

## GROSS SUBLIMATION

### Introduction

**Sublimation** is the process by which a molecule of a solid phase of a substance leaves the surface of that substance and becomes a gas molecule. At no time during that transformation is that molecule a part of a liquid phase. In this paper, we will concern ourselves only with the sublimation of solid water into water vapor.

**Net Sublimation** is gross sublimation minus gross deposition. When the term sublimation is used in this series without a modifying adjective, gross sublimation is intended. If net sublimation is intended, net sublimation will be specified.

**Ubiquity of Sublimation:** Much of the Earth's surface is permanently covered by ice and snow—particularly in the polar areas. Many parts of the mid-latitudes are seasonally covered by ice and snow during the cooler months. Even in the tropics, mountain summits will often be snow and ice covered.

Clouds cover more than sixty percent of the Earth's surface, and are usually composed of liquid water droplets. However, ice crystals begin to appear when cloud temperatures drop below  $-5^{\circ}\text{C}$  and most clouds will be largely composed of ice crystals at cloud temperatures below  $-20^{\circ}\text{C}$ . All in all, the interface between solid water and the Earth's atmosphere is fairly ubiquitous.

**Spontaneity of Sublimation:** Wherever and whenever this interface occurs, sublimation occurs. That is, ice molecules leave the surface of the ice and become vapor molecules without becoming liquid water molecules first. This sublimation is spontaneous. It does not need any triggering event. It does not need any outside

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source of heat. The mathematics of probability ensures that sublimation happens under any combination of ice surface temperature and bonding forces.

**Genesis of Sublimation:** Generally speaking, the rate at which this sublimation occurs is strictly a function of the characteristics of the ice surface, and is largely independent of the characteristics of the overlying or surrounding atmosphere.

### Dynamic Balance

Like so much else in the atmosphere, the process of gross sublimation can be viewed as a dynamic balance between two sets of opposing forces: constraining forces that tend to bond individual ice molecules to one another and to a substrate; and liberating forces that tend to stretch, bend, and break those bonds.

**Constraining Forces:** Constraining forces are essentially forces of intermolecular attraction. They bind ice molecules to one another and to the substrate. They constrict and constrain molecular movements. They force the ice molecules into fairly rigorous alignments with one another. They oppose random movements of all kinds. They support spatially aligned movements and temporally rhythmic movements. They oppose any translatory movement of the molecules and they oppose and random movements. They especially oppose any attempt of an ice molecule to leave the ice surface to become a vapor molecule.

**Liberating Forces:** Liberating forces are generally keyed to temperature and the thermal activity that temperature measures. Temperature measures the means of the various intermolecular motions within their equally various intermolecular constraints. These individual ice molecules vibrate and librate (bend and flex their intermolecular axes) within the constraints of their solid phase. On occasion, they will rotate and move about from place to place.

The variety of these movements is such that—at any given instant—a wide distribution of molecular impulses is being received by the ice surface molecules from ice molecules below the surface. Statistical mechanics ensures that at least some of those impulses are of sufficient magnitude to enable some of those surface molecules to break their restraining bonds and become vapor molecules.

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Since temperature is a measure of this molecular vigor, the higher the ice temperature the more vigorously the ice molecules try to break the bonds that bind them together. Consequently, the higher the ice surface temperature, the greater the proportion of surface molecules that break loose of these constraining bonds and become vapor molecules. This is gross sublimation.

### The Zone of Attraction

**Zone of Attraction:** Every glacial substrate is surrounded by a zone of attraction. This is the volume of space where the speeds of vapor molecules leaving the surface of the substrate are decelerated by the various attractive forces of that substrate. At the same time, it is the volume of space where the speeds of vapor molecules approaching the surface of the substrate are accelerated by the various attractive forces of that substrate.

The zone extends out from the substrate as far as those effects are evident. The zone is not necessarily uniform in its extension from the surface, but varies topographically and temporally as the individual attractive forces vary from place to place and from time to time over the substrate. This zone of attraction is created by many different forces. It is useful to group some of these forces together because it is often difficult to separate them experimentally.

**Surface Energy:** The most obvious group is those forces of attraction that exist between water molecules and water molecules. The strongest force of this group is the hydrogen bond. It is this bond and other similar attractive forces that create what we see as surface tension in water and surface energy in ice.

Diagrams of surface energy in ice often show representations of the surface molecules bonding together into a smooth unbroken and regular two-dimensional planar network. This is artistic license. In reality, this surface is extremely irregular and always three-dimensional. Transient molecular impulses continually stretch and bend the intermolecular bonds along all three axes of movement. In addition, surface molecules frequently break loose from these bonds and fly away, to be quickly replaced by a nearby ice molecule. “Frequently” is actually a gross understatement. At  $-25^{\circ}\text{C}$ , the average surface ice molecule is replaced some thirty billion times each second.

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These subsurface impulses range from the gentlest of “nudges” through impulses great enough to break one or more (but not all four) of a surface molecule’s hydrogen bonds and on to powerful blows that blast a surface molecule from all of its bonds and send it flying into space away from the surface at speeds many times the speed of sound.

Even when the impulse is insufficient to completely break all four of the surface molecule’s H-bonds it may break one, two, or three of them. This leaves the surface molecule still attached to the surface but aligned with one of its polar ends attached and the other “dangling”. Such dangling but still aligned molecules form what are called “quasi-liquid layers” (qls).

At the same time, this surface network is continually being bombarded by vapor molecules with a variety of kinetic energies. Almost all of these vapor molecules “stick”. The depositing vapor molecules will eventually align themselves with the ice molecules and share that kinetic energy. Some of the high-velocity vapor molecules will break through the surface layer of molecules and penetrate deeper into the ice. This is especially true if that surface layer is a quasi-liquid layer.

Finally, non-water molecules of the atmosphere also strike the ice surface. Most will be adsorbed to the surface for some period of time. Since these air molecules are not subject to the same attractive forces as are vapor molecules, some of them will rebound from the surface of the ice and immediately return to the atmosphere. Some of the adsorbed molecules will be returned later to the overlying air when impelled from below, and some will be absorbed into solution in the ice.

Thus we see that the ice surface consists of molecules in perpetual motion. These motions result in a variety of intermolecular distances and angles. These intermolecular distances and angles are constantly changing as molecular impulses are transmitted from molecule to molecule. The surface of the ice is hardly ever smooth, and is continually being broken—both by ice molecules sublimating and by incoming high-velocity humid air molecules. The crystalline surface may be covered by patches of quasi-liquid layers or many superimposed complete layers of them. Finally, it is littered with other adsorbed gas molecules and (on a considerably larger scale) a wide variety of atmospheric particulates.

Nevertheless, this surface bonding effect is very real and the forces that create it are fairly strong ones. The proportion of ice molecules that manage to

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break these bonds is small (in the parts per hundred range) at common atmospheric temperatures. Generally speaking, surface energy makes up a bit over one-eighth of the total forces bonding an ice molecule to the ice surface.

**Ionic Forces:** A very powerful set of attractive forces is due to ionic attraction. This ranges from ion mediated nucleation to the strong attraction between an ionized substrate and ionized ice molecules. At the normal range of tropospheric temperatures, ice crystals tend to possess a substantial negative electrostatic charge.

Ice, however, is self-ionizing; and atmospheric ice is often additionally ionized by winds, lightning, and other atmospheric phenomena. Finally, the process of vaporization itself tends to ionize the ice surface as departing molecules may leave behind an electron or two. Strong liberating impulses may actually fragment the molecule or its common dimer and result in the vaporization of a hydronium ion ( $\text{H}_3\text{O}^+$ ) or a hydroxide ion ( $\text{OH}^-$ ).

In the free atmosphere, pure ice does not exist. All atmospheric ice is a solution of whatever solutes happen to be available at that time and place. Raoult's Law mandates that solutions will sublime at a slower rate than the rate of the pure solvent. This means that the more concentrated the solution, the less the rate of sublimation. Cloud crystals formed about icing nuclei that are also solutes generally sublime at a slower rate than cloud crystals that form about non-solutes.

When and where quasi-liquid layers exist, these layers are often chemically-enhanced and more highly ionized than the true ice below. This is because pure water freezes at a higher temperature than water containing solvents. As a body of water gradually freezes, the remaining liquid portion contains a higher and higher concentration of solvents. Many of them will end up in the quasi-liquid layers.

**Quasi-Liquid Layers (QLL):** Studies show that as ice warms to near the melting point, the abundance of quasi-liquid layers increases—both in the ice surface area covered and in the thickness of the layers. These are layers where the surface molecules are bonded to the molecules below with fewer than four hydrogen bonds. Consequently, the molecules align themselves normal to the surface with one or the other polar segments outward.

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Usually, this is the end of the molecule with the two unmatched electron pairs (“dangling-O”). This gives the qll a negative surface charge. Sometimes, however, the loose end is the end with the two hydrogen molecules (“dangling-H”). This gives the qll a positive surface charge. Generally speaking, the two groups do not mix. If both groups are present, they will be in separate patches on the ice surface.

