349. *Hydration of Salts with Heavy Water, and Remarks on the Constitution of Salt Hydrates.*

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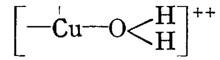
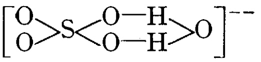
A comprehensive treatment of the problem of the constitution of crystalline salt hydrates was first given by Werner (" Neuere Anschauungen," 1905), who attempted a hypothetical allocation of the water of crystallisation as between the cation and the anion. His main argument was to the effect that the number of water molecules in crystalline salts is often identical with the co-ordination number of the cation, and that deviations can usually be interpreted by making simple auxiliary assumptions about the hydration of anions and the occurrence of double water molecules. The results of this theory are well known : *e.g.*, in $SrCl_2,6H_2O$ the water is assumed to belong to the cation ; in Li_2SO_4,H_2O it is allocated to the anion ; in $CuSO_4,5H_2O$ four molecules are allotted to the cation and one to the anion.

Sidgwick has developed the general thesis that the co-ordination linking of Werner is really a covalency ; and he has applied this conception to salt hydrates, thus achieving a structural theory of these substances (" Electronic Theory of Valency," 1927). Werner's allocation of the water as between the individual ions is adopted ; water bound to a cation is considered to be linked through oxygen, which thus assumes the oxonium condition, whilst water joined to an anion is regarded as being linked through hydrogen, *i.e.*, by the " hydrogen bonds " of Latimer and Rodebush. A third mode of binding is also recognised, inasmuch as the water might add to the carbonyl double bond possibly present in such salts as sodium carbonate and potassium oxalate. The three types of linking may be illustrated as follows :



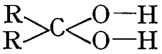
$\left[-\overset{|}{\mathrm{Cu}}-\mathrm{O}<\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right]^{++}$

(I.) Cation hydration.



$\left[\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}>\mathrm{S}<\begin{matrix}\mathrm{O-H}\\ \mathrm{O-H}\end{matrix}>\mathrm{O}\right]^{--}$

(II.) Anion hydration.



$\begin{matrix}\mathrm{R}\\ \mathrm{R}\end{matrix}>\mathrm{C}<\begin{matrix}\mathrm{O-H}\\ \mathrm{O-H}\end{matrix}$

(III.) Carbonyl hydration.

Independently of this chemical conception, a physical theory of ion hydration has been evolved by Fajans (*Deut. physikal. Ges.*, 1919, **21**, 549, 709) and Born (*Z. Physik*, 1920, **1**, 45). This theory is not structural, but electrostatic, and is concerned, not so much with the electronic or protonic constitutions of the interacting species, as with their bulk characteristics or general molecular properties such as size, charge, dipole moment, and coefficient of polarisability. The essential proceeding is the calculation from these physical quantities of the electrostatic energy of hydration. Magnus (*Z. anorg. Chem.*, 1922, **124**, 305) computed the energy of electrostriction by an ion of gradually increasing numbers of water molecules, and found that this energy became maximal for a particular number, depending on the size and charge of the ion ; thus he achieved an electrostatic calculation of the co-ordination number assumed to be effective in ion hydration. Garrick (*Phil. Mag.*, 1930, **9**, 131 ; **10**, 76 ; cf. *ibid.*, 1931, **11**, 741) has extended the theory by taking account, not only of Coulomb, but also of non-Coulomb, forces ; and thus, for a large number of simple ions, he has derived effective co-ordination numbers in excellent agreement with general chemical experience.

These two theories illustrate respectively two alternative, opposing ideas concerning the condition of water in ion hydrates. According to one view the molecules may be considered as separately bound each into its place in a rigid structure, so that the intermolecular cohesions which characterise ordinary water are inhibited for these molecules by reason of their fixed positions and fixed modes of attachment to the central ion. Alternatively, the water of a hydrated ion might be regarded as much like a microscopic sample of ordinary water, permitting, in particular, similar molecular interaction, but with this principal difference, *viz.*, that upon the continually varying intermolecular forces a permanent central force is superimposed. Of course, it is unnecessary exclusively to entertain either of these two antithetical extremes, and intermediate views are both possible and reasonable; for, on the one hand, structures may vary in stability all the way from permanence to non-existence, and, on the other, the electrical analysis, if pursued, might reveal loci of maximal attraction equivalent to a more or less definite tendency towards structure. It therefore appears that one of the most important of the outstanding general questions concerning the constitution of ion hydrates relates to the extent to which water molecules, when present in hydrates, retain their normal properties of mutual cohesion.

