GROSS CONDENSATION

Definitions

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.

Gross Condensation: Gross condensation refers to the process of condensation without any consideration of whatever vaporization may be taking place. Throughout the balance of this paper, the term condensation will refer to gross condensation. If net condensation is intended, net condensation will be specified. Nevertheless, for the ease of understanding, we will quite often use the term gross condensation instead of simply condensation.

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

Free Atmospheric Considerations

Ubiquity of Gross Condensation: Gross condensation takes place on every surface of any substance (except for those that actively repel water) exposed to the free atmosphere. It occurs on water surfaces, on ice surfaces, and on any exposed surface of animal, vegetable, or mineral nature. The water molecule possesses extremely strong bonding forces, and it will bond whenever and wherever given a chance. For all practical purposes, gross condensation may be assumed to be occurring on every surface that is exposed to the atmosphere.

Although intermittent on the molecular level, this process may be considered to be virtually continuous on the macroscopic level. Such gross condensation is

not always visible to the naked eye, nor measurable by our relatively crude instruments, but it is always occurring.

Spontaneous Condensation: It is extremely difficult to bring about spontaneous condensation in clean air. Temperatures may be dropped many degrees below the dew point without any visible condensation taking place. In fact, without the presence of cloud condensation nuclei (CCN), vapor pressures may easily exceed twice the equilibrium value before spontaneous condensation occurs. Supersaturation is thus an extremely common phenomenon in clean air. On the other hand, condensation may easily be initiated at vapor pressures as low as 75% of the equilibrium value in the presence of certain common hygroscopic nuclei.

This situation is analogous to the difficulty in causing pure water to freeze by dropping its temperature below the triple-point. In this case, icing nuclei must be present to facilitate freezing.

Luckily, both hygroscopic particles and icing nuclei appear to be fairly common in our none-too-clean atmosphere—at least in its lower reaches. Both supersaturation and super-cooling appear to be common in the upper levels of the troposphere.

Condensation Nuclei: For condensation to occur most readily, a little assistance seems to be required in the form of surfaces that attract water vapor. This attraction can be any one or any combination of attractive forces. It can be physio-chemical, as in the attraction of water to silica and in the absorption of water by salt and sulfates. And, it can be electrostatic, as in the case of both simple ions and ionized surfaces[1].

The most common of these condensation nuclei are salt (from the sea and playas) and sulfates (from volcanoes, industrial emissions, automotive emissions, and the decay of phytoplankton). Such particles can initiate condensation; and—once initiated—increase the attractive forces of the droplets thus created.

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[1] The potency of ionized particles in initiating and accelerating condensation is graphically demonstrated by cloud chamber experiments.

Zone of Attraction: Surrounding every object that attracts water vapor is a zone of attraction. Vapor molecules that enter that zone will have their trajectories modified by those forces of attraction. Most will continue to pass through the zone. Some, however, will be captured and become part of the substrate.   Faster molecules are most likely to pass through; slower ones are most likely to be captured.

Vapor molecules already in that zone cannot escape capture unless and until their kinetic energies normal to and away from the zone exceed the bonding energies.

The strength and range of the zone of attraction varies with the strengths and ranges of the three groups of forces that are characteristic of that particular substrate. These are—firstly—the attractive forces of surface tension in liquid water and surface force and/or surface energy in ice. Secondly, we have the various hygroscopic attractions of various condensation nuclei. Thirdly, we have the electrostatic attraction between an ionized substrate and ionized vapor molecules.

The resulting zone of attraction is not necessarily uniform from place to place over the substrate. Ice crystals have extremely varied zones. On the one hand, we have the variations from points to edges to flats in the hydrogen bonds due to the structural variations in the number of "neighboring" molecules. On the other hand, we have the electrostatic variation from flats to edges to points in the concentration of free electrons and water ions as they migrate to more favored locations.

Even water droplets can have variations in the zone strengths and ranges due to irregular condensation nuclei and variations in the concentrations of solutes.

Vapor Molecule Inflow Rates

In *Gross Vaporization*, we saw how the vapor molecule outflow from a wet substrate represented an imbalance. This imbalance was between two different sets of forces. On the one hand we had the cohesive forces of intermolecular attraction which acted to keep the molecules in liquid and solid phases or attached to a substrate. On the other hand we had the various kinetic energies of thermal agitation which tended to force them apart.

THE KINETIC ATMOSPHERE
Gross Condensation

Statistical mechanics ensures that there will always be some portion of the surface molecule population that has sufficient energy to escape the cohesive forces and become free vapor molecules. This is the vapor outflow.

In a similar but opposite fashion, statistical mechanics ensures that there will always be some vapor molecules of the free atmosphere that interact with the attractive substrate and are captured by these same cohesive forces. These molecules cease to be vapor molecules and become part of the substrate, whatever this substrate may be. This is the vapor inflow.

The imbalance occurs because, in the free atmosphere, these two opposing sets of forces are virtually never equal. Moreover, the sheer magnitude of the numbers involved ensures that the two flow rates are never really absolutely identical.

The Nature of Vapor Inflow: Water vapor is present in every part of the atmosphere, although its presence may be difficult to measure at very low vapor pressures and temperatures. Consequently, there will always be vapor molecules moving toward and eventually interacting with any object of interest.

Unforced and Forced Inflows: In condensation studies, it is extremely important to distinguish between "unforced" and "forced" inflows of vapor molecules toward the substrate. All the interactions that would occur if the substrate involved had no attraction for the vapor molecule can be considered "unforced". Those that occur solely because of some attraction for the vapor molecule (and would not occur otherwise) must be considered "forced".

