

NET VAPORIZATION AND CONDENSATION

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.

Condensation: Condensation is the process by which vapor molecules leave the gaseous phase and attach themselves to a water surface or an ice surface or to some other substrate. After such attachment, they are no longer gas molecules.

Substrate: A substrate is any surface bearing water molecules. In the free atmosphere, most substrates are surfaces of either liquid water or ice. In addition, any surface exposed to the free atmosphere that does not actively repel water may be considered (and—in fact—is) a substrate.

Gross Vaporization: Gross vaporization refers to the process of vaporization without any consideration of the reverse process of gross condensation.

Gross Condensation: Gross condensation refers to the process of condensation without any consideration of whatever vaporization may be taking place.

Net Vaporization: Net vaporization occurs when the rate of gross vaporization exceeds the rate of gross condensation upon any substrate of interest.

Net Condensation: Net condensation occurs when the rate of gross condensation exceeds the rate of gross vaporization upon any substrate of interest.

Intermolecular Attraction: Water molecules are attracted to other water molecules by various intermolecular forces. These other water molecules can be vapor molecules or a droplet of liquid water or a crystal of ice. In addition, water molecules are attracted to what are called hygroscopic substances by various physio-chemical forces. Finally, water ions are attracted to ionized surfaces. Any

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and all of these forces of intermolecular attraction can and do cause water molecules to move toward one another and to bond together.

Zone of Attraction: The resulting zone of attraction has two parts. The core is composed of the substrate and any water molecules bonded to it. The second part is the force field surrounding the substrate and its bonded water molecules. This force field extends as far as the various forces are capable of causing variations in the trajectories of nearby vapor molecules.

The force field acts so as to diminish the speed of water molecules moving away from the substrate and its zone of attraction; and to increase the speed toward the substrate of those molecules moving toward the substrate and its zone of attraction.

Latent Heat of Vaporization: Because of the attractive forces of the zone of attraction, water molecules leaving the substrate undergo diminution of their escape velocities and become vapor molecules with less kinetic energy of translation than they had when first leaving the substrate. This loss of enthalpy is carried on the books as the latent heat of vaporization.

Latent Heat of Condensation: Because of the attractive forces of the zone of attraction, water molecules leaving the gaseous phase undergo acceleration of their arrival velocities and become liquid or solid phase molecules with more kinetic energy of translation than they had when first leaving the vapor phase. This gain of enthalpy is carried on the books as the latent heat of condensation.

Free Atmosphere Considerations

Ubiquity: Every surface exposed to the free atmosphere is undergoing **both** gross vaporization and gross condensation unless that surface actively repels water. Every such surface exposed to the free atmosphere is undergoing either net vaporization **or** net condensation. There are no exceptions unless that surface actively repels water.

This means that every such surface is either undergoing a net gain in water molecules or a net loss of water molecules; a net gain of enthalpy or a net loss of enthalpy. There is no equilibrium.

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The Equilibrium Fallacy: The concept of equilibrium is a useful concept, but—like the concepts of infinity and centrifugal force—it is not a reality. It is a useful fiction. Equilibrium can be very closely approximated in the laboratory under controlled conditions; but, in the free atmosphere it does not exist. This is especially true at the molecular level where the mathematical mandates of statistical mechanics apply.

The idea that in one second some 517,727,454,042,331,290,445 vapor molecules should be arriving at one square centimeter of ocean surface, while exactly 517,727,454,042,331,290,445 molecules are leaving that square centimeter is beyond belief. The idea that the enthalpy loss and the enthalpy gain in that same second are equal down to the last quantum of energy is equally ludicrous.

The illusion of equilibrium is assisted by the time spans and spatial parameters that we human beings are forced to live with. If we reduce the area to one square micron or the time to one millionth of second, we produce even greater disparities from one area to another or one time span to another.

No, Virginia, equilibrium does not exist. It is a well-meant lie; but a lie nonetheless. The most that we can hope for is pseudo-equilibrium. When your instruments tell you that a state of equilibrium exists, what they are really telling you is that they are not sensitive enough to measure the non-equilibrium that is really there.

The Primal Opposition—Attraction versus Repulsion

Whether some portion of the atmosphere is undergoing net vaporization or net condensation at any give time and place depends upon the relative strengths of a variety of different forces and processes.

