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ADSORPTION SYSTEMS AT TEMPERATURES BELOW THE FREEZING POINT OF THE ADSORPTIVE

by G.G. Litvan

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SOMMAIRE

Des études portant sur l'adsorption isotherme et la mesure des variations dimensionnelles au-dessous du point de congélation de l'adsorbat indiquent que les substances adsorbées dans des solides poreux ne peuvent geler in situ. Un procédé de désorption permet d'éliminer la différence entre la pression de la vapeur ou l'énergie libre de l'adsorbat non gelé et celle de l'adsorbant à l'extérieur du système poreux; la matière sujette à la désorption gèle à l'extérieur du système tandis que la pression de la vapeur de l'adsorbat dans les pores diminue par formation de ménisque. La défaillance mécanique du système se produit à ce moment, lorsque le cycle de désorption ne peut être complété et que l'état d'équilibre n'est pas atteint.

On a trouvé que ce mécanisme est valable pour le verre de silice poreux, le mastic de ciment hydraté, les briques et même pour des substances biologiques tels les tissus animaux et végétaux et les aliments. Cette recherche a permis la mise au point de nouvelles méthodes d'essai de la durabilité des matériaux de construction et la clarification de certains problèmes posés par la méthode de détermination de surface BET, en plus de proposer une explication pour l'action des agents cryoprotecteurs.

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ADSORPTION SYSTEMS AT TEMPERATURES BELOW THE FREEZING POINT OF THE ADSORPTIVE

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ABSTRACT

Isothermal adsorption studies and the measurement of dimensional changes below the bulk freezing point of the adsorbate indicate that substances adsorbed in porous solids are unable to freeze in situ. The difference between the vapour pressure or free energy of the unfrozen adsorbate and that of the bulk adsorptive outside of the porous system is resolved by a desorption process; the desorbed matter freezes outside of the system while the vapour pressure of the adsorbate remaining in the pores decreases through meniscus formation. Mechanical breakdown of the system occurs only then, when this process cannot be completed and an equilibrium state is not attained.

This mechanism was found to be valid for porous silica glass, hydrated cement paste, bricks, and even for biological substances such as animal and plant tissue, and foodstuff. This understanding has led to the development of new methods for testing the durability of building materials, clarification of some problems of the BET surface area determination method and it suggests an explanation for the action of cryoprotective agents.

I. INTRODUCTION

Adsorption of vapours on solids at temperatures below the bulk triple-point of the substance and the anomalous behaviour exhibited by porous solid-adsorbate systems on cooling are phenomena of great interest. Several questions arise, but perhaps the two most important are concerned with: 1) the potential modification of the adsorption forces due to solidification of the adsorbate, and 2) the features of phase relations for substances in the adsorbed state. Answers are sought not only to satisfy theoretical curiosity but for practical application in the diverse fields of frost heaving of soils, freeze-thaw susceptibility of porous building materials (concrete, brick, stone), winter hardiness of plants, and low temperature preservation of foodstuff and biological materials. Numerous studies have been undertaken to clarify various aspects, but the inherent links among the widely diverse fields have not been considered. This is the purpose of the present review.

II. THEORETICAL CONSIDERATIONS

According to the phase rule, pure bulk water has one degree of freedom when present in two phases such as liquid and vapour. At the triple-point three phases coexist and the system is invariant. If the phases are separated by curved instead of planar surfaces, the phase rule in its usual form is no longer valid. The vapour pressure of curved surfaces is different from that of planar surfaces and, therefore, equilibrium among the three phases of a single-component

substance can be achieved at temperatures other than the triple-point if the radii of curvature of the interfaces assume the appropriate values.

The dependence of the triple-point on the radii of curvature was derived by Defay et al [1] for a single-component system consisting of a droplet and a crystal, both surrounded by vapour. By writing the Gibbs-Duham equation for each phase, eliminating the pressure terms by the substitution of the Laplace equation, simplification and integrating yields the relation

$$\ln \frac{T}{T_0} = \frac{2}{\Delta_f h} \left(\frac{V_{\sigma}^{\ell, g}}{r^{\ell, g}} - \frac{V_{\sigma}^{s, g}}{r^{s, g}} \right) \quad (1)$$

In this equation T denotes the temperature, T_0 the triple-point of the system comprising bulk phases, $\Delta_f h$ the heat of fusion, $r^{\ell, g}$ radius of the droplet, $r^{s, g}$ that of the crystal, V the volume and σ the surface tension. The new triple-point of the system may be either below or above T_0 , depending on the relative size of the droplet and crystal.

Various possibilities can best be surveyed by means of a schematic illustration of the coexistence curves of liquid-vapour and solid-vapour in the coordinates T and p^g (Figure 1). The value of T at the intersection of the curves is the freezing point. A shift of either or both curves to higher or lower p^g values alters the freezing point. Such a shift occurs if the surface of the condensed

Fig. 1. Schematic phase diagrams of water with planar and curved surfaces.

phase is either convex or concave instead of planar, or if the concentration of a new constituent increases from zero to a finite value.

Early and even contemporary work [2] utilized this concept to explain the well-known observation that water in soils, concrete, or plants does not freeze at 0°C , or at the temperature predicted on the basis of the ionic strength of the solutions, but at a significantly lower temperature. This concept, however, could not account for the other features of the freezing phenomenon in porous solids [3] or solve the many engineering problems caused by it. Neither could unequivocal experimental evidence be found to support the theory, but this may be attributed to the inherent difficulties of the techniques applied.

III. EXPERIMENTAL METHODS

Vapour pressure measurements, dilatometry and calorimetry are perhaps the most important classical experimental techniques employed in the study of adsorbate phase transitions. Unfortunately, all suffer serious difficulties. In conventional dilatometry, the presence in the adsorption system of fluid such as toluene or ligroin is obviously undesirable. In determining vapour pressure, particular care has to be exercised to avoid condensation of the substance on the cell walls during cooling. Furthermore, as the maximum vapour pressure realizable experimentally is that of the bulk phase, the validity of the hypothesis concerning the elevated pressure of the solidified adsorbate can never be directly assessed.

In calorimetry, the specific heat determination of the adsorbate is made difficult by the presence of the adsorbent, the mass of which acts as a heat sink. The ratio of adsorbate to adsorbent masses is seldom greater than 1:4, but it can be as small as 1:20. Because calorimeters operated in the cooling mode yield results of considerable uncertainty, the calorimeter was operated in the conventional manner in all the work reported in the literature, thus requiring that the system be cooled to low temperatures prior to the experiment. As will be described, adsorption systems exhibit marked hysteresis in low temperature cycles with respect to their dimensional behaviour. Calorimetric measurements thus commence not from a uniquely defined equilibrium state but from one that depends on the path followed to reach it.

Another difficulty is presented by the extremely long period of time required to attain equilibrium. At low temperatures, the rate of change is so slow and the observable effect so small that it is indistinguishable from that caused by calorimeter drift. Moreover, in calculating the heat capacity of the adsorbate the heat capacity of the adsorbent is always assumed to be its value in the pure state. Dimensional changes observable during such measurements indicate, however, that the adsorbent is perturbed. It is very probable that the heat capacity of the adsorbent is altered by the presence of an adsorbate but, because

the magnitude of the effect is unknown, it has to be neglected.

Common to all methods is the difficulty of preventing change of adsorbate content, i.e., of maintaining isosteric conditions during change in cell temperatures; seldom, if ever, can mass transfer be ruled out with certainty. In isosteric measurements, a temperature gradient across the cell is created that may cause evaporation from the sample and condensation on the walls of the container during cooling. The system can thus be described as being in the desorption branch of the isotherm. The rate of mass transfer is directly proportional to the rate of cooling and can be avoided only at infinitely low rate of cooling, i.e., at constant temperature. To minimize this effect in practice, the temperature is changed by very small increments and a long constant-temperature period is imposed to re-establish equilibrium. In some cases inert gas is added to the cell to retard distillation; this addition, of course, precludes vapour pressure measurement.

The inherent difficulty of carrying out an isosteric measurement, however, can hardly be circumvented even with the greatest care. With lowering of temperature, the vapour pressure in the cell decreases so that the excess condenses on the adsorbent. However small the dead space in the cell, the adsorbate content increases, resulting in the system described by the adsorption branch of the isotherm. On warming, the opposite effect, desorption, occurs and the relation between the variables is expressed by the desorption branch. It follows that at relatively high adsorbate content the dimensions of the system depend on the sign of temperature change that occurs when a particular state is reached.

In order to test this assumption the following experiment was carried out [3]. With a fixed amount of water adsorbed, the length of a porous silica glass rod was measured at $+2.50^{\circ}\text{C}$. After the temperature of the system was changed (raised, lowered or both), the original temperature, 2.50°C , was restored as closely as possible (within 0.5°C) and the length measured again. The results are shown in Table I. It may be seen that when the reference temperature was restored by heating (desorption branch) as in points Nos. 1, 4, 8 and 11, the rod appears to be of the same length and about $\Delta L/L = 11 \times 10^{-5}$ units shorter than in those cases where temperature was restored by cooling (adsorption branch), points Nos. 6 and 13. This difference is consistent with the fact that the desorption branch of the extension isotherm is below the adsorption branch.

