## The Structure of Water and Its Relationship to Hydrocarbon-Water Interactions

Stig R. Erlander[a]

[a] Ambassador College, Pasadena, California

## PLEASE SCROLL DOWN FOR ARTICLE

# The Structure of Water and Its Relationship to Hydrocarbon – Water Interactions

STIG R. ERLANDER

*Ambassador College,*
*Pasadena, California*

## SUMMARY

A comparison of entropy and enthalpy values for the dissolution of a hydrocarbon in water with those for the formation of ice show that in the dissolving process both the formation and melting of ice structures are involved. Instead of 20 or more water molecules per molecule of hydrocarbon as required for clathrate formation, about −1 to 6 water molecules per molecule of hydrocarbon at most are associated with the process. The solubility of hydrocarbons in concentrated salt solutions, partial molal volumes, and nuclear magnetic resonance data support the conclusion that clathrate structures around such relatively inert molecules cannot exist. The solubility of a hydrocarbon depends on the amount of water that is unbonded (does not exist in clusters) since water clusters appear to react more unfavorably with hydrocarbons than unbonded water molecules. The physical properties of water suggest the presence of two types of water clusters: compressible and noncompressible. It is proposed that from about 60 or 65°C to 100°C the hydrogen bonding of water molecules produces exclusively noncompressible water clusters which have either the structure of ice II (rhombohedral crystallites) or tetrahedrally bonded water molecules. From 0 to about 18°C the main process in hydrogen-bond formation is the aggregation of these water clusters to form compressible clusters. Both processes coexist in the transition region of approximately 18-60°C. Hydrogen bonding between different-sized crystallites produces empty pockets that decrease the density of these cluster aggregates. The final aggregation of these aggregates to form ice produces unbonded water molecules as liquid microinclusions in the interstitial areas

of the final aggregate. Ice I at 0°C therefore consists of interlocked water clusters, interdispersed $H_2O$ molecules, and about 20 vol.% of empty pockets. The proposed model for water explains such diverse phenomena as the decreases and increases in solubility of hydrocarbons with an increase in temperature; the formation of insoluble water clathrates around methane under high pressure; the ability of inert molecules to raise the freezing-point temperature of pure water; viscosity-pressure isotherms; specific heat capacities; and the positive and negative values of $\Delta H$ and the decreases and increases in the values of $\Delta S$ for the solubilization of hydrocarbons and inert gases at different temperatures.

## INTRODUCTION

From both biological and industrial aspects, water is the most important liquid and solvent known. Present knowledge and proposed theories concerning the structure of water have been reviewed extensively by Kavanau [1]. Although the literature is voluminous, no definite model exists that correctly explains the properties of water.

The most famous theory concerning the structure of water is the "iceberg" theory of Frank et al. [2-4], which has been expanded by Némethy and Scheraga [5, 6] and by others. Their iceberg or "flickering cluster" theory has two main facets: (1) the structure of pure water and (2) the structure of water surrounding inert molecules, such as those of hydrocarbons or inert gases. Concerning the first facet, Némethy and Scheraga have formulated a detailed statistical model for pure water. They calculated that at 20°C the average cluster of water molecules or iceberg contains about 57 molecules. Moreover, 70% of all water molecules is in clusters, and about 23% (about 33% of those in clusters) at 20°C is quadruply bonded inside these flickering clusters.

Recently Wicke [7] has shown that the above models and other models [8-10] do not correctly explain some of the observed properties of water and consequently must be wrong. To explain these properties, Wicke [7] proposed that a third state of water exists. According to his model, tetrahedrally bonded flickering clusters, as proposed by Frank and Wen [3] and Némethy and Scheraga [5, 6] and others [7], exists together with unbonded water. However, in addition, the existence of more dense aggregates at first increases with temperature and finally decreases.

Although his model answers certain questions, the model proposed by Wicke [7] does not coordinate the properties of water. For example, the shallow minimum in heat capacity of water at 30-40°C is stated by Wicke [7] to be due to the overlap of the thermal breakdown of both the large clusters and the small dense aggregates. Yet

he proposes that the large clusters are the main cause of the density anomalies, compressibility, and viscosity of water. However, this minimum in heat capacity as observed by Ginnings and Furukawa [11] coincides with the elimination of the pressure dependence of the viscosity of water at about 34°C, as observed by Bett and Cappi [12]. Furthermore, even though Wicke [7] states that the minimum in viscosity is due to the flickering clusters, he does not give any model as to how this is accomplished. In apparent contradiction to Wicke's statements, Némethy and Scheraga [5], state that a weakness of the flickering cluster model is that it cannot explain the transitional changes in viscosity, refractive index, surface tension, and thermal expansion that occur in the neighborhood of 30 and 40°C. This inability is, of course, characteristic for the particular mathematical model chosen by Némethy and Scheraga. However, no matter how exact the mathematical expression, it would seem impossible to correlate the large clusters with such data as the minimum in density at 4°C, the minimum in viscosity at 34°C, and the existence of these clusters at 60°C or higher temperatures. Consequently, Wicke's [7] proposed model cannot explain these phenomena, and therefore it also is in error.

A model will now be proposed that retains some of the features of previous models but, in addition can explain the above and associated phenomena. In essence, the proposed model states that single or individual clusters exist at 60 to 100°C. They may be formed either from tetrahedrally hydrogen-bonded water molecules or from ice-II type structures. These clusters are relatively stable and begin to aggregate below about 60°C to form less dense structures which contain empty pockets between the unequally sized aggregates. As the aggregation process continues, the density of the cluster aggregates decreases until it is much less than that of unbonded water. It will be shown that this model can readily explain the properties of water.

This paper therefore considers two problems concerning liquid water: (1) What is the structure of pure water, and (2) do clathrate water structures form around non-polar molecules such as hydrocarbons? The latter question will be considered first.

## ENTROPY AND ENTHALPY DATA CONTRADICT PROPOSED CLATHRATE STRUCTURES

The cluster model has been applied to the structure of water surrounding inert molecules [1, 3-6, 13], i.e., molecules with low electrostatic fields, such as hydrocarbons. The basis for such models is the structure of crystal hydrates. That is, X-ray patterns show that under proper conditions water molecules can form hydrates around such gas molecules as xenon or methane [1, 9, 13]. These permanent water clathrates form polyhedron structures, con-

taining almost spherical cavities having inside radii of 3.95 and
4.3 Å. As pointed out by Némethy [6], the formation of a complete
cage is only possible for very small molecules such as those men-
tioned above and is impossible for molecules larger than butane,
tetraalkyl ammonium, or trialkyl sulfonium salts, since larger mole-
cules than these do not fit into the cage structure. Therefore partial
cages have been proposed to circumvent this problem. Such clath-
rate or partial clathrate structures must consist of at least 20 or
more hydrogen-bonded water molecules [1, 13, 14]. Also according
to the light-scattering studies of Mysels [15], empty clathrates do
not exist. Moreover, assuming the existence of clathrate structures,
Némethy and Scheraga [5] have concluded that the possible net de-
crease in the number of water molecules in such clathrate struc-
tures is the driving force for the formation of the hydrophobic bond.

The validity of the presence of clathrates in water will now be
examined with respect to thermodynamic data. Listed in Table 1
are observed changes in entropy and enthalpy for the solubilization
of various hydrocarbons and inert gases. The approximate number
of water molecules involved in any water clathrate is obtained by
dividing the observed values of $\Delta S$ and $\Delta H$ by those values for the
formation of ice. That is, the energy for the formation of the gas
hydrates per mole of water is essentially the same as that for the
freezing of water [1]. The values of $\Delta H/\Delta H_1$ and $\Delta S/\Delta S_1$ in Table 1
contradict the clathrate theory in a number of ways: (a) the values
are much too small; (b) both negative and positive values are ob-
tained; (c) methane, ethane, propane, and n-butane have similar values
even though these molecules differ grossly in size, and yet all have
smaller values than those listed for radon even though radon is
about the same size as methane; (d) values for $\Delta H/\Delta H_1$ decrease in-
stead of increase as the size of the hydrocarbon increases (1.9 for
methane and 0.7 for butane); (e) the values of $\Delta S/\Delta S_1$ range from
less than two to as much as six times greater than the values of
$\Delta H/\Delta H_1$; (f) the values of $\Delta S/\Delta S_1$ and $\Delta H/\Delta H_1$ for radon dras-
tically decrease with an increase in temperature even though the
postulated clathrate structure should have the same number of hy-
drogen-bonded water molecules no matter what the temperature;
and (g) these values for helium decrease at a much lower rate with
an increase in temperature as compared to those for radon. These
statements can be explained by employing changes in the structure
of water (see below) but cannot be explained on the basis of the for-
mation of water clathrates. Consequently, the thermodynamic data
contradict the clathrate theory.

