GROSS VAPORIZATION

Definitions

Vaporization: Vaporization is the process by which molecules leave their previous liquid or solid phase or attachment to a substrate and become gas molecules.

In some papers, the term *sublimation* is used to describe vaporization directly from the solid phase, while the term *evaporation* is restricted to vaporization from the liquid phase. Since the process is the same in each case and the resulting gas molecules indistinguishable from one another, this is a distinction without a measurable difference. We shall use both the term vaporization and—on occasion—the term evaporation to describe either process.

Substrate: Vaporization takes place from any surface bearing or containing water molecules. Most commonly, this surface is water or ice. Sometimes, however, it is the surface of an atmospheric particulate, a blade of grass, a rock face, or the glass surface of a window. When we are not particularly concerned with the nature of this surface, but primarily with the process of vaporization itself, we will simply refer to this undifferentiated surface as the substrate.

Gross Vaporization: Gross vaporization refers to the process of vaporization without any consideration of the reverse process of gross condensation. Throughout this paper, use of the terms vaporization, evaporation, and sublimation will refer to gross vaporization. If net vaporization is meant, net vaporization will be specified.

Net Vaporization: Net vaporization occurs when the rate of gross vaporization exceeds the rate of gross condensation.

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Water Vapor and Steam: It is customary in physics texts to refer to gaseous water at temperatures greater than the boiling point as steam. Gaseous water at temperatures less than the boiling point is referred to as water vapor.

Again, this is a distinction without a relevant difference. The processes by which the gas molecules are formed are identical in each case. Moreover, except for differences in the mean temperature of the gas as a whole, there are no measurable differences in the two populations. Both populations will contain molecules whose individual thermal energies are identical to one another. Consequently, we will use the term vapor to refer to all gaseous water molecules, regardless of both the mean temperature of the population and the boiling point temperature at the ambient pressure.

The Zone of Attraction

Zone of Attraction: Every aqueous substrate is surrounded by a zone of attraction. This is a volume of space where the speeds of vapor molecules leaving the surface of the substrate are diminished by the various attractive forces of that substrate. The zone extends out from the substrate as far as that diminution of speed exists. The zone is not necessarily uniform in its extension from the surface, but varies topographically as the individual attractive forces vary from place to place over the substrate.

Surface Tension: This zone of attraction is created by three different groups of forces. The first group is those forces of attraction that exist between water molecule and water molecule. The strongest force of this group is the hydrogen bond. It is this bond and the other forces that create what we see as surface tension in liquid water and surface force and surface energy in ice.

Diagrams of surface tension often show representations of the surface molecules forming a smooth unbroken "skin" to keep the sub-surface molecules within. This is artistic license. In reality, this surface network is continually being bent outward by the impulses transferred to it by the molecules within. In addition it is continually being bent inward by the bombardment of air and vapor molecules. It is hardly "smooth".

This “skin” is also continually being broken and ruptured as the more energetic molecules within break through the bonds of surface tension to escape; and as high energy air and vapor molecules penetrate it from without. Sometimes, it is the surface molecule that escapes or submerges, leaving a rapidly-filled gap in the net.

Nevertheless, this “skin” effect is very real and the forces that create it are extremely strong ones. As we shall see later, the proportion of water molecules that manage to break these bonds is quite small at most tropospheric temperatures.

Hygroscopic Forces: The second group of attractive forces is due to the hygroscopic nature of one or more condensation nuclei or a substrate of some kind. These forces may also include the hydrogen bond, but the attraction is between water molecules and some other substance. Common cloud condensation nuclei include silica, salt, and various sulfates. Hygroscopic forces act to increase both the strength and the range of the zone of attraction.

Ionic Forces: The third set of attractive forces is due to ionic attraction. This ranges all the way from ion mediated nucleation (IMN) all the way to the strong attraction between an ionized substrate and ionized vapor molecules. The power of ionized water molecules to attract other water molecules is graphically illustrated by the condensation trails in a Wilson cloud chamber.