**Hypothesis:** I believe that these qlls are formed by sub-surface impulses that are sufficient to loosen one or more of the bonds, but insufficient to loosen all four and send the molecule into space. This hypothesis is supported by the fact that these qlls are strongly temperature dependent. They are also a direct function of the rate of deposition. This suggests that thermal relaxation is not yet complete and the impulse generated by the deposition is still in effect.

**Hygroscopic Forces:** Another group of attractive forces is due to the hygroscopic nature of one or more icing nuclei or a substrate of some kind. These forces may also include the hydrogen bond, but the attraction is between water molecules and molecules of some other substance. Common icing nuclei include kaolinite, other mineral particulates, and certain bacteria. Hygroscopic forces act to increase both the strength and the range of the zone of attraction.

**Spatial Variation of the Attractive Forces:** Irregularly-shaped substrates produce irregular zones of attraction. Cloud icing 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 ice crystals, ionic forces of attraction vary with the concentration of solutes and ionized areas from place to place on or within the substrate.

Because of these variations, the escape velocity needed by an 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

Surface molecules are continually receiving impulses from sub-surface molecules. For the moment, let us consider only that part of the impulse that is

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normal to and away from the surface. Molecular reactions on receiving these impulses can be divided into five groups.

**1. Rebuffs** – The subsurface impulse will give the surface ice molecule insufficient kinetic energy normal to the surface to enable it to break any of the bonds of surface energy. It will stretch the bonds of surface energy, but it will not break them. It will remain an ice molecule. The solid phase suffers no loss of enthalpy.

**2. Dangles** – The impulse results in the surface molecule temporarily breaking one or more (but not all four) of its hydrogen bonds. The molecule then becomes part of the quasi-liquid layer as a “dangling” molecule. It is still an ice molecule, and the solid phase suffers no loss of enthalpy.

**3. Departures** – The surface ice molecule will possess sufficient kinetic energy to enable it to break all of the bonds of surface energy and to move completely away from the surface. At that point, it becomes a vapor molecule. Most of these departing molecules will very shortly return to the ice surface but some will remain vapor molecules. The solid phase suffers a loss of enthalpy. This loss may be temporary or it may be permanent. This depends upon what happens next to that departing molecule.

**4. Returns** – These are of two kinds. In the first case, the departing vapor molecule will have insufficient velocity to escape the sum total of the various bonding forces. It will take a parabolic path and return to the ice surface with the same kinetic energy that it possessed when it left. It will remain an ice molecule. Its enthalpy is returned to the solid phase.

In the second case, the departing vapor molecule will be struck by an incoming humid air molecule and be knocked back onto the ice surface. It will become an ice molecule once more. The solid phase regains that molecule's enthalpy. If the struck molecule returns to the surface with more kinetic energy than it had when it left, the ice surface may actually gain enthalpy thereby.

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**5. Escapes** – The departing vapor molecule will escape from all of the various bonding forces. The solid phase suffers a loss of enthalpy and the vapor phase enjoys a gain in enthalpy. As we shall see, however, the two do not balance.

### **Zones within the Zone of Attraction**

Let us postulate an ice crystal suspended in the humid air of the atmosphere. The presence of this crystal automatically creates several zones within the zone of attraction.

**Solid Zone:** This is the innermost zone, the core of the whole. It consists of the body of the crystal itself. Here we have ice, with each ice molecule bonded by four hydrogen bonds (however ephemerally) to neighboring ice molecules. This zone may have a slight negative charge, since the negative pole of the polar ice molecule is less fully saturated than is the case with the positive pole.

**Quasi-Liquid Zone:** Studies have shown that at certain temperatures ice will have quasi-liquid layers (qll) of water molecules on its surfaces. These quasi-liquid molecules may range from a few scattered molecules through patches of molecules to complete layers many molecules thick. The range of temperatures where qlls are found starts at the triple point, and qll are virtually ubiquitous at that point. As the ice gets colder, the layers get thinner and patchier. Scholars disagree on the question of when the layers disappear.

This quasi-liquid water differs from either ordinary water or super-cooled water in that the molecules that make up these layers do not show the random polar alignments of liquid water, but are strongly aligned normal to the surface. This alignment may utilize either the hydrogen atom (producing a “dangling-O”) or the oxygen atom (producing a “dangling-H”). There appears to be a preference for the “dangling-O” orientation in sublimation.

Naturally, when the ice surface is completely coated with qll, sublimation occurs from the qll. However, the significant differences between the enthalpy of sublimation and the enthalpy of vaporization plus the significant differences between the equilibrium vapor pressures of vapor over ice and vapor over water suggest that the presence or absence of qll does not strongly affect the rate of



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sublimation. This is probably because most of the sublimating impulses originate in the underlying ice layer.

It should not be imagined that these molecules in the quasi-liquid layers persist in their alignments and fractured states for any appreciable period of time. As soon as a hydrogen bond is broken it starts to rebond and will rebond unless (as is often the case) further subsurface impulses prevent it from so doing. The relaxation time of a disturbed molecule may be measured in picoseconds. On the other hand, at  $-25^{\circ}\text{C}$  the average surface molecule experiences some 423 billion sub-surface impacts per second.

**Congested Vapor Zone (Knudsen Layer):** This zone is composed of molecules that have broken the bonds of ice surface energy and become—at least for the moment—vapor molecules. The vast majority of these molecules are pursuing a parabolic course that will take them once more back to the surface of the crystal. Some few will escape to join the vapor molecules of the ambient zone. The number density within this zone decreases with distance from the surface, following the form of a complementary cumulative probability density function curve.

Just above the quasi-liquid zone, the number density of vapor molecules is only about one fifteenth of the density of the ice itself and more than one-hundred thousand times the number density of “saturated” air at that temperature. The mean free path for these molecules is virtually that of a single molecular diameter. This vapor molecule number density drops rapidly as we move away from the ice surface, as fewer and fewer molecules have the necessary velocity to get that far. Eventually, the number density drops to the level of the equilibrium vapor pressure for that temperature. Here, we enter the final zone.

Before we take up the characteristics of this final zone, the ambient zone, it is worth noting that the congested vapor zone also contains vapor molecules that have penetrated into this space from the surrounding ambient zone. Some of these alien vapor molecules will be caught by the attractive forces of the substrate and pulled directly onto that substrate. Some of these alien vapor molecules will collide with other vapor molecules in the congested zone and will be eventually pulled onto the substrate. Finally, some may pass on through unmolested.

As we shall see in *Condensation*, it is the slower aliens that are most likely to be captured.

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**Ambient Zone:** This is the zone where the vapor molecule number density is that produced by the ambient vapor pressure. If that ambient vapor pressure is less than the equilibrium value, there will still be more vapor molecules moving away from the crystal than will be moving toward it. If the ambient vapor pressure is equal to the equilibrium value, the two flows will be theoretically equal.

### Escape Velocities

The escape of an ice molecule from the bonding forces of the zone of attraction may be viewed as analogous to the escape of a rocket from the zone of attraction of the Earth's gravitational field. Both must attain escape velocity normal to and away from the attracting surface.

Obviously, this velocity is generated by a sub-surface impulse. This concept brings up a number of related questions: Firstly, how do we measure the velocity of a subsurface impulse? Secondly, what is the distribution of these subsurface impulse velocities? What mathematical function does this distribution follow? What is the mean velocity? The standard deviation? How do we measure the escape velocity? And so on.

Since molecular velocities are one element of molecular kinetic energies, these questions lead to the larger question of just exactly what are the kinetic energies of the ice surface.

### Equivalence of Phase Temperatures

Let us postulate three sealed and rigid laboratory containers. The first contains natural water vapor at a temperature of 0°C and at a vapor pressure that is the equilibrium vapor pressure for that temperature. The second container contains liquid natural water at the same temperature. The third container contains natural water ice at that same temperature. All three containers also contain well-calibrated contact thermometers. These thermometers are in conductive and radiative equilibrium with their surrounding vapor, water, and ice.

That conductive equilibrium is mediated by the molecular impulses transmitted to and from the surrounding phase and the surface of the thermometer.

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We must assume that those impulses will have translatory, rotational, and vibratory components.

Obviously, all three thermometers show the same temperature, 0°C. We may justifiably argue that, whatever the form or forms of energy that the three thermometers are measuring, that the mean molecular impulse conducted to the thermometers is the same per unit area of sensing surface in each of the three cases.

However, quantum physical theories dealing with solids, liquids, and gases do not assume that all three kinetic modes are equally possible. A diamond, for instance, is assumed to have no significant molecular kinetic energies of translation or rotation at all. Its kinetic energies are solely vibrational. Yet a diamond most definitely does possess a temperature.

Solids are assumed to possess all three modes, with the vibratory mode dominant. The proportion of energy in each mode varies with both the temperature and the nature of the solid.

The only logical conclusion is that the effective mean molecular axial impulse remains constant for any given temperature, while the amount of impulse each mode contributes to that mean varies with the nature of the material and with its temperature.