It is not suggested that the results of the isosteric experiments should be dismissed because of the problems and shortcomings of the method. Valuable information can be obtained from these measurements, but great care has to be exercised to avoid misinterpretation. In assessing results it has to be remembered that adsorption systems subjected to temperature cycling are not as a rule isosteric.

TABLE I

Length changes due to temperature variation with fixed amount of water [3]

Point Number	Temperature, °C	$\Delta L/L \times 10^{-5}$
1	+ 2.50	0
2	+25.0	
3	- 6.5	
4	+ 2.30	- 1.01
5	+30.0	
6	+ 2.07	+13.33
7	-31.5	
8	+ 2.85	- 3.60
9	+22.0	
10	0.0	
11	+ 2.92	- 0.12
12	+20.0	
13	+ 2.02	+10.25

Fig. 2. Expansion isostere of porous silica glass containing 0.0839 g/g water adsorbed. (Reproduced by permission of the National Research Council of Canada from the Canadian Journal of Chemistry, Volume 4, pp. 3095-3107, 1963) [3].

IV. LENGTH CHANGE STUDIES

Work in the field of phase changes of adsorbates commenced with the measurement of dimensional changes. At first [3] a porous, 96 per cent, silica-glass rod containing known amounts of adsorbed water was taken in steps through a temperature cycle between +5 and -165°C. At each stage the temperature was kept constant until changes in length were not detectable with a capacitance type extensometer. Representative curves are shown in Figures 2 to 4, where it may be seen that the length of the adsorbent-adsorbate system does not change in a linear manner. In several temperature regions, anomalous changes in dimension occurred.

The most important findings of the experiments can be summarized as follows:

1. No length anomaly can be detected if the amount of water adsorbed is less than that at inception of the hysteresis loop of the adsorption isotherm. This condition is equivalent to two adsorbed layers.
2. If concentration is greater than two layers on cooling, anomalies in length changes are observable near -7 and -22°C.
3. The exact temperature at which the anomaly occurs depends upon the adsorbate content for the -7°C transition, but the other anomaly always occurs at -22°C.

Fig. 3. Expansion isostere of porous silica glass containing 0.1389 g/g water adsorbed. (Reproduced by permission of the National Research Council of Canada from the Canadian Journal of Chemistry, Volume 41, pp. 3095-3107, 1963.) [3]

4. Transitions, if anomalies can be accepted as indicators, are not sharp but take place between 5 and 10°C.
5. Anomalies during warming occur at higher temperatures than during cooling.
6. All isosteres exhibit hysteresis.
7. After completion of a cycle, the length of the adsorbent is different from its initial length.

These results, though interesting, are in themselves insufficient to provide understanding of the low temperature behaviour of adsorption systems. The anomalies cannot be interpreted in terms of physical events with any degree of confidence.

V. HEAT CONTENT AND LENGTH CHANGES

In order to establish the link between length anomalies and phase changes, and to learn more about the nature of the latter, simultaneous measurement of heat content and dimensional changes were undertaken. A calorimeter design originally developed by Antoniou [4] that incorporated an optical strain gauge was utilized. Results of the experiments with porous silica glass-water system,

Fig. 4. Expansion isostere of porous silica glass containing 0.1754 g/g water adsorbed. (Reproduced by permission of the National Research Council of Canada from the Canadian Journal of Chemistry, Volume 41, pp. 3095-3107, 1963.) [3]

Fig. 5. Specific heat of water adsorbed on porous silica glass as a function of temperature. Numerical values indicate the water content of the adsorbate. (Reproduced by permission of the National Research Council of Canada from the Canadian Journal of Chemistry, Volume 44, pp. 2617-2622. 1966.) [5]

shown in Figure 5, in addition to confirming the findings listed above [5], yielded the following conclusions:

1. Length anomalies do indeed signify phase changes.
2. The specific heat of the adsorbate is, below the melting anomaly at -11°C , consistently and significantly more than that of bulk ice ($0.45 \text{ cal deg}^{-1}$).
3. The heat of fusion of adsorbed water is 55.5 cal g^{-1} when the water content is equivalent to 7.7 monolayers. This value is uncertain to the extent that the quantity of water involved in the transition is not known. According to conclusion No. 1 (Section IV), the first two layers remain unfrozen when present in themselves, but the behaviour of these layers at higher concentrations can only be surmised.
4. The length curves show good reproducibility in a qualitative sense, but vary significantly in a quantitative sense.

VI. VAPOUR PRESSURE AND EXTENSION ISOTHERMS

It is clear that isosteric adsorption studies suffer from uncertainties. This situation is most unfortunate because the mechanism of frost action cannot

be understood without knowledge of adsorptive properties at temperatures below bulk freezing point of the adsorbate. Interest in this field is heightened by surprising observations.

As the heat of adsorption is exothermic, any increase in temperature results in diminution of adsorptive capacity; cooling should bring about an increase. Although this behaviour is, in fact, found at temperatures above the bulk triple-point, isotherms determined below this temperature indicate decreased adsorptive capacity. In addition, the shapes of the vapour pressure and extension isotherms become distorted as temperature is lowered. The results obtained with the porous silica glass-xenon system shown in Figure 6 illustrate this point.

To clarify the question, the vapour pressure and extension isotherms of the porous silica glass-water system were determined simultaneously at temperatures below 0°C [6]. Uncertainties concerning the quantity of adsorbed water vapour, due to potential condensation on the walls, were avoided by measuring the adsorbate content gravimetrically with a quartz balance. Because of this arrangement a companion specimen had to be used for length change measurements. The small vapour pressures at low temperatures necessitated all metal and glass construction of the equipment and bake-out to reduce degassing. The isotherms

Fig. 6. Adsorption and expansion isotherms of the porous glass-xenon system. (Reproduced by permission of the National Research Council of Canada from the Canadian Journal of Chemistry, Volume 41, pp. 3095-3107, 1963.) [3]

are shown for relative pressure based on the vapour pressure of super-cooled liquid $\left\{p_{\ell}^0\right\}$ in Figures 7 and 8(a) and for relative pressure based on the vapour pressure of ice $\left\{p_s^0\right\}$ in Figure 8(b).

The following conclusions are valid:

1. If the relative pressure p/p^0 is expressed as p/p_s^0 , the amount of adsorbate, a , decreases with decreasing temperature.
2. The isotherms can be superimposed if the relative pressure is based on p_{ℓ}^0 .

Fig. 7. Vapour pressure isotherms of the porous glass-water system at +1.5, -6.4, -14.6, -25.4 and -35.3°C (from top to bottom). Adsorption $\circ$, desorption $\bullet$. (Reproduced by permission of The Chemical Society from Transactions of the Faraday Society [6]).

Fig. 8. Vapour pressure isotherms superimposed (a) a against p/p_l^0 (b) a against p/p_s^0 . —, $+1.5$; ----, -6.4 ; ·····, -14.6 ; —·—, -25.4 and —·—·—, -35.3°C . (Reproduced by permission of The Chemical Society from Transactions of the Faraday Society [6]).

These conclusions are consistent with previous findings concerning the liquid-like non-frozen state of the adsorbate below the normal triple-point [7 - 13]. The decrease in adsorptive capacity was suggested to be only apparent. It was agreed that because the adsorbate is known to be in a liquid-like state, adsorption is governed by the magnitude of p in relation to p_l^0 not p_s^0 . As condensation on the walls prevents the rise of vapour pressure above the value of p_s^0 , this value is the upper limit of the experimentally realizable p ; and p_l^0 can never be achieved except at the bulk freezing point. Because p_l^0 exceeds p_s^0 by an increasing margin as the temperature is lowered, the isotherms are terminated at values of p/p_l^0 that become progressively lower and always less than unity.

On the other hand, if a , the amount of adsorbed substance, is expressed in terms of p/p_s^0 , the limiting relative pressure is made equal to unity, implying

complete saturation. This method of plotting results in distortion of the constructed isotherm and an apparent reduction of a for a given p/p_s^0 . Accordingly, when a is plotted against p/p_ℓ^0 the isotherms can be superimposed (Figure 8(a)).

The isotherm at -35.3°C (Figure 7) is of special interest. After obtaining by isothermal adsorption the point marked A, with excess water on the cell walls, the temperature was raised approximately 2 deg, which resulted, as expected, in further adsorption. Restoration of the original temperature caused desorption, but at the original pressure a net increase of a was found (point B). By repeating this warming/cooling process, successive increments of water were transferred to the specimen. The upper limit of the hysteresis loop, as established by the isotherm at $+1.5^\circ\text{C}$, was not attained in this work, but in theory there is no reason why it should not be achieved if a sufficient number of warming/cooling cycles are carried out. The desorption points obtained subsequently were all in stable equilibrium (at -35.3°) and were above those obtained on adsorption. Under these conditions, the adsorption isotherm is a vertical line at the maximum relative pressure that can be realized experimentally.

