

In applying a crystal-like model to the liquid state, it is necessary to allow for intermixing between molecules occupying lattice point sites and interstitial sites, due to the disappearance of long-range order. With water, the mechanism by which the voids of the ice-like carcass are filled is superimposed on the former process. It is shown that the first process makes a contribution of about 30% to the observed entropy of fusion of ice, while the second process contributes about 26%.

## 1. Introduction

The generally accepted similarity between the structures of water and ice [1-4] has given rise to numerous models for the structure of water which emphasize its close structural relation to ice [5-7]. If, however, an absolute significance [7-8] is ascribed to this similarity, then several very important ways in which liquid water differs from crystalline ice may be overlooked. This difference is most clearly manifested in the calculation of the configurational entropy of water, and the quasicrystalline models for the structure of water must be treated with caution.

The principal difference between the solid and liquid states is the absence of long-range order [9, 10] in the latter. In a solid body, the molecules are located at the lattice points in the crystal, and that part of the configurational space of the crystal which corresponds to the transfer of its molecules into the interstices is practically inaccessible to molecules, providing that the dimensions of the voids in the crystal lattice are small. This is the case for the overwhelming majority of substances (water, of course, is an exception to this).

Molecular exchange, which also exists in the solid state, does not reduce the differences between the lattice point sites and the interstitial sites. On the other hand, all points of a space filled by a liquid are equivalent. Hence, when speaking of the similarity between the structures of water and ice, it should be kept in mind that the similarity only extends to close-range order, which expresses the spatial correlations in the arrangement of molecules of the liquid in the vicinity of a certain fixed molecule [9]. Close-range order includes large regions around the central molecule. In the case of liquid water, close range order is manifested to a greater degree, perhaps, than in other substances.

The absence of specific spatial positions means that in liquids the molecules possess greater possibilities for the filling of the space. If a liquid is described within the framework of the quasicrystalline model, then it is absolutely essential to augment this by making allowance for the peculiar intermixing between the different types of sites. The increase in entropy which occurs with fusion is also probably connected with this phenomenon. In the case of water an additional possible mode of filling the voids with molecules is superimposed on the process involving the intermixing of the lattice point sites and the voids of the ice-like carcass. An additional configurational entropy term from the intermixing of the occupied and unoccupied cavities is associated with this. This fortuitous circumstance is not however, generally speaking, the principal distinguishing idiosyncrasy of liquid water as one of the three fundamental aggregate states of matter.

## 2. Melting as the Intermixing of Lattice Point and Interstitial Sites

Let us now consider in more detail the processes involved in the fusion of a conventional molecular crystal. We shall assume that  $N$  molecules of the liquid can be in  $(M + N_s)$  temporal positions of equilibrium. Of these we shall call  $N_s$  crystal-like sites ( $s$ ), while  $M$  are called hole vacancies ( $h$ ). The two classes of equilibrium sites differ

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All-Union Scientific-Research Institute of Petrochemical Processes, Leningrad. Translated from *Zhurnal Strukturnoi Khimii*, Vol. 11, No. 4, pp. 590-594, July-August, 1970. Original article submitted December 14, 1967.

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sharply in their potential energies. The nearest environment around the crystal-like sites is the same as that about a lattice site in a crystal. The interstices in a crystal correspond to the hole vacancies. Molecules which have crossed over into these positions possess significantly higher potential energies than those at crystal lattice sites. Hence a definite potential energy,  $\varepsilon_s$  and  $\varepsilon_h$ , respectively, may be ascribed to each class of equilibrium site. We further assume that  $\varepsilon_s \ll \varepsilon_h$ . The difference between the solid and liquid states lies mainly in the fact that in the crystal, the  $N_s$  crystal-like sites and the  $M$  voids occupy strictly determined positions in space, while in the liquid, any of the  $M + N_s$  equilibrium sites belong to class  $s$  for part of the time and to class  $h$  for a part of the time.

In calculating the statistical probability for the model under consideration, it is necessary to find the number,  $\Omega$ , of different ways of distributing  $N_s$  crystal-like sites among the total number ( $M + N_s$ ) of equilibrium sites. This number is given by [11]:

$$\Omega = \frac{(M + N_s)!}{N_s!M!}. \quad (1)$$

The total partition function for such a system has the form:

$$Q(N, V, T) = \psi_s^{N_s} \exp \{-N_s \varepsilon_s / kT\} \Omega, \quad (2)$$

where  $\psi_s$  is the partition function for the vibrational and rotational motion of the molecule in an equilibrium crystal-like site.

Since in the model taken,  $N_s = N$ , the free energy of the liquid becomes equal to

$$\frac{F_l}{N} = \varepsilon_s' - kT \ln \psi_s' - kT \left\{ \ln(\nu + 1) + \nu \ln \frac{\nu + 1}{\nu} \right\}, \quad (3)$$

where  $\nu = M/N$ , the number of additional equilibrium positions at one lattice point site which arise during the fusion process. The state parameters in Eq. (3) have been marked with a stroke in order to emphasize that both the density and the (quasi)lattice constant change during the fusion process.