Temperature: First and foremost among these forces are the repulsive forces made manifest in thermal agitation. Increases in the temperature of the substrate always lead to increased gross vaporization. Gross condensation, on the other hand, is inversely proportional to the square-root of the temperature; and so tends to decrease with an increase in temperature.

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Increases in temperature thus favor net vaporization, while decreases in temperature favor net condensation—as experiment and observation both clearly show.

Intermolecular Forces: The intermolecular forces of attraction obviously act to favor condensation. If it weren't for thermal agitation, these forces would ensure that everything that is would be solid. The liquid and vapor phases would not exist. The forces that bond water molecules to one another and to various substrates and solutes are many and extremely complex. For the sake of simplicity, let us consider four groupings and how they affect net condensation or net vaporization.

Water to Water Bonding – Water molecules attract one another at moderate distances, and repel one another at very close distances. In both liquid water and ice, the balance between these opposing forces establishes the effective inter-molecular distances. The strength of these bonds is also affected by particle size. Large droplets and crystals will undergo net condensation at combinations of temperature and vapor pressure that cause smaller droplets and crystals to undergo net vaporization.

Thus, for any combination of vapor pressure and temperature, there will be a droplet or crystal size that represents a balance between gross condensation and gross vaporization. It doesn't take much, however, to upset that balance. Given the natural variability of the free atmosphere, the life of a cloud droplet or ice crystal is a brief one.

This tendency for the smaller droplets and crystals to vaporize may be overcome by the incorporation of strongly hygroscopic substrates into the droplet or crystal, by higher concentration of solutes, or by greater ionization of the smaller particles.

Hygroscopic Bonding – Water molecules bond strongly to certain hygroscopic substances. Ordinary silica is one such substance. The water molecules do not ordinarily combine chemically with the hygroscopic substrate or act to dissolve it, but simply adhere to the surface of it. The bonding forces are unsaturated by this adhesion, and may continue to attract water molecules until they are covered by water to a considerable relative depth.

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However, the strength of the hygroscopic force diminishes with the depth from the surface of the droplet or crystal. Thus it leads to net condensation at certain combinations of vapor pressure and temperature only up to the point where it is once again balanced by the forces of thermal agitation.

Nevertheless, droplets and crystals with strongly hygroscopic substrates tend to undergo net condensation and growth when similarly-sized droplets of pure water will be undergoing net vaporization and diminution.

Solute Bonding – Strong chemical bonds exist between water and certain solutes, such as common sea salt or common atmospheric sulfates. This bonding tends to decrease gross vaporization, and therefore tends to increase net condensation. A salty or acidic droplet will grow under conditions where a similar droplet of pure water will diminish.

Quite naturally, however, the growth of the droplet decreases its concentration of the solute. Once again, it will reach a droplet size where gross vaporization and gross condensation balance momentarily. And once again, this delicate balance does not last for long.

Ionic Bonding – There are numerous processes in the atmosphere that tend to ionize atmospheric molecules—water included. Ionization is a very strong force compared to some of the forces described above. As such, it is capable of bonding both molecules and small droplets or crystals together from much greater distances than the weaker forces normally act through in the time available to them.

Ionization produces both negatively (excess of electrons) and positively (deficiency of electrons) charged ions and particles. Like charges repel and unlike charges attract. Free electrons have a tendency to migrate to points and edges. Since snowflakes grow at those very same points and edges, it is likely that ionic forces play a role in the growth of snowflakes and other ice crystals—probably by attracting hydroxyl ions.

Similarly, small ionized droplets can be attracted to one another, producing the “collision and capture” mechanism by which cloud droplets are assumed to grow. The power of ionic forces in creating condensation is graphically illustrated by the Wilson cloud chamber.

Conclusions - The net effect of all of the various intermolecular bonding forces is to increase net condensation and diminish net vaporization. We are thus

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back to our starting point where the forces of thermal agitation tend toward net vaporization and the forces of intermolecular attraction (bonding) tend toward net condensation.

Decreasing temperatures also tend to net condensation, but—by themselves—do not appear to be sufficient to explain most atmospheric condensation processes. We need the forced inflow brought about by the intermolecular forces of attraction.

Inflows and Outflows

As we saw in [Gross Condensation](#), we can divide up the population of molecular inflows into four groups. Each group has a different motive force that impels its vapor molecules toward the surface of the substrate.

