TABLE III

Relaxation times and activation parameters for structure I hydrates and ices I and III at 0 °C

	P/bar	$\tau/\mu s$	E_A (kcal mole^{-1})	$\Delta S^{\ddagger}$ (cal deg^{-1} mole^{-1})	$\Delta V^{\ddagger}$ (cm^3 mole^{-1})	Reference
Argon hydrate	2000	16	5.7	−17.5	3	This work
Nitrogen hydrate	1200	15	7.9	− 9.4	2	This work
Ethylene oxide hydrate	1	0.027	6.7	− 1.2		8
Trimethylene oxide hydrate*	1	0.005	5.8	− 1.3		9
Ice I	1	21.5	13.25	+ 9.5	2.9 (−23 °C)	1, 2
Ice III†	3000	0.19	11.6	+13.0	4.5 (−30 °C)	3

*Extrapolated from data below −74 °C.
†Extrapolated from data below −22 °C.

gives a g value of 2.5. This is significantly smaller than the value of 3.3 for ice I, but is comparable to the value of 2.7 found for ice III (3) and for structure II hydrates (9). Clearly again the hydrogen bonding imposes a considerable local correlation between the directions of the dipole moments of water molecules.

Relaxation Times

Reorientation of the water molecules in argon and nitrogen hydrates is remarkably slow in comparison with their reorientation in the clathrate hydrates previously studied. The relaxation times at 0° C (Table III) are larger by several orders of magnitude than those of the isostructural hydrates of ethylene oxide (8) and trimethylene oxide, the latter extrapolated from results at much lower temperatures (9).[3] The structure II hydrates of several ethers and ketones (7, 9–11), have relaxation times of about 0.1 μs at 0 °C.

At relatively high temperatures, argon and nitrogen hydrates relax as slowly as ice I, the slowest of the disordered ices to relax. The relaxation times depend much less on temperature, however, and the activation energies (Table III) are similar to those of other hydrates.

The activation volumes (2 or 3 cm^3 mole^{-1}) are indistinguishable from the activation volume of ice I. Because of small differences between samples, and the small effect of pressure on the relaxation times, activation volumes were derived only from measurements on the same sample. They almost certainly refer to hydrates of constant composition, rather than to hydrates whose compositions attain new equilibrium values in response to a change of pressure.

Shape of the Dispersion Curves

The shapes of the dispersion loci of structure II hydrates and their change with temperature appear to be characteristic of the crystal structure (9–11). This is not the case for the four structure I hydrates for which information is available if the shapes are compared at the same temperatures. Values of α of about 0.1 are found above 0 °C for argon and nitrogen hydrates, at −80 °C for ethylene oxide hydrate, and at −110 °C for trimethylene oxide hydrate, at which temperatures the relaxation times of all these hydrates are similar. However, if the width of the dispersion is entirely dictated by the degree of non-equivalence of water molecule sites and hydrogen bonds in the lattice, identical structures should lead to identical α's at the same temperature. The size of the unit cell is known to vary slightly for different encaged molecules (23, 24). The extent to which the positions of the water molecules vary within the unit cell is unknown, but is likely to be too small to markedly affect the value of α. The relatively broad loci shown by argon and nitrogen hydrates are probably partly due to factors other than non-equivalence of the hydrogen bonds (see next section).

Mechanism of Relaxation

There are several suggestive regularities in the activation parameters for relaxation of the various phases of "ice" listed in Table III of this paper and in Table III of the following paper (25). The Arrhenius activation energies fall into two groups, with values in the ranges 5.7 to 8.7 (average about 7) and 11.0 to 13.3 kcal mole^{-1}, respectively. The group with high

---

[3] In addition to a hydrate of structure II, trimethylene oxide forms a second hydrate (9) which Calvert's X-ray diffraction studies (22) have now confirmed to be structure I.

activation energies is also characterized by relatively high positive entropies of activation, 9 to 13 cal deg^{-1} mole^{-1}. The group with low activation energies may be subdivided into the ether and ketone hydrates, with entropies of activation close to zero, and argon and nitrogen hydrates, with large negative activation entropies.

