TABLE II

Effect of the gap corrections for nitrogen hydrate

t (°C)	P/bar	ε_0(exp)	τ(exp)/μs	α	ε_0 (eq. [9])	τ/μs (eq. [8])	$10^3\,\delta$
−3.03	1234	54.3	16.8	0.17	57.3	17.9	1.3
−3.24	1888	48.4	15.6	0.17	57.6	19.2	4.7
−3.26	601	52.2	15.9	0.17	57.0	17.7	2.0
−3.32	1233	47.1	14.5	0.17	57.3	18.3	5.1

$(a/b)x^\beta = \omega^\beta(a/b)\tau^\beta$, that is, the apparent relaxation time is now

[6] $\qquad \tau(\exp) = (a/b)^{1/\beta}\tau.$

To the extent that the observed dispersion loci are Cole–Cole arcs the adequacy of this model may be tested by the consistency of the values of τ derived from experimental relaxation times by use of eq. [6]. For this purpose the proper values of ε_0 and ε_∞ are required. A knowledge of k is not explicitly required for eq. [6], but is necessary for an estimation of the effective gap thickness

[7][2] $\qquad \delta = k\left[\dfrac{\epsilon_0}{\epsilon_0(\exp)} - 1\right](\epsilon_0 - k)^{-1}.$

If δ and ε_∞ are small, and $\varepsilon_0 \gg \varepsilon_\infty$, little error is introduced by putting $a/b = \varepsilon_0(\exp)/\varepsilon_0$, whence

[8] $\qquad \tau = [\varepsilon_0/\varepsilon_0(\exp)]^{1/(1-\alpha)}\tau(\exp).$

Application of the Gap Model to the Data

For application of eq. [8], ε_0 as a function of temperature and pressure is required. For argon and nitrogen hydrates we take

[9] $\quad \varepsilon_0 = (4.0 + 14200/T)(1 + 0.010P),$

where P is the pressure in kbar. This equation fits the experimental values of ε_0 (± 2) at high temperatures, when the gaps are inappreciable, and allows for variations of ε_0 with temperature and pressure similar to those of the other forms of ice (1–3).

Values of ε_0 from [9] and of τ from [8] are included in Table I, along with the estimates of

the relative gap thickness δ from [7]. Values of k were crudely evaluated by extrapolating to lower temperatures the dielectric constants of gaseous argon and nitrogen measured under pressure (18, 19). Values of δ did not exceed 0.015 for nitrogen hydrate and 0.018 for argon hydrate.

The gap correction reduces considerably the variability of the original relaxation time $\tau(\exp)$. The data in Table II for sample 2 of nitrogen hydrate at -3 °C illustrate this. The relaxation times for the two sets of measurements at 1230 bar are brought into close agreement and the τ's now clearly increase with increasing pressure as they do for other ices (2–4). Figure 4 shows the general improvement in consistency which results.

The series-gap treatment does not reduce the scatter of the relaxation times, particularly between different samples, to the level of uncertainty (ca. 1 %) with which τ may be measured in the absence of gaps. Some of the residual scatter suggests overcorrection for the larger gaps. This may arise because the real static dielectric constants are somewhat less than those given by eq. [9] or the gaps are not of uniform thickness. However, certain consistent differences between results for different samples suggest some variation of the relaxation behavior with the conditions of preparation and history of the sample. Thus initial measurements on sample 3 of nitrogen hydrate at a number of temperatures (not shown in Fig. 4) yielded smaller α's and τ's than those previously measured. These anomalies, which do not seem attributable to the presence of ice, disappeared after several days of conditioning.

Discussion

High-Frequency Dielectric Constants

Values of ε_∞ for both argon and nitrogen hydrate (2.85 $\pm$ 0.05 at -30 °C after small gap