Since  $\Omega = 1$  for a system with long-range order, we obtain for the free energy of the crystal:

$$\frac{F_K}{N} = \varepsilon_s - kT \ln \psi_s'.$$

The melting curve is determined by the condition

$$\varepsilon_s - \varepsilon_s' + kT_0 \ln \frac{\psi_s'}{\psi_s} = kT_0 \left\{ \nu \ln \nu - (1 + \nu) \ln(1 + \nu) \right\}, \quad (4)$$

where  $T_0$  is the melting point.

It follows from Eq. (4) that the entropy of fusion (per mole) is made up of two contributions:

a) a configurational part

$$\Delta S_{\text{conf.}} = R \{ (\nu + 1) \ln(\nu + 1) - \nu \ln \nu \}, \quad (5)$$

b) a potential part

$$\Delta S_{\text{pot.}} = R \ln \frac{\psi_s'}{\psi_s} + RT \frac{d}{dT} \ln \frac{\psi_s'}{\psi_s},$$

caused by the change in the force field in which the molecules are situated.

When  $\nu = 1$ , which corresponds to cubic close packing, Eq. (5) yields  $\Delta S_{\text{conf.}} = 2.77$  eu. It is known that the entropy of fusion of the majority of simple substances which crystallize with the above structure lies in the range from 2 to 3 eu [12]. Upon fusion, the entropy of the inert gases increases by 3.4 eu [13]. Hence, the configurational contribution constitutes a large part of the entropy of fusion.

### 3. The Configurational Entropy of Water

In the case of water the additional mechanism whereby some of the cavities become filled by molecules is superimposed on the process involving the intermixing of the lattice point sites with the voids of the ice-like carcass. If we assume that all cavity molecules are equivalent, which corresponds to the original treatment of the model due to Samoilov [1, 2] then both mechanisms can be considered as statistically independent. In considering a carcass with filled cavities it is convenient to employ an isothermal isobaric ensemble [7, 11], since the volume of the system does not remain constant during this process and the expression:

$$Q(N, p, T) = \sum_{N_h=0}^M \frac{M!}{N_h! (M - N_h)!} \psi_s^{N_s} \psi_h^{N_h} \exp \left\{ - \frac{N_s \varepsilon_s + N_h \varepsilon_h + N_s p v_s}{kT} \right\}. \quad (6)$$

is written for the partition function. Here  $N_s = N - N_h$ , the number of lattice point sites in the carcass;  $N_h$  is the number of cavity molecules;  $\varepsilon_s$ ,  $\varepsilon_h$ ,  $\psi_s$ , and  $\psi_h$  are the energies and free volumes of the molecules at the lattice point sites in the carcass and in the cavities;  $v_s$  is the volume (per molecule) of the idealized carcass (without any filling of the interstitial cavities). The total volume of the system is  $V = N_s v_s$  and the molar volume,  $v = f v_s$ , where  $f = N_s/N$ , the fraction of molecules situated at lattice point sites. In liquid water the state parameters acquire new values due to the change in the intermolecular distances upon fusion.

In order to allow for the absence of long-range order in water in the proper manner, it is necessary to augment Eq. (6) by including an additional factor (1) which describes the intermixing of the lattice point sites and the voids, independently of whether the latter are filled or not. The total partition function then becomes equal to

$$Q(N, pT) = \sum_{N_h=0}^M \frac{(M + N_s)!}{N_s! N_h! (M - N_h)!} \psi_s'^{N_s} \psi_h'^{N_h} \exp \left\{ - \frac{N_s \varepsilon'_s + N_h \varepsilon'_h + N_s p v'_s}{kT} \right\}. \quad (7)$$

The factor

$$\bar{\Omega} = \frac{(M + N_s)!}{N_s! N_h! (M - N_h)!} \quad (8)$$

can be interpreted as the number of different ways of distributing  $N_s$  crystal-like molecules with energy  $\varepsilon'_s$  and  $N_h$  cavity molecules with energy  $\varepsilon'_h$  among a total number  $(M + N_s)$  of equivalent sites. In a formal approach it might be thought that Eq. (8) does in fact take the indistinguishable permutations of the carcass and cavity molecules within the unchanged ice-like carcass into account. The same applies to the exchange of the molecular sites together with their energy states, which is very typical of the liquid state. Such permutations lead to different configurations. One can convince oneself on this point by taking, as an example, the Ising model, which was intended to describe statistical ordering in systems of identical particles, capable of existing in two different spin states [11]. The number of ways of distributing  $N_s$  spins, which are antiparallel to an external magnetic field, over  $M + N$  equivalent lattice points is exactly given by the expression (1) [11].