Moreover, in the free atmosphere pure water does not exist. All atmospheric water and ice is a solution of whatever solutes happen to be available at that time and place. Raoult’s Law mandates that solutions will vaporize at a slower rate than the rate of the pure solvent. This means that the more concentrated the solution, the less the rate of vaporization. Cloud droplets formed about solutes such as sea salt may well vaporize at a slower rate than cloud droplets that form about non-solutes.

Other Molecules and the Zone of Attraction: For our purposes, we are concerned only with the attraction of the aqueous substrate for vapor molecules. It may well be, however, that other gaseous molecules are attracted as well.

Spatial Variation of the Attractive Forces: Irregularly-shaped substrates produce irregular zones of attraction. Cloud condensation nuclei are often irregular in shape. The points of ice crystals exert weaker attractive forces than do the edges, and the edges exert weaker attractive forces than the flats.
In both droplets and ice crystals, ionic forces of attraction vary with the concentration of solutes and ionized areas from place to place on the substrate.

Because of these variations, the escape velocity needed by a water or ice molecule to leave the zone of attraction and become a vapor molecule will likewise vary from place to place on the substrate.

Departure and Outflow

Maxwell Distribution of Thermal Energies: There are very good reasons for believing that gases, liquids, and solids at the same temperature have the same mathematical distribution of molecular kinetic energies. The arguments, however, are not particularly germane to the present discussion. We will simply postulate that the same mathematical distribution exists in all three phases.

The distribution of kinetic energies of those vapor molecules whose next interaction is with an object of interest (here, a substrate) during some appreciable period of time is:

$$d\bar{f}_i = \frac{\bar{f}_i}{\mathrm{k_B}\bar{T}} \exp - \frac{u_i}{\mathrm{k_B}\bar{T}} du_i \qquad \text{VAP01}$$

Here, $\bar{f}_i$ is the mean number of molecular interactions per square meter per second, u_i is the individual molecular kinetic energy of translation (measured normal to the surface) of those molecules whose next interaction is with that surface.

Since we have postulated that the distribution of energies of translation is the same for water molecules and vapor molecules, we can rewrite VAP01 to read:

$$d\bar{f}_{-i} = \frac{\bar{f}_i}{\mathrm{k_B}\bar{T}} \exp - \frac{\underset{\sim}{u}_{-i}}{\mathrm{k_B}\bar{T}} d\underset{\sim}{u}_{-i} \qquad \text{VAP02}$$

Here, the ***–i*** subscript indicates that the molecules under observation have had their last interaction with the object of interest (the substrate), rather than their next interaction. They are leaving the surface, not arriving at it. Expression VAP01 measures inflow and arrivals at the substrate, while expression VAP02 measures outflow and departures. The dimensions of both equations are number per unit area per unit time—or, more precisely, the ***probability*** associated with that number.

Note: In this expression and in future expressions, we will use the *tilde* (~) under the parameter to indicate that the parameter applies to water molecules in the expression.

Thermal Distributions: In *The Nature of Gas Temperatures*, we defined temperature to be a function of the mean value of the total kinetic energies (translation, rotation, and vibration) expressed normal to the thermometric surface. This definition was expressed in the formula:

$$\bar{T} = \frac{\bar{u}_i^{\Sigma}}{\mathrm{k_B}} \qquad \text{NGT04}$$

If we are discussing the temperature of the sub-system of water molecules leaving a surface, we can also say:

$$\underset{\sim}{\bar{T}} = \frac{\underset{\sim}{\bar{u}}_{-i}^{\Sigma}}{\mathrm{k_B}} \qquad \text{VAP03}$$

Here, $\underset{\sim}{\bar{u}}_{-i}^{\Sigma}$ is the mean total kinetic energy (measured normal to the evaporating surface) of that sub-set of water molecules leaving the surface during some appreciable period of time, and the other two terms have their previous meanings.

