel covers itself externally with an ice crust from the precipitated moisture of the atmosphere; even strong agitation is insufficient to put a stop to this abnormal fluidity. When the temperature has finally sunk very low, a sudden formation of ice takes place, which propagates itself in a few seconds from λ to μ. The whole vessel is filled down to this limit with milky turbid leaves and needles of ice, the water mass from μ to the mercury surface β is on the contrary unfrozen. Now begins, under continued cooling, the first formation of the ice cylinder, which is allowed to increase until its walls have attained a thickness of about 6 to 10^{mm}. That part of the very regularly formed ice crust which lies below μ appears perfectly amorphous, clear and transparent as the purest crystal glass; the portion above μ reaching to λ appears turbid and of a texture not dissimilar to the confused coarse-fibrous, after the instrument has stood several days ready for use at 0° C. in the snow this coarse-fibrous texture changes entirely. The ice mass between λ and μ consists now of small rounded transparent grains of spherical habitus; if, after long use, the instrument be exposed to the temperature of the room, the individual spheres melt off on their surfaces, detach themselves thereby from the adjacent mass, and rise in the fluid; they then appear at times connected with one another like the cells of yeast.

[To be continued.]