

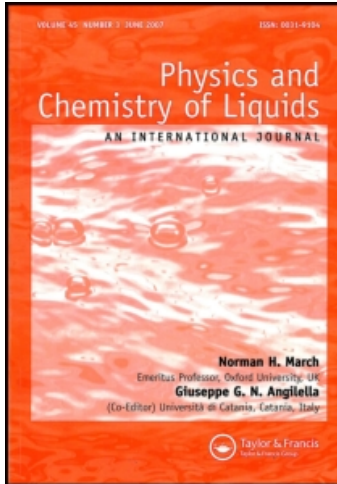
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H. T. Hammel^a

^a Department of Physiology, Medical Science Program, Meyers Hall, Indiana University School of Medicine, Bloomington, Indiana, USA

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INTERNAL PRESSURES, HARD CORE AND FREE SPACE VOLUMES AND BOLTZMANN'S RULE

H. T. HAMMEL

*Department of Physiology, Medical Science Program,
Meyers Hall, Indiana University School of Medicine, Bloomington,
Indiana 47405, USA.*

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Two fundamental relationships describing natural phenomena are posited to be functions of the free space in which atoms and molecules are confined and interact. These relationships are the Boltzmann energy distribution principle and the equation of state. In both cases the free space is that space available to the centers of mass of the atoms and molecules as they move randomly in translational motion. The hard core volume of atoms and molecules is not available for translational motion of their centers of mass and is excluded from the volume function in both Boltzmann's principle and the equation of state. Only in this way is it possible: 1) to apply Boltzmann's principle to the distribution of atoms or molecules between the two energy states of two phases in equilibrium; solid-gas, liquid-gas or solid-liquid and 2) to apply the equation of state to the gas, liquid or solid phase in order to determine the internal pressure exerted by the translational motion of atoms or molecules and to deduce the internal tension in the cohesion between atoms or molecules. These relationships are applied to water for the determination of the molar free space and molar hard core volumes of pure water.

KEY WORDS: Equation of state, Boltzmann law.

INTRODUCTION

Boltzmann's principle describes the distribution of molecules (or atoms) between two energy states provided there is a reversible exchange of molecules between the energy states and provided they are in equilibrium. The molar internal energy, molar enthalpy and molar entropy of the molecules (or atoms) may differ, depending on the phase of the molecules or the external force field applied to them. However, at constant and uniform temperature, the Gibbs free energy is the same for all molecules (or atoms) of pure species *i* when two of its phases are in equilibrium. Distribution of molecules (or atoms) between differing energy states due to phase changes in pure species *i* will be considered first; and this treatment will serve to introduce the concepts of internal pressure and tension, free space volume and hard core volume of pure species *i*. I shall posit that the free space volume is required for the Boltzmann energy distribution principle as well as for calculating the internal pressure and tension of species *i*. Then, these concepts and the Boltzmann principle will be applied to pure water molecules in equilibrium in two energy states: between liquid and vapor, between ice and vapor and between ice and liquid.

Internal energy of pure species i

In this section and the next, there are restatements of well known concepts expressed in the notation used by McGlashan¹. The molar internal energy of pure species *i* is denoted $U_i^{\alpha}(T, p_e^{\alpha})$ and is a function of the phase of *i* as well as a function of the temperature and external pressure applied to it. α denotes the phase of species *i* and the asterisk denotes purity, i.e. only one component. The molar internal energy of species *i* changes with change of phase at the same temperature and applied pressure. For a change from pure solid *i* to pure liquid *i*, the change in molar internal energy at the same T_i^{s*+l*} (melting temperature of solid *i*) and applied pressure ($p_e^{s*} = p_e^{l*} = p_e^{s*+l*}$) is $\Delta U_i^{s*+l*}(T_i^{s*+l*}, p_e^{s*+l*}) = U_i^{l*}(T_i^{s*+l*}, p_e^{l*}) - U_i^{s*}(T_i^{s*+l*}, p_e^{s*})$. For a change from pure liquid *i* to pure vapor *i* at the same *T* and applied pressure ($p_e^{l*} = p_e^{g*} = p_e^{l*+g*}$), $\Delta U_i^{l*+g*}(T, p_e^{l*+g*}) = U_i^{g*}(T, p_e^{g*}) - U_i^{l*}(T, p_e^{l*})$.

Effects of heat and pressure volume work on internal energy at constant, applied T and p

During a phase change at constant temperature and constant external pressure, there is a change of internal energy requiring an amount of heat, $\pm \delta Q$, added to or removed from the constituents and/or an amount of pressure work, $\pm \delta W$, done on or by the constituents according to the first law of thermodynamics, that is,

$$\Delta U = \pm \delta Q \pm \delta W. \quad (1)$$

In order for the temperature to remain constant during a change of phase, heat may be added to or removed from the molecules of *i* when and as they react physically in changing phase. Pressure volume work is always done on or by the constituents as they react physically during a change of phase. Pressure volume work is performed by the system when there is a volume increase at constant applied pressure, $p_e \Delta V$. At the same time, any decrease of applied pressure will increase the pressure volume work performed by the system an amount $V \Delta p$ at constant volume. Change of pressure (and internal energy) as pure *i* changes phase may result from a change in the external pressure applied to it, $\pm \Delta p_e$, and it always results from a change of internal pressure of species *i* during a phase change. One purpose of this article is to examine the consequences of the change in internal pressure of pure species *i* when it changes phase. But first, the free space volume of species *i* is required before its internal pressure and internal tension can be determined in pure *i*.

Volumes occupied by pure species i

The molecules (or atoms) of a mole of pure species *i* may be viewed as occupying three spaces concurrently: its molar volume, its molar hard core volume, and its molar free space volume. The center of mass of each molecule of species *i* is excluded from moving within a hard core space as it collides with other molecules in the same total space. This excluded space depends on the size, shape and charge distribution of the molecules which collide. It also depends on the number of molecules (or atoms)

involved in each collision and, therefore, it depends on the phase. However, the excluded space per collision is the same whether the molecule collides with only one molecule or with many molecules at the same time. For a mean radius of molecule i , σ_i , the excluded space for each of its collisions, v_{hci} , is the forward half of a hemisphere of radius $2\sigma_i$ when it collides with another of the same species, i.e. $v_{hci} = 2/3\pi(2\sigma_i)^3$ (c.f. Loeb²). When all collisions are binary, as in a gas at low temperature, the volume of the excluded space in a mole of species i is Lv_{hci}^* , since there are L (Avagadro's constant) molecules of i in one mole. Each of the L molecules collides with only one other molecule at a time so that there are L exclusions altogether in a mole of gas. When collisions include ternary and higher order collisions, as in the liquid phase, then there are many fewer than L exclusions altogether in a mole. The exclusion space for a collision of a molecule with two or more molecules at the same time remains about $2/3\pi(2\sigma_i)^3$ for pure liquid i . However, the molar exclusion volume of pure i in liquid phase is much less than Lv_{hci}^* by an amount depending on the proportion of higher order collisions. Increasing temperature increases the number of collisions per unit time and also increases the proportion of higher order collisions and, for this reason, reduces the molar hard core volume of pure liquid i .

The total volume occupied by a molecule of species i is more variable than its hard core volume and is determined by its random translational motion as it collides with and is reflected by surrounding atoms or molecules. The total volume occupied by species i in phase α is $V^{\alpha*} = n_i^{\alpha*} V_i^{\alpha*}$ where $n_i^{\alpha*}$ is the moles of species i in phase α and $V_i^{\alpha*}$ is the molar volume of pure i in phase α . Within the total volume, $V^{\alpha*}$, there is the total hard core volume, $V_{hc}^{\alpha*}$, not available for the motion of the center of mass of the molecules i . There is a third volume associated with these molecules. It is the volume available for the random translational motion of the center of mass of its molecules and is denoted $V_{fs}^{\alpha*}$ for the total free space volume. Thus, the total volume of the pure substance i is the sum of the total hard core and free space volumes, $V^{\alpha*} = V_{hc}^{\alpha*} + V_{fs}^{\alpha*}$, where $V_{hc}^{\alpha*} = n_i^{\alpha*} V_{hci}^{\alpha*}$ and $V_{fs}^{\alpha*} = n_i^{\alpha*} V_{fsi}^{\alpha*}$ and where $V_{hci}^{\alpha*}$ is the molar hard core volume of species i and $V_{fsi}^{\alpha*}$ is its molar free space volume. It should be noted that $V_{fsi}^{\alpha*}$ is much more variable than $V_{hci}^{\alpha*}$ with respect to temperature and pressure applied to substance i .