If the clathrate structure were made spontaneously from either
existing clathrates or from water molecules as in the case of water
clusters, then the $\Delta H$ values for their formation would be negligible.
Such values would agree with the magnitude of $\Delta H$ values given in
Table 1 [point (a) above]. However, then $\Delta S$ values for the formation

of the hydrophobic bond would also be zero or opposite to that proposed by Némethy and Scheraga since the clathrate structures for <u>both</u> the aggregated and the nonaggregated species would be formed spontaneously and the structure of the clathrate could not play any role in the entropy changes. Thus in addition to the other points listed above [(b) to (g)], the formation of the hydrophobic bond argues against such spontaneously formed clathrates. Moreover, from a mechanistic viewpoint the clathrate could not be formed from exis<u>ting</u> clathrate structures because (1) empty clathrates cannot exist [15] and (2) it would be impossible to displace the water molecules

**Table 1.** Enthalpy and Entropy Values for the Solubilization of Inert Molecules in Water and the Calculated Number of Water Molecules in Any Possible Surrounding Clathrate[a]

| Solute | Temp., °C | $\Delta S$, eu. | $\Delta S/\Delta S_1$ | $\Delta H$, cal/mole | $\Delta H/\Delta H_1$ |
|---|---|---|---|---|---|
| Benzene | 18 | −14 | 2.6 | 0 | 0 |
| Benzene | 25 | −10.3 | 1.9 | 1574 | −1.1 |
| Benzene | 60 | −9.7 | 1.8 | | |
| Methane | 25 | −18 | 3.4 | −2800 | 1.9 |
| Ethane | 25 | −20 | 3.8 | −2200 | 1.5 |
| Propane | 25 | −23 | 4.3 | −1800 | 1.2 |
| n-Butane | 25 | −23 | 4.3 | −1000 | 0.7 |
| Helium | 0 | −19.0 | 3.6 | −980 | 0.7 |
| Helium | 20 | −18.6 | 3.5 | −897 | 0.6 |
| Helium | 50 | −18.1 | 3.4 | −710 | 0.5 |
| Helium | 80 | −17.6 | 3.3 | −550 | 0.4 |
| Radon | 0 | −33.9 | 6.4 | −7070 | 4.9 |
| Radon | 20 | −27.7 | 5.2 | −5500 | 3.8 |
| Radon | 50 | −20.2 | 3.8 | −3100 | 2.2 |
| Radon | 80 | −13.2 | 2.5 | −720 | 0.5 |
| Ice | — | −5.3 | 1.0 | −1440 | 1.0 |

[a]Data obtained from Kauzmann [16], Erlander and McGuire [17], and Eley [18]. The number of water molecules in any possible surrounding clathrate structure ($\Delta H/\Delta H_1$ and $\Delta S/\Delta S_1$) is calculated by dividing the $\Delta S$ and $\Delta H$ values by those corresponding values for the formation of ice ($\Delta S_1$ and $\Delta H_1$).

in a filled clathrate even if a stable clathrate with a hole in it could be formed. The mechanism for the displacement of water molecules would have to be similar to the forcing of a broom stick into a milk bottle filled with marbles. Even though the stick is slightly smaller than the opening of the bottle, the space between the stick and the opening is too small to let the marbles out. Similarly, water molecules in a clathrate could not be forced out by a hydrocarbon chain, nor can they be spontaneously expelled. Hence, the task is impossible. Consequently, from the observed entropy and enthalpy data and from the mechanistic viewpoint, it is concluded that unbonded (free) water molecules rather than clathrate structures surround molecules such as hydrocarbons. Moreover, as will be shown below, organized water molecules such as those in any possible clathrate structure actually repel or "salt-out" hydrocarbons.

## OTHER PHENOMENA CONTRADICT CLATHRATE THEORY

As the temperature is increased from 0 to 18°C, the solubility of benzene and other hydrocarbons decreases as shown in Fig. 1. In light of the clathrate theory, these results indicate that as the temperature is increased, the clathrates are destroyed. Such reasoning is consistent with the fact that the ability of the water molecules to form hydrogen bonds decreases with an increase in temperature. In other words, the solubilities of the hydrocarbons decrease because there is a decrease in the ability of the water molecules to form clathrates.

This conclusion sounds reasonable until the solubilities of these hydrocarbons and others are examined at higher temperatures. At 18°C and higher, the solubility of benzene increases with an increase in temperature. Moreover, the data given in Fig. 1 for methane and ethane indicate that the aliphatic hydrocarbons approach a minimum in solubility at approximately 50 or 60°C. That is, the experimental points for ethane, and particularly methane, begin to level off at 40-50°C. Only two points are given for propane and butane, and therefore no such conclusions can be made for these molecules. However, other hydrophobic-type molecules also exhibit the minimum in solubility shown by benzene in water. Such compounds as 3-methyl pyridine [20] and polyethylene oxide [21] (molecular weight 3000) go through minimum solubilities in water as the temperature is increased. If the clathrate theory is correct, then these results suggest that the stability of the clathrate first decreases and then increases as the temperature is increased. However, hydrogen bonds between water molecules should continue to decrease in stability as the temperature is increased. Consequently, these minimums cannot be explained by
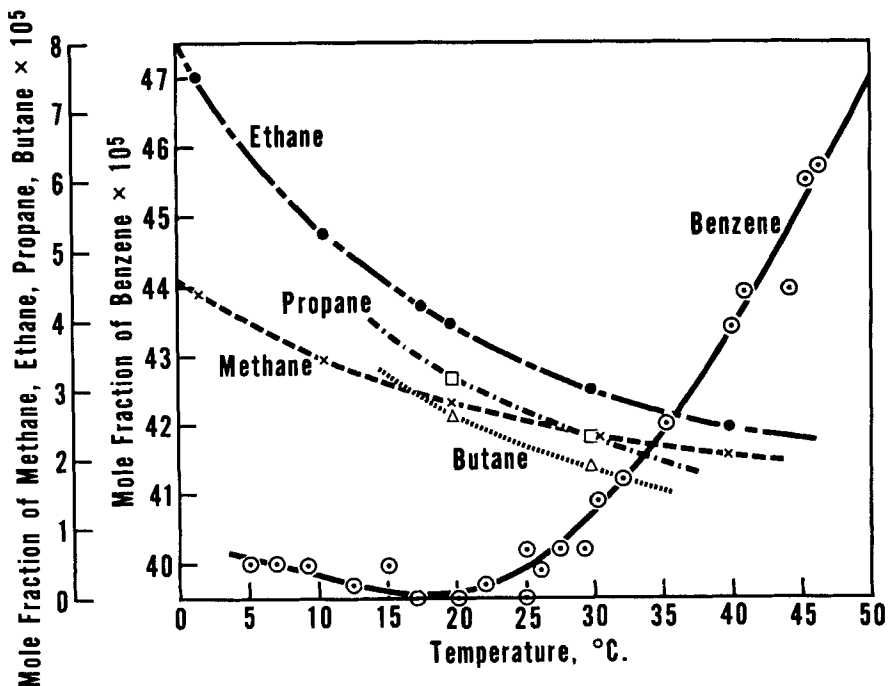
Fig. 1. Solubility of methane, ethane, propane, n-butane, and benzene in water versus temperature. The solubility of benzene is at a minimum at 18°C, whereas that of the aliphatic hydrocarbons is at approximately 40-50°C. (Data on benzene from Franks et al.[19] and data on aliphatic hydrocarbons from Claussen and Polglase [14]).

the clathrate theory. Rather, they must be due to changes in the structure of water.