Unforced Inflows – Unforced inflows are those molecular movements toward the substrate originating in the surround humid air that are thermally driven and would occur even if no forces of attraction existed. They can be expressed by:

$$\tilde{n}_i = \tilde{p} \left(\frac{1}{2\pi\tilde{m}_\sigma k_B T} \right)^{\frac{1}{2}} \quad \text{NET01}$$

Here, \tilde{n}_i is the vapor flux rate in number of vapor molecules per unit area of substrate surface per unit time, \tilde{p} is the vapor pressure, \tilde{m}_σ is the effective molecular mass at temperature T , and k_B is Boltzmann's Constant in units of energy per degree Kelvin per molecule.

As we saw in [Gross Condensation](#), in still air this flux can be more simply expressed as:

$$\tilde{n}_i = \tilde{n}_p \bar{v}_p \quad \text{CON01}$$

and in moving air by:

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$$\tilde{n}_i = \frac{\tilde{n} \bar{v}_{\tilde{p}}}{2(\omega + 1)} \quad \text{CON07}$$

Here, \tilde{n}_p is the number of vapor molecules in unit volume of humid air that have a component of motion toward our substrate, $\bar{v}_{\tilde{p}}$ is their mean speed toward that substrate, \tilde{n} is simply the number of vapor molecules in unit volume of humid air, and ω is the wind velocity in unit distance per unit time.

This flux is purely a function of the characteristics of the atmosphere surrounding the substrate. The characteristics of the substrate play no role in its magnitude or direction.

Forced Inflows – Forced inflow does not include any unforced inflow, but consists only of those vapor molecules whose impact on the substrate is solely due to the combined forces of attraction of the substrate. If it were not for these forces, the vapor molecule would have passed by the substrate unscathed.

Because of the enormous variability in the strengths and ranges of the various zones of attraction, it is not possible (at this time) to develop a simple expression for the forced inflows on the order of NET01. We can, however, produce some general rules.

1. The longer a vapor molecule is in a zone of attraction, the more likely it is to become part of a forced inflow. This means that vapor molecules having a slow speed relative to the substrate are more likely to be captured than ones moving more quickly. This, in turn, translates out to molecules have lower kinetic energies of translation relative to the substrate being more likely to be captured. Finally, when placed in the construct of individual molecular “temperatures”, the cooler ones are more likely to be captured than the hotter ones.
2. Droplets or ice crystals with a hygroscopic component are more likely to capture ambient vapor molecules than those lacking in these additional attractive forces. This explains why condensation and freezing are so difficult to bring about in the absence of such nuclei. It also supports the hypothesis that forced inflow is necessary to explain condensation phenomena.

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- Hygroscopic attraction is often not enough. The much stronger forces of ionic attraction are frequently necessary to promote rapid growth of condensation in both droplets and ice crystals.

Knock-Backs – The surfaces of water droplets and ice crystals are subject to a continual bombardment by air molecules. What, then, are the chances that water molecules that otherwise might escape the zone of attraction to become vapor molecules might be knocked back to the substrate by collision with non-aqueous air molecules?

Rejection by ambient vapor molecules is not counted in this population, since that must be considered a simple transfer of impulse resulting in either forced or unforced inflow. In any case, as we shall see, this phenomenon is insignificant.

In still air, the dry air molecular flux against the surface of a droplet or crystal is given by a variation of NET01:

$$\dot{n}_i = p \left(\frac{1}{2\pi \hat{m}_\sigma k_B T} \right)^{\frac{1}{2}} \quad \text{NET02}$$

Here, \dot{n}_i is the molecular flux in number of impacts per unit area and time, p is the dry air pressure, \hat{m}_σ is the effective molecular mass of the dry air, and the remaining terms have their previously agreed-upon meanings.

Once again, this expression can be simplified to:

$$\dot{n}_i = \dot{n}_p \bar{v}_p \quad \text{NET03}$$

in still air, and:

$$\dot{n}_i = \frac{\dot{n}_p \bar{v}_p}{2(\omega + 1)} \quad \text{NET04}$$

in moving air. The dot under the parameter signifies that the parameter applies to dry air molecules only.