The volume of the molar free space available to the centers of mass of species i is an important volume conceptually. It is the principal volume that is compressible in the gaseous, liquid, as well as in the solid phase of species i . This volume varies as temperature and pressure applied to species i vary and as the forces between molecules of species i are affected by their order at a given T and p_e in phase α . Thus, $V_{fsi}^{\alpha*}(T, p_e^{\alpha*})$ is variable in any phase α largely (but not exclusively) because $V_{fsi}^{\alpha*}$ is variable and depends on T and $p_e^{\alpha*}$ and on the internal energy and the extent the molecules of species i are ordered at a given T , $p_e^{\alpha*}$. As we shall see, the volume of the molar free space available to the centers of mass of species i is the volume into which molecules of species i are distributed in each of two energy states when they are in equilibrium. It is also the volume to be used in the equation of state of species i , that is, the equation which relates pressure, volume and temperature for species i in any phase.

Boltzmann energy distribution principle applied to physical reactions

A fundamental relationship affecting the atoms or molecules of a substance in two or more energy states in equilibrium is the Boltzmann distribution principle. This statistical principle governs the distribution of atoms or molecules between an initial molar energy state, U_i , before and a final molar energy state, U_f , after a chemical or a physical reaction. The principle assumes the reaction is reversible, proceeds until equilibrium is established between atoms or molecules in the two energy states and provided that quantum mechanical effects are not important, that is, $(U_f - U_i) \gg RT$ or $(U_f - U_i) \ll RT$. Boltzmann's principle was derived from the theory of probability applied to an assemblage of N similar molecules in a gaseous phase. The energies of the molecules may differ in amount and kind. However, if there are N_i each with an amount and form of energy ε_i , then the total number of molecules would be $N = \sum_i N_i$ and the total energy would be $Q = \sum_i N_i \varepsilon_i$. Using the principles of statistical mechanics, Glasstone³ shows that the number of molecules N_i possessing the energy ε_i at any absolute temperature T is

$$N_i = C e^{-\varepsilon_i/kT},$$

where C is a constant and k is Boltzmann's constant. The principle makes no restrictions as to the nature of the energies obtaining to the molecules; their energies might be kinetic energy of translation or rotation or vibration or their potential energy might vary in a non-uniform force field applied to them. The principle is often applied to gases subject to the gravitational field of the earth and is thereby called the law of the atmosphere as it describes the distribution of gases of the atmosphere as a function of altitude, assuming uniform temperature throughout the atmosphere.

Perrin⁴ applied Boltzmann's principle to the distribution of dense colloidal particles of gamboge and mastic. From his observations of their distribution in liquid water in the earth's gravity field, he was able to explain Brownian motion and to establish the reality of atoms and molecules. Moreover, he obtained a good approximation of Avogadro's constant from these observations.

Feynman⁵ notes "It turns out that there are many, many phenomena in nature which are characterized by having to borrow an energy from somewhere, and in which the central feature of the temperature variation is e to the minus energy over kT ." Feynman considers that an evaporating liquid is one of the phenomena to be studied, albeit relatively complicated. He states further "Now we use the general principle that the number of atoms per unit volume in two different regions is $n_2/n_1 = e^{-(E_2 - E_1)/kT}$." Feynman supposes "that there is a force of attraction between the molecules to hold them together in the liquid. Otherwise we cannot understand why it condenses." Furthermore, he supposes "that there is an energy of binding of the molecules in the liquid which is lost when they go into the vapor. That is—in order to take a single molecule out of the liquid into the vapor, a certain amount of work W has to be done. There is a certain difference, W , in the energy of a molecule in the liquid from what it would have if it were in the vapor, because we have to pull it away from the other molecules which attract it." Feynman then uses the general principle stated by Boltzmann: "So the number n per unit volume in the vapor, divided by the number

$1/V_a$ per unit volume in the liquid, is equal to $nV_a = e^{-W/kT}$, because that is the general rule." Feynman gives no examples to illustrate the value of W for any liquid. Nevertheless, there is no reason to disallow the application of Boltzmann's general principle to the liquid phase of water or to its equilibrium with its vapor.

When atoms or molecules A are involved in a physical reaction between two energy states such that atoms or molecules A_1 in energy state 1 are in equilibrium with atoms or molecules A_2 in energy state 2, then n_{A1} moles of A_1 in a unit volume available to the centers of mass of atoms or molecules A_1 and n_{A2} moles of A_2 in a unit volume available to the centers of mass of atoms or molecules A_2 are distributed according to Boltzmann statistics, namely,

$$\frac{n_{A2}}{n_{A1}} = e^{-(U_{A2} - U_{A1})/RT}, \quad (2)$$

where U_{A1} and U_{A2} are the molar energies in states 1 and 2, respectively, and where $R = kL$, the product of Boltzmann constant and Avogadro constant. Equation (2) is rigorous only if $(U_{A2} - U_{A1}) \gg RT$ or $(U_{A2} - U_{A1}) \ll RT$.

Maxwell's principle was derived for the distribution of velocities of molecules in a gas and his principle may also be derived from Boltzmann's principle. The distribution of velocities of the molecules in the liquid and vapor phases of the same species are identical at the same temperature. It follows that Boltzmann's principle as well as Maxwell's principle apply to the distribution of molecules of species i in any phase when these molecules, which for any reason differ in energy, are in equilibrium and can reversibly change from one energy state to another. For example, the energy of molecules in the vapor phase is higher than the energy of molecules of the same species in its liquid phase at the same T . Likewise, the molecules in the liquid phase have higher energy than those in the solid phase at the same T . Nevertheless, the molecules may reversibly pass from one phase to another and remain in equilibrium all the while. The molecules are distributed between two energy states such that fewer per unit volume are in the higher energy state (vapor) and more per unit volume are in the lower energy state (liquid). Since Boltzmann's principle was derived without regard for the nature of the energies of the molecules, it applies also to the distribution of molecules between the liquid and vapor phases or between the solid and liquid phases of species i . However, as we shall see, it can be made to apply to these two phases 1) only if the unit volume is taken to be the unit free space volume for the molecules in each phase, 2) only if the enthalpy of transition from liquid to vapor phase (or from solid to liquid) is known and 3) only if the pressure-volume work from liquid to vapor phase can be assessed. The total pressure-volume work must include the work performed when the molecules expand in volume when going from the liquid to the vapor phase against a constant external pressure applied to each, namely, $p_a^g(V_1^g - V_1^l)$ and it must also include the work resulting from a change in internal tension in the cohesion between molecules in the two phases.

When molecules A_1 and molecules A_2 are at the same temperature, their average kinetic energies and the distribution of their translational velocities in x , y and z are identical in the two energy states. Nevertheless, forces acting on molecules A_1 and A_2 may yield potential energy states which differ. The force field may be external to

the molecules or it may be internal between the molecules. In each case, the unit volume is a unit of volume available to the centers of mass of the molecules. The hard core of molecules A is not included in the unit volume. Thus, if there are $n_{A2}L$ molecules in energy state 1 in a unit volume, the total volume occupied by these molecules is $V_1 = 1 + n_{A1}V_{hcA1}$. Likewise, in energy state 2, for which there are $n_{A2}L$ molecules in a unit free space volume, the total volume occupied by these molecules is $V_2 = 1 + n_{A2}V_{hcA2}$. V_1 also equals n_{A1} times the molar volume of A_1 , V_{A1} , so that a unit volume equals $n_{A1}(V_{A1} - V_{hcA1})$. Likewise, $V_2 = n_{A2}V_{A2}$ and a unit volume also equals $n_{A2}(V_{A2} - V_{hcA2})$. Thus, the left side of Eq. (2) becomes

$$\frac{n_{A2}}{n_{A1}} = \frac{(V_{A1} - V_{hcA1})}{(V_{A2} - V_{hcA2})} = \frac{V_{fsA1}}{V_{fsA2}}$$

Melting is a physical reaction, a phase change from pure solid A to pure liquid A at or above its melting temperature $T_A^{s^*+l^*}$ at a given pressure. The equilibrium distribution of molecules of A between the molar energy states $U_A^{s^*}$ and $U_A^{l^*}$, i.e., the solid and liquid phases in the reaction $A^{s^*} \leftrightarrow A^{l^*}$ at $T_A^{s^*+l^*}$, becomes

$$\frac{n_A^{l^*}}{n_A^{s^*}} = e^{-(U_A^{l^*} - U_A^{s^*})/RT_A^{s^*+l^*}}, \quad (3)$$

where $n_A^{l^*}$ is the moles of pure liquid A in a unit volume and where $n_A^{s^*}$ is the moles of pure solid A in a unit volume. Since a unit volume excludes the hard core volume in both cases, Eq. (3) can be written

$$\frac{n_A^{l^*}}{n_A^{s^*}} = \frac{V_{fsA}^{s^*}}{V_{fsA}^{l^*}} = e^{-\Delta U_A^{s^*+l^*}/RT_A^{s^*+l^*}}, \quad (4)$$

where $\Delta U_A^{s^*+l^*} = (U_A^{l^*} - U_A^{s^*})$.