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The concept of individual molecular "temperatures": Equation VAP03 shows that the temperature of a sub-population of evaporating gas molecules is a direct function of the mean kinetic energy of those molecules normal to the surface at the moment of evaporation. It does not stretch a point too much to apply this concept to individual molecules. That is,

$$\underset{\sim}{\boldsymbol{T}}_{-i} = \frac{\underset{\sim}{\boldsymbol{u}}_{-i}^{\boldsymbol{\Sigma}}}{\mathbf{k}_{\mathbf{B}}} \qquad \text{VAP04}$$

Here, $\underset{\sim}{\boldsymbol{T}}_{-i}$ is the temperature of an individual water molecule having total kinetic energy $\underset{\sim}{\boldsymbol{u}}_{-i}^{\boldsymbol{\Sigma}}$ normal to the surface at the moment of leaving that surface.

If we combine equations VAP02 and VAP04, we get the distribution function of molecules leaving the surface of the substrate in terms of their individual molecular temperatures:

$$d\underset{\sim}{\overline{\boldsymbol{f}}}_{i} = \frac{\overline{\underset{\sim}{\boldsymbol{f}}}_{i}}{\underset{\sim}{\boldsymbol{T}}} \mathbf{exp} - \frac{\underset{\sim}{\boldsymbol{T}}_{-i}}{\underset{\sim}{\boldsymbol{T}}} d\underset{\sim}{\boldsymbol{T}}_{-i} \qquad \text{VAP05}$$

Note that the most probable molecular temperatures are close to 0°K[1]; and that the higher the individual molecular temperature the less likely some surface molecule is to have that temperature. This is entirely apart from the selective process inherent in the escape mechanism itself, where the "hotter" molecules are the only ones allowed to escape.

Selection and Escape

Escape Velocity: For any particular bonding situation, there will exist some molecular velocity along the proximity axis that represents the escape velocity, $\underset{\sim}{\boldsymbol{v}}_{-i}^{\boldsymbol{escape}}$. Molecules moving away from the substrate with less than that critical

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[1] Quantum considerations mandate against a true zero value.

velocity will not escape to become free vapor molecules. Molecules moving away from the substrate that possess that velocity or greater will escape[2].

Diminution of Escape Velocities: As a prospective vapor molecule moves away from the surface, the various attractive forces serve to reduce its velocity along the proximity axis and consequently its kinetic energy of translation along that same axis. This means that when the successful molecules join the vapor phase, they will have less thermal energy than when they first left the substrate. This process may be expressed as:

$$\underset{\sim}{\boldsymbol{u}}_{-i}^{vapor} = \underset{\sim}{\boldsymbol{u}}_{-i}^{substrate} - \underset{\sim}{\boldsymbol{u}}_{-i}^{escape} \qquad \text{VAP06}$$

Note that the loss of energy (heat of vaporization) is solely along the proximity axis. There is no reason to believe that any of the other kinetic energies manifested in any of the other degrees of freedom are affected or diminished in any way.

Derivation of Escape Energy: We may readily derive a value for the escape energy by simply dividing the experimental heat of vaporization per unit mass of a substance by the number of molecules in that unit of mass. This will produce:

$$\underset{\sim}{\boldsymbol{u}}_{-i}^{escape} = \frac{\underset{\sim}{\boldsymbol{Q}}^{vaporization}}{\underset{\sim}{\boldsymbol{N}}} \qquad \text{VAP07}$$

Here, $\underset{\sim}{\boldsymbol{u}}_{-i}^{escape}$ is the kinetic energy of escape (measured normal to and away from the vaporizing surface), $\underset{\sim}{\boldsymbol{Q}}^{vaporization}$ is the heat of vaporization per unit of mass and $\underset{\sim}{\boldsymbol{N}}$ is the number of water molecules per unit of mass.