We have endeavoured to contribute to this question by a study of salt hydration with water containing protium and deuterium in known proportions.

In explanation of the method employed, we shall provisionally adopt the viewpoint of the structural theory, according to which the hydration of an ion involves the rupture and formation of various chemical bonds. It is necessary to consider how the stability of such bonds should be changed when the protium of the water is replaced by deuterium.

The hypothesis of Lewis and Schutz (*J. Amer. Chem. Soc.*, 1934, **56**, 493, 1002) that " hydrogen bonds " containing deuterium (H^2) are more stable than those containing protium (H^1) appears to be well grounded : the hydrogen-isotopic forms of compounds such as water and ammonia, which are generally believed to contain many " hydrogen bonds " in the liquid state, have widely different vapour pressures, whilst the isotopic forms of other compounds, such as hydrogen chloride and hydrogen cyanide, which can scarcely contain any " hydrogen bonds," have almost identical vapour pressures. It is directly clear from the vapour-pressure relations that a water molecule, in particular, becomes more difficult to remove from its normal liquid surroundings when its protium is replaced by deuterium.

The other type of bond to be considered is the covalency of the hydroxyl group. It is generally recognised that, largely on account of the existence of zero-point energy (Cremer and Polanyi, *Z. physikal. Chem.*, 1932, *B*, **19**, 443; Eyring, *Proc. Nat. Acad. Sci.*, 1933, **19**, 78), the covalency of the deuteroxyl group ($O—H^2$) must be more stable than that of the protoxyl group ($O—H^1$). From these premises it follows immediately that the three forms of hydration which are assumed in the structural theory of salt hydrates should, in general, be distinguishable from each other by differences of selectivity for light and heavy water.

In the formation of cation hydrates, the hydrogen of the water plays no direct part (formula I), and therefore the only apparent reason for preferential selection in this case is one which is common to hydration in general, *viz.*, that it is easier to extract a light water molecule than a heavy one from solvent water. Therefore cations, on hydration, should discriminate in favour of light water.

The hydration of anions necessitates the formation of " hydrogen bonds " (formula II). Therefore, *as compared with cations*, anions should show a relative preference for heavy water.

In carbonyl hydration one hydroxyl covalency is broken whilst another is formed (formula III), so that there will be a certain balancing of the energy differences which arise when deuterium replaces protium. If the balancing is exact, and no other factor operates, the case will be like that of cation hydration; but the hydroxyl links which are formed and broken are differently situated (one is in an alcoholic, and the other in an aqueous, hydroxyl group), and therefore they could have slightly different bond-energies. Consequently, the balancing which results when deuterium replaces protium might be only approximate, and in that event the resemblance to cation hydration would be approximate also. However, there is another important factor : in formula (III) the hydrogen is still only unicovalent and the oxygen only bicovalent, so that a carbonyl hydrate, unlike a cation hydrate or an anion hydrate, can still form intra- or inter-molecular hydrogen bonds. It would certainly be expected to do so, and, if it does, the effect must tend to nullify the type of isotopic discrimination described as resemblance to cation hydration.

It must be noted that the above conclusions are not affected by consideration of the possibility of hydrogen-ion exchange, independently of water-molecule exchange, between the ion hydrate and the solvent : alternative routes to an equilibrium cannot influence the energy relations on which that equilibrium depends. The same statement is obviously true also for the equilibrium between liquid water and its vapour, where there is a notable isotopic discrimination.

In reference to our results we shall make the simplifying assumption that the water found in any crystalline salt hydrate is a fair sample of the water associated with the ions of that salt just before crystallisation. It will be evident that the preceding discussion of the possible selectivity of various ions for light and heavy water relates essentially to this pre-crystalline, and thus to the crystalline, state; for, were it otherwise, account would have to be taken of the effect on the stability of an ion hydrate of interaction between the hydrate water and surrounding layers of solvent water, and particularly of the differences which arise when deuterium replaces protium in these outer layers: in the crystalline and pre-crystalline states such outer layers are absent. The real implication of this simplifying assumption is that any possible effect of each ion in the crystal on the isotopic selection of the others is neglected. Of course, some such effect may exist, but it is difficult to see on what general grounds.