Similarly, when pure liquid A vaporizes at T , the moles of A are distributed between the energy states of the liquid and vapor according to

$$\frac{n_A^{g^*}}{n_A^{l^*}} = \frac{V_{fsA}^{l^*}}{V_{fsA}^{g^*}} = e^{-\Delta U_A^{l^*+g^*}/RT}. \quad (5)$$

Likewise, when pure solid A vaporizes at T , the moles of A are distributed between the energy states of the solid and vapor according to

$$\frac{n_A^{g^*}}{n_A^{s^*}} = \frac{V_{fsA}^{s^*}}{V_{fsA}^{g^*}} = e^{-\Delta U_A^{s^*+g^*}/RT}. \quad (6)$$

Equation of state of pure species i: free space volume, external and internal pressures and internal tension

An equation of state for a mole of pure substance i in any phase relates its volume to the pressure and temperature applied to it. However, the external pressure, $p_e^{s^*}$, applied to phase α of pure substance i is not the only pressure affecting the molar volume of substance i . An internal pressure attributable to the Brownian motion of

its molecules also affects its volume. In all phases of pure species *i*, its molecules (or atoms) are in thermal, random, translational (also rotational and vibrational) motions. All molecules (or atoms) reflected at the boundaries within which they are contained change momenta. The momentum change normal to a boundary per unit time is an internal force and, per unit area of boundary, an internal pressure, $p_i^{\alpha*}$, which is always positive and depends on the temperature of substance *i*. Some fundamental equation must relate this internal pressure to the temperature and to some molar volume of substance *i*. I shall posit that: 1) the molar free space volume of *i* in phase α is the appropriate molar volume for this fundamental equation and 2) the fundamental equation is

$$p_i^{\alpha*} V_{f_{si}}^{\alpha*} = RT. \quad (7)$$

In the gaseous phase, this outwardly directed internal pressure, p_i^{g*} , due to the translational motion of molecules of *i* is opposed largely by the walls of the containing vessel, namely, the external applied pressure p_e^{g*} .

In all phases of species *i*, there is a cohesive force between its molecules (or atoms) when they are in close range. In the higher energy and gaseous phase, this cohesion diminishes the pressure exerted by the gas molecules of species *i* against the walls containing them. Thus, p_e^{g*} is slightly less than p_i^{g*} . Because there is a cohesive force between the molecules, there is also a tension in it, τ_i^{g*} , (a negative pressure) such that $p_i^{g*} + \tau_i^{g*} = p_e^{g*}$. It is this cohesion and the attendant tension that allows p_e^{g*} to be less than p_i^{g*} . The same cohesion between molecules of *i* also insures that they can exist in lower energy and condensed phase (liquid and solid) in which the average spacing between molecules is only a few molecular diameters. Therefore, I shall posit that this internal pressure of substance *i* in any phase is related to the external pressure as

$$p_i^{\alpha*} + \tau_i^{\alpha*} = p_e^{\alpha*}, \quad (8)$$

where $\tau_i^{\alpha*}$ is a tension (negative pressure) in the cohesive force between atoms or molecules of *i* so that $\tau_i^{\alpha*}$ allows the pressure applied to *i* in any phase to be less than its internal pressure. If the pressure applied to a condensed phase were zero, the internal thermal pressure and the internal tension would be the same magnitude but opposite in sign.

Combining Eqs. (7) and (8), I shall posit that the equation of state for pure substance *i* in phase α to be

$$(p_e^{\alpha*} - \tau_i^{\alpha*}) V_{f_{si}}^{\alpha*} = RT$$

or

$$(p_e^{\alpha*} - \tau_i^{\alpha*})(V_i^{\alpha*} - V_{h_{ci}}^{\alpha*}) = RT, \quad (9)$$

where $V_{h_{ci}}^{\alpha*}$ is the molar hard core volume of *i* unavailable for the motion of the centers of mass of the atoms or molecules of *i*. Equation (9) for the gaseous phase of pure substance *i* has the form of van der Waals' equation for which $-\tau_i^{g*} = a_i^{g*}/(V_i^{g*})^2$ and $V_{h_{ci}}^{g*} = b_i^{g*}$ where a_i^{g*} and b_i^{g*} are the van der Waals' constants for pure gaseous *i*.

The magnitude of $a_i^{g^*}$ for each of the gaseous substances i listed on page D-146 of the CRC Handbook of Chemistry and Physics 53rd Edition or, specifically, the value of $a_i^{g^*}[V_i^{g^*}(T, p_e^{g^*})]^{-2}$ is a measure of the cohesion between the molecules of gaseous substance i when it is in equilibrium with its pure liquid at T and applied pressure $p_e^*(T) = p_e^{g^*}(T)$. The greater the value of $a_i^{g^*}[V_i^{g^*}(T, p_e^{g^*})]^{-2}$, the more the molecules of i cohere in the gaseous phase and the extent to which the applied pressure is less than the internal pressure is greater. That is, the extent to which $[p_i^{g^*}(T) - p_e^{g^*}(T)]$ is greater than zero is increased as $a_i^{g^*}$ increases or as $V_i^{g^*}$ decreases. Cohesion between molecules i in the gaseous phase is less than in the liquid phase only because cohesion is a short range interaction between molecules of i so that they are seldom near enough to interact and cohere to one another in the gaseous phase, i.e. when $T \ll T_{ci}$. In a condensed phase, below the critical temperature T_{ci} , nearly all molecules cohere to one another. As the temperature increases toward T_{ci} , the liquid molecules cohere to one another to a lesser extent and the vapor molecules cohere to one another to a greater extent so that at $T = T_{ci}$ the extent of the cohesion is the same in both liquid and vapor phases and there is no distinction between the two phases. Cohesion between molecules of i in any phase is also related to the energy of transition from one phase to another. The greater the cohesion, the higher is the energy of transition. When liquid i is in equilibrium with its vapor only, the pressure applied to the upper surface of the liquid is the same as the pressure applied to the vapor by the walls containing the vapor at the same level, $p_e^{g^*}$, and is designated the vapor pressure of the liquid. In this case, $p_e^* = p_e^{g^*}$. For the liquid, $p_i^* = RT/V_{fsi}^*$ so that $RT/V_{fsi}^* + \tau_i^* = p_e^*$ at its upper surface. For the vapor, $p_i^{g^*} = RT/V_{f_{si}^{g^*}}$ so that $RT/V_{f_{si}^{g^*}} + \tau_i^{g^*} = p_e^{g^*}$. When $p_e^* = p_e^{g^*}$, $RT/V_{fsi}^* + \tau_i^* = RT/V_{f_{si}^{g^*}} + \tau_i^{g^*}$. For temperature $T = T_{ci}$, the critical temperature for species i , τ_i^* equals $\tau_i^{g^*}$ and the liquid and vapor phases are no longer distinguishable. At $T = T_{ci}$, the critical applied pressure is $p_{ec}^* = p_{ec}^{g^*} = RT_{ci}/V_{fsi}^* + \tau_i^*(T_{ci}) = RT_{ci}/V_{f_{si}^{g^*}} + \tau_i^{g^*}(T_{ci})$. Since $\tau_i^*(T_{ci}) = \tau_i^{g^*}(T_{ci})$, it follows that $V_{fsi}^*(T_{ci}, p_{ci}) = V_{f_{si}^{g^*}}(T_{ci}, p_{ci})$.