### The Nature of Temperature

In [\*The Nature of Gas Temperatures\*](#) we defined the gas temperature as:

$$\bar{T} = \frac{\bar{u}_i}{k_B} \quad \text{SUB01}$$

Here,  $\bar{T}$  is the mean gas temperature in Kelvins. The term  $\bar{u}_i$  is the mean kinetic energy of translation in Joules per impacting molecule, measured normal to and toward the sensing surface. The constant  $k_B$  is Boltzmann's Constant in Joules per molecule per Kelvin.

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Note that  $\bar{u}_i$  is **not** the mean kinetic energy of translation of the general population of gas molecules, but only of that sub-population of gas molecules that actually impact upon the sensing surface of the thermometer during some significant period of time (see [Kinetic Energies of Translation](#)).

**Generalized Definition of Temperature:** We may generalize this definition of gas temperatures to include all three classical phases of matter. The equation now becomes:

$$\bar{T} = \frac{\bar{u}_i^{\Sigma}}{k_B} = \frac{\bar{u}_i^{\text{translational}} + \bar{u}_i^{\text{rotational}} + \bar{u}_i^{\text{vibrational}}}{k_B} \quad \text{SUB02}$$

Thus, temperature measures the mean total kinetic energies transmitted to the sensing surface of the thermometer by the impulses of a substance's molecules upon that surface. The impulse energies may be translational, rotational, vibrational or any combination of the three modes.

Boltzmann's Constant plays the role of the constant of proportionality relating substance temperature to this total kinetic energy.

We may then reasonably argue that—at the same temperature—the mean impulse exerted against a surface molecule of liquid water by the “nudging” of molecules around it is the same as the mean impulse of a vapor molecule impacting upon a surface and the same as the mean impulse exerted by an ice molecule against the bonds holding it in place on the surface of an ice crystal.

Since the dimensions of impulse are mass times velocity, if the mass remains the same (which, of course, it does) then the *effective* axial impulse velocity must be the same. For ice, this effective axial velocity may well be the sum of the translatory, rotational, and vibrational movements. It would be nice to know how much of each, but we don't need to know this. It is sufficient for our purposes to hypothesize that the distribution of effective axial impulse velocities in ice is the same as the distribution of translatory axial impulse velocities in water vapor at the same temperature.

As we see below, this working hypothesis will enable us to ascertain both the escape velocity of ice molecules and the proportion of ice surface molecules that have this escape velocity at any instant. We may thus readily calculate the

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number of ice molecules that actually escape from one square meter of ice surface in one second of time.

### Working Hypothesis

*The distribution of effective ice molecular axial velocities has the form of a probability density curve. The mean and the standard deviation of that probability density curve is the same as the mean and standard deviation of the probability density curve for axial velocities of water vapor molecules at the same temperature.*

**Distribution of Effective Molecular Axial Velocities:** The relationship between the mean axial impulse velocity ( $\bar{v}_i$ ) and the mean axial velocity ( $\bar{v}_p$ ) and the standard deviation velocity ( $\sigma$ ) is a rigorous one. This relationship is thoroughly covered in [Molecular Speeds and Velocities](#). Although we are primarily interested in the mean axial impulse velocity, we must start with the mean axial velocity.

Since we are hypothesizing that the distribution of effective ice axial velocities is essentially the same as that of axial vapor molecule velocities, we may adapt the latter's distribution function:

$$\frac{d\bar{n}}{dv_p} = \frac{1}{\sqrt{2\pi}} \frac{\bar{n}}{\sigma} \exp - \frac{v_p^2}{2\sigma^2} \quad \text{SUB03}$$

Here,  $\bar{n}$  is the number of ice molecules per cubic meter,  $v_p$  is the individual ice molecule's effective axial impulse velocity toward an object of interest,  $\sigma$  is the standard deviation, and  $d\bar{n}_p$  is the limited number of ice molecules having effective axial impulse velocities between  $v_p$  and  $dv_p$ .

**The Mean Effective Axial Velocity:** Under conditions of equilibrium, we may assume that the ice has no net flow, and the mean effective axial velocity for the total population of impulses is zero.

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$$\bar{v}_{\sim \pm p} = \frac{1}{\bar{n}} \sum_1^{\bar{n}} v_{\sim \pm p} = 0 \quad \text{SUB04}$$

**The Standard Deviation Velocity:** The standard deviation ( $\sigma$ ) is defined as the square-root of the mean of the squares of the individual deviations. Since the mean velocity is zero, the individual effective molecular axial impulse velocities are themselves deviations. Thus,

$$\sigma = \left( \frac{1}{\bar{n}} \sum_1^{\bar{n}} v_{\sim p}^2 \right)^{\frac{1}{2}} \quad \text{SUB05}$$

The combination of SUB02 and our working hypothesis more or less mandates that:

$$\sigma = \left( \frac{k_B \bar{T}}{\bar{m}} \right)^{\frac{1}{2}} \quad \text{SUB06}$$

### Sub-Surface Impulses

**Impulse Arrivals at the Ice Surface:** Impulses travel freely through the solid ice. However, the only direction of travel that might facilitate a surface molecule's escape from its bonding forces must have a component of direction that is normal to and toward that molecule. Therefore, we are interested only in half of the effective axial impulse velocity distribution function. Equation SUB03 thus becomes,

$$\frac{d\bar{n}_{\sim p}}{dv_{\sim p}} = \sqrt{\frac{2}{\pi}} \frac{\bar{n}_{\sim p}}{\sigma} \exp - \frac{v_{\sim p}^2}{2\sigma^2} \quad \text{SUB07}$$

Since we keep mentioning impulses, the curious reader might wonder why we are still dealing with the proximity velocity ( $\bar{v}_p$ ) rather than the impulse

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velocity ( $\bar{v}_i$ ). The answer is that although the magnitude of the impulse is a function of  $\bar{v}_i$ , the rate at which the various impulses arrive at the surface is still a function of  $\bar{v}_p$ . Therefore, to ascertain flux rates we must use the latter velocity.

Since we are now dealing with only the positive half of the axial population, the mean effective axial impulse velocity is no longer zero. It has become,

$$\bar{v}_p = \sqrt{\frac{2}{\pi}} \sigma \quad \text{SUB08}$$

The mean effective axial impulse velocity of those impulses that actually impact upon surface molecules from below over some significant period of time is now:

$$\bar{v}_i = \sqrt{\frac{\pi}{2}} \sigma \quad \text{SUB09}$$

The derivation of all molecular velocities is covered in [\*Molecular Speeds and Velocities\*](#).

**Surface-Bound Flux:** Molecular flows are described in [\*Molecular Flows\*](#). In keeping with our analogy with vapor molecules, the flow of impulses toward the surface will thus be:

$$\bar{f}_i^\uparrow = \frac{1}{2} n \bar{v}_p \quad \text{SUB10}$$

Here,  $\bar{f}_i^\uparrow$  is the molecular impulse flux in number of impulses per square meter per second. Keep in mind that this is the flux of kinetic impulses, not the flux of any actual ice molecules themselves.

### Disturbances

We now have the flow rate of kinetic impulses reaching the surface ice molecules from below. The next step is to ascertain how many of these impulses result in surface ice molecules being impelled to break one or more of their

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intermolecular bonds, leave the ice surface temporarily, or effectively leave for good.

Impulses, of course, are measured in Newtons. Bonding energies are measured in Joules. However, when a subsurface impulse is transmitted to a surface ice molecule the impact is exerted over both time and distance. This converts the impulse into kinetic energy. This enables us to consider both the impulse and the bonding energy in the same terms.

There is an additional obstacle, however. As described below, our only “yardstick”, the error function distribution, is calibrated in *sigmas* ( $\sigma$ ), a unit of velocity. This requires us to state our critical kinetic energy levels in terms of their effective axial velocities. This is rather easily accomplished with the general formula:

$$v_i = \left( \frac{u_i}{\tilde{m}} \right)^{\frac{1}{2}} \quad \text{SUB11}$$

Here,  $v_i$  is the effective molecular axial velocity of an individual ice molecule in meters per second,  $u_i$  is the kinetic energy of an individual impulse in Joules, and  $\tilde{m}$  is the mass of our ice molecule in kilograms.

**Minimal Departure Impulse Velocity:** For any particular bonding situation, there must be some molecular impulse velocity (along the axis normal to the bonds) that represents the minimum velocity necessary to break those bonds. For prospective departees, that bonding force is the surface energy. The effective axial velocity necessary to break loose of that surface energy will be:

$$v_{+i}^{sfe} = \left( \frac{\dot{\tilde{\Gamma}}}{\tilde{n}_{\square} \tilde{m}} \right)^{\frac{1}{2}} \quad \text{SUB12}$$

Here,  $v_{+i}^{sfe}$  is the effective axial impulse velocity in meters per second normal to and away from the surface necessary to break the bond of surface energy,  $\dot{\tilde{\Gamma}}$  is that surface energy in Joules per square meter of ice surface,  $\tilde{n}_{\square}$  is the number of



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surface molecules per square meter of ice surface, and  $\bar{m}$  is the mean molecular mass in kilograms. The positive subscript indicates that this bonding energy is directed toward the surface, thereby acting against any attempt to move away from the surface.