We have studied the hydration of all the salts mentioned in the foregoing discussion as illustrating possible types of hydrates, *viz.*, strontium chloride, copper sulphate, lithium sulphate, sodium carbonate, and potassium oxalate. Employing specimens of water the deuterium contents of which corresponded to densities of more than 2000 parts per million above the normal, we formed the hydrates of these salts and measured the densities of the solvent water and of the water recovered from the crystalline hydrates and from the solutions. The density determinations (made with 3 c.c. pyknometers) were accurate to within ± 1 part per million, but, as noted below, the error inherent in the rest of the manipulation is somewhat greater than this.

Our results are summarised in the following table, most of the headings of which are self-explanatory. Recorded in the last col. is what we call the " isotopic discrimination " (denoted by *I.D.*), which, for mixtures as dilute with respect to deuterium as those we have employed, is sufficiently accurately defined * as the difference between the proportions of deuterium in the solid and liquid phases, divided by the proportion of deuterium in one of them. These percentage discriminations are seen to be very small, and it is necessary to enquire into their possible reality.

(All the data relate to room temperature, except those for $Na_2CO_3,10H_2O$, which refer to 0°.)

			Excess density (p.p.m.) of					
Salt.	Wt. (g.) anhydr. salt.	Wt. (g.) heavy water.	solvent water.	crystal water.	solution water.	Total density loss, p.p.m.	Density diff. (soln. —salt), p.p.m.	*I.D.*, %.
Example from early series (illustrating effect of short atmospheric contact).								
Li_2SO_4,H_2O	50	50	2225	2216	2216	9	±0	±0·00
Final series.								
$SrCl_2,6H_2O$	15	15	2159	2157	2154	3	—3	—0·14
$CuSO_4,5H_2O$	15	25	,,	2154	2156	3	+2	+0·09
Li_2SO_4,H_2O	20	20	,,	2156	2157	2	+1	+0·05
$Na_2CO_3,10H_2O$ ...	7	20	,,	2156	2152	5	—4	—0·19
$K_2C_2O_4,H_2O$.........	40	20	,,	2159	2157	2	—2	—0·09

The preparation of the water samples with a precision equivalent to the accuracy with which the density determinations were carried out would require the fulfilment of the following conditions, *inter alia*: (1) Ordinary water must be removed from the salt to be employed until the proportion of the original water remaining does not much exceed

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* The separation coefficient for a heterogeneous equilibrium may be defined analogously to that for a heterogeneous process. Just as for a process we have $\alpha = [\delta(H^1)/(H^1)]/[\delta(H^2)/(H^2)]$, where the parentheses denote molar isotopic quantities and the differentials refer to escape through a phase-boundary during a small time-interval, so for a heterogeneous equilibrium we may write $\beta = \{[H^1]_A/[H^1]_B\}/\{[H^2]_A/[H^2]_B\}$, where the square brackets connote molar isotopic concentrations, and the subscript letters indicate the phases. With β thus defined, our " percentage discrimination " is equal to $100(\beta - 1)$.

1 part in 10^4. (2) The water, which after hydration is contained in the salt and the solution, must be separated substantially completely and purified by distillation until the proportion of retained salts does not amount to 1 in 10^6. (3) The total quantity of water lost during the distillations should not amount to 1 part in 10^2, because of the ease with which the isotopic forms of water are separated by distillation. (4) The total access of ordinary water during manipulation, either from the atmosphere or from incompletely desiccated glass surfaces, should not be of greater order than 1 part in 10^4. Condition (2) can be satisfied with comparative ease and certainty, but conditions (1) and especially (3) and (4) are less easily controlled; and their incomplete fulfilment leads to diminutions of density which are difficult entirely to eradicate (distillation losses occur chiefly in the tail). However, the circumstance that these residual errors are all in the same direction renders the loss of density, which is obtained when the *whole* recovered water is compared with the original water, a particularly reliable measure of the over-all value of the manipulative imperfections. These density reductions, which represent loss of deuterium plus contamination by protium, are shown in col. 7 of the table. The example at the top illustrates how much larger the losses of density were when the experimental method involved atmospheric exposures amounting perhaps to several tens of seconds. In col. 8 will be found the differences in the densities of the water recovered from the salts and from the solutions, and it will be seen that these differences are, on the whole, numerically smaller than the differences of col. 7 which we take to indicate the over-all uncertainty of the experiments. Furthermore, it will be appreciated that our methods were only gradually evolved, and that the final series of experiments, which alone we quote in full, had many predecessors: in some of these we thought we observed an isotopic separation; but with each technical refinement the density differences became smaller to the limits shown, and there is no reason to suppose that they would not continue to diminish if our methods were further improved. Therefore the conclusion to be drawn from the figures of col. 9 is that any isotopic discrimination associated with the hydration of these typical salts is not of greater order than 0·1%.*