Concentrated salt solutions should destroy clathrate structures because of the strong interactions between the ions and the water molecules. If the solubility of a hydrocarbon in water depends on the existence of clathrate structures, then all salts should salt-out hydrocarbons. However, results show that some salt solutions salt-in hydrocarbons. In particular, we [17] observed that in 6 M guanidinium thiocyanate the solubility of benzene is approximately six times its value in water, whereas in 6 M lithium chloride the solubility of benzene is approximately one-sixth that in water. In these concentrated salt solutions all the water should be involved as hydrated water (either in the A or B regions), as shown in previous calculations [22], and consequently clathrate structures cannot exist. If the solubility of the hydrocarbon depends upon entropy effects

of a water clathrate, then the solubility of benzene should be the same in both salt solutions, since a clathrate structure of water could not surround the benzene in either salt solution. The unequal solubility effects observed experimentally therefore support the proposal that clathrate structures do not exist.

Masterton [23] concluded from data for a plot of the partial molal volume of benzene as a function of temperature that no water clathrate structures or cages surround the benzene molecule in water. This idea is in contrast with his conclusion concerning less compact hydrocarbons, such as methane and ethane [23]. If a clathrate structure is to surround one hydrocarbon, it should also surround others. Consequently, Masterton's data are also inconsistent with the water-clathrate theory.

The experimental findings observed and pointed out by Wicke [7] also indicate the absence rather than the presence of clathrate structures. He compared the static dielectric constants of various aqueous inorganic salt solutions with those for aliphatic compounds or salts. According to Wicke [7] the data show that for such hydrocarbons there is "... no evidence of effects that increase the dielectric constant, such as formation or stabilization of frameworks with tetrahedral H-bonds (e.g., clusters)." Wicke [7] proposed the presence of a new type of clathrate water structure. However, the polar or ionic groups of the hydrocarbon will become hydrated. Consequently, this hydration can explain the results rather than any new type of water structure.

Wicke [7] points out that the chemical shifts in nuclear magnetic resonance (NMR) studies of Hertz and Zeidler [24] is always positive for various tetraalkyl ammonium ions and polar hydrocarbons. According to Wicke [7], this indicates that the intensified structure of water around such ions or polar molecules does not involve ice-like structures. Rather, the protons of the adjacent $H_2O$ groups must be involved in stronger electrostatic screening. Again, rather than invoke a new type of clathrate structure as done by Wicke, the results can be explained on the basis of the interaction of the surrounding water molecules with the electrostatic charge of the ionic or polar group.

To explain the observation that $(C_2H_5)_4N^+$ ion has the same orientation time as the $NH_4^+$ ion, Wicke [7] proposes that the $(C_2H_5)_4N^+$ ion has complete freedom to rotate inside its clathrate structure. In other words, instead of a clathrate structure surrounding each aliphatic chain, the clathrate structure must surround the entire ion. But such a model contradicts experimental observations [6]; that is, the clathrate structure in the gas hydrate surrounds each chain and thus allows no freedom for rotation. Consequently, if a clathrate structure surrounded the $(C_2H_5)_4N^+$ ion, then the increase in volume of the $(C_2H_5)_4N^+$ ion would be enormous and the hydrated $NH_4^+$ ion would have a much greater orientation time.

A more plausible explanation of the result is to consider that the $NH_4^+$ ion is hydrated and the $(C_2H_5)_4N^+$ ion is not. Such a conclusion agrees with the hydration studies of Nightengale [25]. The negatively hydrated water (B region) of the $NH_4^+$ ion could very well have the same effective volume as the four $CH_3CH_2-$ groups on the tetraethyl ammonium ion. Consequently, the same reorientation time for both the more bulky $(C_2H_5)_4N^+$ ion and the smaller $NH_4^+$ ion is obtained because the $NH_4^+$ ion is hydrated, whereas the $(C_2H_5)_4N^+$ ion is not. That is, the difference in hydration counteracts the difference in size and thus produces the equal orientation periods. Again, the results are explanable when the clathrate theory is discarded.

The extrapolated partial molar heat capacities (C) of a number of organic salts show "surprisingly large" shifts in the series $HCO_2-$, $CH_3CO_2-$, and $C_2H_5CO_2-$ as well as the series $(CH_3)NH_3^+$ and $(C_2H_5)NH_3^+$. As noted by Wicke [7], the positive values of C are due chiefly to contributions of the vibrations and internal rotations in the organic ions. Wicke considers that the large increment cf 15 to 20 cal/mole/deg resulting from the introduction of one $CH_2$ group must be due to the formation of a larger clathrate structure ("hydration of the second kind"). But Wicke [7] has failed to recognize that the addition of a $CH_2$ group also changes the pK and consequently the degree of hydration of the ionic group. For example, the $HCO_2^-$ ion is positively hydrated (A-regions) and has a pK of 3.75, whereas the $CH_3CO_2^-$ ion is negatively hydrated and has a pK of 4.75. This change in charge density with a consequent change in the degree of hydration is therefore quite large and is the same as that encountered in going from the fluoride to the chloride ion [26]. The results concerning the partial molar heat capacities can therefore be explained on the basis of a change in the affinity of the ionic group for water molecules, i.e., a change in the charge per unit surface area of the ion. The greater the degree of hydration of the ionic group, the smaller will be the contributions of the vibrations and internal rotations of the organic ion. Consequently, the shift in C can be explained on the basis of ion-water interactions rather than the formation of clathrate structures.

Other data obtained from NMR studies [24] can be explained on the basis of a change in the number of water clusters with a change in temperature or the ability of a polar group to hydrate $D_2O$ or $H_2O$.

Within experimental error, Gordon et al. [27] cannot measurably detect from NMR studies the presence of any bound water on deoxyribonucleic acid (DNA), suggesting that such clathrates are absent. Furthermore, the small amount of water that may be present does not change during denaturation or unfolding of DNA, again suggesting the absence of any clathrate water structures. The small amount of water hydrated to DNA can readily be accounted for by the hydration

of ionic and polar groups on the DNA. Moreover, in view of my previous calculations [26], action of perchlorate ions reported by Gordon et al. [27] is to be expected. That is, unlike $Na^+$ and $Cl^-$ ions, the $ClO_4^-$ ion has an effective dielectric constant greater than that of water [26]. Hence, $ClO_4^-$ ions can destroy hydrogen bonds in both water clusters and in DNA molecules, just as an increase in temperature destroys these bonds. Moreover, as discussed above, if clathrates were attached to DNA, then they would be destroyed by the 5. 2 M $NaClO_4$. No such change or destruction is detectable [27]. Consequently, these NMR results are further proof that clathrate water structures do not exist in aqueous solutions.

Thus the thermodynamic, solubility, and NMR evidence cited above clearly shows that in aqueous solutions hydrocarbons or other relatively inert compounds, such as some noble gases, do not exist in cage structures or water-clathrates. It will be shown below that the entropy and enthalpy values obtained in the dissolving of inert molecules and other related data can readily be explained by using the proposed model for the structure of water.

## SOME PROPERTIES OF WATER AS A SOLVENT AND AS A PURE LIQUID

Perhaps the most significant experimental study with regard to the structure of water clusters below 20°C was recently done by Horne and Johnson [28]. They measured the viscosity of pure water as a function of pressure for various specific temperatures from 2. 2 to 20. 4°C. From their results they concluded [28]: "The structured regions in liquid water are less dense than the 'free' water; thus cluster breakup results in a volume decrease and is therefore enhanced by the application of pressure."