Let us postulate a parcel of atmospheric air with the following parameters:

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$$\begin{aligned}T &= 273.15^\circ\text{K} \\p &= 1.007143 \times 10^5 \text{ Pascals} \\ \hat{m}_\sigma &= 4.75 \times 10^{-26} \text{ kilograms} \\ \mathbf{k}_B &= 1.38065 \times 10^{-23} \text{ Joules per degree per molecule}\end{aligned}$$

The dry air flux against a droplet or crystal surface then becomes:

$$n_i = 3.00 \times 10^{27} \text{ impulses per square meter per second.}$$

If we assume that there are some 1.04×10^{19} water molecules per square meter of surface, then each of those surface molecules undergoes some 2.89×10^8 impulses from above each second¹. Let's double that number to allow for glancing blows.

At NTP, the average speed normal to the surface of an escaping water molecule is some 445 meters per second or some 1.14×10^{12} molecular diameters. This means that the average escaping molecule will get some 2.48×10^3 diameters away from the surface before being hit by an incoming air molecule. This distance is well in excess of the normal free path, and such molecules must therefore be considered to be part of the ambient vapor at that time.

In short, “knock-backs”—whether from incoming air molecules or incoming vapor molecules—are an insignificant part of the inflow population.

Weaklings – We must assume that water molecules leaving the surface of a droplet or crystal do so with a wide range of velocities normal to the surface. Some of these velocities will be less than the escape velocity. Such “weak” molecular efforts will follow the standard parabolic trajectory and return to the substrate. The net effect is zero. There is neither a gain or loss of mass, or a gain or loss of enthalpy. Such efforts are therefore meaningless in considerations of either inflow or outflow.

In consequence, only unforced inflow and forced inflows play any significant role in either the net vaporization process or the net condensation process. Moreover, the total outflow must of necessity equal the sum of both the

¹ Of course, at the same time each surface molecule is undergoing roughly a thousand times as many impulses from below.

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forced inflow and the unforced inflow under conditions of so-called equilibrium vapor pressure.

$$\bar{n}_{-i}^{outflow} = -\bar{n}_i^{unforced\ inflow} + \bar{n}_i^{forced\ inflow} \quad \text{NET05}$$

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Summary of Net Vaporization and Condensation Concepts

01. Unless a surface actively repels water, every surface exposed to the free atmosphere undergoes both gross condensation and gross vaporization.
02. True equilibrium does not exist in the free atmosphere. The mathematics of probability mandate that either net vaporization exists or net condensation exists.
03. Which of the two processes is in effect depends upon the local relative strengths of the combined forces of attraction and the combined forces of repulsion.
04. The combined forces of attraction include water-to-water bonding forces, hygroscopic attractive forces, solution forces, and ionic forces.
05. The combined forces of repulsion include the repulsive van der Waal's force and the forces of thermal agitation.
06. Net condensation occurs when molecular inflows to the substrate exceed molecular outflow from the substrate.
07. Molecular inflows include both unforced inflows and forced inflows.
08. Unforced inflows are those that would occur even in the complete absence of any forces of attraction. They are a function solely of vapor characteristics.
09. Forced inflows are those that occur solely because of the attractive forces of the substrate. They are a function of both vapor characteristics and substrate characteristics.

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10. Forced inflows are usually some two orders of magnitude greater than unforced inflows.
11. In the free atmosphere, most condensation is initiated by forced inflows. Indeed, in the absence of such forced inflows, supersaturation is the norm.
12. Outflows are a function solely of the substrate characteristics.
13. In moving against the forces of attraction, an escaping water molecule loses kinetic energy of translation. This energy loss is carried on the books as the latent heat of vaporization.
14. In arriving at the surface of a substrate a vapor molecule undergoes acceleration due to these same attractive forces. It thus joins the substrate with increased kinetic energy of translation. This energy gain is carried on the books as the latent heat of condensation.
15. During net vaporization, the substrate loses enthalpy and the free atmosphere gains it. The loss is greater than the gain by the amount of the latent heat of vaporization.
16. During condensation, the free atmosphere loses enthalpy and the substrate gains it. The gain is greater than the loss by the amount of the latent heat of condensation.
17. The diminution of temperature during net vaporization is due the loss of the “hotter” molecules to the vapor phase by the liquid or solid phase. Since temperature is an average, the temperature is diminished.
18. The increase in temperature of the free atmosphere during net condensation is due to the loss of the “cooler” molecules to the substrate. Since temperature is an average, the temperature goes up.
19. Neither “knock-backs” nor “weaklings” play any significant role in the transfer of either mass or enthalpy during net vaporization or net condensation.
20. The gross vaporization and gross condensation processes are, in essence, symmetrical.