We may enquire what order of discrimination might have been expected according to the structural viewpoint provisionally adopted. First, regarding the essential factor of selection for cation hydration, *viz.*, the more facile separation from association in the liquid of a light water molecule than a heavy one, a guide is available in the equilibrium between liquid water and its vapour. The vapour pressures of the isotopic forms are known (Lewis and Macdonald, *J. Amer. Chem. Soc.*, 1933, **55**, 3057), and, for low concentrations of deuterium at least, ideal mixture laws may safely be assumed : it can be calculated that in the neighbourhood of the ordinary temperature the isotopic discrimination amounts to 15%, so that we might reasonably have expected a separation of this order accompanying the hydration of cations. Further, if this degree of selection can be caused by the rupture of "hydrogen bonds," and if anion hydration is characterised by the formation of such bonds, then the discrimination shown by anions should differ from that of cations by an amount of at least the same order. In carbonyl hydration compensating influences are foreseen, so that the separation in this case might well be comparatively small.

Our results therefore show that all the discriminatory effects above considered, if they exist, are negligibly small in comparison with what might have been anticipated (except with regard to carbonyl hydration) on the basis of an uncompromisingly structural theory; and it is to be observed that the particular feature of that theory which primarily is responsible for these unfulfilled expectations is the implication that water molecules in ion-hydrate structures (carbonyl hydrates again excepted) are inhibited from mutual associations analogous to those in which they would engage in the state of liquid.

What of the electrical theory? In its completely antithetical form it may be taken to imply that there is no appreciable inhibition of the associations of bound water molecules. Therefore this theory requires that in general there can be no notable isotopic discrimination in the formation of ion hydrates—an inference which is much more like our finding.

Thus, if we correctly read the evidence, the conclusion would seem to be that the water

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* A preliminary report of this result was made in May (*Chem. and Ind.*, 1934, **53**, 492).

bound by a dissolved ion is a very fair sample of the molecular species present in ordinary water; that the intermolecular associations of normal water must, in bound water, be largely unimpaired; and that any structure involved in the linking of hydrate water can at best have but a loose and evanescent character.

EXPERIMENTAL.

Materials.—The salts employed, purchased from the British Drug Houses, Ltd., were marked " pure A.R." The " heavy water " was part of a batch of about 5 l., which was recovered from a previous research (this vol., p. 493); it had been fully purified by passage over red-hot copper oxide (*Chem. and Ind.*, 1934, **53**, 492) and distillation, as described below.

Purification of Heavy Water.—Our apparatus for the treatment with copper oxide consisted of an iron (mild steel) tube of 13 mm. bore, the central portion (45 cm.) of which was heated to 1000° in an electric furnace, whilst the ends were cooled with closely wound water coils. The copper oxide, in origin commercial wire-form oxide, had been alternately completely reduced with cylinder hydrogen and reoxidised with purified air until the water obtained during reduction was quite free from traces of chlorides, sulphides, etc. It was finally oxidised with purified air. The water was introduced by means of a capillary dripping-tube of glass, delivering 1 drop in about 3 seconds with the head which was usually maintained. Each drop falling on the hot metal was instantly vaporised, and the passage of the steam through the tube containing the oxide cooled it to an equilibrium temperature a little below 1000°. The water, together with any steam issuing from the other end of the iron tube, passed through a water-jacketed glass condenser into a receiver, the necessary rubber joint being placed in such a position as to avoid contact with the liquid. Any decomposition into hydrogen was imperceptible.

