

flow set up below the surface. With a solid sphere that is rough or wet, the phenomena are quite different from the earliest moments of contact, and very similar to those produced by a liquid sphere.

Although a few theoretical or conjectural points are touched on, the authors prefer to abstain at present from even general explanations, and to put forward the photographs simply as a record of facts of fluid motion, hoping that the puzzling nature of some of the phenomena may evoke attention and interest among those most competent to explain them.

II. "A New Method of Determining Freezing Points." By MEYER WILDERMANN, Ph.D. Communicated by LORD KELVIN, F.R.S. Received January 13, 1896.

(Abstract.)

The subject of this paper is the best means of determining freezing points in dilute as well as in concentrated solutions. Two things have to be considered: the proper arrangement of equilibrium in the heterogeneous system, and the proper treatment of the instrument used for measuring temperature.

A. *Arrangement of Equilibrium.*—I begin with the statement that the equilibrium between the solid and liquid solvents in the heterogeneous system (ice and water) is a "perfect" one, and this is characterised by the fact that, at the slightest change of the temperature of equilibrium, one of the two parts of the heterogeneous system disappears; above freezing temperature, the solid, below it, the liquid. In carrying out an experiment the heterogeneous system is simultaneously cooled down or warmed by the arrangements of the experiment (air bath, &c.), and the velocity with which the given liquid is cooled down must also come into consideration. This isolated process must be expressed by Newton's equation,  $dt/dz = c(t_g - t)$ , in which  $c$  is inversely proportional to the quantity of liquid and to the heat capacity, and directly proportional to the surface of the whole volume of the liquid, and  $t_g$  is the convergence temperature of the liquid if no ice be present, and can be above or below the freezing temperature. If the convergence temperature be *above* the freezing temperature, the liquid is, at the freezing temperature, continuously warmed by the experimental arrangements to a higher than the freezing temperature  $t_0$ , and the process of ice melting takes place. If the convergence temperature be *below* the freezing temperature, the liquid is, at the freezing temperature, continuously cooled to a lower temperature, and the process of ice separation takes place. The velocity of *ice melting* has been found to be expressed by the

s 2

equation  $dt/dz = K(t_0 - t)$ , in which  $K$  is directly proportional to the surface of the separated ice,  $t_0$  is the freezing temperature of the liquid, and  $t$  is the temperature of the liquid at the time  $z$ . The velocity of ice separation has been found to be expressed by the equation  $dt/dz = c''(t_0 - t)$ , in which  $t_0$  is the freezing temperature of the given liquid,  $t$  the temperature of the liquid at the time  $z$ . If the convergence temperature is above the freezing temperature the general equation will therefore be:  $dt/dz = K(t_0 - t_g)$ , process of ice melt.  $+ c(t_g - t_g)$  arrang. exper.

Equilibrium takes place when  $dt/dz = c(t_g - t') + K(t_0 - t') = 0$  and  $t' = t_0 + \frac{c}{K}(t_g - t')$ , i.e., the mercury thread comes to equilibrium, not at the real freezing temperature  $t_0$ , but at the temperature  $t'$  (apparent freezing temperature), which is more or less different from  $t_0$  (Nernst), and  $t'$  will be between  $t_0$  and  $t_g$ . In order that  $t'$  may be as nearly equal to  $t_0$

as possible,  $\frac{c}{K}(t_g - t')$  must be kept as small as possible, and for

this it is necessary for a successful freezing point determination that (a)  $c$  be kept very small (the quantity of liquid used for the experiment must be as large as possible, an air bath preferred to a liquid bath), (b)  $K$  be as great as possible (the overcooling of the liquid before ice separation must be sufficiently great, the ice must be separated into fine needles, and not allowed to form conglomerate masses; subsidiary to this are good stirring arrangements, the proper choice of the beaker, &c.), (c)  $t_g - t'$  or  $t_g - t_0$  be kept very small, i.e., the convergence temperature must be as near as possible to the freezing temperature (the temperatures of the air bath and ice bath most suitable to the given temperature of the room must be experimentally found). For the freezing point depressions we get  $t' - t'' =$

$t_0 - t_0' + \left[ \frac{c}{K}(t_g - t') - \frac{c'}{K'}(t_g' - t'') \right]$ , in which  $t' - t''$  is the apparent freezing point depression as obtained from the apparent freezing points, and  $t_0 - t_0'$  is the real freezing point depression as obtained from the real freezing points. As in dilute solutions it has been found that  $c$  can be put  $= c'$ ,  $K = K'$ , we have  $t' - t'' = t_0 - t_0'$   $+ \frac{c}{K}[(t_g - t_g') - (t' - t'')]$ . In order that the apparent freezing point

depression may be, as far as possible, equal to the real,  $\frac{c}{K}[(t_g - t_g') - (t' - t'')]$  must be kept as small as possible. In dilute solutions  $t' - t''$  may be neglected,  $t_g - t_g'$  being of importance; but in concentrated solutions  $t' - t''$  becomes of more importance. So we get for the freezing point method in dilute solutions the rule: the same convergence temperature, the same temperature of the ice bath, at the same temperature of the room, the same regular stirring in all concentra-