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[2]Strictly, δ is the ratio of gap thickness to electrode separation only for parallel plate electrodes. For cylindrical coaxial electrodes of radii u and v, δ in the above equations is replaced by $\Delta r/[r \ln (v/u)]$, where r is the radial position of a small gap of uniform thickness Δr. In the likely event that contraction occurs by shrinkage away from the outer electrode, δ is replaced, for the actual electrodes used, by $0.78\delta'$, where $\delta' = \Delta r/(v-u)$.
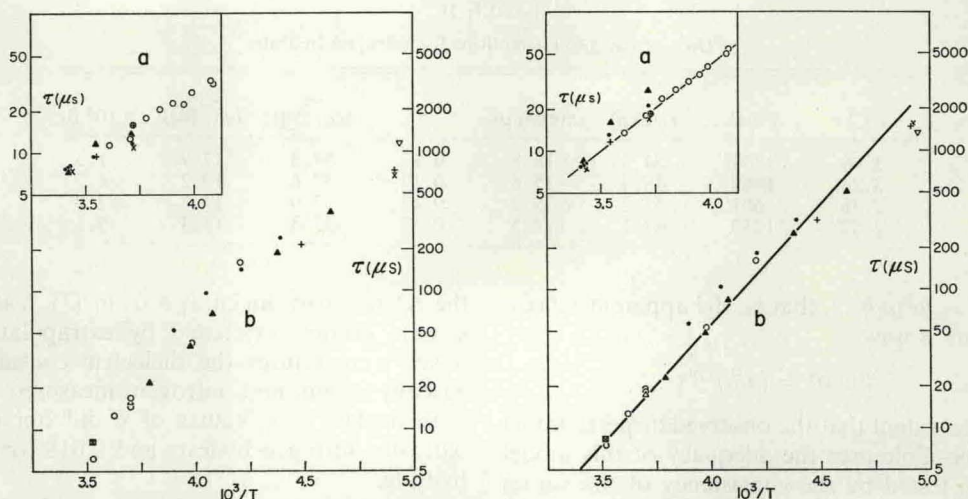
FIG. 4. Experimental (left) and gap-corrected (right) relaxation times at various pressures. (a) Argon hydrate. Sample 1: ⊕, 300; +, 800; ×, 1100; ●, 2000; ▲, 3000 bar. Sample 2: ○, 2000 bar. (b) Nitrogen hydrate. Sample 1: ▲, 600; ●, 1240 bar. Sample 2: △, 620; ▽, 810; ○, 1240 bar. Sample 3: +, 1; ×, 310; □, 1800 bar.

corrections) are similar to that of ice (3.1), in contrast to the much higher values found for the hydrates of dipolar molecules, to which the reorientation of the guest molecules makes a large contribution (6, 9, 10).

For a solution of argon or nitrogen in the structure I hydrate lattice the Onsager equation may be written (20)

$$[10] \quad \frac{(\epsilon_\infty - 1)(2\epsilon_\infty + 1)}{3\epsilon_\infty}$$

$$= \frac{4\pi N_0 \alpha_0}{1 - f_0 \alpha_0} + \frac{4\pi N_1 \alpha_1}{1 - f_1 \alpha_1},$$

where N is the number density of molecules, α is the molecular polarizability, $f\alpha$ allows for the reaction field, and the subscripts 0 and 1 refer respectively to water and argon or nitrogen. The empty lattice contribution cannot be evaluated in terms of the polarizability of the isolated water molecule since lattice vibrations make important contributions. Instead, we take

$$[11] \quad \frac{4\pi N_0 \alpha_0}{1 - f_0 \alpha_0} \simeq \left[\frac{(\epsilon_\infty - 1)(2\epsilon_\infty + 1)}{3\epsilon_\infty N_0} \right]_{\text{ice I}} N_0,$$

in which ϵ_∞ and N_0 in the square brackets refer to ice I. Equation [11] assumes a contribution, per water molecule, of the empty hydrate lattice equal to that of ice and leads to a value of ϵ_∞ of 2.78 for the empty lattice if the unit cell dimension is 12.05 Å. Addition of the contri-

bution of the encaged molecules gives $\epsilon_\infty = 2.90$ for argon hydrate and $\epsilon_\infty = 2.91$ for nitrogen hydrate if all the cages are occupied.

Thus eq. [11] appears to provide a good approximation to the effective polarizability of the water lattice in these hydrates. As in ice, ϵ_∞ is considerably greater than n_D^2 which is ∼ 1.72 for both hydrates and ice. It is probable that the lattice vibrations are similar, especially the translational modes which are associated with the optical density maximum in ice at 229.2 cm^{-1} at 100 °K (21). Even after correction for gaps, values of ϵ_∞ for nitrogen hydrate decrease slightly with decrease of temperature, despite the increase of density. This decrease amounts to 0.08 ± 0.04 between -30 and -94 °C and probably arises from a general shift toward higher frequencies of the lattice modes.

Static Dielectric Constants

Since encaged argon and nitrogen molecules contribute only about 0.1 to the dielectric constants, the static dielectric constants are essentially those of the ice-like lattice. Substitution of $\epsilon_0 = 56$ at 0 °C into the Kirkwood equation in the form

$$[12] \quad \epsilon_0 - \epsilon_\infty = 2\pi N_0 [(n^2 + 2)/3]^2 g\mu^2/kT,$$

with $n^2 = 1.60$ (from the Lorentz–Lorenz equation and $n^2 = 1.72$ for ice) and $\mu = 1.84$ D,