Behaviour leading to the vertical portion of the -35.3°C isotherm is similar to that described by Emmett and Cines [9] and can be explained in the following way. With increasing temperature, p_s^0 / p_ℓ^0 increases, eventually becoming unity at 0°C . Warming of the cell containing bulk ice causes an increase in a . On cooling, a decreases, but if the system is in the hysteresis region it will, on desorption, follow a scanning curve (path within the extreme boundaries of the hysteresis loop). Thus, a warming cycle results in an increase in a and a cooling cycle in a decrease.

Two findings lend further support to the conclusion that the adsorbate is liquid-like: the isosteres constructed from the isotherms have no break point indicative of a phase change, and the extension isotherms below 0°C are of the same shape as those above this temperature so that they can be superimposed (Figure 9).

VII. SURFACE AREA DETERMINATION

The fact that the adsorbate is in a liquid-like state below the bulk triple-point has direct consequences for the BET surface area determination. When using gases other than nitrogen, for example krypton or argon, the experiments are usually carried out at the boiling point of nitrogen for the sake of convenience. Because this temperature is 39 deg below the triple-point for krypton, application of the vapour pressure of solid krypton, p_s^0 , would be justified in computing the results. This mode of calculation, however, yields surface areas that differ significantly from those calculated from nitrogen adsorption. The discrepancy vanishes when p_s^0 is replaced by p_ℓ^0 , calculated by

Fig. 9. Extension isotherms at temperatures of +1.5, -6.4, -14.6, -25.4 and -35.3°C (from top to bottom). Adsorption ○, desorption ●. For sake of clarity of presentation the measured points of the isotherm at -35.3°C are not shown. Arrows indicate direction of adsorption path, broken lines presumed path between measured points. (Reproduced by permission of the Chemical Society from the Transactions of the Faraday Society [6]).

an extrapolation, which quantity is considered to be merely an adjustable parameter whose value is identical to that of p_{ℓ}^0 . The close agreement between these quantities was thought to be fortuitous [14, 15]. It is important to realize that the use of p_{ℓ}^0 is not only warranted for pragmatic reasons but is also

theoretically correct. Consequently, the application of p_{ℓ}^0 is not restricted to krypton adsorption but is required with all other gases, with no regard for the relation of their triple-point to the temperature of the experiment.

It should be noted that the results of adsorption studies carried out below the normal melting point of the adsorbate will be distorted and lead to erroneous conclusions; for example, apparent supersaturation will be indicated by p/p_s^0 greater than unity, if the adsorbate is assumed to be solidified.

VIII. INTERPRETATION OF THE EXTENSION CURVES OBTAINED IN NON-EQUILIBRIUM TEMPERATURE CYCLES

Insight gained in isothermal studies makes it possible to identify some of the physical events responsible for the anomalies of the dimensional change curves obtained in cooling/warming cycles. To this end, experiments were carried out in non-equilibrium temperature cycles in which heat effects were measured by differential thermal analysis, and simultaneously, the length changes were measured with a differential linear transformer [16]. Representative results for a porous silica glass - water system are shown in Figure 10.

Length Anomaly in the Vicinity of 0°C

The extension isosteres and thermograms of the saturated samples (Figure 10) show that an anomalous change in dimensions, occurring in the region between -0.2 and -8°C, was accompanied by sudden release of heat. This proves solidification of at least a fraction of the adsorbed water. It may be concluded that ice formed on the outside surface of the specimen and was in the bulk state because (a) on visual inspection at -10°C, the sample was covered with ice, (b) the established melting point of ice formed at -8.6°C was 0°C (Figure 11), and (c) on freezing, the released heat warmed the system to about 0°C.

When the glass sample was immersed in water and cooled, the surrounding water froze at 0°C but the surface water solidified only at -0.4°C, as indicated by the sudden change in length (Figure 12). Because the glass was in contact with ice crystals, this result indicates that the lower freezing point cannot be attributed to undercooling. Experimentally established facts (that ice formed on the outer surface, below 0°C, and in the absence of undercooling) suggest that water failed to solidify at 0°C because it was located in pores where it could not freeze; also, that as the temperature became colder than 0°C the water migrated to the surface where it formed ice.

The cause of this mechanism is the liquid-like state of the adsorbate, as discussed previously. The temperature at which water becomes available for freezing on the external surface depends on the temperature at which the actual adsorbate content, a , exceeds $a_{\max}^0$, the maximum adsorbate content determined by p_s^0 . The onset of this condition depends on the shape of the adsorption isotherm.

If $a = a_{\max}$ at 0°C , migration of water will start as soon as the temperature is decreased below this value. When it reaches the external surface, it freezes or remains in a supercooled state (Figure 12). On the other hand, if the specimen is partly saturated at $T > 0^\circ\text{C}$, then at $T = 0$, $a < a_{\max}$ and a exceeds

Fig. 10. Dimensional changes and thermograms of the porous glass-water system (a) 2-mm thick glass, water saturated, cooling rate $0.25^\circ\text{C}/\text{min}$; (b) 5-mm thick glass, water saturated, $0.25^\circ\text{C}/\text{min}$; (c) 5-mm thick glass, water saturated, $0.33^\circ\text{C}/\text{min}$. (Reproduced by permission of the Academic Press from Journal of Colloid and Interface Science [16]).

$a_{\max}$ only when $T < 0^\circ\text{C}$. If the water content is very low, $a \ll a_{\max}$, a does not exceed $a_{\max}$ in the region between 0 and -20°C and no freezing occurs on the surface (Figure 13).

Below the bulk triple-point, p_s^0 is the limiting value of p . Figure 14(a) shows values of the limiting relative pressure, p_s^0 / p_ℓ^0 as a function of T . With the aid of the adsorption isotherm, which is the relation between adsorbed

Fig. 11. Dimensional changes and thermograms of 5-mm thick porous glass saturated with water during a $+5$ to -15°C temperature cycle ($0.33^\circ\text{C}/\text{min}$). (Reproduced by permission of the Academic Press from Journal of Colloid and Interface Science [16]).

Fig. 12. Dimensional changes of a 5-mm thick porous glass sample immersed in water. (Reproduced by permission of the Academic Press from Journal of Colloid and Interface Science [16]).

amount and relative pressure, $a_{\max}$ can be related to T for this system. The derivative of a with respect to T is also given (Figure 14(b)). It can be seen that because of the shape of the isotherm, a significant amount of water moves only below -5°C . This result agrees well with the previously observed external surface freezing temperature of -7°C .

In view of the dynamic nature of the factors causing expansion, it is to be expected that, if the cooling rate is very slow, no anomalous dimensional changes can be observed. This effect, in fact, was found with the cement-water system [17] at a cooling rate of $0.0417^{\circ}\text{C}/\text{min}$. The suggested explanation is not specific to water as the adsorbate. The extension "isosteres" of porous glass containing adsorbates such as cyclohexane, chloroform, xylene, carbon tetrachloride, benzene and octanol exhibit similar features (Figure 15). It may be seen that in every system there are at least two freezing ranges. The existence of the anomaly at the higher temperature remained undetected in most former studies because of either experimental difficulties or erroneous interpretation.

Fig. 13. Dimensional changes and thermograms of (a) 2-mm and (b) 5-mm thick glass samples partly saturated with water. (Reproduced by permission of the Academic Press from Journal of Colloid and Interface Science [16]).

The values exhibit remarkably uniform behaviour. It appears that first freezing on the external surface occurs between 0.92 and 0.98 T_0 , where T_0 is the bulk freezing point of the adsorbate in degrees Kelvin. The suggested mechanism is supported also by the fact that melting of the adsorbate always occurs at T_0 .

Freezing at Low Temperatures

For transitions occurring at lower temperatures, the adsorbate solidifies in the pores. The process is associated with an exothermic heat effect and expansion, both extending over a temperature range of approximately 15 degrees. Despite the gradual nature of the transition for a given type of specimen (e.g., 5-mm thick porous glass), the inception temperature of the process is constant ($\pm 0.3^\circ\text{C}$).

Fig. 14. (a) Maximum realizable vapour pressure of water as a function of temperature; (b) $\Delta a/\Delta T \times 100$ vs T for 5-mm thick porous glass-water system based on isotherm of $+0.5^\circ\text{C}$. (Reproduced by permission of the Academic Press from Journal of Colloid and Interface Science [16]).

Fig. 15. Dimensional changes and thermograms of 5-mm thick porous glass with various adsorbates. (Reproduced by permission of the Academic Press from Journal of Colloid and Interface Science [16]).

The sign of the specific volume change on freezing in the bulk state has no bearing on the dimensional changes of the adsorbent-adsorbate system. Expansion occurred with all systems (Figure 15), although water is the only substance in the group that expands on freezing in the bulk state.