**Dangles:** This minimum effective axial velocity  $v_{+i}^{sfe}$  is the velocity necessary for a ice surface molecule to break loose of all four of its hydrogen bonds and become (however temporarily) a vapor molecule. The effective axial velocity necessary for a molecule to break a single bond and become a “dangle” (a qll molecule) should then be:

$$v_{+i}^{dangle3} = \left( 0.25 \frac{\dot{\Gamma}}{\bar{n}_{\square} \bar{m}} \right)^{\frac{1}{2}} \quad \text{SUB13}$$

Here,  $v_{+i}^{dangle3}$  is the minimum effective axial molecular velocity necessary for a surface ice molecule to break a single one of its four hydrogen bonds and to become (again, however temporarily) a qll molecule. The “3” in the velocity superscript denotes that the molecule is still bonded by three of the four hydrogen bonds.

For the minimum effective molecular axial velocity to break two of the four hydrogen bonds, we get:

$$v_{+i}^{dangle2} = \left( 0.5 \frac{\dot{\Gamma}}{\bar{n}_{\square} \bar{m}} \right)^{\frac{1}{2}} \quad \text{SUB14}$$

For the minimum effective molecular axial velocity to break three of the four hydrogen bonds, we get:

$$v_{+i}^{dangle1} = \left( 0.75 \frac{\dot{\Gamma}}{\bar{n}_{\square} \bar{m}} \right)^{\frac{1}{2}} \quad \text{SUB15}$$

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### Calculating the Number of Molecules in Each Group

Let us start our calculations of the proportion of impulses that are sufficient to generate each of our five groups of ice molecules with what is both the largest group and the one requiring the smallest effective molecular axial velocity, the formation of a qll molecule with but a single broken hydrogen bond.

At this point, we return to the original distribution function (SUB03) with its mean of zero. By setting the variance ( $\sigma^2$ ) to one we produce a standard normal curve. The ordinate of the curve ( $x$ ) for any specific minimum effective molecular axial velocity ( $v_{+i}^x$ ) will be:

$$(x) = a \frac{v_{-i}^x}{\sigma} \quad \text{SUB16}$$

Here, ( $a$ ) is an empirically-derived coefficient. It is necessary to make our calculations come out correctly because ice is not an ideal solid. The coefficient has the value:

$$a = \left( \frac{238}{T - 10.5} \right)^{0.3725} \quad \text{SUB17}$$

**Dangle Rate:** The proportion of received impulses that will force a surface ice molecule into breaking a single bond and becoming a qll molecule will then be:

$$\bar{f}_{-i}^{\mapsto} = 2 \operatorname{erfc}(x) \bar{f}_i^{\uparrow} \quad \text{SUB18}$$

Here,  $\bar{f}_{-i}^{\mapsto}$  is the number of dangles produced per square meter of ice surface per second. The coefficient is two because we are dealing with only half of the population—that half that have a component of motion toward the surface molecule. [See the Note at the end of the text for definitions of *erf* and *erfc*.]

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**Rebuff Rate:** The difference, of course, between the impulse rate and the dangle rate is the number of molecular impulses received that are insufficient to overcome any portion of the surface energy. Hence, they do not result in a surface ice molecule's either leaving that surface or becoming a dangle.

$$\bar{f}_{-i}^{\downarrow} = \bar{f}_{-i}^{\uparrow} - \bar{f}_{-i}^{\mapsto} \quad \text{SUB19}$$

Here,  $\bar{f}_{-i}^{\downarrow}$  is the rebuff rate,  $\bar{f}_{-i}^{\uparrow}$  is the impulse rate, and  $\bar{f}_{-i}^{\mapsto}$  is the dangle rate.

**Departure Rate:** To calculate the proportion of impulses that result in an ice surface molecule's breaking all four of its hydrogen bonds and escaping (however momentarily) from the surface, we start with:

$$(x) = a \frac{v_{+i}^{sfe}}{\sigma} \quad \text{SUB20}$$

Substituting this into the complimentary error function equation gives us:

$$\bar{f}_{-i}^{\nearrow} = 2erfc(x) \bar{f}_i^{\uparrow} \quad \text{SUB21}$$

Here,  $\bar{f}_{-i}^{\nearrow}$  is the number of surface water molecule departures per square meter of surface per second.

**Escape Rate:** Simply breaking the bonds of surface energy is not sufficient for an ice molecule to become part of the permanent vapor population. To do this, the molecule must have sufficient escape velocity to overcome all of the bonding forces—not just the surface energy.

This minimal escape velocity may be readily calculated from the specific enthalpy of phase change. This enthalpy is usually given in terms of Joules per kilogram of ice. Converting that into Joules per molecule, dividing by the molecular mass, and taking the square root of the result should give us the minimal escape velocity. After all of these algebraic manipulations, it turns out that:

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$$\bar{v}_{+i}^{bonding} = \left( W_{kg}^{\leftrightarrow} \right)^{\frac{1}{2}} \quad \text{SUB22}$$

Here,  $\bar{v}_{+i}^{bonding}$  is the minimal escape velocity in meters per second, and  $W_{kg}^{\leftrightarrow}$  is the enthalpy of phase change in Joules per kilogram. The double-headed arrow in this latter symbol recognizes that the work done in breaking the bonding force is reversible. The positive subscript in the escape velocity term recognizes that the bonding energies serve to decelerate the initial velocity of the escaping water molecule.

The ordinate now becomes:

$$(x) = a \frac{v_{+i}^{bonding}}{\sigma} \quad \text{SUB23}$$

The escape function takes the form:

$$\bar{f}_{-i}^{\uparrow} = 2erfc(x) \bar{f}_i^{\uparrow} \quad \text{SUB24}$$

**Return Rate:** The rate at which departing surface molecules return to that surface is simply the departure rate minus the escape rate, i. e.;

$$\bar{f}_{-i}^{\nearrow} = \bar{f}_{-i}^{\nearrow} - \bar{f}_{-i}^{\uparrow} \quad \text{SUB25}$$

**Summary:** We now have procedures for calculating the rates at which all five of our molecular sublimation groups are produced. Let us now look at what happens next.

### Latent Heat of Sublimation

**Diminution of Escape Velocities:** As prospective vapor molecules move away from the surface, the various attractive forces serve to reduce their velocities along the proximity axis by the amount  $v_{+i}^{bonding}$ , and consequently their kinetic energies of translation along that same axis. This means that when the successful ice

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molecules join the vapor phase, they will have a lower velocity and less thermal energy than when they first left the substrate. The difference between the initial kinetic energy and the final kinetic energy is equal to the energy required to break the intermolecular bonds; that is, the enthalpy of phase change per molecule.

Note that the loss of both velocity and kinetic energy is solely along the translational axes. There is no reason to believe that kinetic energies of rotation or vibration are affected or diminished in any way. The enthalpy of phase change, expressed as a slowdown in escape velocity ( $v_{+i}^{bonding}$ ) represents the molecule's "departure fee"; that is the velocity loss, work done, or energy expended in overcoming the intermolecular forces of attraction.

**Mean Terminal Velocities:** Under isothermal conditions, the mean temperature of the resulting vapor molecules is the same as the mean temperature of the surface molecules. Thus they will have essentially the same distribution of velocities.

### Addenda

**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 an ice body will increase over time.

**Limitations of Table Values for the Free Atmosphere:** All of the table values are for a system consisting of clean humid air in contact with a pure natural ice surface. The problem with applying these values to the free atmosphere lies in the facts that the free atmosphere does not have either clean air or pure ice. Under such circumstances, surface energies and enthalpies of phase change are both likely to be higher in the free atmosphere. Other parameters may change, as well. Whether or not these values will be significantly different from free atmosphere values will depend upon specific conditions from place to place and from time to time.

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Consequently, the best way to view these tables and their values are as base lines, points of departure and limiting cases. The relationships will be the same, but the actual numerical values for the free atmosphere are likely to be different—slightly in some cases, significantly in others.

### Testing the Working Hypothesis

If the working hypothesis is correct, then SUB24 should produce a flux rate that is identical to or a close approximation of the flux formula for equilibrium vapor pressure. This latter flux formula is:

$$\bar{f}_i^\downarrow = \frac{1}{2} \bar{n}^e \bar{v}_p \quad \text{SUB26}$$

Here,  $\bar{f}_i^\downarrow$  is the vapor molecule flux in number of vapor molecules per square meter per second,  $\bar{n}^e$  is the number density of vapor molecules in number per cubic meter at the equilibrium vapor pressure, and  $\bar{v}_p$  is the mean axial molecular velocity normal to and toward the sensing surface in meters per second.

Comparing the flux rates produced by SUB24 and SUB26, we get the results shown in Table SUB01.