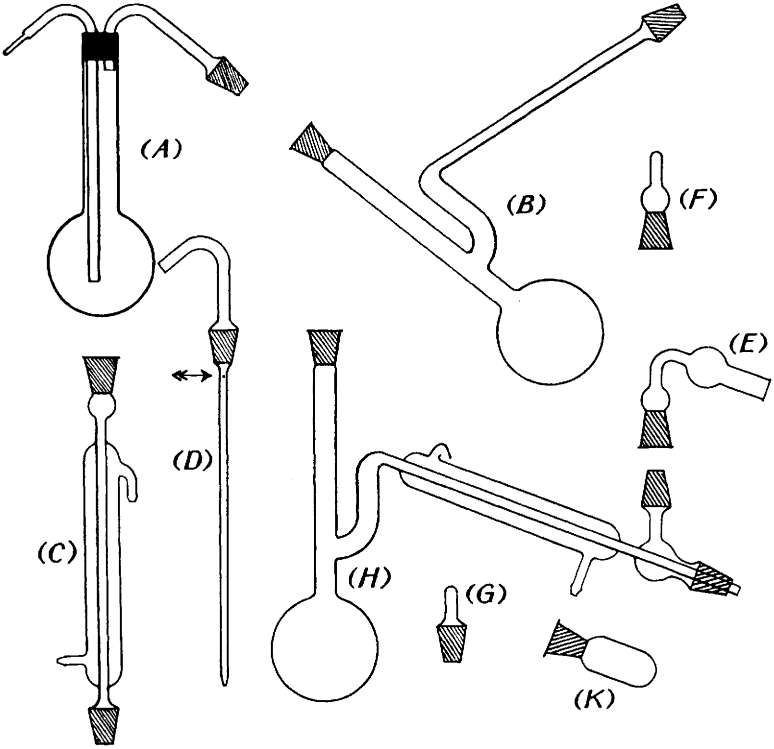
The distillations, carried out in rubber-free Pyrex-glass apparatus, involved refluxing with acid permanganate, distilling from this reagent, distilling from sodium hydroxide introduced as sodium, and distilling alone, adequate " tails " being always neglected, from which a further quantity of heavy water could be recovered by more complete distillation and repetition of the whole treatment. The criterion of purity was an unchanging density (to 1 in 10^6) on complete distillation, and the absence of detectable traces of the reagents used from the interior of the empty distilling flask.

Drying of Salts.—The difficulty of drying many hydrated salts, except by complete fusion, is well known; but initial fusion always led to subsequent inconvenience, and in some cases was impossible by reason of the limited thermal stability of the salt. The amount of light water contained in the salts to be employed was therefore reduced as much as possible by first roughly drying them for several days in a clean, electrically heated air oven at 240°, crystallising them from some of the heavy water with which they were finally to be hydrated, and then drying for some days at 250—290° over phosphoric oxide in a high vacuum. This drying was done in an apparatus from which the bulb containing the phosphoric oxide could be detached by means of a ground joint for replacement by fresh oxide as often as was necessary. The salts were contained in a 50 c.c. bulb of Pyrex glass, the neck of which, 2 cm. in bore, had a constriction to 1 cm. a little way below the branches leading to the pump and the phosphoric oxide.

Hydration of Salts.—The bulb was detached, and, after addition of the requisite amount of heavy water, was sealed at the constriction with exclusion of atmospheric moisture. It was heated at 100° for several hours, then kept at room temperature or at 0° for a further considerable period, placed in water at the ordinary temperature, or alternatively in ice-water, contained in one of the cups of a centrifuge, and finally centrifuged. The tube was opened, the solution was poured into one of the units *B* (see below), whilst the residual solid was distilled directly into another of the same units. This transference by distillation involved the use of a rubber joint (unit *A*, below) which could be partly protected by tin-foil. From this point forward there were no further transferences in air or exposure to rubber, and the total exposures of the samples are therefore as follows : the water originally used receives exposure to air when it is poured on to the dry salt; the solution water is subjected to a further exposure when it is poured from the hydration bulb into unit *B*; the crystal water makes contact through its vapour with rubber when transferred by distillation from the hydration bulb.