Compressibility relates change of applied pressure to change in volume and volume

External pressure applied to all boundaries of a condensed phase alters the spacing between its molecules. Increasing a positive external pressure diminishes the average spacing and decreasing a negative applied pressure increases the spacing. The relationship between a change in the applied pressure and a change in spacing between molecules, i.e. volume, is determined experimentally and is termed compressibility of the condensed phase. For a liquid, the compressibility is $\kappa^l = -\Delta V^l/V^l(\Delta p_e^l)^{-1}$. Compressibility varies with species, temperature and pressure applied to the condensed phase.

There are two pressures acting at the boundaries of pure liquid A: an external pressure compressing the liquid, when this pressure is positive, and an internal pressure always distending the liquid. The net effect of these two pressures is $(p_e^* - p_A^*) = \tau_A^*$, the internal tension in the cohesive force between the molecules of liquid A. Furthermore, since $p_A^* = RT \div V_{fsA}^*$, which is temperature dependent, the spacing between molecules of liquid A is temperature dependent. Similarly, for pure

A in solid phase, the pressure affecting the spacing between its molecules is $(p_e^{s*} - p_A^{s*}) = \tau_A^{s*}$ where p_e^{s*} is the external pressure applied to the solid and p_A^{s*} is the internal pressure due to the thermal motion of molecules A at the boundaries of the solid.

Melting and vaporization of solvent A (water): V_{f,sH_2O}^{s*} and V_{f,sH_2O}^{l*}

According to the first law of thermodynamics, Eq. (1), the increase of energy during melting one mole of solid A to one mole of liquid A at constant temperature and constant external pressure is possible only if an amount of heat δQ is added to the system and/or an amount of pressure volume work δW is performed on the system. By definition and in accord with the second law of thermodynamics, $\delta Q = T\Delta S_A^{s*+l*}$ where $\Delta S_A^{s*+l*} = [S_A^{l*} - S_A^{s*}]$, the molar entropy of liquid A minus the molar entropy of solid A at the same temperature and applied pressure. The amount of pressure volume work in melting one mole of solid A is the change from $[p_e^{s*} - p_A^{s*}]V_A^{s*}$ to $[p_e^{l*} - p_A^{l*}]V_A^{l*}$, i.e. from $\tau_A^{s*}V_A^{s*}$ to $\tau_A^{l*}V_A^{l*}$. Since work is done on the system when the volume change is negative, $\delta W = -\{[p_e^{l*} - p_A^{l*}]V_A^{l*} - [p_e^{s*} - p_A^{s*}]V_A^{s*}\}$ in melting one mole of A. If the externally applied pressure remains constant during melting, i.e. $p_e^{l*} = p_e^{s*} = p_e^{s*+l*}$, and since the molar volume change is $[V_A^{l*}(T_A^{s*+l*}, p_e^{l*} - p_A^{l*}) - V_A^{s*}(T_A^{s*+l*}, p_e^{s*} - p_A^{s*})] = \Delta V_A^{s*+l*}$, the external pressure volume work done on (or by) the system due to a change in volume during melting is $p_e^{s*+l*}\Delta V_A^{s*+l*}$, and depends on whether the volume decreases (or increases). Thus, if the external pressure remains constant and if the temperature remains T_A^{s*+l*} , then during melting the change in internal energy is

$$\begin{aligned} \Delta U_A^{s*+l*}(T_A^{s*+l*}, p_e^{s*+l*}) &= T_A^{s*+l*}\Delta S_A^{s*+l*} - p_e^{s*+l*}\Delta V_A^{s*+l*} \\ &\quad + p_A^{l*}V_A^{l*} - p_A^{s*}V_A^{s*}. \end{aligned} \quad (10)$$

Enthalpy is defined as $H = U + pV$ so that $\Delta H = \Delta(U + pV)$ and the enthalpy change when one mole of solid A melts at constant T and constant applied pressure is

$$\Delta H_A^{s*+l*} = \Delta U_A^{s*+l*} + p_e^{s*+l*}\Delta V_A^{s*+l*} - p_A^{l*}V_A^{l*} + p_A^{s*}V_A^{s*}; \quad (11)$$

so that Eq. (4) can be written

$$\frac{V_{f,sA}^{s*}}{V_{f,sA}^{l*}} = e^{-[\Delta H_A^{s*+l*} - p_e^{s*+l*}\Delta V_A^{s*+l*} + p_A^{l*}V_A^{l*} - p_A^{s*}V_A^{s*}]/RT_A^{s*+l*}} \quad (12)$$

Comparing Eqs (10) and (11), it is evident that $\Delta H_A^{s*+l*} = T_A^{s*+l*}\Delta S_A^{s*+l*}$ at constant temperature and external pressure so that ΔH_A^{s*+l*} is the amount of heat required to melt (increase the entropy by ΔS_A^{s*+l*} and decrease the order of) one mole of solid A at T_A^{s*+l*} and p_e^{s*+l*} . This amount of heat can be determined experimentally by calorimetry. Equation (12) also determines the distribution of molecules between a unit volume of liquid A and a unit volume of solid A, n_A^{l*}/n_A^{s*} , at T_A^{s*+l*} and p_e^{s*+l*} , where the unit volume is that available to the motion of the centers of mass of the molecules.

Evaporating a mole of pure liquid A to a mole of pure vapor at T requires an enthalpy change $\Delta H_A^{l \rightarrow g} = H_A^g(T, p_e^g) - H_A^l(T, p_e^l)$ and a volume change $\Delta V_A^{l \rightarrow g} = V_A^g(T, p_e^g) - V_A^l(T, p_e^l)$. At constant T and applied pressure $p_e^g = p_e^l$, the ratio of molar free space volume of liquid A to molar free space volume of vapor A is, according to Eq. (5),

$$\frac{V_{fsA}^l}{V_{fsA}^g} = e^{-[\Delta H_A^{l \rightarrow g} - p_e^g \Delta V_A^{l \rightarrow g} + p_A^g V_A^g - p_A^l V_A^l]/RT} \quad (13)$$

The distribution of molecules A between a unit free space volume of vapor A and liquid A is also given by Eq. (13). At the critical temperature and pressure for A, we have already deduced that $V_{fsA}^l(T_{cA}, p_{cA}) = V_{fsA}^g(T_{cA}, p_{cA})$ so that molecules of A are distributed equally between the two phases and the left side of Eq. (13) equals unity.

Likewise, Eq. (6), the distribution of pure solvent molecules A between its solid and gaseous phases can be written

$$\frac{V_{fsA}^{s \rightarrow g}}{V_{fsA}^g} = e^{-[\Delta H_A^{s \rightarrow g} - p_e^g \Delta V_A^{s \rightarrow g} + p_A^g V_A^g - p_A^s V_A^s]/RT} \quad (14)$$

where $\Delta H_A^{s \rightarrow g}$ is the molar enthalpy of evaporation from solid to gaseous A.

Eqs (12), (13) and (14) are readily applicable to pure water, since the molar enthalpy of melting ice and the molar enthalpies of vaporization of ice and liquid water are well known. First, Eq. (13) will be used to calculate the free space volume of liquid water at 0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 200, 300 and 374.15°C as well as 33, 34, 35, 36, 37, 38, 39, 40, 42, 52, 62°F. Next, the free space volume of ice at its triple point temperature, 0.0098°C, will be calculated from Eq. (14).

In order to calculate the molar free space volume of liquid water from Eq. (13), it is necessary to assess the molar free space volume of its vapor, $V_{fsH_2O}^g$, as well as the internal tension in the cohesive force between the molecules of water vapor. For these terms, let us assume that the a and b terms for water vapor in van der Waals' equation of state, namely, $[p_e^g + a_{H_2O}^g/(V_{H_2O}^g)^2][V_{H_2O}^g - b_{H_2O}^g] = RT$, provide the appropriate values when T is near 0°C. $b_{H_2O}^g$ is interpreted to be a volume occupied by a mole of the vapor molecules, i.e. the volume in a mole of gas not available for the motion of the centers of mass of the molecules, so that $V_{hcH_2O}^g = b_{H_2O}^g = 30.49 \text{ cm}^3/\text{mole}$ and $V_{fsH_2O}^g = V_{H_2O}^g - b_{H_2O}^g$.