In isothermal adsorption studies [6], it was not possible to achieve solidification of the adsorbing water in the voids of porous glass at either -35°C , $a_{\text{max}} = 0.12 \text{ g/g}$, or -25°C , $a_{\text{max}} = 0.17 \text{ g/g}$. These results are surprising because even at -35°C , $p/p_g^0 = 0.7$ was attained, and at this value of the relative pressure (according to the Kelvin equation), pores of less than $66\text{\AA}$ diameter are filled with water, which has an estimated freezing point as high as -13.5°C . On the other hand, a transition took place on "isosteric" cooling with $a = 0.12 \text{ g/g}$ [5] and even with $a = 0.084 \text{ g/g}$ [3]. If the hypothesis that cooling brings about desorption is correct, these findings imply that freezing takes place only in states defined by the desorption branch of the isotherm. The theory that the sole cause of freezing point lowering is the meniscus effect, the magnitude of which is assumed to be inversely proportional to the extent of the vapour pressure reduction, appears to be contradicted by this conclusion; for a given value of a , the adsorbate has a lower vapour pressure on desorption than on adsorption, so that the latter should have a higher freezing point. The opposite, however, is true.

One may argue that because water remains in the liquid state (being unable to freeze in the pores it filled on isothermal adsorption), it drains on cooling into the partly filled larger pores when the maximum realizable relative pressure becomes less than the vapour pressure of the adsorbate. The sharp rise of the $\Delta a/\Delta T$ curve indicates that below -15°C , a large amount of water has to leave the porous system. This depletion is probably seldom possible at this low temperature because of the low vapour pressure, high viscosity, and partly blocked pores. Equilibrium can be attained, however, if the trapped water freezes, reducing the vapour pressure to that of ice so that equilibrium conditions are attained. The well-established difference between the freezing and melting points of the adsorbate can then be expected because freezing occurs at the temperature at which water is transported to a pore in which it can form ice; the melting point is determined by the characteristics of the formed ice.

Interpretation of the Extension Isosteres

On the basis of the preceding hypothesis, an attempt can be made to specify the physical processes causing anomalies in the length changes. The specimen saturated at $T > 0^{\circ}\text{C}$, point 0, Figure 10(b), contracts on cooling as a result of the thermal effect. At the temperature represented by A (because $a > a_{\text{max}}$), freezing occurs on the surface and the latent heat of freezing warms the system to 0°C . Point B reveals a net contraction for this temperature cycle resulting

from loss of water on cooling to A. The system contracts between B and C again because of thermal contraction and continuous loss of water. At C, the water in the pores commences to solidify, a process that extends to point D.

The large expansion between C and D is associated with freezing and may be the result of the changed interaction between the glass and the solidified adsorbate. Dimensional changes normally occurring in response to change in ambient conditions (temperature, vapour pressure) cannot take place freely in the presence of solids in the pores, and strain develops. This expansion appears to be partly reversible; the system contracts to E on warming, where the low temperature melting process is completed. The net increase of length at this temperature is a measure of the damage suffered between C and D. It must be recognized, however, that the dimensions of the adsorbent at constant coverage depend also on whether it is in an adsorption or desorption state, according to the extension isotherms (Figure 9). This situation may well also exist for non-isothermal conditions.

Expansion between E and F is due to adsorption brought about by increasing relative pressure and loss of mechanical strength of the glass. This effect manifests itself when the ice in the crevices melts.

IX. AQUEOUS SODIUM CHLORIDE SOLUTIONS ADSORBED IN POROUS SILICA GLASS

Most natural systems contain solutions rather than pure water, so that their freezing mechanism is of great interest. In studying water adsorption on porous silica glass in the presence of NaCl, specimens were prepared by vacuum impregnation with NaCl solutions of various concentrations [18].

The concentration of the pore solution at complete saturation can be calculated from the water uptake and the salt content of the glass (determined from the increase of the dry weight due to impregnation.) The twenty calculated values were smaller than that of the impregnating solution by approximately 10 per cent. If, however, the concentration of the adsorbed liquid is calculated by assuming that one monomolecular layer is completely free of salt, the aforementioned differences vanish. This analysis is consistent with the reported salt rejection phenomenon in porous glass [19 - 23] and haemoglobin [24, 25], which presumably is due to the fact that the structured nature of the first layer is unavailable to the solute.

The adsorption isotherms, obtained by exposure of salt-impregnated samples to various relative humidities, are shown in Figure 16. Distortion is caused, at least in part, by the changing adsorbate concentration in the course of the adsorption process, a result of the constant salt and varying water content. Initially, the amount of water is insufficient to dissolve all the salt, so that solid salt and saturated solution are present. In later stages when all the salt has been dissolved, water uptake leads to dilution of the solution. Only

when the available pore volume has been completely filled does the concentration become equal to that of the impregnating liquid.

The water uptake of a salt-impregnated solid is not governed by relative pressure expressed in terms of pure water, but rather in terms of the vapour pressure of a bulk solution having a concentration identical to that existing in the pores at the current stage of adsorption. Because the concentration of the liquid held in the capillaries varies during adsorption, relative pressure has to be expressed in terms of appropriately changing saturation pressure values. Accordingly, the results of Figure 16 were recalculated. For each point, the concentration was calculated and the relative pressure expressed with the appropriate p^0 value. The results are shown in Figure 17.

The isotherms are very similar in shape but cannot be superimposed for two reasons: as salt concentration increases, the horizontal section of the curves at high relative pressures shifts to lower water content values and the hysteresis loop occurs at lower relative pressures. These effects are caused by reduced adsorptive capacity and diminished pore sizes due to the presence of salt.

The experiments lead to the conclusion that the adsorbed salt solution outside the first salt-free monolayer has properties - vapour pressure, density, solubility - that appear to be similar to those of the bulk state.

Fig. 16. Adsorption isotherms for water on porous glass impregnated with NaCl solutions of various concentrations. Relative pressure is based on the saturation pressure of pure water. (Reproduced by permission of the Academic Press from Journal of Colloid and Interface Science [18]).

Thermograms and Length Changes

The extension diagrams, Figure 18(a), and differential thermograms, Figure 18(b), of porous glass samples fully saturated with salt solutions of various concentrations show: (1) on cooling, anomalies 2 to 5 degrees below the bulk freezing point of the respective solutions, and (2) on heating, anomalies at a temperature closely approaching the bulk freezing point. Such results are consistent with the proposed model: on cooling, desorption takes place due to formation of ice on the wall of the container, followed by freezing on the surface of the specimen; on warming, melting occurs at the bulk freezing point. The double peaks in the thermograms for high salt concentration (18 and 22 per cent, marked A and B in Figure 18(b)) are caused by formation of ice in the undercooled liquid and the eutectic solid, respectively. Exothermic effect between the peaks is an indication of continuous freezing, as expected. Significantly, if the impregnating solution is saturated NaCl, only a single peak occurs.

In the temperature range -19 to -40°C , anomalies were obtained in the dimensional changes and heat content of the water-saturated sample (Figure 18). These anomalies are manifestations of second freezing and are assumed to result from the following circumstances.

Fig. 17. Adsorption isotherm for water on porous silica glass impregnated with NaCl solutions of various concentrations. Values of Figure 16 replotted as explained in text. (Reproduced by permission of the Academic Press from Journal of Colloid and Interface Science [18]).

Maximum relative pressure (based on vapour pressure of undercooled water), on cooling, decreases continuously until it reaches a value of 0.8 at -10°C (see Figure 14), the inception point of the steep, descending section of the desorption branch of the isotherm (Figure 7). At constant rate of cooling, the rate of desorption increases greatly in this region; as relative pressure changes from 0.8 to 0.6, the equilibrium water content is reduced from 0.24 to 0.08 g/g, the difference being equal to 65 per cent of the ultimate uptake and 92 per cent of the capillary-held water. The transfer of such an amount of water causes significant disturbance even under equilibrium conditions, conditions seldom established owing to the inadequate migration rate. The dynamic character of the phenomenon was demonstrated by very much reduced expansion at slow cooling rates compared with that observed at higher rates.

In another experiment (Figure 19), water-saturated glass was cooled at a rate of $0.33^{\circ}\text{C}/\text{min}$ until after the commencement of freezing at -18°C , when (apart

Fig. 18. Porous silica glass samples saturated with NaCl solutions of various concentrations during temperature cycle ($0.33^{\circ}\text{C}/\text{min}$). (a) dimensional changes, (b) differential thermograms. (Reproduced by permission of the Academic Press from Journal of Colloid and Interface Science [18]).

from a drift of approximately 1 C deg) constant temperature was maintained for 17 h. In this period, almost all of the strain of 53×10^{-5} that occurred during freezing was recovered. On resumption of cooling at a rate of 0.33 C deg/min, an over-all expansion of 70×10^{-5} took place, an amount very similar to that obtained at a rate of cooling of 0.0417 C deg/min. This expansion is in contrast with an expansive strain of about 400×10^{-5} usually found at the higher rate of 0.33 C deg/min (Figure 18(a)). These results indicate that a part of expansion is associated with non-equilibrium conditions caused by too-rapid cooling for a given permeability and diffusion rate.