Let us now explain what has been discussed above in greater detail. Both in the solid state and in the liquid state, systems composed of  $N$  particles can be classified in terms of the distribution of the particles (or quasiparticles such as phonons) over the energy levels of the correctly chosen single particle Hamiltonian. In the Einstein model of a crystal these could be the independent harmonic oscillations of the particles about the lattice points. Upon transferring a molecule into an interstitial position, however, its energy state is described by a different one-particle Hamiltonian, if only because the symmetry of the environments of molecules at lattice points and interstitial positions is different. In the calculation of the number of microstates of a multiparticle system only those permutations are indistinguishable which differ in a permutation of the particles between states of the one and the same Hamiltonian. The permutation of particles between states corresponding to different single particle Hamiltonians leads to physically different configurations. In an analogous manner, in the Ising model only those permutations are indistinguishable which change both the spatial positions as well as the direction of the spins. If the spins do not change direction, the configurations are considered as distinguishable. In the liquid state, those permutations of the lattice point and cavity molecules, under which each particle retains its belonging to a definite single particle Hamiltonian, are distinguishable. In systems with long-range order such permutations are impossible. We must take them into consideration, however, if we wish to obtain a correct description of the liquid state. The

TABLE 1. The Entropy of Fusion of Water

$\nu$	[7, 14, 15]	$\Delta S_h$ , eu	$\Delta S_p$ , eu	$\Delta S_{\text{conf.}}$ , eu	$\Delta S_{\text{fusion}}$ , eu (exptl.)
0,5	0,85	1,35	1,62	3,1	5,2

partition function [Eq. (6)], in which the additional possibilities for distributing the equilibrium crystal-like sites in space are not taken into consideration, describes, according to what has been said above, a system with long range order and refers to ice crystals with filled voids which do not exist in nature. Analogous remarks also apply to [8] in which clathrate structures serve as the model.

Let us now return to the partition function (7). By separating out the largest term and recalling that  $M/N = \nu f$ , we obtain the thermodynamic potential of liquid water:

$$\begin{aligned} \mu_l = & f\varepsilon_s' + (1-f)\varepsilon_h' - kTf \ln \psi_s' - kT(1-f) \ln \psi_h' + p\nu_s' \\ & + kT\{-\nu f \ln f + (1-f) \ln (1-f) + [(\nu+1)f-1] \ln [(\nu+1)f-1] \\ & - (\nu+1)f \ln (\nu+1)\}, \end{aligned} \quad (9)$$

where  $f$  is defined by the equation

$$kT \ln \left\{ \left[ \frac{(\nu+1)f-1}{\nu+1} \right]^{\nu+1} \cdot \left( \frac{f-\nu}{1-f} \right) \right\} = \varepsilon_h' - \varepsilon_s' + kT \ln \frac{\psi_s'}{\psi_h'} - p\nu_s' \quad (10)$$

The substitution of (10) in (9) yields the equilibrium magnitude of the thermodynamic potential

$$\begin{aligned} \bar{\mu}_l = & \varepsilon_s' - kT \ln \psi_s' + p\nu_s' + kT\{\nu \ln [(\nu+1)f-1] - \nu \ln f \\ & - (\nu+1) \ln (\nu+1)\}. \end{aligned}$$

The thermodynamic potential of ice, in which all the cavities are vacant, has the form

$$\mu_{\text{ice}} = \varepsilon_s - kT \ln \psi_s + p\nu_s. \quad (11)$$

Comparing (10) and (11), we obtain for the entropy of fusion of ice (per mole)

$$\Delta S_{\text{fusion}} = \Delta S_{\text{conf.}} + \Delta S_{\text{pot.}}$$

where  $\Delta S_{\text{pot.}} = R \ln \frac{\psi_s'}{\psi_s} + RT \frac{d}{dT} \ln \frac{\psi_s'}{\psi_s}$ , the potential part of the entropy of fusion. The configurational entropy of fusion can be broken up into two contributions:

a)  $\Delta S_h = -R\{(1-f) \ln (1-f) - \nu f \ln \nu f + [(\nu+1)f-1] \times \ln [(\nu+1)f-1]\}$ . This is the contribution from the distribution of the molecules over the voids.

b)  $\Delta S_p = Rf\{(\nu+1) \ln (\nu+1) - \nu \ln \nu\}$ . This is the contribution determined by the process of the intermixing of the lattice point sites and cavities of the ice-like carcass which takes place as the long range order is reduced. The results of the calculation of  $\Delta S_h$  and  $\Delta S_p$  for water at 0°C are shown in Table 1.

It can be seen that the entropy change  $\Delta S_h$  associated with the distribution of a fraction of the molecules over the voids of the ice-like carcass, only constitutes one quarter of the over-all entropy change which occurs during the fusion of ice, while the intermixing of the lattice point sites and cavities of the carcass gives about a third of the observed change. On the whole, the configurational entropy makes up about 60% of the total entropy of fusion. The remaining part is probably associated with a change in the nature of the thermal vibrational motion of the carcass molecules in the liquid state.

I express my deep thanks to F. M. Kuni for valuable comments.

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