The disappearance of expanded ice-like structures, as implied by the viscosity-pressure isotherm studies, can also be seen by examining the changes in volume of water with temperature. In Fig. 2, the relative volume of water (V) and also the change in this volume of water with temperature (dV/dt) are plotted against temperature. From approximately 55 to 100°C, the linear dV/dt line signifies that a mechanism different from that for lower temperatures governs the change in volume of water. At lower temperatures, the value of dV/dt decreases nonlinearly. Thus as in the viscosity-pressure isotherms, the dV/dt versus temperature curve signifies the formation of expanded ice-like structures at low temperatures. Hence, just as in the viscosity-pressure isotherm studies of Horne and Johnson [28], the continuous dV/dt versus temperature curve shows that the maximum in density (or minimum in volume) of water at 4°C is not due to some erratic change in structure but rather is a
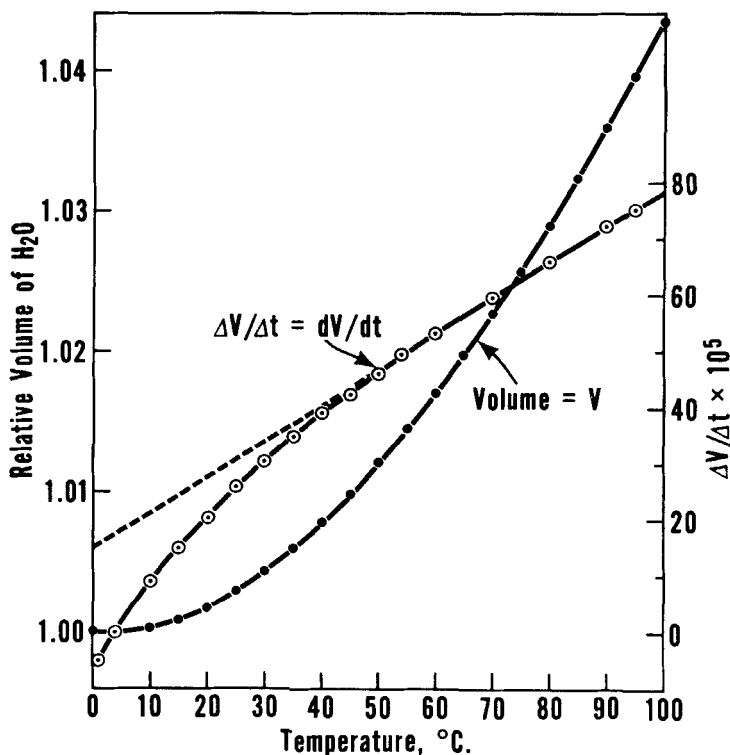
**Fig. 2.** Volume of water (V) and the change in this volume with temperature (dV/dt) are plotted versus temperature. The linear dV/dt versus t plot at 55-100°C is the result of the formation or destruction of clusters and a change in the thermal motion of water molecules and its aggregates. The nonlinearity for lower temperatures is due to the aggregation of clusters accompanied by the formation of empty spaces at their junctures. The empty space amounts to about 10% of the volume of the aggregate at or near 0°C (see the text). (Data from *Handbook of Chemistry and Physics* [29].)

result of a continuous change which commences at a higher temperature.

It should be noted that the value of dV/dt in Fig. 2 does not abruptly change at any given temperature but does begin to taper off between 15 and 20°C. That is, the second derivative (or $d^2V/dt^2$) has a maximum at around this temperature. The more precise and thorough investigations of Horne and Johnson [28] also show that this mimimum becomes less prominent around 20°C. This is slightly earlier than suggested by the results of Bett and Cappi [12]. However, their [29] results at 15.1°C are essentially the same as those

by Bett and Cappi at 20°C. Moreover, Feates and Ives [30] con-
cluded that even at temperatures higher than 30 or 40°C there are
still signs of a corresponding curvature, showing that a remnant
of a viscosity reducing pressure effect remains. They [28] also
stated that "it may be safely concluded that at some slightly higher
temperatures the structure-breaking effect of pressure vanishes."
Consequently, the dV/dt and viscosity-pressure isotherms illus-
trate that the expanded water clusters begin to gradually disappear
as the temperature is raised from 15 or 20°C to about 50 or 60°C.

Another peculiar property of water which is not seen in other
liquids or in solids is the minimum in its heat capacity at about 35°C.
Thus the specific heat or heat capacity of water first decreases with
an increase in temperature until 35°C is reached and then continual-
ly increases as in the case of ice and other solids and liquids. This
increase in specific heat at higher temperatures for water or for
other materials at any temperature must be due to the increase in
the distance between the molecules (expansion of the material).
Thus, because at higher temperatures the molecules are on the aver-
age separated from each other by greater amounts of empty space,
it takes more heat per gram to increase the temperature of the par-
ticular material. In other words, there is a decrease in the ability
of the molecules to exchange heat (photons) because of an increase
in the space between them. Why then does a decrease in the specific
heat of water occur during a period when the water is expanding?
It certainly cannot be due to the destruction of clusters because clus-
ters are continually being destroyed up to 100°C. Hence, the data at
temperatures above 35°C show that the destruction of clusters to
form unbonded water (an increase in the distance between the mole-
cules) produces an increase and not a decrease in the specific heat.
The minimum at 35°C must therefore be due to two opposing specific heat
factors: destruction of clusters and destruction of cluster aggregates.
In other words, the destruction of cluster aggregates decreases the
average distance between water molecules by destroying the empty
pockets in the cluster aggregates, whereas the destruction of clus-
ters increases the average distance between molecules. The mini-
mum in specific heat thus occurs when the effects due to the des-
truction of clusters and the increase in the thermal motion of the
unbonded and bonded water molecules overcome the effect due to the
destruction of the empty pockets of the cluster aggregates.

As noted in the Introduction, other various phenomena occur in
the properties of water in the temperature range of about 20-40°C.
In addition to the minimum in the heat capacity of water, Salama
and Goring [31, 32] observed a transition in the structure of water
using infrared absorption at 2100 and 1900 $cm^{-1}$ from 5 to 75°C.
The difference in transmission between the maximum at 2100 $cm^{-1}$
and the minimum at 1900 $cm^{-1}$ was designated as $\Delta Tm$. This $\Delta Tm$
was plotted versus temperature (t). Although they [31, 32] con-

cluded from their plot that the transition occurs from 30 to 40°C, a close examination of their $\Delta Tm$ versus temperature figure shows that the transition occurs from about 20 to 45°C. The same is true for linear lines obtained on their [26] $d(\Delta Tm)/dt$ versus t curves. Consequently, the transition is quite broad, just as the minimum in heat capacity is not sharp. These transitions are therefore in agreement with those for the Fig. 2 plot of $dV/dt$ and for the viscosity-pressure isotherms.

By comparing the solubilities of the aliphatic hydrocarbons of Fig. 1 with observed values of partial molal volumes for the corresponding alcohols, it can be shown that the solubility of a hydrocarbon increases or decreases according to whether the space or domain it occupies in the water increases or decreases. Friedman and Scheraga [33] and Masterton [23] have examined the partial molal volumes $(\overline{V}_i)$ of hydrocarbons in water. By subtracting the volume of 1 mole of a pure hydrocarbon. $V_i{}^0$ from its effective volume in water $\overline{V}_i$, Friedman and Scheraga [33] obtained the difference between the space occupied by a hydrocarbon molecule in water as compared to its space in the pure hydrocarbon $(\overline{V}_i - V_i{}^0 = \Delta \overline{V}_i)$ for various temperatures. Since all these values for the temperature range that they covered were negative, a hydrocarbon molecule occupies less space (a smaller domain) in liquid water than it does in its own or another hydrocarbon liquid.

Examination of a change in this difference with a change in temperature $[d(\Delta \overline{V})/dt]$ is given in Table 2. The values of $d(\Delta \overline{V})/dt$ follow the same pattern as the corresponding solubilities given in Fig. 1. That is, values of $d(\Delta \overline{V})/dt$ are negative for a corresponding decrease in solubility (the aliphatic alcohols) and positive for a corresponding increase in solubility (benzyl alcohol). It should be noted that the minimum in solubility for benzene occurs between 0 and 20°C. (see Fig. 1). Hence the value of $d(\Delta \overline{V})/dt$ for benzyl alcohol in this temperature range is meaningless.

As the decreases in solubility of the hydrocarbons in Fig. 1 begin to taper off, the negative values of $d(\Delta \overline{V})/dt$ for the alcohols tend to become smaller at higher temperatures. The negative or positive values for $d(\Delta \overline{V})/dt$ mean that the space or domain occupied by an alcohol molecule is either decreasing or increasing with an increase in temperature. Consequently, the production of more positive values of $d(\Delta \overline{V})/dt$ at the higher temperatures indicates an increase in the space occupied by the alcohol molecule.