Great similarities exist in the behaviour of the low temperature freezing and thawing anomalies for the condition of water with and without salt. This fact strongly suggests that the adsorbent-adsorbate system re-establishes equilibrium, in both cases, by desorption instead of freezing, when the vapour pressure of the pore-held adsorbate exceeds that of the external crystal.

Fig. 19. Changes in dimensions and heat content of porous silica glass saturated with water during temperature cycle; cooling rate $0.33^{\circ}\text{C}/\text{min}$ between 0 and -18°C ; $0.12^{\circ}\text{C}/\text{min}$ between -18 and 21°C ; arrest for 17 h at -21°C ; $0.33^{\circ}\text{C}/\text{min}$ rate in remainder of the cycle. (Reproduced by permission of the Academic Press from Journal of Colloid and Interface Science [18]).

X. FROST ACTION IN CEMENT AND CONCRETE

Durability of concrete is greatly impaired by freeze-thaw action. Air entrainment, in which a surface-active agent is added during the mixing operation to create small air bubbles in the paste and subsequently in the hardened concrete, has proved to be beneficial in engineering practice. In spite of this, certain problems remain. The most important include deterioration of bridge decks due to the action of de-icing salts and lack of a test method for evaluating frost resistance.

The conclusions reached in the study of the low-temperature behaviour of the better defined porous silica glass-water system were utilized in cement and concrete durability investigations. Initially, the experiments were carried out with neat cement paste, i.e., the samples contained neither sand nor stone.

The pore structure of hardened cement paste depends mainly on the ratio of water to cement (W/C ratio) in the original mix. In order to achieve the required plasticity, known in practice as workability, water is always added in excess of the amount needed for hydration. The presence of such an excess results in higher porosity and altered pore size distribution, the effects of which are directly proportional to the W/C ratio. In practice, cement in concrete has a W/C ratio in the range of 0.4 to 0.6. For the experiments, specimens with W/C ratios between 0.4 and 1.0 were prepared.

Investigation of hardened cement paste is made very difficult by the dependence on time of physical and chemical properties due to continuing hydration. In addition, most changes of concrete properties due to environmental factors have an element of irreversibility. By employing samples several years old, an age at which the rate of hydration becomes very low, the difficulty due to the former cause can be minimized. Circumvention of the problem caused by irreversibility is more formidable, although certain difficulties can be lessened. For example, by not exposing, even during pumping, hardened cement specimens to relative humidities of less than 10 per cent, part of the irreversible drying shrinkage can be avoided. The dimensional changes of saturated cement specimens were determined during a cooling/warming cycle in a manner similar to that applied in the porous glass case discussed in Section VIII. The results are shown in Figure 20(a) and (b) for specimens 1.25 mm and 3.125 mm thick respectively; the W/C ratios are indicated on the curves.

The first and most important observation to be made is that, notwithstanding differences, the extension curves are very similar to those obtained for the porous glass-water system. Compare the curve for 0.4 W/C sample in Figure 20 with that for porous glass in Figure 10(b). The same explanation may be assumed as a working hypothesis for the present system and the results will now be examined for consistency.

Fig. 20. Fractional length changes of vacuum-saturated plain cement specimens in temperature cycles (0.33°C/min). Curves have been shifted along the temperature axis; starting temperature, each case, +5°C. (Reproduced by permission of the American Ceramic Society from Journal of the American Ceramic Society [17]).

The anomaly near -8°C in the length changes is associated with an exothermic heat effect and is caused by the freezing of water driven to the external surface by the vapour pressure difference that exists between the liquid-like, pore-held water and external ice. Evidence for desiccation is presented in Figure 21, which shows the weight change of two fully saturated cement samples during a cooling/warming cycle, when at each point the temperature was kept unchanged until constant weight had been achieved.

Samples equilibrated at 84 per cent relative humidity at room temperature (Figure 22) failed to exhibit an anomaly at high temperatures because the vapour pressure of the adsorbate becomes greater than that of bulk solid only at temperatures below -18°C . Freezing of desorbed water occurred consistently at -21°C . At lower temperatures, -40°C , a length anomaly associated with an exothermic heat effect takes place, corresponding to that of the porous glass system observed at -20°C and attributed to a higher order transition of the water that was originally adsorbed in small pores but is, during cooling, in the larger pores. On warming, the semi-amorphous metastable ice melts at approximately -10°C .

Fig. 21 Weight change of cement specimens vacuum-saturated with water during a temperature cycle. Results were obtained in gravimetric adsorption experiments and represent equilibrium values. (Reproduced by permission of the American Ceramic Society from Journal of the American Ceramic Society [17]).

Fig. 22. (A) Fractional length changes and (b) thermograms of plain cement specimens equilibrated at 84% rh. (Reproduced by permission of the American Ceramic Society from Journal of the American Ceramic Society [17]).

Mechanical Failure

The volume change at -40°C , a temperature to which concrete structures are seldom, if ever, exposed, is small and of little practical importance. On the other hand, the following observations suggest that residual expansion is associated with the dilation at -8°C and leads to the destruction of cement paste: (1) this dilation can be very large (0.7 per cent for a sample of 0.7 W/C ratio and 0.125-in. thickness (Figure 20(b))); and (2) its value is related to the degree of frost susceptibility as established by field experience (W/C ratio, dimensions of specimen, etc). The severe damage resulting from repeated cycling between $+5$ and -10°C , while full saturation was maintained, provided direct proof of the inter-relation (Figure 23). Significantly, while the strain at -10°C changes little, the residual strain is additive.

Fig. 23. Fractional length changes of cement specimen during repeated temperatures cycles. Full saturation was maintained. (Reproduced by permission of the American Ceramic Society from Journal of the American Ceramic Society [17]).

The assumption that the expansion at -8°C is caused by the 9 per cent increase of the water volume on freezing cannot be accepted because in two slowly cooled samples, 33 and 40 per cent, respectively, of the total water present was expelled (Figure 21). this amount is equivalent to more than 3 to 4 times the specific volume increase. Furthermore, similar freezing behaviour was found with adsorbates other than water that decrease in volume on freezing (Figure 15).

The length changes of a vacuum-saturated cement sample ($W/C = 0.7$) during very slow cooling are plotted in Figure 24. Although the thermogram indicates that freezing occurred at -4°C , there was no expansion above -40°C , suggesting that the rate of the process causing dilation is a controlling factor. On this evidence, the process must be the desorption or expulsion of water due to reduction of the effective relative humidity in the cell.

The implication is that expansion occurs if the water concentration is higher than the equilibrium value at the prevailing relative humidity. This conclusion is supported by the observation that, on freezing, the length of a specimen 0.125 in. thick increases more than that of a specimen 0.050 in. thick (Figure 20 (a) and (b)). As most of the water reaches the outer surface by migration along

Fig. 24. Thermogram (top) and fractional length changes (bottom) of cement specimen, 3.125 mm thick (W/C ratio = 0.7) during a temperature cycle with slow cooling and heating rate ($0.0417^{\circ}\text{C}/\text{min}$). (Reproduced by permission of the American Ceramic Society from Journal of the American Ceramic Society [17]).

the shortest path (in this case the thickness), an increase of this distance understandably reduces the amount of water leaving the specimen and dilation occurs. In addition, the relaxation effect observed after freezing at constant temperature (Figure 19) is proof of the existence of non-equilibrium conditions, a state consistent with the proposed mechanism.

It must be emphasized that the absolute value of the permeability of the solid does not determine frost resistance. The quantity of water to be exuded in unit time is determined by the cooling rate (rate of relative humidity decrease), the shape of the desorption isotherm (number of pores to be emptied for a given relative humidity change), and the initial degree of saturation at 0°C . A solid having many pores of large diameter and fully saturated at 0°C may be severely damaged at moderately fast cooling rates, whereas a solid with only small pores is essentially invulnerable under the same conditions. If the specimens are not fully saturated, desorption begins only at low temperatures when the water flows into the partly empty large pores where it freezes without causing expansion (Figure 22(a)).

In solids with larger external dimensions, the path of diffusion to the outer surface is too long to achieve the required degree of desiccation unless the rate of cooling is very slow. Under normal conditions and a high degree of saturation on freezing, a great deal of expansion occurs, causing cracks. These fissures are the sites to which water migrates on further cooling and are therefore soon filled. Here the water expands on freezing, extending the break and creating new voids. Thus, the expansive force associated with ice formation is located at the weak areas of the solid (the reason the fissure formed there) and on repeated cycling leads to its destruction.

XI. FACTORS AFFECTING FROST RESISTANCE OF CEMENT

The mechanism described explains the observations made under field conditions and can be utilized in designing for durability. The factors are now considered in three groups relating to paste, water and environment.

The pore structure of the cement matrix and the stone is perhaps the most important property affecting durability. Ideally, porosity should be very low in order to reduce water content. In any case, very large and very small pores are preferable to those of medium size because large pores are seldom full and small ones become involved in the freezing mechanism only at very low temperatures.