For water vapor near 0°C, $a_{H_2O}^g = 5.464 \text{ liter}^2 \text{ atm mol}^{-2}$ or $0.55364 \text{ liter}^2 \text{ joule cm}^{-3} \text{ mol}^{-2}$ or $5.536398 \times 10^5 \text{ cm}^3 \text{ joule mol}^{-2}$. $a_{H_2O}^g/(V_{H_2O}^g)^2$ has the dimensions of a pressure attributed to the attraction between the molecules of water vapor; it lessens the external pressure applied by the wall of the containing vessel, so that $\tau_{H_2O}^g = -a_{H_2O}^g/(V_{H_2O}^g)^2$. Since $p_{H_2O}^g + \tau_{H_2O}^g = p_e^g$, then the third term in the numerator of the exponential in Eq. (13), $p_{H_2O}^g V_{H_2O}^g$, equals $[p_e^g + a_{H_2O}^g/(V_{H_2O}^g)^2] V_{H_2O}^g$. Also, the second term in the same numerator is $-p_e^g [V_{H_2O}^g(T, p_e^g) - V_{H_2O}^l(T, p_e^l)]$ so that the second and third terms may be combined to equal $+p_e^g V_{H_2O}^l + a_{H_2O}^g/V_{H_2O}^g$. I have posited that $p_{H_2O}^l V_{fsH_2O}^l = RT$, so that the term for $p_{H_2O}^l V_{H_2O}^l$ in Eq. (13) becomes $RT V_{H_2O}^l/V_{fsH_2O}^l$. Equation (13) can now be written

$$\frac{V_{fsH_2O}^l}{V_{H_2O}^g - b_{H_2O}^g} = e^{-[\Delta H_{H_2O}^{l \rightarrow g} + p_e^g V_{H_2O}^l + a_{H_2O}^g/V_{H_2O}^g - RT V_{H_2O}^l/V_{fsH_2O}^l]/RT} \quad (13a)$$

There is a term for $V_{fsH_2O}^{I*}$ on the left side of Eq. (13a) as well as on the right side. All other terms are known from experimental determinations as noted in Table 1. By iteration, the value of $V_{fsH_2O}^{I*}$ in Eq. (13a) can be determined and is shown in the last column of Table 1 for each temperature. Since $V_{hcH_2O}(T, p_e^{g*}) = V_{H_2O}^{I*}(T, p_e^{g*}) - V_{fsH_2O}^{I*}(T, p_e^{g*})$, the molar hard core volume is the difference between the fourth and last columns and is shown in the next to last column of Table 1 at each temperature. Although it is known that van der Waals' constants a and b vary to some extent with temperature, they were assumed to be constants for the calculations of $V_{fsH_2O}^{I*}$ in Table 1 from 0 to 100°C. Thus, the free space volume for the motion of the centers of mass of water molecules in a mole of liquid water, $V_{fsH_2O}^{I*}(T)$, increases from 3.07759 cm³/mole at 0°C to 4.38469 cm³/mole at 100°C. It is greater (by 1.424714178 ×) at 100°C causing thermal expansion of the liquid water (by 1.043224326 ×) even though there was a reduction of the hard core volume due to an increasing number of high order collisions. Distensibility and thermal expansion are related properties of any liquid A. Increasing temperature increases the internal pressure (since $p_A^{I*} V_{fsA}^{I*} = RT$) against the boundary of the liquid and thereby increases the volume of the distensible liquid an amount depending, in part, on its distensibility (negative compressibility).

The molar hard core volume of liquid water diminished by a factor of 0.964645002 × from 14.94122 cm³mol⁻¹ at 0°C to 14.41297 cm³mol⁻¹ at 100°C. As expected, the hard core volume of liquid water (14.94 cm³mol⁻¹ at 0°C) is less than half its value for its vapor (30.49 cm³mol⁻¹). Many collisions in the liquid are ternary and higher order so that there are many fewer exclusion volumes from which the center of mass of a molecule is excluded. Likewise, as the temperature increases, the proportion of higher order collisions increases so that the hard core volume is diminished.

In Figure 1 the molar hard core volume and the molar free space volume of liquid water are plotted as a function of temperature from 0°C to 100°C. The cubic regression lines for these are, respectively,

$$V_{hcH_2O}^{I*} = 14.93960119 - 10.48454364 \times 10^{-3} T + 82.52599697 \times 10^{-6} T^2 - 305.1299425 \times 10^{-9} T^3 \text{ cm}^3/\text{mole.}$$

where the correlation coefficient $R^2 = 0.999950074$; and

$$V_{fsH_2O}^{I*} = 3.007437132 + 10.03634476 \times 10^{-3} T + 24.92521700 \times 10^{-6} T^2 + 54.10119605 \times 10^{-9} T^3 \text{ cm}^3/\text{mole,}$$

where $R^2 = 0.999999666$. The sum of these equations is the molar volume of liquid water as a function of temperature, namely,

$$V_{H_2O}^{I*} = 18.01703825 - 0.448184787 \times 10^{-3} T + 107.4508272 \times 10^{-6} T^2 - 251.0261511 \times 10^{-9} T^3 \text{ cm}^3/\text{mole,}$$

where $R^2 = 0.999971154$. As shown in Figure 2, the molar volume of liquid water is a minimum at 3.8°C even though its constituent volumes are without minima. The molar hard core volume decreases continuously with increasing T and the molar free

Table 1 Molar free space volume $V_{fsH_2O}^{l*}(T, p_e^{g*})$, molar hard core volume $V_{hcH_2O}^{l*}(T, p_e^{g*})$ and molar volume $V_{H_2O}^{l*}(T, p_e^{g*})$ of pure liquid water as a function of temperature.

$$R = 8.31441 \text{ joule mol}^{-1} \text{ K}^{-1}; 0.0^\circ\text{C} = 273.15 \text{ K}; M_{H_2O} = 18.015 \text{ gm mol}^{-1}.$$

T C	p_e^{g*} joule $\text{cm}^{-3} \cdot 10^4$	$V_{H_2O}^{g*}$ $\text{cm}^3 \text{ mol}^{-1}$ 10^{-4}	$V_{H_2O}^{l*}$ $\text{cm}^3 \text{ mol}^{-1}$	$\Delta H_{H_2O}^{l*+g*}$ joule mol^{-1}	$V_{hcH_2O}^{l*}$ $\text{cm}^3 \text{ mol}^{-1}$	$V_{fsH_2O}^{l*}$ $\text{cm}^3 \text{ mol}^{-1}$
0.0	6.108068	371.6596873	18.01881494	45101.23968	14.9412206	3.0775943
0.556	6.359037	357.7141543	18.01818019	45076.07860	14.9347786	3.0834015
1.111	6.618970	344.3534349	18.01764528	45055.11103	14.9292458	3.0883995
1.667	6.888555	331.5550350	18.01720819	45029.94995	14.9229530	3.0942552
2.222	7.167103	319.2852157	18.01686714	45004.78887	14.9167394	3.1001278
2.778	7.456683	307.5214842	18.01662032	44983.82130	14.9114360	3.1051843
3.333	7.755916	296.2525943	18.01646600	44958.66022	14.9053554	3.1111106
3.889	8.065490	285.4335602	18.01640249	44933.49913	14.8993645	3.1170380
4.444	8.386097	275.0643820	18.01642824	44912.53157	14.8942676	3.1221606
5.556	9.061783	255.5631293	18.01674119	44862.20940	14.8826176	3.1341236
10.0	12.269915	191.7285790	18.02127510	44673.50129	14.8410000	3.1802756
11.111	13.213808	178.7277438	18.02317881	44627.37264	14.8313880	3.1917908
16.667	18.956453	126.9943168	18.03689465	44388.34236	14.7847186	3.2521761
20.0	23.365652	104.1978698	18.04823065	44249.95640	14.7600242	3.2882065
30.0	42.415185	59.3247451	18.09454390	43822.21801	14.6919407	3.4026032
40.0	73.749800	35.2124695	18.15708778	43394.47961	14.6347643	3.5223234
50.0	123.354151	21.6999235	18.23385268	42962.54770	14.5856147	3.6482380
60.0	199.203406	13.8330685	18.32350796	42522.22877	14.5421604	3.7813476
70.0	311.622468	9.0904628	18.42516939	42077.71632	14.5044958	3.9206736
80.0	473.601064	6.1416575	18.53826891	41624.81684	14.4708152	4.0674537
90.0	701.059197	4.2538372	18.6624877	41163.53033	14.4408143	4.2216645
100	1013.253930	3.0139220	18.79766607	40689.66329	14.4129738	4.3846923
100	1013.253930	3.0139220	18.80285143	40689.66329	14.426098	4.376753
200	15548.78696	0.2290779	20.83957396	34948.74305	14.249830	6.589744
300	85926.63598	0.0390003	25.29314724	25349.79023	14.160123	11.133024
374.15	221197.69	0.0057109	57.10920483	0.0	30.490001	26.619204
374.15	221197.69	0.0057109	57.10920483	0.0	14.1	43.009205
0.0098	6.108068	371.4010201	18.01880286	45101.23968	14.9412030	3.0775998
0.0098	6.108068	371.4010201	$V_{H_2O}^{l*}$ 19.64558343	$\Delta H_{H_2O}^{l*+g*}$ 51111.96659	$V_{hcH_2O}^{l*}$ 17.2629753	$V_{fsH_2O}^{l*}$ 2.3826081