Now the domain per carbom atom required for the benzene molecule in the water will not be so great as that of a corresponding aliphatic molecule, because the translational and rotational motion of the benzene molecule is less. This property is shown in its density. For example, benzyl alcohol has a density which is 1.28 and 1.32 times as great as that of hexanol and methanol at 20°C. Also, benzene has a density of 1.33 times that of hexane [29]. Because

**Table 2.** Change in $\Delta V$ with a Change in Temperature $[d(\Delta V)/dt]$ for Various Alcohols[a]

| Temp. range, °C | $10^3(\Delta V_2 - \Delta V_1)/(t_2 - t_1)$ | | | | | $10^3 d(\Delta V)/dt$ | | | |
|---|---|---|---|---|---|---|---|---|---|
| | MeOH | EtOH | n-PrOH | i-PrOH | n-BuOH | i-BuOH | n-BuOH | n-PeOH | Benz. OH |
| 1-20 | −43 | −43 | −55 | −53 | −64 | −56 | −46 | −53 | 2 |
| 20-40 | −43 | −44 | −50 | −45 | −53 | −39 | −39 | −53 | 53 |
| 40-50 | −31 | −36 | −38 | −34 | −50 | −30 | −35 | −46 | 95 |

[a]Data obtained from Table IV of Friedman and Scheraga [33], where $\Delta \overline{V}_i = \overline{V}_i - V_i^0$ at temperature $t_i$. Here $\overline{V}_i$ = partial molal volume of the alcohol and $V_i^0$ = molecular weight divided by density of the pure alcohol $(M_i/\rho_i)$.

the aliphatic compounds require a larger domain than the benzyl alcohol and benzene, their molecules occupy more space per carbon atom in the water. Moreover, the solubility of benzene is about 10 times greater than that of the aliphatic compounds (see Fig. 1). The correlation of domain and solubility therefore again shows, as in the correlation of Fig. 1 and Table 2, that the solubility of an aliphatic compound depends on its required space or domain which in turn is determined by its translational and rotational motion.

But solubility studies (Fig. 1) show that the space or domain allotted for a hydrocarbon changes irregularly. This irregularity is particularly evident for benzene molecules, since the solubility of benzene decreases slightly in going from 0 to 18°C and then commences to increase as the temperature is further raised. The same, of course, is true for the 3-methyl pyridine [17] and the polyethylene oxide [18] cited earlier. Based on the above correlation of solubility and space occupied, it is concluded that above 18°C a structural change is occurring in water which enables the formation of more available space for the relatively inert hydrocarbons. This change in structure occurs in exactly the same temperature range as that related above for various phenomena. It will be shown below that this reduction in available space, i.e., the suggested minimum in $d(\Delta V)/dt$ of Table 2, is due to the salting-out of the hydrocarbon by the water clusters.

In summary, the properties of water show that the unusual changes in the solubilities of hydrocarbons are governed by the space available in the water. This available space must change because of a change in the structure of water. Other properties of water show that this change is accompanied by the loss of expanded ice-like structures with an increase in temperature. However, these less dense water clusters disappear when the temperature is raised above 50 or 60°C. Yet phenomena such as the value of the dielectric constant show that water clusters should still exist at the higher temperatures. Therefore, two forms of clusters must exist in pure water.

## SOME PROPERTIES OF ICE AS A SOLVENT OR AS A HETEROGENEOUS SOLID

Until recently, it was thought by many scientists that ice (ice I) was a continuous tetrahedrally hydrogen bonded structure which contained defective bonds or "Bjerrum faults." However, recent evidence [34-36] has shown that such a model is not true. Thus ice I just as water is a heterogeneous mixture.

Recently, Grant and Alburn [34] produced some very interesting chemical reactions in ice. Previous work cited by them illustrated that several chemical reactions occur faster in ice than in

liquid water. Their investigations of this phenomenon led them to conclude that (1) "liquid microinclusions" exist in the ice structure, and (2) the reactant molecules become entrapped or enclosed in "clathrate-like" structures. It is apparent that the "liquid micro-inclusions" can be the "clathrate-like" structures. That is, the ice I exists as a mixture of crystalline material plus interdispersed non-crystalline water molecules which can be designated as the above-mentioned "liquid microinclusions." The existence of such non-crystalline regions in impure ice suggests that these regions—or similar smaller regions—can exist in pure ice.

But if such noncrystalline interstitial areas exist, then water molecules should be able to migrate or diffuse in such areas. That such a phenomenon occurs has been shown by Onsager and Runnels [35]. Kuhn and Thürkauf [36] showed that the diffusion coefficients of deuterium and oxygen-18 in ice are equal. From these results Onsager and Runnels [35] illustrated that water molecules in ice I are capable of diffusion and that this diffusion must occur by migra-tion of interstitial or noncrystalline molecules. They estimated that the mean-square displacement per trip for such a water molecule is about $8d^2$, where d is the oxygen-oxygen distance of 2.76 Å.

As noted by Kavanau [1, p. 4], to account for the high dielectric constant of ice I at low and intermediate frequencies, it has been assumed that the orientation of water molecules in the ice I crystal structure is changing constantly ($8.3 \times 10^5$ turns/sec at 0°C). But such rapid changes with all the water molecules would appear to de-stabilize or disrupt the hydrogen bonds. This apparent discrepancy may be explained by the proposal [1, p. 7] that such shifts occur be-tween proton positions along the hydrogen bonds without the occur-rence of free molecular rotation. Alternatively, the high dielectric constant of ice I may be due to the structure proposed above. That is, it may be due to the fast orientation of the molecules in the non-crystalline regions.

Thus it can be concluded that the heterogeneous mixture of water plus water clusters also exists in ice I. That is, ice I must consist of a continuous crystalline network of aggregated clusters attached to each other by hydrogen bonds with interdispersed unbonded water molecules which can be designated as liquid microinclusions.

## PROPOSED STRUCTURE OF LIQUID WATER

From the above properties of water it was shown that cluster aggregates of water molecules which are less dense than the sur-rounding water molecules exist from 0 to about 50 or 60°C. At ap-proximately 15 to 20°C the presence of these cluster aggregates be-gins to decrease dramatically. Moreover, the structure of ice I appears to be an aggregation of these less dense clusters plus inter-

stitial water molecules which exist in liquid microinclusions. The aggregation of these clusters appears to be an unfavorable inter-action, since such an aggregation causes the volume of the water to expand when water is frozen. This unfavorable interaction can there-fore account for the formation of the liquid microinclusions on ice I. In addition, the aggregation reaction involves a definite phase transition because there must be present a minimum amount of water to maintain the aggregates in a liquid state. Thus just as in the formation of solid polymers the transition from the liquid to the solid state is not a gradual change but rather must be abrupt once the amount of free water (monomer) is reduced below a minimum. Supercooled water can exist when the water molecules between the cluster aggregates are not orientated properly and when impurities which could initiate the aggregation of cluster aggregates are ab-sent. It is known that supercooled water is changed rapidly to ice by means of sound vibrations. The energy from these vibrations could reorientate a few of the water molecules between crystal faces and thus start the chain reaction of crystallization.

Based on the evidence presented, the proposed model for water is as follows. In the temperature range from approximately 60 to 100°C, water molecules are in equilibrium with clusters. Moreover, water clusters are most likely quite stable and the short observed dielectric relaxation time of water [1, p. 11] is most likely due to a more unstable cluster aggregate. These stable clusters are crystal-line structures and hence involve hydrogen bonding between all water molecules in a specific cluster. This hydrogen bonding con-trasts with the Pauling model [9, 10] of a clathrate-water structure surrounding non-hydrogen-bonded water molecules. The densities of these clusters may be greater than that of water (may have the struc-ture of ice II). However, it must be emphasized that the structure of the clusters is not critical. That is, to explain the properties of water they may be constructed either from tetrahedrally hydrogen-bonded water molecules or from ice-II-type crystalline structures. At this time it cannot be said definitely which structure exists. The size of the average cluster as well as their population no doubt decreases as the temperature increases.

At temperatures below approximately 60°C, it is proposed that another phenomenon takes place in addition to the formation of water clusters. This phenomenon is the aggregation of these water clusters. Aggregation of water clusters occurs below 60°C because of the scarcity of unbonded water molecules and because of the in-creasing abundance of water clusters. In other words, the constant collisions of the highly concentrated water clusters and the lack of sufficiently large areas of unbonded water molecules for the forma-tion of new water clusters produces a situation where the aggrega-tion process can occur more rapidly than the formation of new water clusters. Between approximately 18 and 60°C, there is a transition

region where both mechanisms (the formation of clusters from water molecules and the aggregation of these clusters) occur simultaneously.