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Table SUB01

TESTING THE WORKING HYPOTHESIS

SYSTEM TEMP	ENTHALPY OF PHASE CHANGE	EQUILIBRIUM VAPOR PRESSURE	OUTFLUX	INFLUX	OUTFLUX INFLUX RATIO
°C	$\dot{W}_{kg}^{\leftrightarrow}$	$p^e$	$\bar{f}_{-i}^{\uparrow}$	$\bar{f}_{-i}^{\downarrow}$	$\frac{\bar{f}_{-i}^{\uparrow}}{\bar{f}_{-i}^{\downarrow}}$
	kilojoules kg <sup>-1</sup>	pascals m <sup>-2</sup>	x 10 <sup>23</sup> m <sup>-2</sup> sec <sup>-1</sup>	x 10 <sup>23</sup> m <sup>-2</sup> sec <sup>-1</sup>	
00	2834	610.70	213.69	229.47	0.93
-05	2836	402.30	146.64	152.57	0.96
-10	2837	260.70	98.66	99.80	0.99
-15	2837	166.10	65.19	64.20	1.02
-20	2838	103.85	42.19	40.53	1.04
-25	2838	63.70	26.66	25.11	1.06
-30	2838	38.27	16.40	15.24	1.08
-35	2838	22.50	9.81	9.05	1.08
-40	2839	12.92	5.69	5.25	1.08
-45	2839	7.24	3.20	2.98	1.08
-50	2840	3.95	1.73	1.64	1.06
-55	2840	2.09	0.91	0.88	1.03
-60	2841	1.08	0.45	0.46	0.99
-65	2841	0.54	0.22	0.23	0.94
-70	2841	0.26	0.10	0.11	0.88
-75	2842	0.12	0.04	0.05	0.80

All table values are for a system consisting of clean humid air at a pressure of 10<sup>5</sup> Pascals in contact with a pure natural ice surface. All data are contingent upon acceptance of the Working Hypothesis (see text).

TESTING THE WORKING HYPOTHESIS

$$\dot{W}_{kg}^{\leftrightarrow} = 0.0009056 \left( \frac{\bar{p}_{ice}}{\bar{m}} \right)^{\frac{1}{3}}$$

This is the enthalpy of phase change in kilojoules per kilogram. It is a function of the mean inter-nuclear distance between the ice molecules.

$$p^e$$

Equilibrium vapor pressure of water vapor over ice in Pascals. Taken from American Institute of Physics Handbook, 3<sup>rd</sup> Ed., 1972. Table 4k-16.

$$\bar{f}_{-i}^{\uparrow} = 2 \operatorname{erfc} \left( a \frac{v_{+i}^{\text{bonding}}}{\sigma} \right) \bar{f}_i^{\uparrow}$$

Working Hypothesis escape flux in number of molecules per square meter per second.

$$\bar{f}_i^{\downarrow} = \frac{1}{2} \bar{n}^e \bar{v}_p$$

Influx at equilibrium vapor pressure in number of molecules per square meter.



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**TABLE SUB02**

**INFLUENCE OF THE ACCOMMODATION COEFFICIENT**

SYSTEM TEMP	OUTFLUX WITH <i>a</i>	INFLUX	RATIO	OUTFLUX WITHOUT <i>a</i>	RATIO
°C	$\bar{f}_{\sim i}^{\uparrow}$	$\bar{f}_{\sim i}^{\downarrow}$	$\frac{\bar{f}_{\sim i}^{\uparrow}}{\bar{f}_{\sim i}^{\downarrow}}$	$\bar{f}_{\sim i}^{\uparrow}$	$\frac{\bar{f}_{\sim i}^{\uparrow}}{\bar{f}_{\sim i}^{\downarrow}}$
	x 10 <sup>23</sup> m <sup>-2</sup> sec <sup>-1</sup>	x 10 <sup>23</sup> m <sup>-2</sup> sec <sup>-1</sup>		x 10 <sup>23</sup> m <sup>-2</sup> sec <sup>-1</sup>	
00	213.69	229.47	0.93	93.07	0.41
-05	146.64	152.57	0.96	73.84	0.48
-10	98.66	99.80	0.99	58.07	0.58
-15	65.19	64.20	1.02	45.40	0.71
-20	42.19	40.53	1.04	35.21	0.87
-25	26.66	25.11	1.06	27.04	1.08
-30	16.40	15.24	1.08	20.52	1.35
-35	9.81	9.05	1.08	15.40	1.70
-40	5.69	5.25	1.08	11.43	2.17
-45	3.20	2.98	1.08	8.37	2.81
-50	1.73	1.64	1.06	6.05	3.69
-55	0.91	0.88	1.03	4.31	4.89
-60	0.45	0.46	0.99	3.02	6.60
-65	0.22	0.23	0.94	2.08	9.03
-70	0.10	0.11	0.88	1.41	12.57
-75	0.04	0.05	0.80	0.94	17.82

All table values are for a system consisting of clean humid air at a pressure of 10<sup>5</sup> Pascals in contact with a pure natural ice surface. All data are contingent upon acceptance of the Working Hypothesis (see text).

It would appear that however ice departs from the behavior of an ideal solid, it does so both at the higher temperatures where “dangles” are virtually ubiquitous and at the lower temperature where they tend to disappear.

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**INFLUENCE OF THE ACCOMMODATION COEFFICIENT**

$$\bar{f}_i^\uparrow = \frac{1}{2} \bar{n} \bar{v}_p \quad \text{Impulse rate}$$

$$\bar{f}_{-i}^\uparrow = 2 \operatorname{erfc} \left( a \frac{v_{+i}^{\text{bonding}}}{\sigma} \right) \bar{f}_i^\uparrow$$

Working Hypothesis escape flux in number of molecules per square meter per second.

$$\bar{f}_i^\downarrow = \frac{1}{2} \bar{n}^e \bar{v}_p$$

Influx at equilibrium vapor pressure in number of molecules per square meter per second.

$$\bar{f}_{-i}^\uparrow = 2 \operatorname{erfc} \left( \frac{v_{+i}^{\text{bonding}}}{\sigma} \right) \bar{f}_i^\uparrow$$

Working Hypothesis (without the accommodation coefficient) escape flux in number of molecules per square meter per second.

# THE KINETIC ATMOSPHERE

## Gross Sublimation

### Summary of Sublimation Concepts

01. Every surface of ice in the atmosphere undergoes continual gross sublimation. Every non-ice surface that carries one or more transient ice molecules undergoes continual gross sublimation. This process is spontaneous and ubiquitous. It is not necessary to add heat to a substrate to bring about sublimation.
02. The amount of gross sublimation 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 energy. 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 molecules.
05. Another set of forces involves ionization. Ionized ice molecules have additional bonding forces due to this ionization.
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 ice. As a general rule, these solutes increase the strength of the bonding forces.
08. The distribution of effective axial velocities in gases, liquids, and solids is postulated to take the same form in each of the phases. This form is that of a probability density curve. Phases with the same temperature are assumed to share the same mean and standard deviation.
09. 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.

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### Gross Sublimation

10. Sublimation is a strongly selective process. Only the hotter (higher kinetic energy of translation) molecules are able to sublimate. Since temperature is an average whereas heat (enthalpy) is a total, this diminishes the mean temperature of those that remain, hence cooling the sublimating surface.
11. Because escape is based on velocity, lighter isotopes are more likely to sublimate than heavier ones. This increases the mean molecular mass of those that remain.
12. Sublimation increases the enthalpy of the vapor system and decreases the enthalpy of the sublimating system.
13. 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.
14. The temperature of the resulting vapor system may be increased or decreased or remain unchanged by the sublimation process. The result depends upon the relative temperatures and masses of the sublimating surface and the vapor system and upon the strength of the bonding forces.

\* \* \* \* \*

### Constants Used in the Tables

$k_B$  =  $1.3806504 \times 10^{-23}$  Joules per molecule per K = Boltzmann's Constant

$\pi$  = 3.1415926 = Pi

$\bar{m}$  =  $2.989681 \times 10^{-26}$  kg = mean molecular mass of natural water

# THE KINETIC ATMOSPHERE

## Gross Sublimation

### A note on the error function

The original use of the denotation *erf* (error function) was to refer to the cumulative probability density function; that is, the area under the curve to the left of the ordinate in a standard normal curve:

$$erf(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^x e^{-t^2/2} dt$$

The complementary error function was then defined as:

$$erfc = 1 - erf$$

Unless I specifically indicate otherwise, these are the ways in which I use the two terms.

Over the years, these two terms have been used to refer to other functions—especially in various engineering fields. I do not use those functions in this series of papers.

Error function calculations in these papers were performed under the *Microsoft Excel* Program (2003, SP3), using the “NORMSDIST” function. They were then converted into the complementary error functions as shown above.

I did not use that program’s **erf** and **erfc** engineering functions.

\* \* \* \* \*

**A Final Note:** The observant reader will quickly see that all of the values in the tables are based on five measurable parameters of ice plus one working hypothesis. The five measurable parameters are: temperature, density, equilibrium vapor pressure, surface energy, and enthalpy of sublimation.