Data for p_e^{g*} (vapor pressure of water at T), $V_{H_2O}^{g*}(T)$, $\Delta H_{H_2O}^{l*+g*}(T)$ and for $V_{H_2O}^{l*}(T \geq 100 \text{ C})$ were taken from the CRC Handbook of Chemistry and Physics 53rd Edition, 1972-1973 pp. E12-E17. Factors converting from British to metric units were 1 psi = 6894.76×10^{-7} joule cm^{-3} , 1 $\text{ft}^3 \text{ lb}^{-1}$ = $1124.639717 \text{ cm}^3 \text{ mol}^{-1}$ and 1 BTU lb^{-1} = $41.93513685 \text{ joule mol}^{-1}$.

$$V_{H_2O}^{l*}(T \leq 100 \text{ C}, p_e^{g*}) = 18.01501 \rho_{H_2O}^{l*}(T, 1 \text{ atm}) e^{\kappa_{H_2O}^{l*}(T)[1.013254 - 10p_e^{g*}(T)]}$$

where

$$\rho_{H_2O}^{l*}(T, 1 \text{ atm}) \text{ kg m}^{-3} = [999.83952 + 16.945176T - 7.9870401 \times 10^{-3}T^2 - 46.170461 \times 10^{-6}T^3 + 105.56302 \times 10^{-9}T^4 - 280.54253 \times 10^{-12}T^5] [1 + 16.879850 \times 10^{-3}T],$$

and

$$10^6 \kappa_{H_2O}^{l*}(T) \text{ bar}^{-1} = [50.88496 + 0.6163813T + 1.459187 \times 10^{-3}T^2 + 20.08438 \times 10^{-6}T^3 - 658.47727 \times 10^{-9}T^4 + 410.4110 \times 10^{-12}T^5] [1 + 19.67348 \times 10^{-3}T].$$

The latter two equations are from Kell⁶.

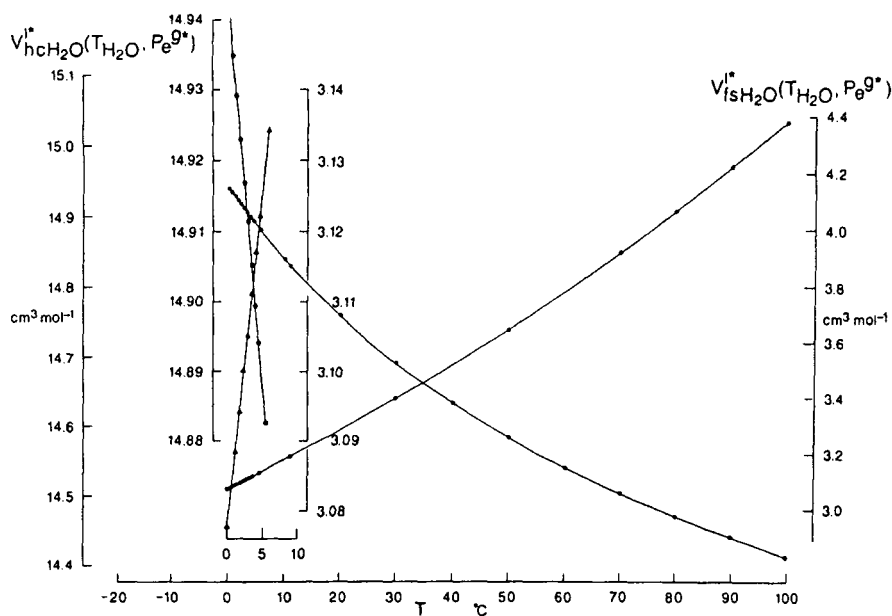


Figure 1 Molar hard core volume, $V_{hcH_2O}^*(T, p_e^{g*})$, and molar free space volume, $V_{fsH_2O}^*(T, p_e^{g*})$, of pure liquid water are plotted as a function of T from 0°C to 100°C and at its vapor pressure at T . Data are from Table 1. In the inset, these functions are redrawn to the same scale as is the molar volume of pure liquid water in the inset of Figure 2 from 0°C to 5°C.

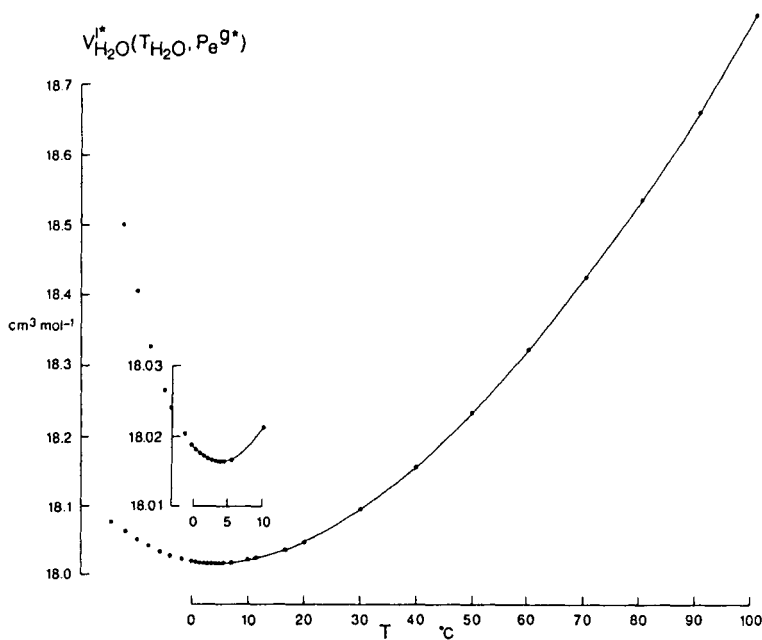


Figure 2 Molar volume, $V_{H_2O}^*(T, p_e^{g*})$, of pure liquid water is plotted as a function of T from 0°C to 100°C at its vapor pressure at T . Data are from Table 1. In the inset, the scale is the same as in the inset in Figure 1 from 0°C to 5°C.

space volume increases continuously with increasing T without inflections in either curve from 0°C to 5°C , Figure 1. The inserts of $V_{\text{H}_2\text{O}}^{l*}(T)$, Figure 2, and of $V_{\text{hcH}_2\text{O}}^{l*}(T)$ and $V_{\text{fsH}_2\text{O}}^{l*}(T)$, Figure 1, are drawn to the same scale. The cubic regression lines for these functions over the range 0°C to 4.44°C are, respectively,

$$V_{\text{hcH}_2\text{O}}^{l*} = 14.94111984 - 10.90673609 \times 10^{-3} T - 28.50052560 \times 10^{-6} T^2 + 23452.00230 \times 10^{-9} T^3 \text{ cm}^3/\text{mole},$$

where $R^2 = 0.999039846$; and

$$V_{\text{fsH}_2\text{O}}^{l*} = 3.077695120 + 9.67326311 \times 10^{-3} T + 193.0430145 \times 10^{-6} T^2 - 25218.48259 \times 10^{-9} T^3 \text{ cm}^3/\text{mole},$$

where $R^2 = 0.999760226$.