As pointed out by Frank [37] (see also review by Kavanau [1, p. 12], it would be a rare event for the faces of two clusters to match exactly. Hence aggregation of the heterogeneous clusters can only be accomplished with the simultaneous formation of empty space near the junctures of the aggregating clusters. The formation of these empty interstices decreases the density of the aggregating clusters. This phenomenon continues until all the clusters are aggregated together at 0°C to form ice. Consequently, the reason why ice floats on water is because of the inability of the clusters to have matching faces. The concave upward curvature of the plot of volume versus temperature in Fig. 4 is therefore due to the decrease in the density of the cluster aggregates. In going from 4 to 0°C this decrease in density is quite pronounced, as shown by Horne and Johnson [28], and hence it has a greater effect on the total volume of the water than the increase in density due to less thermal motion of the water molecules. This mechanism therefore explains the maximum density occurring at 4°C. Furthermore, the aggregated clusters will no doubt be of different sizes and shapes. Consequently, the final aggregation (formation of ice I) of such diverse clusters can readily account for the formation of the liquid microinclusions.

Let us now consider the structure of the individual water clusters. The viscosity-pressure isotherms show that empty pockets or holes almost completely vanish in the clusters near 30-40°C and presumably are completely absent at some higher temperature. The reduction in viscosity of water upon application of pressure at low temperatures is thus due to the decrease in the number of cluster aggregates, i.e., elimination of empty pockets. These and other data presented above suggest that the cluster—in contrast with its aggregate form—is completely crystalline and hence is most likely denser than the unbonded water molecules. That is, application of pressure has no effect on its stability. It has been stated (see Wells [38, p. 426]) that if distilled water is frozen at temperatures below −8°C, or if the temperature of ice is lowered to the range −70° to −160°C, an impure rhombohedral form of ice is obtained. This apparently different form of ice may be due to the elimination of some of the empty pockets during the freezing of water under these conditions. Likewise, if normal ice (ice I) is subjected to high pressure (3000 atm) at −75°C, then a different form of ice (ice II) is obtained which also is rhombohedral in structure and which contains 12 water molecules per unit cell [39]. But this application of pressure on ice I must eliminate the empty pockets in the aggregates just as it did in the case of water between 0 and 30 or 40°C. It is therefore proposed that ice II is obtained by elimination of the empty pockets in ice I. This transformation occurs slowly at lower pressures and

suggests again that holes in ice I are being eliminated by the application of pressure.

Ice I may therefore consist of ice II crystallites interdispersed between unorientated water molecules and empty pockets. The energy necessary to convert ice I to ice II can therefore be due to the reorientation of the disorganized water molecules between the ice II crystallites and the corresponding elimination of the holes in ice I. These unorganized water molecules must be so orientated so that the crystallites of ice II can be joined together to make one large crystallite. Such orientations explain the need for application of large amounts of energy (pressure) to convert ice I to ice II.

Three other factors also suggest that the water clusters have the same structure as ice II. First, ice II is the only ice that has its protons in an ordered state [39]. Such ordering could readily occur by elimination of empty pockets of the cluster aggregates and the alignment of the crystallites by application of pressure. In maximum hydrogen bonding one would expect that ordered water molecules would form. Second, the internal energy of ice II is nearly equal to that of ice I [39]. According to Kamb [39], "considering the rather large distortions from an 'ideal' tetrahedral environment for the water molecules in ice II, it is remarkable that the internal energy of this phase is so nearly equal to that of ice I. . . . " One would suspect that these "large distortions" do not occur and hence that ice II is also formed at high temperatures. Third, the entropy of ice II is 0.77 eu less than that of ice I [39, 40]. This value, as pointed out by Kamb [39], is close to the residual entropy of ice I (about 0.82 eu [39]). And it has been suggested that this negative $\Delta S$ value is due to hydrogen ordering in going from a tetrahedrally disordered hydrogen arrangement of ice I to an ordered hydrogen arrangement of ice II. However, the measured negative value of $\Delta S$ in going from ice I to ice II could also be readily due to the elimination of the empty pockets or holes in ice I and to the organization of the water molecules in the liquid microinclusions. Consequently, it is concluded that the unaggregated water clusters in aqueous solutions may be rhombohedral crystallites of water molecules as in ice II.

## SOME STRUCTURAL PROPERTIES OF THE ICE II CLUSTERS

The density of ice II at −150°C and 1 atm is 1.17 g/ml [39]. The density at higher temperatures will be less than this value. An approximate density of a nonaggregated cluster at high temperatures can be obtained by extrapolating to 0°C the 85-100°C portion of the volume versus temperature plot (Fig. 2). Such an extrapolation yields a density of 1.03 g/ml. Considering the thermal expansion of ice [41], the density of ice II may be approximately equal to 1.15 g/ml at 0°C. Thus the density of the cluster may decrease from 1.15 g/ml at 0°C to 1.03 g/ml at 85-100°C.

By relating the various densities to the densities of water and ice at 0°C it is possible to calculate the percentage of space in the cluster aggregates and ice. The total volume $V_t$ of ice will be the sum of the volume of the clusters $(V_2)$ plus that of the pockets or holes $(V_h)$ or $V_t = V_2 + V_h$, where $V_i = M_i/\rho_i$ = molecular weight divided by density. The density of ice at 0°C is $\rho = 0.9168$ and the density of ice II at 0°C is approximately 1.15 g/ml. The calculated percentage of holes in ice I ($100 \times V_h/V_t$) is then 20%. If the density of ice II is 1.03 g/ml, as determined by extrapolating from values of the volume of water at 80-100°C, then the percentage of holes in ice is 11% or about one-half that of the first calculation. Thus the percentage of volume which consists of empty space is approximately 15 or 20% of the total volume of ice at 0°C.

One can also calculate the approximate volume of the holes in water at 0°C. At this temperature only a small percentage of water molecules will be in the unbonded state and hence the calculation will yield the approximate volume of holes in the cluster aggregates. Since the density of water at 0°C is $\rho = 0.9998$, the calculated percentage of holes in the aggregated clusters is approximately 13% for a density of 1.15 g/ml or 3% for a density of 1.03 g/ml for a cluster. Thus the aggregation of clusters at 0°C is accompanied by the formation of holes or empty pockets which comprise about 10% of the volume of the aggregated clusters. As the average number of clusters per aggregate decreases with an increase in temperature, the percentage of enclosed pockets should also decrease from this 10% value.

## APPLICATION OF MODEL TO SOME PROPERTIES OF WATER

In the above model, as the temperature decreases the water molecules can exist in three predominate states: free or relatively unbonded water, clusters, and cluster aggregates. As seen in Fig. 1, the solubility of hydrocarbons goes through a minimum. The most plausible explanation is that water clusters decrease the solubility of hydrocarbons just as the addition of certain salts decrease their solubility. In other words, the hydrated sodium ion salts-out hydrocarbons because it has tightly bound water (A-regions) rather than loosely bound water (B-regions) and consequently its effective dielectric constant is extremely low. In like manner, those water molecules bound together in clusters will be relatively stationary just as in the case of the hydrated water molecules of the sodium ion's A-region. In contrast, the unbound water behaves as loosely hydrated water or as a B-region. Hence, the unbound water will have an effective dielectric constant much higher than those water molecules on the exterior of a cluster. Consequently, the formation of clusters and the reduction of unbound water molecules decreases the solubility of a hydrocarbon because of a decrease in the effec-
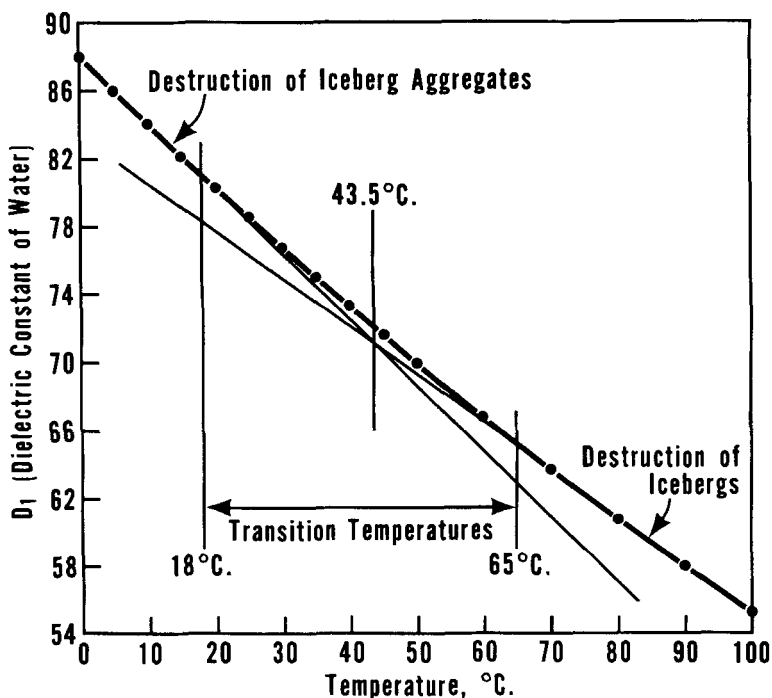
Fig. 3. Dielectric constant of water ($D_1$) plotted versus temperature. The decrease in $D_1$ between 65 and 100°C is due to the destruction of water clusters. The more rapid decrease in $D_1$ from 0 to 18°C is due to the destruction of aggregates of these clusters, i.e., a reduction in size of these aggregates. The transition temperatures (18-65°C) involves both water clusters and their aggregates.
(Data from [29, p. E-36].)

tive dielectric constant (even though the macroscopic dielectric constant may be higher).