Preparation of Samples of Water.—All Pyrex-glass apparatus used in this work was cleaned with ordinary reagents, then with permanganate and concentrated sulphuric acid, followed by sulphur dioxide solution, and finally by prolonged treatment with steam. The pieces were dried above 200° in a clean, electrically heated oven whilst a slow stream of air dried by phosphoric oxide was allowed to flow through them. A grease-free desiccator containing phosphoric oxide was used for the storage of pieces, which, having been cleaned and dried, were not immediately required.

The glass pieces used for the distillations are indicated in the diagram. All ground joints were interchangeable. *A* is the apparatus used for transferring the crystal water; it consists of a long bent tube sealed at the upper extremity, and a short bent tube with a male ground joint, the two tubes being jointed to the hydration bulb with tin-foil-covered rubber. *B* is a bulb which can be used either as a distilling flask or a receiver; several such bulbs were employed. Cooled in ice, one of these bulbs acted as receiver for the crystal water expelled from *A*. The salts in *A* were fused when possible, and, at the end of each distillation, the sealed tube was cut, and the last traces of steam were displaced with a little oxygen delivered through seasoned rubber (Pregl). *C* is a condenser with which, in conjunction with two interchangeable bulbs of type *B*, the water samples were refluxed and distilled as often as necessary; the purifying agents and criteria of purity are mentioned later. *D* is a delivery tube for the oxygen used to displace the steam into the condensing system at the end of a distillation; it has a small hole in the position indicated by the arrow. The drying tube, *E*, excludes atmospheric moisture during the distillations. *F* is a female ground stopper, and *G* a ground plug, by means of which either end or both ends of the apparatus may be closed. *H* holds the distillate of the penultimate distillation, so that it becomes the distilling flask and condensing system in the final distillation. *K* is one of the series of collecting tubes in which the samples were out-gassed for use in the pyknometer.



The solution from the hydration bulb, poured as already indicated into one of the units *B*, was distilled into a second such unit, with fusion of the salt in the case of strontium chloride and lithium sulphate. The subsequent distillations, using two units *B*, and finally unit *H*, were carried out as described for the crystal water. Every effort was made to make all these distillations of water complete, and this seemed possible excepting in the case of primary distillations from copper sulphate, since at the ordinary pressure this salt does not lose the whole of its water without evolution of sulphuric acid.

Samples were distilled until no residue remained in the distilling bulb *B*, the internal surface of which was tested for sulphate, carbonate, hydroxide, chloride, etc., if these were anticipated (reagents : barium chloride, litmus, silver nitrate). If chloride was expected, a little silver oxide was added in advance, and the distillation was continued until freedom from silver ions was proved. When sulphates were present, fused barium oxide was added, and the water was distilled until barium and hydroxide ions were shown to be absent. All samples were refluxed with potassium permanganate, and distilled with this reagent after the addition of sodium. No reagent was added in the final distillation.

Density Measurements.—These were made as described in our previous publication (this vol., p. 498)—always with 3 c.c. pyknometers in the present series of experiments—except for the following modification, which appreciably increased the accuracy.

The pyknometer, instead of being hung in the thermostat, was placed in an immersed aluminium frame, two prongs of which supported the bottom of the **U**. The latter leaned back slightly against the polished aluminium plate of the frame, and lugs from the side of this kept the axis of the **U** in a vertical plane perpendicular to the back plate, without squeezing the pyknometer sufficiently to alter the internal volume. By means of other lugs the frame was fixed in the thermostat in such a way that the pyknometer placed in it came into the right position for setting. Yet another branch of the same frame held a small low-power microscope focused on the setting mark, which was a minute scratch made with a carborundum crystal (a method of marking suggested to us by Professor R. Whytlaw-Gray). Accurate setting was scarcely possible by hand, and the method used was to bring the meniscus to just above the mark as usual with paper wetted with the sample and applied to the tip, and then to employ spontaneous evaporation from the tip, after removal of the paper, as a mechanism of fine adjustment. At the right moment, evaporation was stopped by immersion in a beaker of cooler water, and by the application about a second later of a rubber pad to the dry end of the pyknometer, as previously described. We should have explained in our previous paper that the pad must not be applied prior to, or exactly simultaneously with, the second immersion; for the immediate effect of this is to cool the glass and thus to cause a momentary apparent expansion of the interior liquid, so that the use of the pad at this stage would cause some of the liquid to be ejected. The pad is used only when the liquid begins to contract relatively to the glass.

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