The free space volume for a water molecule in a mole of ice can be similarly calculated with Eq. (12) and is found to be $2.3826081 \text{ cm}^3/\text{mole}$ at 0.0098°C , last column, bottom row, Table 1. Thus, the molar hard core volume of ice is $17.2629753 \text{ cm}^3/\text{mole}$.

In order to calculate the molar free space volume of liquid water from Eq. (13), it was necessary to assess the molar free space volume of its vapor, $V_{\text{fsH}_2\text{O}}^{g*}$, as well as the internal tension in the cohesive force between the molecules of water vapor. It was assumed that the a and b terms for water vapor in van der Waals' equation of state provided appropriate values for these terms. Eq. (13) may be evaluated by noting that $p_{\text{H}_2\text{O}}^{g*}$ in the third term of the numerator of its exponential equals $RT/V_{\text{fsH}_2\text{O}}^{g*}$ and that $\Delta V_{\text{H}_2\text{O}}^{l*+g*}$ in the second term equals $[V_{\text{H}_2\text{O}}^{l*} - V_{\text{H}_2\text{O}}^{g*}]$. The molar volumes of liquid and vapor of water are given in the steam tables as a function of temperature. Equation (13) can be written and evaluated in the form

$$\frac{V_{\text{fsH}_2\text{O}}^{l*}}{V_{\text{H}_2\text{O}}^{g*} - b_{\text{H}_2\text{O}}^{g*}} = e^{-[\Delta H_{\text{H}_2\text{O}}^{l*+g*} - p_{\text{H}_2\text{O}}^{g*} V_{\text{H}_2\text{O}}^{l*} - V_{\text{H}_2\text{O}}^{l*}] + RTV_{\text{H}_2\text{O}}^{g*}/(V_{\text{H}_2\text{O}}^{g*} - b_{\text{H}_2\text{O}}^{g*}) - RTV_{\text{H}_2\text{O}}^{l*}/V_{\text{H}_2\text{O}}^{l*}]/RT}, \quad (13b)$$

where all values except $b_{\text{H}_2\text{O}}^{g*}$ and $V_{\text{fsH}_2\text{O}}^{l*}$ can be obtained from the steam tables as a function of T . Again, assuming that $b_{\text{H}_2\text{O}}^{g*} = 30.49 \text{ cm}^3/\text{mol}$, the molar free space volume, $V_{\text{fsH}_2\text{O}}^{l*}(T, p_{\text{H}_2\text{O}}^{g*})$, was determined by iteration using Eq. (13b) for T between 100°C and 374.15°C , the critical temperature of water, Table 1. As before, the molar hard core volumes in Table 1 were computed as $V_{\text{hcH}_2\text{O}}^{l*} = V_{\text{H}_2\text{O}}^{l*} - V_{\text{fsH}_2\text{O}}^{l*}$. Computed this way, the value of $V_{\text{hcH}_2\text{O}}^{l*}$ decreases toward $14.1 \text{ cm}^3 \text{ mol}^{-1}$ as T increases toward the critical temperature, $T_{\text{cH}_2\text{O}}$. However, at $T_{\text{cH}_2\text{O}}$ the value of $V_{\text{hcH}_2\text{O}}^{l*}$ was computed to be $30.49 \text{ cm}^3/\text{mol}$. It is obvious that as T approaches $T_{\text{cH}_2\text{O}}$ and as $p_{\text{H}_2\text{O}}^{g*}$ approaches $p_{\text{cH}_2\text{O}}$, the critical pressure of water, the value of $b_{\text{H}_2\text{O}}^{g*}$ must approach and become equal to the molar hard core volume of liquid water, that is,

$$b_{\text{H}_2\text{O}}^{g*}(T_{\text{cH}_2\text{O}}, p_{\text{cH}_2\text{O}}) = V_{\text{hcH}_2\text{O}}^{l*}(T_{\text{cH}_2\text{O}}, p_{\text{cH}_2\text{O}}) = V_{\text{hcH}_2\text{O}}^{l*}(T_{\text{cH}_2\text{O}}, p_{\text{cH}_2\text{O}}).$$

So we must conclude that $V_{\text{hcH}_2\text{O}}^{l*}(T_{\text{cH}_2\text{O}}, p_{\text{cH}_2\text{O}}) = 14.1 \text{ cm}^3 \text{ mol}^{-1}$ rather than the value of $b_{\text{H}_2\text{O}}^{g*}$ near 0°C . At the critical temperature and pressure of water, the first two terms in the numerator of the exponential of Eq. (13b) are both zero (c.f. the steam tables)

so that the remaining terms in the numerator must also sum to zero so that the right side of Eq. (13b) equals unity. That is,

$$V_{\text{H}_2\text{O}}^{g*}(T_{\text{cH}_2\text{O}}, p_{\text{cH}_2\text{O}}) - b_{\text{H}_2\text{O}}^{g*}(T_{\text{cH}_2\text{O}}, p_{\text{cH}_2\text{O}}) = V_{f\text{SH}_2\text{O}}^{l*}(T_{\text{cH}_2\text{O}}, p_{\text{cH}_2\text{O}}).$$

Since $V_{f\text{SH}_2\text{O}}^{l*}(T_{\text{cH}_2\text{O}}, p_{\text{cH}_2\text{O}}) = V_{\text{H}_2\text{O}}^{l*}(T_{\text{cH}_2\text{O}}, p_{\text{cH}_2\text{O}}) - V_{\text{hcH}_2\text{O}}^{l*}(T_{\text{cH}_2\text{O}}, p_{\text{cH}_2\text{O}})$ and since $V_{\text{H}_2\text{O}}^{g*}(T_{\text{cH}_2\text{O}}, p_{\text{cH}_2\text{O}}) = V_{\text{H}_2\text{O}}^{l*}(T_{\text{cH}_2\text{O}}, p_{\text{cH}_2\text{O}})$, it is essential that $b_{\text{H}_2\text{O}}^{g*} = V_{\text{hcH}_2\text{O}}^{l*}$ at the critical temperature and pressure of water, Table 1.

Equations (13a) and (13b) justified

The analysis leading to Eqs (13a) and (13b) and the results given in Table 1 and Figure 1 were based on two important statements. 1) The distribution of water molecules in a unit volume of liquid and vapor must be treated with reference to the molar free space volumes of liquid and vapor in these two energy states and 2) the internal tensions in the cohesion between water molecules in both the liquid and vapor phases must be included in the derivation of the work done during vaporization. These statements and Eqs (13a) and (13b) are justified if the values of $V_{f\text{SH}_2\text{O}}^{l*}$ and $V_{\text{hcH}_2\text{O}}^{l*}$ computed from these equations are reasonable and if the computed values of $V_{f\text{SH}_2\text{O}}^{l*}$ and $V_{\text{hcH}_2\text{O}}^{l*}$ are absurd when the novel aspects of Eqs (13a) and (13b) are ignored.

At 0°C, the molar free space of liquid water is $3.077594341 \text{ cm}^3\text{mol}^{-1}$ and the ratio of the moles of water in a unit free space volume of vapor to the moles in a unit of free space volume of liquid is $8.280746323 \times 10^{-7}$ according to the left side of Eq. (13a) and the data in Table 1. From data in Table 1, the value computed for the right side of Eq. (13a) is $8.280746331 \times 10^{-7}$. These two values differ by less than 8×10^{-16} . At 0°C, the most important terms in the numerator of the exponential in Eq. (13a) are the term for the enthalpy of vaporization and the term derived from the internal tension in liquid water. The two middle terms have little effect on the value of the exponential at 0°C. If the term derived from the tension in liquid water were neglected, then the right side of Eq. (13a) would equal 2.373×10^{-9} , which, of course, no longer equals the left side which it must. If the unit volumes had included the molar hard core volumes of liquid and vapor, then the calculation of the distribution of moles of water in the liquid and vapor phases in equilibrium would have been $n_{\text{H}_2\text{O}}^{g*}/n_{\text{H}_2\text{O}}^{l*} = V_{\text{H}_2\text{O}}^{l*}/V_{\text{H}_2\text{O}}^{g*} = 48.4820 \times 10^{-7}$, which, of course, can not be reconciled with any evaluation of the right side of Eq. (13a).