The features of the pore system of cement paste are determined mainly by the W/C ratio. The amount of water that has to be removed to maintain equilibrium during the traversing of a given temperature range is of importance. This quantity depends on porosity. Ease of flow, characterized by permeability, is also of prime interest. Table II [26] shows the approximate amount of water

TABLE II

Amount of water lost by fully saturated cement samples on decrease of relative humidity from 100 to 80% [26]

W/C Ratio	Non-air-entrained		Air-entrained
	gram of water per gram of saturated paste	expressed in multiples of 0.0168 (0.4 W/C paste)	gram of water per gram of saturated paste
0.4	0.0168	1.0	0.0228
0.5	0.0291	1.7	0.0327
0.6	0.0812	4.8	0.0581
0.7	0.0977	5.8	0.0903
0.8	0.1100	6.5	0.1024

TABLE III

Desorption time of half the amount of water lost by non-air-entrained cement samples on decrease of relative humidity from 100 to 80% [26]

Half-time		
W/C Ratio	in seconds	in multiples of 2600 (0.4 W/C)
0.4	2600	1.0
0.5	7056	2.7
0.6	8300	3.2
0.7	11200	4.3
0.8	19600	7.5

lost by fully saturated cement pastes of different W/C ratios when the relative humidity is reduced from 100 to 80 per cent. The quantities of water are approximately equal to those that saturated specimens expel when cooled from 0 to -25°C . According to these values, the amount of water that has to leave a paste with a W/C ratio of 0.8 when it is cooled by 25°C deg is approximately 6.5 times greater than that from a paste with a W/C ratio of 0.4.

Reduction of water content is, of itself, not detrimental; but if the process is impeded, damage ensues. Low permeability, i.e., resistance of the pore structure to water flow, may create such a condition. Cement pastes with large W/C ratios (owing to their higher water content) require greater permeability if damage is to be avoided. In a series of exploratory experiments the "half-times" were determined for desiccation of various cement pastes when the relative humidity was reduced from 100 to 80 per cent. (The term, half-time, is used because it gives the time necessary for desorption of half the amount required to establish equilibrium.) The values shown in Table III indicate that under these conditions the rates of drying of cement pastes of different W/C ratios are similar. For example, paste with a W/C ratio of 0.8 lost 6.5 times the

amount of water desorbed from paste with a W/C ratio of 0.4, and the half-times had a ratio of 7.5 to 1. This finding is somewhat surprising because it would be not unreasonable to expect that the rate of drying would increase as pore volume (porosity) increases.

The essentially unchanged rate of drying explains frost susceptibility of pastes with high W/C ratios: with increase in W/C ratio the amount of water to be exuded increases sharply without the benefit of increased permeability. The mechanism by which air-entrained bubbles protect cement paste is clear. Barring unusual circumstances, the large cavities provided by bubbles serve as reservoirs into which, with cooling, expelled water can escape. Short distances between bubbles eliminate the need for migration of water to distant external surfaces.

Degree of saturation is the second factor affecting durability. It has been shown that freezing is destructive when concrete, whether plain or air-entrained, is fully saturated. On the other hand, when the degree of saturation is low, little damage occurs. Air-entrainment is beneficial because the uniformly and closely spaced voids become filled with water only on prolonged exposure to 100 per cent RH; under normal field conditions, therefore, proportionately fewer voids are filled with water in air-entrained concrete than in non-air-entrained concrete.

Freshly placed concrete is vulnerable to frost damage because of the high water content. Concrete placed late in the autumn has insufficient time to desiccate before freezing occurs. Air-entrainment is helpful in this case also. Incorporation of air bubbles provides reservoirs into which the water can flow from neighbouring smaller capillaries when the temperature falls below 0°C . The total volume of the pores in the cement paste and their size distribution after hydration are given and remain unchanged. Whether voids are filled with water or remain partially empty is determined by external conditions: relative humidity, and the shape of the structure.

Relative humidity of the atmosphere to which concrete is exposed in the field cannot readily be modified, and essentially nothing can be done to alter it so as to prevent frost damage. Concrete may contain water from wetting by rain, from groundwater or from inadequate drainage. Good architectural and engineering design can greatly improve durability by minimizing the time of exposure to water.

The factors of relative humidity and temperature are the environmental conditions most important with regard to frost action. The absolute value of the minimum temperature below 0°C determines the fraction of pores involved in the freezing mechanism. Perhaps not fully realized is the significance of the rate of temperature change. If the rate is slow enough, desorption can take place; but rapid cooling by only a few degrees can result in damage.

XII. AGGRAVATING EFFECT OF DE-ICING AGENTS ON THE FREEZING OF CEMENT PASTE

The so-called "bare pavement" policy adopted by most highway maintenance departments in recent years has resulted in large and ever-increasing use of de-icing chemicals, primarily NaCl , but also CaCl_2 in smaller quantities. As a direct consequence, deterioration of concrete pavements, bridge decks and embedded steel elements has increased alarmingly. Disintegration due to the action of de-icing agents is a serious technical and economic problem for which no satisfactory solution has yet been found.

Representative results of a study of salt impregnated cement samples [27] are shown in Figure 25. The features of the curves are once again similar to those

Fig. 25. (a) Fractional length changes and (b) thermograms of 0.5 W/C ratio cement paste, air entrained and saturated with NaCl solutions of concentrations indicated, during temperature cycles ($0.33^{\circ}\text{C}/\text{min}$). Specimens 1.27 mm thick. (Reproduced by permission of the American Ceramic Society from Journal of the American Ceramic Society [27]).

obtained with the corresponding porous glass system and their description would be superfluous. No qualitative difference could be detected when, instead of NaCl, another de-icing agent, urea, was used as the impregnating substance.

The mechanism of deterioration appears to be universally valid for the various adsorbate-adsorbent systems. The aggravating effect of de-icing agents in concrete and cement paste can be explained as follows: the primary cause of freeze-thaw action is the difference between the vapour pressure of the pore liquid and external ice. This difference is reduced by the lowering of the adsorbate content that normally occurs on cooling when a portion of the warm adsorbate distills to the cold surroundings. A porous solid fully saturated with water at, say, +5°C will be only partially saturated when cooled to 0°C unless special precautions are taken to avoid the creation of a temperature gradient. In contrast, when a solution, as opposed to a single-component substance, is adsorbed in the porous body, no distillation takes place because the vapour pressure of the solution is usually less than the vapour pressure of the external ice or water. The following example illustrates this point: at 22°C the vapour pressure of saturated NaCl solution is 19.8 KPa and that of water 26.4 KPa. In a 100 per cent relative humidity, the system that contains salt is exposed to $p/p^0 = \frac{26.4}{19.8} = 1.33$. This large excess results not only in complete saturation but prevents desorption even if a moderate temperature gradient exists on cooling. The alleviating effect of desiccation does not occur, in most cases, when salts are present. The decisive importance of water content in freeze-thaw action was demonstrated (Figure 22) previously.

XIII. TESTING OF FROST RESISTANCE

Efforts to improve the freeze-thaw durability of porous building materials are seriously hampered by the lack of a reliable test method. In concrete, frost resistance is most commonly assessed by the number of freeze-thaw cycles that specimens are able to endure without serious impairment of their mechanical strength. Usually, the change of the modulus of elasticity is monitored by the resonant frequency method. The results of this test seem to be neither easily reproducible or fully representative of field performance.

Poor reproducibility is due to inadequate control of cooling rate, degree of saturation, sample size, and other factors the importance of which is not fully understood. The specifications of the pertinent ASTM standard testing procedure (C666) are not rigorous. They require only that cooling from 37 to 3°F must be longer than 2 and shorter than 4 hr. The sample width is allowed to vary between 3 and 5 in. and the length between 14 and 16 in. The specifications do not provide safeguards against desiccation by distillation from the relatively warm sample to the cold cooling coils.

Beyond the uncertainties inherent in the execution of the test, the results

are in many cases not representative of field performance. Prediction of future performance suffers from the widely held opinion that frost resistance is an inherent material property and that therefore a given material is either susceptible or is not. The foregoing discussion clearly indicates that performance depends on the ability of the structure to expel the required quantity of water at an adequate rate. This capacity depends not only on the permeability and porosity of the solid but also on the initial water content and cooling rate, the two most important factors determined by the environment. One concrete can be durable in one application and susceptible in another. The intrinsic difficulty in testing freeze-thaw durability is the undetermined nature of the environmental conditions the concrete under consideration will experience. For example, degree of saturation depends, among other things, on the shape of the object, the amount of rain, the extent of condensation from the interior, the length of sunny and windy periods, all circumstances not known in advance, so that personal judgment with respect to the results of a durability test is still necessary. Under those circumstances, comparative testing is all that can be achieved; information can be obtained as to whether the frost resistance of a new sample matches that of an old concrete that proved durable in a similar application. Once these limitations of the test are recognized, useful assessment can be made.

Testing time is usually far too long: a minimum of six and in some cases as much as 18 months. Principally, two ways are open for reducing the time requirement: to shorten the cycle period or to evaluate damage by more sensitive means. The former increases the rate of cooling to an excessively high level and curtails the time allowed for re-saturation on thawing in water. Although the two effects may compensate for one another, they are undesirable because the freezing process deviates greatly from the course that usually occurs under field conditions. Utilization of more sensitive means for earlier detection of deterioration due to freezing and thawing leaves the test conditions unaltered and is, therefore, preferable.