As the temperature is increased from 0 to 18°C, the hydrogen bonds holding the cluster aggregates will "melt" or be destroyed. The result will be the dissociation of many aggregated clusters accompanied by only a relatively small increase in unbonded water. The dissociation of these cluster aggregates to form the individual clusters increases the relative concentration of the clusters just as the dissociation of a salt increases the number of species in solution. This increase in the relative concentration of clusters decreases the solubility of the hydrocarbon (Fig. 1). Consequently, from 0 to 18°C the solubility of benzene and other hydrocarbons decreases.

The solubility of benzene increases above 18°C and higher be-
cause now the destruction of individual clusters as well as their
aggregates occurs. Thus the formation of the free water counter-
acts the greater "salting-out" properties of the clusters and the
solubility of benzene increases. The increase in solubility of ben-
zene in contrast to that of aliphatic hydrocarbons must be due to the
less translational and perhaps rotational motion of the benzene in
comparison to the hydrocarbons. The greater translational and
rotational movement of the linear hydrocarbons in comparison to
benzene would produce a greater interaction (more collisions) of
these hydrocarbons with the water clusters or cluster aggregates.
Consequently, a greater amount of free water is necessary to coun-
teract the salting-out properties of the clusters and the solubility
of aliphatic hydrocarbons reaches minimums at higher tempera-
tures.

The disappearance of cluster aggregates can be used to explain
the variation of the dielectric constant of water versus temperature
(Fig. 3). The larger the cluster of water, the greater the dielectric
constant of water. Hence the nonlinear increase in the dielectric
constant of water at low temperatures can be attributed to the for-
mation of cluster aggregates. The fact that water at 0°C has essen-
tially the same dielectric constant as ice at 0°C [38, p. 429] further
verifies the presence of aggregates of water clusters in both water
and ice.

As noted by Klotz [13], if the concentration of methane is increas-
ed by increasing the pressure of the methane gas to tens of atmos-
pheres, a crystalline hydrate of methane precipitates from the solu-
tion. The methane molecules are encased in a large network of
organized water molecules. Klotz [13] used this observation as
proof that hydrocarbons exist in single clathrate structures in
water. However, his data show exactly the opposite, since the cry-
stals are not single clathrate structures but rather are continuous
crystalline structures involving many methane molecules. Moreover,
if such clathrated structures are stable in water, then they should
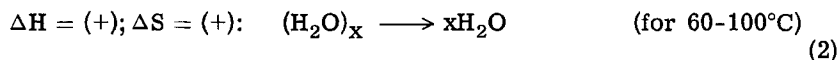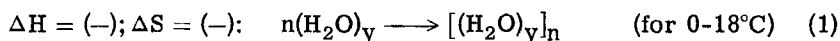remain soluble.

These observations are explainable by application of the pro-
posed model. The methane must exist in domains where there is
free or unbonded water. As the concentration of methane is in-
creased by increasing the pressure, the methane will restrict the
movement of the free water molecules and hence will force these
free water molecules to collide together more frequently. Conse-
quently, at sufficiently high pressures the methane will force the
free water to form hydrogen bonds. At sufficiently low tempera-
tures, this mechanism will freeze the water; i.e., the freezing point
of water will be increased, as is observed experimentally by using
methane. However, if the temperature is sufficiently high so that
ice cannot form, then the concentration of methane will increase

until its molecules occupy all the free space (unbonded water regions). By occupying all these regions, the methane forces the water molecules to hydrogen-bond together to give the most desirable structure. The result is the formation of a stable (not unstable) water clathrate structure which is insoluble in water. Hence the formation of such an insoluble, complex clathrate structure under high pressures is further proof that hydrophobic groups do not have water-clathrate structures surrounding them in aqueous solutions.

This model also explains why the temperature of maximum density of water is lowered when pressure is increased [4]. That is, the application of pressure would hinder the formation of enclosed pockets in the cluster aggregates just as the application of pressure converts ice I to ice II. Hence, under pressure, the quantity of empty pockets in the clusters is not sufficient to overcome the thermal decrease in volume. Therefore, under pressure, the temperature must be lowered below 4°C, before the increase in volume (formation of space pockets) overcomes the decrease in volume (decrease in thermal motion).

## EXPLANATION OF ENTHALPY AND ENTROPY VALUES FOR THE DISSOLVING OF HYDROCARBONS IN LIQUID WATER

From the proposed model, the increase in the solubility of a hydrocarbon is favored by the following reactions:

$$\Delta H = (-); \Delta S = (-): \quad n(H_2O)_y \longrightarrow [(H_2O)_y]_n \qquad \text{(for 0-18°C)} \quad (1)$$

$$\Delta H = (+); \Delta S = (+): \quad (H_2O)_x \longrightarrow xH_2O \qquad \text{(for 60-100°C)} \quad (2)$$

where $(H_2O)_x$ and $(H_2O)_y$ are water clusters of variable sizes containing x and y water molecules and where $[(H_2O)_y]_n$ is a cluster aggregate composed of n water clusters of different sizes. In reaction (1) hydrogen bonds are formed, whereas in (2) hydrogen bonds are destroyed. For the transition temperatures either (1) or (2) could occur, depending on whether the respective thermal motion is great or small. Thus, if a hydrocarbon is dissolved in water under pressure, its thermal movement will tend to force that reaction which gives the least resistance to its presence. From 0 to 18°C or slightly higher temperatures, hydrocarbons or other inert molecules dissolved in water will favor the formation of cluster aggregates and thus will force reaction (1) to occur to decrease the relative concentration of clusters. The result will be a negative value of $\Delta H$.

At temperatures approximately 40 or 60°C and higher, the hydrocarbon cannot induce cluster aggregates, because such structures are unstable at these high temperatures. Hence the only recourse

in order to produce a more favorable interaction with water is to destroy the cluster [reaction (2)]. This reaction produces a positive ΔH and consequently the total ΔH will become more positive.

A positive value of ΔH at high temperatures may not appear even though reaction (2) is the main mechanism. If the space occupied by the inert molecule is less in water than it was in its previous environment, then the inert molecule has, in fact, gone to a more concentrated solution. Moreover, the clusters will occupy less space because of the presence of the inert molecules. Heat is usually absorbed when a solution is diluted. Likewise, if a solute becomes concentrated by reducing the domain it can occupy, then heat would be released; i.e., ΔH will be negative. This negative value of ΔH may obscure the positive value obtained by reaction (2). For benzene, which has less translational energy, these concentrating effects (reductions in space), both for the benzene molecules and the water clusters, will be much less than that for the solubilization of aliphatic hydrocarbons. Consequently, for the solubilization of benzene a positive ΔH is produced at temperatures above 18°C. The mechanism therefore explains the change from negative to more positive values of ΔH for solubilization of benzene and other inert molecules with an increase in temperature.

The introduction of inert molecules into water will limit the freedom of movement of existing water clusters no matter what the temperature. Hence ΔS is always negative. However, the values of ΔS are less at the higher temperatures than at the lower temperatures because of a substitution of reaction (2) for reaction (1). In concentrated salt solutions where water clusters cannot exist, ΔS is also negative, because now the movement of the hydrated ions is restricted due to the presence of inert molecules. Moreover, if there is a reduction in the domain that an inert molecule can occupy, then the value of ΔS will be more negative. Thus in 6 M GSCN, $H_2O$, and 6 M LiCl, the values of ΔS become more negative [17], respectively, because the domain occupied by the benzene molecule decreases.