The lone working hypothesis is that molecular impulses share the same distribution function, mean, and standard deviation regardless of phase.

The rest is just “connecting the dots”.

**TABLE SUB03**

**ICE SURFACE MOLECULAR DEPARTURE RATES**

ICE TEMP	SUB-SURFACE IMPULSES	REBUFFS	DANGLES	DEPARTURES	RETURNS	ESCAPES
°C	$\bar{f}_i^{\uparrow}$	$\bar{f}_{-i}^{\downarrow}$	$\bar{f}_{-i}^{\leftrightarrow}$	$\bar{f}_{-i}^{\nearrow}$	$\bar{f}_i^{\nearrow\searrow}$	$\bar{f}_{-i}^{\uparrow}$
	$\times 10^{24}$ $\text{m}^{-2} \text{sec}^{-1}$	$\times 10^{24}$ $\text{m}^{-2} \text{sec}^{-1}$	$\times 10^{24}$ $\text{m}^{-2} \text{sec}^{-1}$	$\times 10^{24}$ $\text{m}^{-2} \text{sec}^{-1}$	$\times 10^{24}$ $\text{m}^{-2} \text{sec}^{-1}$	$\times 10^{24}$ $\text{m}^{-2} \text{sec}^{-1}$
00	4,343,714	2,572,080	1,346,564	425,069	425,048	21.369
-05	4,309,881	3,912,258	1,325,894	397,622	397,608	14.664
-10	4,276,025	3,905,188	1,304,251	370,837	370,827	9.866
-15	4,237,511	3,892,904	1,280,329	344,607	344,601	6.519
-20	4,196,730	3,877,646	1,254,805	319,084	319,079	4.219
-25	4,155,530	3,861,131	1,228,193	294,399	294,396	2.666
-30	4,115,241	3,844,607	1,200,832	270,634	270,632	1.640
-35	4,074,480	3,826,744	1,172,296	247,736	247,735	0.981
-40	4,033,233	3,807,491	1,142,564	225,742	225,742	0.569
-45	3,991,485	3,786,691	1,111,733	204,794	204,794	0.320
-50	3,949,219	3,764,559	1,079,508	184,660	184,660	0.173
-55	3,906,419	3,740,712	1,046,269	165,707	165,707	0.091
-60	3,863,067	3,715,289	1,011,812	147,778	147,778	0.045
-65	3,819,351	3,688,451	976,188	130,901	130,901	0.022
-70	3,775,040	3,659,941	939,365	115,099	115,099	0.010
-75	3,729,909	3,629,517	901,334	100,392	100,392	0.004

All table values are for a system consisting of clean humid air at a pressure of  $10^5$  Pascals in contact with a pure natural ice surface. All data are contingent upon acceptance of the Working Hypothesis (see text).

# THE KINETIC ATMOSPHERE

## Gross Sublimation

### ICE SURFACE MOLECULAR DEPARTURE RATES

$$\bar{f}_i^\uparrow = \frac{1}{2} \bar{n}_{ice} \bar{v}_p$$

This is the rate at which surface ice molecules receive sub-surface molecular impulses.

$$\bar{f}_{-i}^\downarrow = \bar{f}_i^\uparrow - \bar{f}_{-i}^{\mapsto}$$

This is the rate at which sub-surface molecular impulses fail to cause surface ice molecules to break any of the bonds of surface energy.

$$\bar{f}_{-i}^{\mapsto} = 2erfc\left(0.25a \frac{v_i^{sfe}}{\sigma}\right) \bar{f}_i^\uparrow$$

This is the rate at which sub-surface molecular impulses cause a surface ice molecule to break one or more (but not all four) of its hydrogen bonds.

$$\bar{f}_{-i}^{\nearrow} = 2erfc\left(a \frac{v_i^{sfe}}{\sigma}\right) \bar{f}_i^\uparrow$$

This is the rate at which sub-surface impulses impel a surface ice molecule to break all four hydrogen bonds and become a prospective vapor molecule.

$$\bar{f}_i^{\nearrow\searrow} = \bar{f}_{-i}^{\nearrow} - \bar{f}_{-i}^{\uparrow}$$

This is the rate at which departing molecules return to the ice surface without fully escaping to become vapor molecules.

$$\bar{f}_{-i}^{\uparrow} = 2erfc\left(a \frac{v_i^{bonding}}{\sigma}\right) \bar{f}_i^\uparrow$$

This is the rate at which surface ice molecules escape all of the bonding forces to fully become vapor molecules.

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Gross Sublimation

TABLE SUB04

**SELECTED ICE PROPERTIES**

ICE TEMPERATURE	ICE TEMPERATURE	MASS DENSITY	SURFACE ENERGY	ENTHALPY OF PHASE CHANGE
	$\bar{T}$	$\bar{\rho}_{ice}$	$\dot{\Gamma}$	$\dot{W}_{kg}^{\leftrightarrow}$
°C	°K	kilograms m <sup>-3</sup>	x 10 <sup>-3</sup> Joules m <sup>-2</sup>	kilojoules kg <sup>-1</sup>
00	273.15	916.20	109	2834
-05	268.15	917.50	109	2836
-10	263.15	918.90	109	2837
-15	258.15	919.40	110	2838
-20	253.15	919.50	110	2838
-25	248.15	919.60	110	2838
-30	243.15	920.00	110	2838
-35	238.15	920.40	110	2839
-40	233.15	920.80	110	2839
-45	228.15	921.20	110	2839
-50	223.15	921.60	110	2840
-55	218.15	922.00	110	2840
-60	213.15	922.40	110	2841
-65	208.15	922.85	110	2841
-70	203.15	923.30	110	2842
-75	198.15	923.70	110	2842

All table values are for a system consisting of clean humid air at a pressure of 10<sup>5</sup> Pascals in contact with a pure natural ice surface.



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**SELECTED ICE PROPERTIES**

$$\bar{\rho}_{ice}$$

This is the density of one cubic meter of pure natural water ice in kilograms. Values were taken from: [http://www.engineeringtoolbox.com/ice-thermal-properties-d\\_576.html](http://www.engineeringtoolbox.com/ice-thermal-properties-d_576.html). Data interpolated and checked on 27 June 2010.

$$\dot{\Gamma} = 0.795 \left( \frac{\dot{W}_{kg} \bar{m} \bar{n}}{f_{\circ}} \right)$$

Ice/humid air surface energy in joules per square meter. It is a function of the mean intermolecular distance between the ice molecules.

$$\dot{W}_{kg} = 0.0009059 \left( \frac{\bar{\rho}_{ice}}{\bar{m}} \right)^{\frac{1}{3}}$$

This is the enthalpy of phase change in kilojoules per kilogram. It is a function of the mean intermolecular distance between the ice molecules.

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TABLE SUB05

ICE SURFACE MOLECULAR PARAMETERS

ICE TEMPERATURE	NUMBER DENSITY	SURFACE NUMBER	EFFECTIVE RMS AXIAL VELOCITY*	EFFECTIVE MEAN AXIAL ARM VELOCITY*	EFFECTIVE MEAN IMPULSE VELOCITY*	MEAN IMPULSE FLUX TO SURFACE*
°C	$\bar{n}_{ice}$	$\bar{n}_{\square}$	$\bar{v}$	$\bar{v}_p$	$\bar{v}_i$	$\bar{f}_i^{\uparrow}$
	x 10 <sup>28</sup> molecules m <sup>-3</sup>	x 10 <sup>18</sup> molecules m <sup>-2</sup>	meters sec <sup>-1</sup>	meters sec <sup>-1</sup>	meters sec <sup>-1</sup>	x 10 <sup>28</sup> molecules m <sup>-2</sup> sec <sup>-1</sup>
00	3.0627	9.7889	355	283	445	434
-05	3.0670	9.7981	352	281	441	430
-10	3.0717	9.8081	348	278	437	427
-15	3.0734	9.8117	345	275	433	423
-20	3.0737	9.8124	342	273	428	419
-25	3.0740	9.8131	338	270	424	415
-30	3.0754	9.8159	335	267	420	411
-35	3.0767	9.8188	332	265	416	407
-40	3.0780	9.8216	328	262	411	403
-45	3.0794	9.8245	324	259	407	399
-50	3.0807	9.8273	321	256	402	394
-55	3.0821	9.8302	317	253	398	390
-60	3.0834	9.8330	314	250	393	386
-65	3.0849	9.8362	310	247	388	381
-70	3.0864	9.8394	306	244	384	377
-75	3.0877	9.8422	302	241	379	373

All table values are for a system consisting of clean humid air at a pressure of 10<sup>5</sup> Pascals in contact with a pure natural water ice surface. \*Values are base on acceptance of the working hypothesis on effective axial velocities. See text.