It was mentioned in Section VIII that the length increase of the adsorbent occurring in a cooling/warming cycle is a quantitative measure of the damage inflicted on the system. This finding is now being applied for the early detection of frost damage [27]. The change of the cumulative residual expansion of specimens with the number of freeze-thaw cycles is shown in Figure 26, where it may be seen that residual expansion increases with increasing W/C ratio and is less for air-entrained than for plain cement samples, in accordance with expectations.

Frost resistance of bricks is at present assessed by the so-called saturation coefficient (also called c/b ratio), the ratio of the amount of water absorbed on 24-h submersion in cold water to the quantity contained in the specimen after

5-h submersion in boiling water. Good performance in service is expected if the c/b ratio is less than 0.8. The test was originally devised on the assumption that bricks, which become only partly saturated and have empty pore space available to accommodate increase in volume when water changes to ice, will prove durable. Although this hypothesis is incorrect, the performance of bricks with low c/b ratios is normally superior to those with high c/b values. The method is not reliable enough, however, to fulfil the great need that exists for plant quality control and user's acceptance test.

It follows from the mechanism described that frost resistance depends primarily on the absence of small pores. Large pores become filled only after long exposure to relative humidities of nearly 100 per cent and empty quickly if the humidity level drops. In fact, the durability of brick is due to its very coarse porous network. Because the surface area per unit weight of material increases with decreasing pore size at constant total porosity, the BET nitrogen surface area is expected to be very low for durable bricks.

To determine the validity of this assumption, the surface areas of 27 commercial products were determined [28]. Some of the samples were obtained from bricks that had failed in service, others from unexposed or exposed bricks used locally. The assessment of frost resistance was based on the reputation of the particular product for durability in service. Thus, products were classified

Fig. 26. Change of cumulative residual expansion of cement specimens with the number of freeze-thaw cycles. The W/C ratio of the specimens is indicated on the curves. AE designates air entrainment. (Reproduced by permission of RILEM from Materials and Structures [26]).

TABLE IV

Surface area of bricks related to frost durability [28]

Sample No.	Area $\text{m}^2 \text{g}^{-1}$	Durable	Questionable	Unsound
26	0.21	*		
23	0.35	*		
19	0.45	*		
13	0.52	*		
3	0.57	*		
17	0.63	*		
7	0.76	*		
18	0.78		*	
15	0.85	*		
22	0.98	*		
9	1.01			
14	1.01	*		
8	1.11	*		
6	1.14			*
12	1.25	*		
4	1.35			*
2	1.44			*
11	1.46		*	
21	1.50			*
1	1.65			*
27	1.68			*
25	2.00			*
10	2.65			*
16	2.88			*
5	3.00			*
24	5.60			*
20	8.25			*

as durable (no incidence of failure) questionable (some known cases of failure of product), and unsound (sample originating from brick that failed in service). The results are arranged in order of increasing surface area values in Table IV. It is apparent that durable bricks have low surface area and that bricks with a poor service record have high surface area. It is not implied that a threshold value for surface area can be established or that it even exists, but the value of the BET nitrogen surface area can serve as a good basis for ranking samples with respect to their frost resistance.

XIV. CRYOINJURY IN BIOLOGICAL SYSTEMS

Several theories have been advanced to explain the mechanism of cryoinjury. Lovelock [29] suggested that damage is caused by the high electrolyte concentration inside and outside the cell that increases when water is removed from the solution during ice formation. The observation that intracellular fluids remain in the liquid state well below -15°C [30] served as a basis for several hypotheses. As the free energy of undercooled liquids, as manifested by higher vapour pressure, is higher than their solid modification, a dehydration process

results. Injury was thought to be caused by reduction of the water content in the cell, viz., severe reduction of the cell volume [31] and loss of the protecting water layer leading to denaturation of the protoplasmic proteins [32]. It was also suggested that intracellular freezing of the undercooled water is responsible for injury to the cells [33]. Each theory has good experimental support, but none of the proposed mechanisms is able to account for all the relevant observations.

Perhaps the most important of the unexplained phenomena is the action of cryoprotective agents [34]. When added to biological tissues, these chemicals increase the survival rate from zero to even 100 per cent in a freeze-thaw cycle. Customarily, the additives are divided into two groups according to their ability to migrate through biological membranes.

It appears that most of the observations concerning the freezing phenomena in biological systems can be explained by a single, integrated theory. Adsorbed molecules, including water, in close proximity with inorganic [6, 16, 17] or polymer [35] surfaces remain in a liquid-like state at temperatures below their bulk triple-point as a result of strong attractive forces. No doubt exists that water in the vicinity of surfaces in biological systems also is subjected to strong forces and has properties uncommon in those of bulk water [36 - 43]. Specifically, extensive investigations have been carried out on red blood cells in which the main component is the haemoglobin macromolecule (mol wt 64,500). Water is adsorbed on the relatively large specific surface and in the 15-Å diameter channels formed by adjacent haemoglobin molecules. It has been found that at least part of the water is "bound," that is it is not available as solvent [25, 44] and has higher activation energy for diffusion [45] consonant with significant water surface interaction. Thus it seems reasonable to assume that the water rigidly held in close proximity with cell proteins is also prohibited from crystallization.

At slow cooling rates, crystal formation is restricted to extracellular spaces [30, 46]. With rapid cooling, when intracellular ice forms, cytolysis invariably ensues [47]. This effect occurs for both plant tissues [48] and animal cells. Microscopic study of frozen insect cells [49] has shown that extracellular ice formed in every case of freezing, while intracellular ice, if it occurred at all, formed subsequent to extracellular freezing and was associated with destruction of the cell membrane. Survival after intracellular ice formation has recently been reported. Glycerolated frog blood [50] and ascites sarcoma cells of rats [51], frozen to form a translucent solid, were proved to be viable after thawing. Similarly, rabbit corneal cells were found to survive intracellular ice formation [52]. Disregarding these exceptions for the time being, it may be concluded that, in general, intracellular ice formation is lethal. The present hypothesis is based on the assumption that intracellular

ice does not form in intact cells and where it has been observed did not precede and cause cell destruction but rather followed it.

The coexistence of non-freezable intracellular water and freezable extracellular water leads to the gradual release of bound water (desorption) and subsequent excretion of the free water from the cell. Equilibrium is established in a manner similar to that observed in inorganic systems.

This mechanism accounts for the severe dehydration of the cells and the continuous and gradual nature of the phenomenon. The desiccation process has been found [53] to proceed even at -60°C , a temperature well below the eutectic temperature of most salt solutions. Accordingly, it is understandable that denaturation occurs because the protein molecules lose their protective layer as the amount of water decreases.

If the rate of cooling is sufficiently small, desorbed water leaves the cell in a nondestructive fashion. The chief cause of cellular damage is probably dehydration and consequent denaturation. On rapid cooling, however, water in the cell is released at a rate faster than the permeability of the membrane allows it to flow out, a condition that leads either to total membrane destruction or to the creation of numerous small holes in it. The latter has been noted if erythrocytes are cooled at a rate exceeding $5000^{\circ}\text{C deg per min}$ [54]. It should be emphasized that the value of Δp is small and in itself not damaging. The resulting release of bound water, however, is sudden owing to the extremely steep rise of the adsorption isotherm at high p/p^0 values for the protein-water system [55]. This increase of pressure and transfer from the cell can be lethal.

It has been shown [56] that survival rate versus cooling rate curves exhibit a maximum that is the result of two factors, one directly and the other inversely proportional to rate of cooling. Mazur et al [56] identified them as "solution effects" (increased salt concentration due to desiccation) and intracellular freezing. The proposed mechanism suggests that the two factors are dehydration and membrane destruction.

The freezing behaviour of plant tissues is consistent with the mechanism outlined. Figure 27 [57] shows the differential thermogram and the simultaneously determined length changes of a potato sample during a temperature cycle where the rate of temperature change was $4^{\circ}\text{C deg/min}$. The details of experimentation were similar to those applied in the study of porous glass and cement adsorbents.

The DTA curve on cooling indicates that freezing took place in at least two stages. The first exothermic peak is characteristic of sudden freezing and the second of slow, continuous freezing extending over a wide temperature range. It is proposed that the first peak is caused by nucleation of the undercooled extracellular water at -7°C ; that this triggers desorption, transfer, and finally crystallization; and that ice formation occurs extracellularly from water that

was originally intracellular.

The second process, which immediately follows the first, is associated with large expansion and extends to -40°C because desorption is the rate-controlling process, which in turn is a function of temperature. The process is essentially terminated when, on further cooling, no significant amount of water is frozen.