The effect of a change from reaction (1) to reaction (2) can be observed by examining the ΔH and ΔS values for the solubilization of noble gases as a function of temperature and molecular weight. Both ΔH and ΔS become more positive as the molecular weight of the gas decreases and as the temperature increases [18]. To illustrate this point, the data of Eley [18] are given in Table 3. The increase in the positive character of both ΔH and ΔS with an increase in temperature is in agreement with the proposal that reaction (1) is correspondingly replaced by reaction (2). That is, reaction (2) produces positive values of ΔH and ΔS, whereas reaction (1), which occurs at lower temperatures, produces negative values. As the temperature is increased, the molecular weight sequence disappears and finally reverses itself. That is, the values of ΔS for the solu-

**Table 3.** Values of $-\Delta H$ (in cal/mole) for the Solubilization of Inert Gases[a]

|       | Temp., °C | | | |
| Gas | 0 | 20 | 50 | 80 |
|------|------|------|------|------|
| He | 980 | 870 | 710 | 550 |
| Ne | 2490 | 1990 | 1280 | 580 |
| A | 3730 | 2970 | 1840 | 710 |
| Kr | 5070 | 4000 | 2350 | 740 |
| Xe | 5980 | 4660 | 2680 | 720 |
| Rn | 7070 | 5500 | 3100 | 720 |
| Corresponding values for $-\Delta S$, cal/mole/deg | | | | |
| He | 19.0 | 18.6 | 18.1 | 17.6 |
| Ne | 22.9 | 21.2 | 18.8 | 16.8 |
| A | 25.7 | 22.6 | 19.2 | 15.6 |
| Kr | 29.9 | 25.3 | 19.8 | 15.3 |
| Xe | 31.0 | 26.1 | 20.0 | 14.2 |
| Rn | 33.9 | 27.7 | 20.2 | 13.2 |

[a]From the data of Eley [18].

bilization of noble gases become equal for all the gases at 50°C and become more positive with increasing molecular weight at 80°C. The corresponding change in $\Delta H$ does not occur so rapidly, since the values of $\Delta H$ become equal at 80°C instead of 50°C.

Examination of Table 3 also shows that the degree of change in $\Delta S$ and $\Delta H$ as a function of temperature increases as the molecular weight of the gas increases. These molecular weight sequences can be explained on the basis that the larger the molecular weight of the noble gas, the greater the ability to promote either reaction (1) or (2). That is, the larger molecular weight molecules can interact more forcefully with the clusters and hence will have greater influence in their disappearance. Hence the larger the molecular weight of the noble gas, the larger the $\Delta S$ and $\Delta H$ at high temperatures, and the smaller these quantities at low temperatures. For the same reason, an increase in molecular weight produces the

greatest change in ΔH and ΔS in going from 0 to 80°C. The same explanation can be applied to the solubility studies with hydrocarbons. Those molecules with the greatest collision force will be more effective in promoting reactions (1) and (2).

## REFERENCES

[1]   J. L. Kavanau, *Water and Solute-Water Interactions*, Holden-Day, San Francisco, 1964.

[2]   H. S. Frank and M. W. Evans, *J. Chem. Phys.*, **13**, 507 (1945).

[3]   H. S. Frank and W. Y. Wen, *Trans. Faraday Soc.*, **24**, 133 (1957).

[4]   H. S. Frank, *Federation Proc.*, **24** *(Suppl. 15)*, 5-1 (1965).

[5]   G. Némethy and H. A. Scheraga, *J. Chem. Phys.*, **36**, 3382, 3401 (1962); *J. Phys. Chem.*, **66**, 1773 (1962).

[6]   G. Némethy, *Angew. Chem. Intern. Ed. Engl.*, **6**, 195 (1967); *Federation Proc.*, **24** *(Suppl. 15)*, 38 (1965).

[7]   E. Wicke, Angew. *Chem. Intern. Ed. Engl.*, **5**, 106 (1966).

[8]   R. P. Marchi and H. Eyring, *J. Phys. Chem.*, **68**, 221 (1964).

[9]   L. Pauling, in *Hydrogen Bonding* (D. Hadzi, ed.), Pergamon Press, New York, 1959, pp. 1-6.

[10]  L. Pauling, *The Nature of the Chemical Bond*, Cornell Univ. Press, Ithaca, N.Y., 3rd ed., 1960, p. 472.

[11]  D. C. Ginnings and G. T. Furukawa, *J. Am. Chem. Soc.*, **75**, 522 (1953).

[12]  K. E. Bett and J. B. Cappi, *Nature*, **207**, 620 (1965).

[13]  I. M. Klotz, *Federation Proc.*, **24** *(Suppl. 15)*, 5 (1965).

[14]  W. F. Claussen and M. F. Polglase, *J. Am. Chem. Soc.*, **74**, 4817 (1952).

[15]  K. J. Mysels, *J. Am. Chem. Soc.*, **86**, 3503 (1964).

[16]  W. Kauzmann, *Advan. Protein Chem.*, **14**, 1 (1959).

[17]  S. R. Erlander and J. P. McGuire, *J. Macromol. Sci.*, **A** (1968) in press.

[18]  D. D. Eley, *Trans. Faraday Soc.*, **35**, 1283 (1939).

[19]  F. Franks, M. Gent, and H. H. Johnson, *Trans. Faraday Soc.*, **58** 656 (1962).

[20]  J. D. Cox, *J. Chem. Soc.*, **1954**, 3183.

[21]  G. N. Malcolm and J. S. Rowlinson, *Trans. Faraday Soc.*, **53**, 921 (1957).

[22]  S. R. Erlander and R. Tobin, *Makromol. Chem.*, **107**, 204 (1967).

[23]  W. L. Masterton, *J. Chem. Phys.*, **22**, 1830 (1954).

[24]  H. G. Hertz and M. D. Zeidler, *Z. Elektrochem.*, **67**, 774 (1963).

[25]  E. R. Nightengale, Jr., *J. Phys. Chem.*, **63**, 1381 (1959).

[26]  S. R. Erlander, *J. Macromol. Sci.*, **A** (1968) in press.

[27]  D. E. Gordon, B. Curnutte, Jr., and K. G. Lark, *J. Mol. Biol.*, **13** 571 (1965).

[28]  R. A. Horne and D. S. Johnson, *J. Phys. Chem.*, **70**, 2182 (1966).

[29]  R. C. Weast, S. M. Selby, and C. D. Hodgman (eds.), *Handbook of Chemistry and Physics*, The Chemical Rubber Co., Cleveland, 45th ed. 1964, pp. F-4, F-5.

[30]  F. S. Feates and D. J. G. Ives, *J. Chem. Soc.*, **1956**, 2798.

[31]  C. Salama and D. A. I. Goring, Pulp and Paper Research Institute of Canada, *Tech. Rep. 451*, Feb. 1966.

[32]  D. A. I. Goring, Pulp and Paper Research Institute of Canada, *Tech. Rep. 457*, April 1966.

[33]  M. E. Friedman and H. A. Scheraga, *J. Phys. Chem.*, **69**, 3795 (1965).

[34]  N. H. Grant and H. E. Alburn, *Arch. Biochem. Biophys.*, **118**, 292 (1967).

[35]  L. Onsager and L. K. Runnels, *Proc. Natl. Acad. Sci.(U.S.)*, **50**, 208 (1963).

[36]  W. Kuhn and M. Thürkauf, *Helv. Chim. Acta*, **41**, 938 (1958).

[37]  H S. Frank, *Natl. Acad. Sci. -Natl. Res. Council Publ.*, **42**, 141 (1963).

[38]  A. F. Wells *Structural Inorganic Chemistry*, Oxford, New York, 2nd ed., 1950, pp. 427-432.

[39]  B. Kamb, *Acta Cryst.*, **17**, 1437 (1964).

[40]  W. F. Geanque and M. Ashley, *Phys. Rev.*, **43**, 81 (1933).

[41]  M. Jakob and S. Erk *Chem. Zentr.*, **2**, 397 (1929); **24**, 3936 (1930).