# THE KINETIC ATMOSPHERE

## Gross Sublimation

### ICE SURFACE MOLECULAR PARAMETERS

$$\bar{n}_{ice} = \frac{\bar{\rho}_{ice}}{\bar{m}}$$

This is the number of water molecules in one cubic meter of pure natural ice at the specified temperature and a constant pressure of  $10^5$  Pascals.

$$\bar{n}_{\square} = (\bar{n}_{ice})^{2/3}$$

This is the number of molecules in a mono-molecular layer of pure natural ice exposed to humid air at a constant pressure of  $10^5$  Pascals.

$$\sigma = \left( \frac{k_B \bar{T}}{\bar{m}} \right)^{1/2}$$

**Sigma.** This is the standard deviation (in meters per second) of the distribution of effective molecular axial velocities along any single axis under conditions of equilibrium. It is also the root-mean-square molecular velocity in meters per second for that distribution. The use of the mean molecular mass instead of the effective mass introduces some error. Since pure natural water is largely (99.73%) composed of a single isotope of water, the error is insignificant.

$$\bar{v}_p = \sqrt{\frac{2}{\pi}} \sigma$$

This is the mean effective axial proximity velocity in meters per second of the ice molecules.

$$\bar{v}_i = \sqrt{\frac{\pi}{2}} \sigma$$

This is the mean effective axial impulse velocity in meters per second of the ice molecules.

$$\bar{f}_i^{\uparrow} = \frac{1}{2} \bar{n}_{ice} \bar{v}_p$$

This is the effective molecular axial impulse flux rate normal to and toward the ice surface in number of impulses per square meter per second.

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TABLE SUB06

MOLECULAR ESCAPE RATE FUNCTIONS

SYSTEM TEMP	BONDING FORCES	STANDARD DEVIATION VELOCITY*	ERROR FUNCTION ORDINATE*	ESCAPE POPULATION PROPORTION*	MEAN IMPULSE FLUX TO SURFACE*	ESCAPEE FLUX*
°C	$v_{\sim+i}^{bonding}$	$\sigma$	$(x)$	$2erfc(z)$	$\bar{f}_i^{\uparrow}$	$\bar{f}_{-i}^{\uparrow}$
	meters sec <sup>-1</sup>	meters sec <sup>-1</sup>	$a \frac{v_{\sim+i}^{bonding}}{\sigma}$	parts per million	x 10 <sup>28</sup> molecules m <sup>-2</sup> sec <sup>-1</sup>	x 10 <sup>24</sup> molecules m <sup>-2</sup> sec <sup>-1</sup>
00	1684	355	4.74	4.920	434	21.369
-05	1684	352	4.79	3.402	430	14.664
-10	1684	348	4.83	2.307	427	9.866
-15	1685	345	4.88	1.538	423	6.519
-20	1685	342	4.93	1.005	419	4.219
-25	1685	338	4.98	0.641	415	2.666
-30	1685	335	5.03	0.398	411	1.640
-35	1685	332	5.08	0.241	407	0.981
-40	1685	328	5.14	0.141	403	0.569
-45	1685	324	5.19	0.080	399	0.320
-50	1685	321	5.25	0.044	394	0.173
-55	1685	317	5.31	0.023	390	0.091
-60	1685	314	5.37	0.012	386	0.045
-65	1686	310	5.44	0.006	381	0.022
-70	1686	306	5.51	0.003	377	0.010
-75	1686	302	5.57	0.001	373	0.004

All table values are for a system consisting of clean humid air at a pressure of 10<sup>5</sup> Pascals in contact with a pure natural ice surface. \*Values are base on acceptance of the working hypothesis on effective axial velocities. See text.

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**MOLECULAR ESCAPE VELOCITY FUNCTIONS**

$$\bar{v}_{+i}^{\text{bonding}} = \left( W_{\sim kg}^{\leftrightarrow} \right)^{\frac{1}{2}}$$

This is the slowdown (in meters per second) per molecule that the vaporizing molecule undergoes due to the attraction of the intermolecular bonding forces.

$$\sigma = \left( \frac{k_B \bar{T}}{\bar{m}} \right)^{\frac{1}{2}}$$

*Sigma.* This is the standard deviation (in meters per second) of the distribution of molecular velocities along any single axis under conditions of equilibrium. It is also the root-mean-square molecular velocity in meters per second for that distribution. The use of the mean molecular mass instead of the effective mass introduces some error. Since pure natural water is largely (99.73%) composed of a single isotope of water, the error is insignificant.

$$(x) = a \frac{\bar{v}_{+i}^{\text{bonding}}}{\sigma}$$

This is the ordinate of the normal distribution curve that corresponds to the accommodated bonding velocity.

**2erfc(z)**

The complimentary error function of (x), expressed as parts per thousand. This is the proportion of effective velocities along the proximity axis that meet or exceed the minimal escape velocity. The coefficient of 2 is required by the fact that we are only dealing with the positive half of the population.

$$\bar{f}_i^{\uparrow} = \frac{1}{2} \bar{n}_{\sim ice} \bar{v}_{\sim p}$$

This is the molecular impulse flux rate normal to and toward the water surface in number of impulses per square meter per second.

$$\bar{f}_{-i}^{\uparrow} = \bar{f}_i^{\uparrow} 2erfc(z)$$

This is the molecular flux rate of escapees from the ice surface.

**TABLE SUB07**

**MOLECULAR ESCAPE VELOCITY FUNCTIONS**

ICE TEMPERATURE	ICE TEMPERATURE	MEAN INITIAL ESCAPE VELOCITY*	DECELERATION BY BONDING FORCES	MEAN CONSEQUENT VAPOR VELOCITY*
°C	$\bar{T}$	$\bar{v}_{\sim-i}^{escape}$	$v_{\sim+i}^{bonding}$	$\bar{v}_{\sim-i}$
	°K	m sec <sup>-1</sup>	m sec <sup>-1</sup>	m sec <sup>-1</sup>
00	273.15	2129	1684	445
-05	268.15	2125	1684	441
-10	263.15	2121	1684	437
-15	258.15	2117	1685	433
-20	253.15	2113	1685	428
-25	248.15	2109	1685	424
-30	243.15	2105	1685	420
-35	238.15	2100	1685	416
-40	233.15	2096	1685	411
-45	228.15	2092	1685	407
-50	223.15	2087	1685	402
-55	218.15	2083	1685	398
-60	213.15	2079	1685	393
-65	208.15	2074	1686	388
-70	203.15	2069	1686	384
-75	198.15	2065	1686	379

All table values are for a system consisting of clean humid air at a pressure of 10<sup>5</sup> Pascals in contact with a pure natural ice surface. \*Values are based on acceptance of the working hypothesis on effective axial velocities. See text.

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#### MOLECULAR ESCAPE VELOCITY FUNCTIONS

$$\bar{v}_{-i}^{escape} = \bar{v}_{+i}^{bonding} + \bar{v}_{-i}$$

This is the mean initial velocity (in meters per second) normal to and away from the ice surface that sublimating molecules possess at the instant of departure from that surface.

$$\bar{v}_{+i}^{bonding} = \left( W_{kg}^{\leftrightarrow} \right)^{\frac{1}{2}}$$

This is the slowdown (in meters per second) per molecule that the sublimating molecule undergoes due to the attraction of the intermolecular bonding forces.

$$\bar{v}_{-i} = \sqrt{\frac{\pi}{2}} \sigma$$

This is the mean terminal velocity (in meters per second) that the sublimating molecules possess at the instant of joining the vapor population.

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TABLE SUB08

MOLECULAR ESCAPE ENERGY FUNCTIONS

ICE TEMP	ICE TEMP	MEAN DEGREES OF FREEDOM	THERMAL TERM	MEAN MOLECULAR KINETIC ENERGY	ENTHALPY OF PHASE TRANSFER	ENTHALPY LOSS PER SUBLIMATING MOLECULE
°C	$\bar{T}$	$\bar{f}_\circ$	$k_B \bar{T}$	$\bar{u}^2$	$\dot{w}^{\leftrightarrow}$	$\bar{q}_{-i}$
	°K	degrees per molecule	$\times 10^{-21}$ Joules molecule <sup>-1</sup>	$\times 10^{-21}$ Joules molecule <sup>-1</sup>	$\times 10^{-21}$ Joules molecule <sup>-1</sup>	$\times 10^{-21}$ Joules molecule <sup>-1</sup>
00	273.15	6.0546	3.7712	11.42	84.79	96.21
-05	268.15	6.0512	3.7022	11.20	84.83	96.03
-10	263.15	6.0477	3.6332	10.99	84.87	95.86
-15	258.15	6.0442	3.5641	10.77	84.89	95.66
-20	253.15	6.0408	3.4951	10.56	84.89	95.45
-25	248.15	6.0376	3.4261	10.34	84.89	95.24
-30	243.15	6.0350	3.3571	10.13	84.91	95.04
-35	238.15	6.0324	3.2880	9.92	84.92	94.84
-40	233.15	6.0298	3.2190	9.70	84.93	94.64
-45	228.15	6.0286	3.1500	9.49	84.94	94.44
-50	223.15	6.0253	3.0809	9.28	84.95	94.24
-55	218.15	6.0244	3.0119	9.07	84.97	94.04
-60	213.15	6.0235	2.9429	8.86	84.98	93.84
-65	208.15	6.0227	2.8738	8.65	84.99	93.65
-70	203.15	6.0218	2.8048	8.44	85.01	93.45
-75	198.15	6.0209	2.7358	8.24	85.02	93.26

All table values are for a system consisting of clean humid air at a pressure of  $10^5$  Pascals in contact with a pure natural ice surface.