The main features of these curves remain the same when the cooling rate is half as much, i.e., $2^{\circ}\text{C deg/min}$, but certain quantitative changes are apparent. Extracellular freezing is initiated at a higher temperature (-2.3°C), presumably because the longer time period at sub-zero temperatures increase the probability of nucleation. The amount of heat released during the second phase of freezing appeared to be about the same, as expected, because the amount of water frozen is identical, but the process proceeds at a more even rate and continuously over a wide range of temperature. Most significantly, the fractional expansion dL/L is only 18×10^{-3} instead of 27×10^{-3} . In both cases, freezing is completed at essentially the same temperature of approximately -40°C . Melting in both instances is sharp and occurs at 0°C because the ice is located outside the cell and has bulk properties. It may be mentioned that hardy winter plants

Fig. 27. Fractional length changes of potato during a temperature cycle (4°C/min). (Reproduced by permission of Academic Press from Cryobiology [57]).

show multiple exothermic peaks [53] because the cell membranes are intact and permeable. Conversely, non-hardy plants or dead stems exhibit a single freezing process, presumably due to a fragile or already destroyed membrane structure.

XV. MECHANISM OF CRYOPROTECTION

The proposed mechanism of cryoinjury permits the establishment of conditions under which damage is minimal or totally avoided.

Cooling Rate

It follows that the intermediate velocity renders optimum survival because it is fast enough to minimize dehydration, having less time available for desorption than at slow rate of cooling, but slow enough to avoid membrane injury. In avoiding dehydration, high cooling rates are advantageous because, in spite of the high dehydration rate, the absolute amount of redistributed water is small. Lovelock [29] found, in support of this view, that damage of red cells occurs between -3 and -40°C if the time spent in this temperature region is more than 5 sec. The lower boundary value of the critical region in which damage occurs is probably determined by the drastically decreased mobility of the water molecules.

Although only the cooling process has been discussed, the same considerations apply to the warming process. There is no reason to assume that thawing is less injurious than freezing. In fact, the opposite may be true. On warming, a considerable time is required for the complete disappearance of ice crystals, and during this period the unfrozen cells can warm to well above 0°C . Under these conditions large deleterious vapour pressure differences may exist. The situation is aggravated by the relatively high temperature, at which water diffusion is rapid.

Permeability

It is expected that increased membrane permeability is beneficial by virtue of permitting the application of higher cooling rates without membrane injury or, alternatively, by reducing the extent of the damage at a given cooling rate.

In agreement with this view is the observation that during the increase of winter hardiness, the cell permeability of plants increases. Only plants whose frost resistance actually increased on exposure to "hardening" temperatures showed this change [53,58]. It has also been reported [59] that peptone protects T_4 bacteriophage of *Escherichia coli*, presumably by increasing permeability [60].

Williams and Meryman [61] demonstrated that winter-hardened or artificially protected spinach grana are not injured if a reversible influx of solute is possible. Subsequently, Meryman suggested [62] the increased permeability induced by cryoprotective additives as the efficacy of non-penetrating agents.

TABLE V

Vapour pressure of aqueous solutions of cryoprotective agents at 0°C [57]

Solution	Concentration %	Pressure, torr	Relative pressure
Ammonium Acetate	36	3.27	0.72
DMSO	39	3.48	0.76
Glycerine	40	3.85	0.81

Viscosity

In terms of the proposal presented in this review, cells are damaged during slow cooling mainly by dehydration. Accordingly, a certain degree of protection may be achieved by increasing the viscosity of the intracellular fluid. This increase will retard the flow of water. It seems significant that the aqueous solutions of the penetrating cryoprotective agents (glycerine, DMSO, glycol, ammonium acetate, trimethylamine acetate) are noted for having high viscosity, particularly at low temperatures.

Minimizing Δp

Elimination of Δp , the primary cause of cryoinjury, is theoretically possible in at least two ways: decrease in the vapour pressure of the intracellular fluid or increase in the vapour pressure of the extracellular solid. The first can be achieved by the addition of one of the known penetrating agents. A property common to these additives is the low vapour pressure of their aqueous solutions. The values of p and p/p^0 of three solutions, of a concentration customarily applied for complete protection of biological systems, are given in Table V. Most agents in the undiluted state are deliquescent because the vapour pressure of their saturated solution is less than the partial pressure of water in air.

Increase of the vapour pressure of the extracellular solid in relation to that of crystalline ice can be achieved by glass formation. As glasses do not represent states of thermodynamic equilibrium with respect to configuration changes of their molecular structure, their free energy and vapour pressure are greater than those in the equilibrium crystalline form [63]. Glass formation occurs with certain substances under unique conditions, e.g., amorphous ice is formed below -120°C when water vapour is cooled very rapidly, but other substances undergo glass formation under almost all conditions. Liquids belonging in the latter group are characterized by high viscosity, which is a recognized criterion for glass formation.

Salt Buffering

Farrant and co-workers [64 - 66] demonstrated that the harmful threshold concentration of NaCl occurs at a lower temperature if penetrating cryoprotective

agents of PVP are present and that the reduced salt concentration contributes to protection during freezing.

XVI. ACTION OF CRYOPROTECTIVE AGENTS

Additives possessing cryoprotective qualities greatly affect the pattern of ice formation in solutions, as shown by Luyet and co-workers [67, 68]. Most of the additives that possess cryoprotective qualities are known to form glasses on solidification. Glycerine, DMSO, glycol, ammonium acetate, PVP [35], trimethylamine acetate [62], and sucrose [69] are good examples of such compounds. It is obvious that extracellular glass formation is one of the means by which protection is provided. The concentration of the aqueous solutions of three additives at which the transition is completely glassy has been established in this laboratory. The differential thermograms (Figure 28), obtained at a cooling rate of 130°C/min [57] indicate that no crystalline ice forms in glycerine above 45 per cent concentration, in DMSO above 40 per cent, and in ammonium acetate above 37 per cent. It is most significant that for complete protection of blood the concentration is required to exceed 45 per cent of glycerine [47], 34 per cent for DMSO [70] and 31 per cent for ammonium acetate [71]. PVP provided good but not complete protection when the concentration was 15 per cent in freezing of Chinese hamster and marrow stem cells [56]. This lack of good protection is to be expected in view of the very high concentrations (60 per cent) required to avoid ice formation of PVP solutions [35].

In a classical experiment, Lovelock [72] demonstrated that glycerine must penetrate the red cells to provide good protection. He found that recovery decreased from 97 to 63 per cent when permeation was blocked by added copper ions. The results were puzzling, however, in that survival was 63 per cent instead of 2 per cent, which would be expected in the absence of glycerine. It is suggested that survival increased from 2 to 63 per cent by virtue of glass formation, but could not achieve 97 per cent due to absence of penetration, i.e., vapour pressure lowering of the intracellular fluid.

Figure 29 shows the fractional length changes and thermal effects obtained in a cooling/warming cycle of potato containing DMSO additive. The cryoprotective agents have dramatically reduced the exothermic heat effect, i.e., solidification was essentially glass formation, and the concomitant changes in dimension have also diminished.

It is most probable that the aforementioned survival of ascites tumour [51] and glycerolated frog blood cells [50] during intracellular crystallization was due to the vitreous character of the formed ice. This suspicion is supported by the observation that viability was preserved only if the solid was translucent. In fact, Rapatz and Luyet [50] observed that "the similarity of the results (of the glycerolated blood) with those obtained with non-glycerolated blood cells

frozen at -150° and recrystallized at -10° is striking." It is well known that water cooled rapidly to below -120°C forms vitreous ice.

According to the proposed mechanism, penetrating agents protect by eliminating Δp and thus the free energy, utilizing both the lowering vapour pressure of the fluid and the increasing vapour pressure of the solid; the action of the non-penetrating additives (hitherto not explained satisfactorily) consists mainly of external glass formation. Penetrating agents also increase the viscosity of the intracellular fluid. Although "bound" water excludes salt, it does dissolve non-ionic species such as glucose [73] and, presumably, the penetrating additives.

Fig. 28. Differential thermograms of aqueous DMSO solutions. Concentrations are expressed in v/v% and are indicated on the curves. (Reproduced by permission of Academic Press from Cryobiology [57]).

It should be emphasized that this hypothesis denies neither the operation nor the importance of the "solution," "minimum cell volume," and "sulfhydryl-disulfide" mechanisms. Rather it suggests the primary causes leading to the creation of conditions under which these mechanisms become injurious and demonstrates their compatibility.

XVII. CONCLUSION

It appears that substances are unable to crystallize in the adsorbed state and consequently have higher free energy than bulk crystals outside the adsorption system. The free energy difference is reduced, or eliminated, by desorption of the adsorbate in an appropriate quantity; the adsorptive (desorbed fraction) crystallizes in the external space while the adsorbate remaining in the porous system lowers its free energy by meniscus formation. Mechanical damage is caused when the temperature decreases at such a rate that desorption cannot proceed rapidly enough to eliminate the free energy difference and a glassy solid forms in the pore system. This mechanism was found to be applicable for the various types of adsorbents and adsorbates that were investigated.

Fig. 29. Fractional length changes and thermogram of potato presoaked in 50% DMSO-water solution. Rate of temperature change was 4°C/min. (Reproduced by permission of Academic Press from Cryobiology [57]).

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