tions, and in more concentrated solutions the rule: the bath must be arranged successively cooler, so that the convergence temperature of the solutions falls below the convergence temperature of water by the amount of the freezing point depression. Careful measurements of  $c$ ,  $K$ ,  $t_g - t_g'$  have shown that in the method I use, the apparent freezing point depression cannot differ from the real even by  $\frac{c}{K}(t_g - t_g') = 0.0001^\circ$  to  $0.0002^\circ$ , as far as the equilibrium in the heterogeneous system is concerned. *If the convergence temperature be below the freezing temperature*, we have  $dt/dz = c''(t_0 - t_g)$ , sep. ice  $+ c(t_g - t_g')$ , exp. arr. Equilibrium takes place when  $dt/dz = c''(t_0 - t') + c(t_g - t') = 0$  and  $t'$  is  $= t_0 + \frac{c}{c''}(t_g - t')$ , i.e., the point of rest of the mercury thread is not at the real freezing temperature  $t_0$ , but at the apparent freezing temperature  $t'$ , which is more or less different from  $t_0$ , and  $t'$  will be between  $t_0$  and  $t_g$ . In order that the apparent and real freezing points, as well as the apparent and real freezing point depressions, may be as equal as possible, the same conditions and rules of the freezing point method must be fulfilled as in the case when the convergence temperature is above the freezing temperature. Careful measurements of  $c$ ,  $c''$ ,  $t_g - t'$ ,  $t_g - t_g'$  have shown that in the method I use  $t'$  cannot differ from  $t_0$  even by  $-0.00006^\circ$  to  $-0.00018^\circ$ , and  $t' - t''$  from  $t_0 - t_0'$  even by  $\frac{c}{c''}(t_g - t_g') = 0.00006^\circ$  to  $0.00012^\circ$ . These rules, which we now explain theoretically, were found at first *empirically*, after a very detailed investigation, by my late friend, P. B. Lewis, and then by myself, and form to a great extent the subject of this paper.

Under these arrangements of the equilibrium we get the result that the freezing temperature can be kept within the very narrow limits of one, two, three ten-thousandths of a degree (including other experimental errors) during a time of 15—20 minutes, and longer, as well when the convergence temperature is *above* as when it is *below* the freezing temperature.

B. *The Proper Treatment of the Instrument used for Measuring the Temperature.*—I used the  $1/100^\circ$  and the  $1/1000^\circ$  thermometers simultaneously. On the  $1/100^\circ$  thermometer the reading error is, even under the most favourable conditions, one to two thousandths of a degree, often less, seldom more. Through this the *upper* limit to which we can get *quantitative* results is, in the method I use, with the  $1/100^\circ$  thermometer *c.a.*  $0.04$  mol. normal, in the case of non-electrolytes. The  $1/1000^\circ$  thermometer allows much more accurate readings, gives us the possibility of investigating more dilute solutions, but requires a great series of precautions if a good result be obtained. (1.) The thermometer must always be kept at  $0^\circ$ . (2.) It is

necessary that the equilibrium be maintained during a long time within very narrow limits of temperature, in order that the quick-silver of the thermometer and the glass of the bulb may completely attain the temperature of the liquid (for this the velocity with which this takes place was measured), in order that the atmospheric pressure and the inner pressure of the mercury column may completely exert their influence on the read freezing temperature. It was found in the limits of 250 mm. that if the increase of the outer pressure against the inner be 0.96 mm., a rising of the read freezing point by  $0.00031^{\circ}$  corresponds, and that the velocity with which the inner and outer pressures completely exert their influence is about two minutes in duration. (3.) Great precautions must be taken to bring the mercury thread to its maximum, and this must be controlled. (4.) Care must be taken for "dead" points, that no vacuum is formed in the mercury bulbs, and for this a certain kind of tapping of the thermometer cork must be used, the mercury must not be allowed to rise, while a series of experiments is being carried out, into the upper reservoir, &c.

*Presents, February 6, 1896.*

Transactions.

- Batavia :—Koninkl. Natuurkundige Vereeniging in Nederlandsch-Indië. *Natuurkundig Tijdschrift*. Deel LIII. 8vo. *Batavia* 1893. The Society.
- Berlin :—Gesellschaft für Erdkunde. *Verhandlungen*. Bd. XXII. No. 10. 8vo. *Berlin* 1895. The Society.
- Bhavnagar :—Archæological Department. *A Collection of Prakrit and Sanskrit Inscriptions*. 4to. *Bhavnagar*.  
H. H. The Maharaja of Bhavnagar.
- Boston :—Boston Society of Natural History. *Memoirs*. Vol. V. Nos. 1—2. 4to. *Boston* 1895; *Proceedings*. Vol. XXVI. Part 4. 8vo. *Boston* 1895. The Society.
- Chicago :—Field Columbian Museum. *Publications*. Nos. 2—4. 8vo. *Chicago* 1895. The Museum.
- Cracow :—Académie des Sciences. *Bulletin International*. Décembre, 1895. 8vo. *Cracovie*. The Academy.
- Halifax, N.S. :—Nova Scotian Institute of Science. *Proceedings and Transactions*. Vol. VIII. Part 4. 8vo. *Halifax, N.S.* 1895. The Institute.
- Liverpool :—Geological Society. *Proceedings*. Vol. VII. Part 3. 8vo. *Liverpool* 1895. The Society.
- London :—British Astronomical Association. *Journal*. Vol. VI. No. 3. 8vo. *London* 1896. The Association.