According to the Bjerrum model of relaxation in ice (26), reorientation of water molecules occurs by the diffusion of D and L defects, that is, of O - - - O "bonds" which have either two hydrogen atoms or none near them. In pure ice I these defects are formed by thermal excitation of normal hydrogen bonds N

$$2\text{N} \rightleftharpoons \text{D} + \text{L},$$

for which an enthalpy and entropy of formation of 15.7 kcal mole^{-1} and −4.2 cal deg^{-1} mole^{-1} may be estimated (27). The activation enthalpy and entropy for the diffusion of the defects are then 4.9 kcal mole^{-1} and 11.6 cal deg^{-1} mole^{-1}, where the dielectric Arrhenius energy (Table III) has been converted to an enthalpy of activation at 0 °C.

Ices III, V, VI, and VII have (high) energies and entropies of activation like ice I and appear to relax by essentially the same mechanism (2–4). The hydrogen bonding between the water molecules of the clathrate hydrates of types I and II approaches more closely that in ice I than does the hydrogen bonding in the high-pressure ices. All water molecules are four-coordinated and in the structure I ethylene oxide hydrate at −25 °C (12) for example the average nearest-neighbor O - - - O distance is 2.79 Å and the average departure of the O - - - O - - - O angles from tetrahedral is only 3.7°. It is therefore likely that the clathrate hydrates also relax by diffusion of orientational defects, although the details of the Bjerrum mechanism must be modified to account for the appreciable lowering of the energies and entropies of activation.

The similarity of the activation parameters shown by the ices proper, despite their diverse structures, suggests that the thermodynamic parameters for the formation and diffusion of the defects responsible for relaxation are similar in these phases. We neglect small differences and assume, because of the structural similarities, that the parameters for the *intrinsic* formation and diffusion of the defects are the same in the clathrate hydrates as in ice I.

The fact that the ether and ketone hydrates relax faster than ice suggests that, in addition to intrinsic defects, defects are introduced into the lattice of these clathrate hydrates by interaction of the water with guest molecules. This is further indicated by the existence of differences between the relaxation rates of the isostructural hydrates of different ethers and ketones. The most probable form of this interaction with a guest molecule M produces something resembling an L defect

$$\text{M} + \text{N} \rightleftharpoons \text{M} \cdots \text{H—O} + \text{L},$$

where N stands for a normal hydrogen bond. The equilibrium constant is

$$K = \frac{c_\text{N}}{c_\text{M}}\alpha^2,$$

where α is the fraction of normal bonds converted to defects. The ratio c_N/c_M of the concentration of normal bonds to the concentration of guest molecules varies from 11.5 for structure I hydrates with all cages occupied to 34 for structure II hydrates. From the representative Arrhenius energy and entropy of activation of 7 kcal mole^{-1} and 0 cal deg^{-1} mole^{-1} for these hydrates, the energy and entropy of formation of defects are about 3 kcal mole^{-1} and −23 cal deg^{-1} mole^{-1}, K is about 2×10^{-8} at −10° C, and α is about 3×10^{-5}. In ice I the fraction α of defect to normal bonds is much less, about 10^{-7} at −10 °C. The energy of defect formation is reasonable: the geometry is less favorable than for hydrogen bonding within the lattice and very roughly half the energy of a hydrogen bond has to be paid. The entropy of formation is also reasonable since a large part of the translational and rotational entropy of the guest is lost when it is tied at one point.

It is not possible to explain the large negative apparent entropies of activation of argon and nitrogen hydrates by such an interaction between the encaged and host molecules as has been suggested above for the ether and ketone hydrates. The most likely explanation is that argon or nitrogen molecules occasionally substitute for water molecules as "impurities" in the lattice during the formation of the hydrate at about 2 kbar gas pressure. The van der Waals radii (1.90 Å for argon and 2.05 Å for nitrogen)