Escape Velocity for Liquid Water at NTP: An approximation of the escape energy for a molecule of liquid water at NTP may be calculated by using the values found in *Water: Some Useful Values*.

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[2] Some of the escaping molecules, of course, will be struck by incoming air or vapor molecules and returned to the substrate. Since these molecules cannot be distinguished from vapor molecules arriving from the surrounding atmosphere, we must treat them as simply another part of the inflow. The proportion of such "rejects" is not very large.

Let us postulate a water molecule mass of 2.99 x 10^{-26} kilograms (the mass of the most common isotope of water) as the individual molecular mass ($\underset{\sim}{\dot{\boldsymbol{m}}}_{-i}$). Then, the escape velocity becomes:

$$\underset{\sim}{\boldsymbol{v}}_{-i}^{escape} = \left(\frac{2\underset{\sim}{\boldsymbol{u}}_{-i}^{escape}}{\underset{\sim}{\dot{\boldsymbol{m}}}_{-i}}\right)^{\frac{1}{2}} \qquad \text{VAP08}$$

This gives us an escape velocity ($\underset{\sim}{\boldsymbol{v}}_{-i}^{escape}$) of some 884 meters per second from a surface of pure water at NTP under laboratory conditions.

The Escape Population: To ascertain the proportion of surface molecules likely to have this escape velocity or greater normal to and away from the surface of the substrate, we have to know the standard deviation ($\boldsymbol{\sigma}$) of the speeds along the proximity axis of the surface population. This is given by the expression:

$$\boldsymbol{\sigma} = \left(\frac{\mathbf{k}_{\mathbf{B}}\bar{\boldsymbol{T}}}{\underset{\sim}{\dot{\boldsymbol{m}}}}\right)^{\frac{1}{2}} \qquad \text{VAP09}$$

This gives us a root-mean-square speed ($\boldsymbol{\sigma}$) of some 355 meters per second.

That makes the ratio of $\underset{\sim}{\boldsymbol{v}}_{-i}^{escape}$ to $\boldsymbol{\sigma}$ equal 2.49. The area under a normal curve to the left of the ordinate of 2.49 standard deviations is 0.0128. This is the proportion of the surface population that possesses velocities normal to and away from the surface equal to or greater than the escape velocity.

If we assume (this is the weakest part of the argument) that the subsurface impulse flux toward the surface is $\underset{\sim}{\bar{\boldsymbol{n}}}_p\underset{\sim}{\bar{\boldsymbol{v}}}_p$ (see *Molecular Speeds and Velocities*), this gives us a mean impulse flux of some 4.74 x 10^{30} impulses per unit area and time. Multiplying that value times the escape proportion given above gives us an escaping population of molecules of some 6.06 x 10^{28} per unit area of surface in unit time. All of this is delineated in **Table WSV06** in *Water: Some Useful Values*.

Therefore, the odds of a water molecule breaking away from a plane surface of water at 0° are a little bit better than one in a hundred attempts. This success ratio goes up as the temperature increases.

Isotope Selection: Because escape is based on velocity and not energy, lighter isotopes are more likely to escape than heavier ones. This is just the opposite of the condensation process, where heavier molecules are more likely to be captured by the zone of attraction than are the lighter ones. The net effect of these two selection processes is that—in the absence of replenishment—the mean molecular mass of a water droplet will increase over time.

Vaporization from Ice: Weaker bonding at the points and edges of ice crystals leads to differential rates of vaporization. The points go first, becoming rounded. Then, the edges become rounded. This same differentiation, of course, takes place in the melting process. The points melt first, then the edges. The general effect of these processes is one of rounding.

Water droplets have a very strong tendency to adopt a spherical shape even when the condensation nucleus or substrate is irregular. The tendency in ice is not as strong and nowhere near as fast, but it is still there.

Heat of Vaporization

Transfer of Enthalpy during Vaporization: The net transfer of mass from the liquid and/or solid phase to the vapor phase results in a net gain in enthalpy for the vapor phase and a net loss of enthalpy for the evaporating phase. This is always true.