At 100°C, the molar free space of liquid water is $4.384692292 \text{ cm}^3\text{mol}^{-1}$ so that the value of the left side of Eq. (13a) is $1.456286042 \times 10^{-4}$ whereas the right side equals $1.456286042 \times 10^{-4}$ and these differ by less than 1×10^{-13} . All terms in the numerator of the exponential are important for the evaluation of the right side of Eq. (13a) at 100°C. Without the last term (the term from tension in liquid water), the right side would equal $200.1601836 \times 10^{-8}$ and this would mean that the molar free space volume of water was only 0.06026 cm^3 , i.e. absurdly low. Without the third term (the term from tension in the vapor), the right side would equal $1.464934486 \times 10^{-4}$. Without the second term, the right side would equal $1.457180350 \times 10^{-4}$. All of these values differ significantly from the value of the left side. Therefore all terms

must be included in the evaluation of the right side of Eq. (13a). On the other hand, had the unit volumes included the molar hard core volumes of liquid and vapor then $n_{\text{H}_2\text{O}}^{g^*}/n_{\text{H}_2\text{O}}^{l^*} = V_{\text{H}_2\text{O}}^{l^*}/V_{\text{H}_2\text{O}}^{g^*} = 6.243261077 \times 10^{-4}$ at 100°C , which cannot be equated to any evaluation of the right side of Eq. (13a). At the critical temperature and pressure of water, the first two terms in the exponential of Eq. (13b) are zero so that the molar hard core volumes of liquid and vapor water are about $14.1 \text{ cm}^3 \text{ mol}^{-1}$.

CONCLUSIONS

The Boltzmann energy distribution principle and the equation of state for atoms and molecules in any phase are applicable to pure species *i* only if the hard core volume of the atoms or molecules is excluded from their molar volume. Only the free space volume available for the random translational motion of the centers of mass of atoms or molecules is to be used in these two fundamental relationships. The internal tension in the cohesion between atoms or molecules of a single species in any phase also depends on the molar free space volume. Thus, the only workable analysis of the thermodynamic data pertaining to liquid water and its vapor from 0°C to 100°C must be based on unit volumes which exclude the hard core volumes of water in its liquid and vapor phases. The analysis must also include the effects of cohesion between water molecules, in both liquid and vapor phases, on the pressure volume work during vaporization.

When species *i* is the solvent A in a solution, the internal pressure exerted by solute and solvent against a free boundary of the solution exceeds the internal pressure exerted by pure solvent against a free boundary by an amount equal to the osmotic pressure of the solvent in the solution, π_A^l , (Hammel⁷). This lowers the vapor pressure of the solvent in the solution exactly as would increasing the applied tension in pure A an amount π_A^l . The extent to which this alters the distribution of molecules between the vapor and liquid phases may be determined by modifying the numerator of the exponential in Eq. (13) so as to include the effects of the increased tension applied to the pure water. The increased tension will have small (but not insignificant) effects on the enthalpies of the liquid and the vapor and on the molar volumes of the liquid and the vapor. However, the primary effect of the increased tension will be on the internal energy of the liquid, i.e. a term $-\pi_A^l V_A^l$ must be added to the numerator of Eq. (13). Thus, the work resulting from change of applied tension during vaporization becomes $(p_A^l + \pi_A^l)V_A^l$. When the solvent A is water, Eq. (13a) for pure water becomes

$$\frac{V_{f_{\text{H}_2\text{O}}}^{l^*}}{V_{\text{H}_2\text{O}}^{g^*} - b_{\text{H}_2\text{O}}^{g^*}} = e^{-[\Delta H_{\text{H}_2\text{O}}^{l^*+g^*} + p_e^* V_{\text{H}_2\text{O}}^{l^*} + a_{\text{H}_2\text{O}}^{l^*} V_{\text{H}_2\text{O}}^{l^*} - RT V_{\text{H}_2\text{O}}^{g^*} V_{\text{H}_2\text{O}}^{l^*} - \pi_{\text{H}_2\text{O}}^l V_{\text{H}_2\text{O}}^{l^*}]/RT}, \quad (13c)$$

where

$$\Delta H_{\text{H}_2\text{O}}^{l^*+g^*} = H_{\text{H}_2\text{O}}^{g^*}(T, p_e^*(T, p_e^* - \pi_{\text{H}_2\text{O}}^l)) - H_{\text{H}_2\text{O}}^{l^*}(T, p_e^*(T, p_e^* - \pi_{\text{H}_2\text{O}}^l) - \pi_{\text{H}_2\text{O}}^l),$$

$$V_{\text{H}_2\text{O}}^{l^*} = V_{\text{H}_2\text{O}}^{l^*}(T, p_e^*(T, p_e^* - \pi_{\text{H}_2\text{O}}^l) - \pi_{\text{H}_2\text{O}}^l), \quad V_{\text{H}_2\text{O}}^{g^*} = V_{\text{H}_2\text{O}}^{g^*}(T, p_e^*(T, p_e^* - \pi_{\text{H}_2\text{O}}^l))$$

and where $V_{f_{\text{H}_2\text{O}}}^{l^*} = V_{f_{\text{H}_2\text{O}}}^{l^*}(T, p_e^*(T, p_e^* - \pi_{\text{H}_2\text{O}}^l) - \pi_{\text{H}_2\text{O}}^l)$. The left side of Eq. (13c) also equals the ratio of the moles of water in the vapor phase to the moles of water in

the liquid phase, $n_{\text{H}_2\text{O}}^{g^*}/n_{\text{H}_2\text{O}}^{l^*}$, i.e. the distribution of molecules between the two phases when the applied tension in the pure liquid water was increased by $\pi_{\text{H}_2\text{O}}^l$. This distribution is the same for the water in an aqueous solution in which its osmotic pressure is $\pi_{\text{H}_2\text{O}}^l$. The fact that Eq. (13c) yields the distribution of water between its vapor and liquid phases when the pressure applied to the pure liquid water is decreased to $p_e^{g^*}(T, p_e^{g^*} - \pi_{\text{H}_2\text{O}}^l) - \pi_{\text{H}_2\text{O}}^l$, reinforces the validity of Eq. (13a) which accounts for the distribution when the pressure applied to the pure liquid water is $p_e^{g^*}(T, p_e^{g^*})$. Tension in the cohesive force between the molecules of pure liquid water, whether altered by the thermal motion of its molecules reflecting from its boundaries or caused by an applied negative pressure, effects the internal energy of the liquid water. The change in this internal energy during the transition to vapor is an essential part of the pressure-volume work of vaporization and it must be included when applying the Boltzmann distribution principle to liquid in equilibrium with its vapor.

Calculations of the molar free space and molar hard core volumes of pure liquid water as a function of temperature reveal that $V_{fs\text{H}_2\text{O}}^{l^*}$ increases with increasing temperature without an inflection between 0°C and 5°C and that $V_{hc\text{H}_2\text{O}}^{l^*}$ decreases with increasing temperature without an inflection between 0 and 5°C even though the molar volume of water, $V_{\text{H}_2\text{O}}^{l^*}$, has a minimum at 3.8°C. At the critical temperature and pressure of water, the molar free space and hard core volumes of liquid water are identical with these volumes of water vapor.

References

1. M. L. McGlashan, *Chemical Thermodynamics*. Academic Press, London (1977).
2. L. B. Loeb, *The Kinetic Theory of Gases*, p. 149, Second Edition. McGraw-Hill Book Co., Inc. New York (1934).
3. S. Glasstone, *Textbook of Physical Chemistry*. Second Ed. pp. 270–272. D. Van Nostrand Co. N.Y. (1946).
4. M. J. Perrin, *Brownian Movement and Molecular Reality*, Taylor and Francis, London (1910).
5. R. P. Feynman, R. B. Leighton and M. Sands, *The Feynman Lectures on Physics*, Chapt. 41 Vol. I. Addison-Wesley Publishing Co. Reading, Mass. (1963).
6. G. S. Kell, Density, thermal expansivity, and compressibility of liquid water from 0° to 150°C: correlations and tables for atmospheric pressure and saturation reviewed and expressed on 1968 temperature scale. Eqs (16) and (20). *J. Chem. Eng. Data* **20**, 97–105 (1975).
7. H. T. Hammel, Internal pressures, partial molar free space volume and Boltzmann's principle applied to species *i* in solution. (To be submitted to *Physics and Chemistry of Liquids*.)