**MOLECULAR ESCAPE ENERGY FUNCTIONS**

$$\bar{f}_{\sim} = \frac{2C_v}{k_{ukg}}$$

This is the mean number of degrees of freedom per vapor molecule at the indicated temperature.

$$k_B \bar{T} = \bar{u}_{-i}$$

This is the thermal term in Joules per molecule found in so many of these equations. It is equal to the mean impulse kinetic energy of translation measured normal to and away from any surface at the instant of departure of a molecule from that surface. With a change in subscript sign, it becomes the mean impulse kinetic energy of translation measure normal to and toward any surface at the instant of impact.

$$\bar{u}_{-i}^{\Sigma} = \bar{f}_{\sim} \frac{1}{2} k_B \bar{T}$$

This is the mean total molecular kinetic energy in Joules per vapor molecule. It is the sum of the kinetic energies of translation, rotation, and vibration.

$$\dot{w}_{\sim}^{\leftrightarrow} = \frac{\dot{W}_{\sim}^{\leftrightarrow}}{\bar{N}_{kg}}$$

This is the enthalpy of phase transfer per ice molecule in Joules per molecule.

$$\bar{q}_{-i} = \bar{u}_{-i}^{\Sigma} + \dot{w}_{\sim}^{\leftrightarrow}$$

This is the mean amount of enthalpy in Joules that the substrate must give up to vaporize a single molecule of ice.

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TABLE SUB09

**SPECIFIC ENTHALPIES OF ICE SUBLIMATION**

SYSTEM TEMP	SYSTEM TEMP	ENTHALPY OF PHASE CHANGE	ENTHALPY GAIN BY VAPOR PHASE	ENTHALPY LOSS BY ICE PHASE
°C	$\bar{T}$	$\dot{W}_{kg}^{\leftrightarrow}$	$\Delta\bar{U}$	$\Delta\bar{Q}$
	K	kJ kg <sup>-1</sup>	kJ kg <sup>-1</sup>	kJ kg <sup>-1</sup>
00	273.15	2834	382	3216
-05	268.15	2836	374	3210
-10	263.15	2837	367	3204
-15	258.15	2838	360	3198
-20	253.15	2838	353	3191
-25	248.15	2838	346	3184
-30	243.15	2838	339	3177
-35	238.15	2839	332	3170
-40	233.15	2839	324	3163
-45	228.15	2839	317	3157
-50	223.15	2840	310	3150
-55	218.15	2840	303	3144
-60	213.15	2841	296	3137
-65	208.15	2841	289	3130
-70	203.15	2842	282	3124
-75	198.15	2842	275	3117

All table values are for a system consisting of clean humid air at a pressure of 10<sup>5</sup> Pascals in contact with a pure natural ice surface. Note that these values are dependent only on the mass sublimated and not upon the rate of sublimation.

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#### SPECIFIC ENTHALPIES OF ICE SUBLIMATION

$$\dot{W}_{kg}^{\leftrightarrow} = 0.0009059 \left( \frac{\bar{\rho}_{ice}}{\bar{m}} \right)^{\frac{1}{3}}$$

This is the enthalpy of phase change in kilojoules per kilogram. It is a function of the mean intermolecular distance between the ice molecules.

$$\Delta U_{\sim} = \bar{N}_{kg} \bar{u}_{\sim-i}^{\Sigma}$$

This is the total vapor kinetic energy in Joules per kilogram, although the table shows it in kilojoules. This is the enthalpy gained by the humid air consequent to the sublimation of one kilogram of ice at the specified system temperature.

$$\Delta Q_{\sim} = \Delta U_{\sim} + \dot{W}_{kg}^{\leftrightarrow}$$

This is the total enthalpic (heat) loss by the ice surface consequent to the sublimation of one kilogram of ice at the specified system temperature.

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TABLE SUB10

**POTENTIAL ICE TO VAPOR TRANSFERS**

SYSTEM TEMP	POTENTIAL NUMBER TRANSFER*	POTENTIAL MASS TRANSFER*	POTENTIAL VOLUME TRANSFER*	POTENTIAL ICE COLUMN EROSION*
°C	$\Delta \tilde{N}$	$\Delta \tilde{M}$	$\Delta \tilde{V}$	$\Delta \tilde{Z}$
	$\times 10^{28}$ $\text{m}^{-2} \text{sec}^{-1}$	kilograms $\text{m}^{-2} \text{sec}^{-1}$	cubic meters $\text{m}^{-2} \text{sec}^{-1}$	millimeters $\text{sec}^{-1}$
00	22.94739	0.68589	8.65408	0.74863
-05	15.25693	0.45603	5.64847	0.49703
-10	9.98034	0.29831	3.62606	0.32464
-15	6.42007	0.19189	2.28822	0.20872
-20	4.05344	0.12116	1.41673	0.13176
-25	2.51124	0.07506	0.86038	0.08162
-30	1.52415	0.04556	0.51167	0.04952
-35	0.90545	0.02706	0.29771	0.02940
-40	0.52539	0.01570	0.16912	0.01705
-45	0.29751	0.00889	0.09371	0.00965
-50	0.16409	0.00490	0.05055	0.00532
-55	0.08800	0.00263	0.02651	0.00285
-60	0.04579	0.00137	0.01348	0.00148
-65	0.02307	0.00069	0.00663	0.00075
-70	0.01123	0.00034	0.00315	0.00036
-75	0.00526	0.00016	0.00144	0.00017

All table values are for a system consisting of clean humid air at a pressure of  $10^5$  Pascals in contact with a pure natural ice surface. The values in this table should be viewed as limiting cases, since they assume no compensating gross deposition and unlimited diffusion. In reality, gross deposition does exist and transfers are limited by rates of diffusion at the molecular level and rates of convection and advection (wind velocity) at the meteorological level. Still, these are interesting concepts. \*Values are based on the substitution of the equilibrium vapor pressure flux rate for the working hypothesis flux rate.

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#### POTENTIAL ICE TO VAPOR TRANSFERS

$$\Delta \tilde{N} = \bar{f}_i^\downarrow$$

This is the potential number of ice molecules that could leave the ice surface to become vapor molecules per square meter of ice surface per second. The value is based on the equilibrium vapor pressure flux rate rather than the working hypothesis flux rate.

$$\Delta \tilde{M} = \Delta \tilde{N} \bar{m}$$

This is the potential mass transfer from ice to vapor in kilograms per square meter of ice surface per second.

$$\Delta \tilde{V} = \frac{\Delta \tilde{N}}{\bar{n}}$$

This is the potential increase in atmospheric volume in cubic meters per square meter of ice surface per second. It is also the upward wind flow velocity in meters per second.

$$\Delta \tilde{Z} = \frac{\Delta \tilde{N}}{\bar{n}_{ice}}$$

This is the ice column erosion in meters per second. Multiply by  $10^3$  to get the table value in millimeters.

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#### OUTSIDE REFERENCES

TEMPERATURE: The ice temperatures and the overlying and surrounding vapor temperatures are postulated as being in equilibrium.  $^{\circ}\text{K} = ^{\circ}\text{C} + 273.15$

ICE DENSITY: This is the density of one cubic meter of pure natural water ice in kilograms. Values were taken from *The Engineering Toolbox*, “Ice – Thermal Properties”, [http://www.engineeringtoolbox.com/ice-thermal-properties-d\\_576.html](http://www.engineeringtoolbox.com/ice-thermal-properties-d_576.html) on 10 August 2010.

EQUILIBRIUM VAPOR PRESSURE: Taken from Table 4k-16 on page 4-301 of *American Institute of Physics Handbook*, Third Edition, McGraw Hill, 1972, and converted from bars to Pascals.

ENTHALPY OF VAPORIZATION: Enthalpy of phase change between solid and vapor phases in kilojoules per kilogram. The formula used in Table SUB04 is a partially theoretical and partially empirical fit to the data in Table 2.1 of R. R. Rogers and M. K. Yau, *A Short Course in Cloud Physics*, Butterworth & Heinemann, 1988, page 16.

SURFACE ENERGY: Experimental data were scarce. The partially theoretical and partially empirical values used in Table SUB04 are a fairly close fit to the few published data that I could find.

#### INTERNAL REFERENCES

[MOLECULAR SPEEDS AND VELOCITIES](#)

[MOLECULAR IMPULSES](#)

[MOLECULAR KINETIC ENERGIES](#)

[THE NATURE OF GAS TEMPERATURES](#)

[THE PROBABILITY DENSITY CURVE](#)