However, this does not mean that the resulting cooling of the evaporating surface results in an equivalent warming of the vapor system. If the evaporating surface is cooler than the air, the net result may be a cooling of the air despite the increase in enthalpy.

Moreover, the loss of enthalpy by the substrate is not balanced by the gain in enthalpy by the atmosphere. The enthalpy lost by the diminution of escape velocities and energies due to intermolecular forces of attraction must be carried on the books as latent heat.

It should be noted that latent heat is not real heat. It cannot be either measured or detected—although it can be calculated. It is strictly a bookkeeping device.

Because enthalpy and heat are **totals**, whereas temperature is an **average**, it is entirely possible to add heat (enthalpy) to a system and effect a reduction in that system's temperature. And, as we shall see in *Gross Condensation*, it is also possible to remove heat (enthalpy) from a system and simultaneously effect an increase in that system's temperature.

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Summary of Vaporization Concepts:

01. Every surface of water or ice in the atmosphere undergoes continual gross vaporization. Every non-water surface that carries one or more transient water molecules undergoes continual gross vaporization. This process is spontaneous and ubiquitous. It is not necessary to add heat to a substrate to bring about vaporization.

02. The amount of gross vaporization that takes place from any particular surface at any particular time depends upon the relative strengths of the intermolecular bonding forces on the one hand and the intensity of thermal agitation (temperature) on the other.

03. Water molecules strongly attract one another. The various forces of water to water attraction are subsumed under the rubric of surface tension. It is a very strong set of forces.

04. The bonding forces also vary with the hygroscopic nature of the substrate. Some materials are strongly hygroscopic, some less so, some neutral, and some actually repel water.

05. The third set of forces involves ionization. Ionized substrates can be powerful condensation nuclei, and can attract ionized water molecules that might otherwise be unattracted to the substrate.

06. The bonding forces vary with the topology of the surface, especially as this topology affects the number of other molecules in close enough proximity to exercise their attractive forces.

07. The bonding forces vary with the various solutes dissolved in the water or ice. As a general rule, these solutes increase the strength of the bonding forces.

08. The combination of the various attractive forces in the zone of attraction may attract gas molecules other than simply vapor molecules.

09. The distribution of thermal energies in gases, liquids, and solids is postulated to take the same form in each of the phases. Phases with the same temperature are assumed to share the same thermal mean and the same distribution of kinetic energies of translation.

10. Thermal agitation, specifically kinetic energy of translation directed away from the surface, varies with surface temperatures. No matter what that surface temperature is, however, some molecules will have sufficient thermal energies to escape the bonding forces.

11. Vaporization is a strongly selective process. Only the hotter (higher kinetic energy of translation) molecules are able to vaporize. This diminishes the mean temperature of those that remain, hence cooling the evaporating surface.

12. At NTP, for a plane surface of liquid water, a bit over one percent of the molecules moving away from the surface will have enough velocity to completely escape and are thus able to vaporize.

13. Because escape is based on velocity, lighter isotopes are more likely to vaporize than heavier ones. This increases the mean molecular mass of those that remain.

14. Vaporization from ice varies with location of the molecule on the crystal surface. Points vaporize first, followed by edges.

15. Vaporization increases the enthalpy of the vapor system and decreases the enthalpy of the evaporating system.

16. Overcoming the bonding forces reduces the kinetic energy of the escaping molecules and therefore the enthalpy of the system as a whole. This loss of energy must be carried on the books as latent heat.

17. The temperature of the resulting vapor system may be increased or decreased or remain unchanged by the vaporization process. The result depends upon the relative temperatures and masses of the evaporating surface and the vapor system and upon the strength of the bonding forces.

18. In considering heat transfer and temperature changes, it is essential to keep in mind that heat is a total while temperature is an average. This is particularly important in understanding the nature of latent heat.