Unforced Inflows: *Molecular Speeds and Velocities* gives the number of molecules that interact with unit area of the object of interest in unit time as:

$$\underset{\sim}{n}_i = \underset{\sim}{n}_p \overline{\underset{\sim}{v}}_p \qquad\qquad \text{CON01}$$

Here, $\underset{\sim}{n}_i$ is the number of vapor molecules whose next interaction will be with our object of interest per unit area and unit time, $\underset{\sim}{n}_p$ is the number density of vapor molecules in the system per unit volume having a component of movement toward

the object of interest, and $\overline{\underset{\sim}{v}}_p$ is the mean vapor molecule speed along the proximity axis.

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

Unforced Inflows in Moving Air: The free atmosphere is virtually never still; and both the water droplets and the ice crystals in clouds are always surrounded by moving air. In addition, moving air is the norm over most free terrestrial water surfaces. To understand the effect of this moving air on condensation flow rates, it helps to understand how moving air differs from still air on the molecular level.

The Molecular Nature of Moving Air: Let us start by defining wind as air in net motion in any direction. Let us postulate a parcel of air moving in direction $\rightarrow$ at velocity ω. Let us stipulate that there are no changes occurring in either the mean molecular mass of the parcel of air in motion or in its temperature. That being the case, there are no changes in any of the mean molecular velocities or speeds.

Now, when a wind is blowing, there are more molecules moving in the wind direction than in any other direction. On a molecular level, this means that:

$$n_{\rightarrow} = \omega n + n_{\leftarrow} \qquad\qquad \text{CON02}$$

Here, $n_{\rightarrow}$ is the number of molecules entering unit area of an imaginary plane from the windward side, ω is the wind velocity in units per second, n is the number density in number of molecules per unit volume, and $n_{\leftarrow}$ is the number of molecules passing through that same unit area from the leeward side.

Logic compels us to define $n_{\leftarrow}$ as:

$$n_{\leftarrow} = n - n_{\rightarrow} \qquad\qquad \text{CON03}$$

which leads to:

$$n_{\rightarrow} = \tfrac{1}{2}n(\omega + 1) \qquad\qquad \text{CON04}$$

for an imaginary plane through which the wind is passing.

For passages from the leeward side we get:

$$n_{\leftarrow} = n - \tfrac{1}{2}n(\omega + 1) \qquad \text{CON05}$$

Vapor Flow Rates in Moving Air: For vapor flow rates, we need only substitute $\underset{\sim}{n}$ for n in equations CON02 through CON05.

Vapor Flow Rates and Real Objects: The above flow rates for passages through an imaginary plane are interesting, but are not of much use in the real atmosphere. Both common sense and experience tell us that moving air flows around real objects, not through them. Except for the turbulent boundary layer, winds tend to move more or less parallel to exposed surfaces.

Vapor Flow Rates in Moving Air: Let us postulate a parcel of humid air with a vapor molecule density of $\underset{\sim}{n}$ moving across a plane surface at speed ω. Let us stipulate, for the nonce, that the flow is laminar and not turbulent.

During unit time, the number of vapor molecules that pass out through unit area of the bottom of the parcel will be:

$$\underset{\sim}{n}_i = \underset{\sim}{n}_p \bar{\underset{\sim}{v}}_p = \tfrac{1}{2}\underset{\sim}{n}\bar{\underset{\sim}{v}}_p \qquad \text{CON06}$$

Those vapor molecules will impact on $\omega + 1$ unit area or surface over unit time. This means that the vapor molecule flow rate per unit area and time will be:

$$\underset{\sim}{n}_i = \frac{\underset{\sim}{n}\bar{\underset{\sim}{v}}_p}{2(\omega + 1)} \qquad \text{CON07}$$

This is the number of vapor molecules that will impact on unit area of surface in unit time. Some of these molecules will rebound, of course, and some will be absorbed by or otherwise adhere to that surface.

It should be noted that this expression also applies to a non-planar surface (such as the spherical surface of a cloud droplet), as long as the flow is essentially laminar.

Forced Inflows: It would be nice if expressions for forced inflows could be produced with the same level of simplicity that the above expressions for unforced flow display. Unfortunately, this does not appear to be possible at this time. The water molecule displays a wide variety of bonding forces of varying strengths. Hygroscopic and ionized condensation nuclei vary considerably, and their attractive forces vary as well. Some of these forces appear to follow the familiar inverse square law and some do not. Thus the strength and extent of the resulting zones of attraction vary tremendously from one condensation nucleus to another.

All we can say at this point is that, in the free atmosphere, it is forced inflow that usually initiates condensation and it is forced inflow that is necessary for the growth of water droplets and ice crystals. Part of this is explained by the relative flow rates of the two processes. Forced inflows are generally two orders of magnitude greater than unforced flows (see **Table WSV07** in *Water: Some Useful Values*).

Molecular "Capture" Rates: It is important to keep in mind that forced inflow is not limited to only those molecules that have a component of motion toward the substrate (v_p). Molecules with a component of motion away from the substrate (v_{-p}) that can be overcome by the sum of the attractive forces of the substrate will also be "captured". This capture is made considerably easier by the fact that the most probable velocities away from the substrate are close to zero. *Molecular Speeds and Velocities* gives the distribution of speeds toward any object of interest as:

$$\frac{dn_p}{dv_p} = \frac{n_p}{\sigma} \sqrt{\frac{2}{\pi}} \exp-\frac{v_p^2}{2\sigma^2} \qquad\qquad \text{MSV07}$$

Modified to apply to water molecules and with a change of sign to indicate speeds away from the object of interest, this becomes:

$$\frac{d\underset{\sim}{n}_{-p}}{d\underset{\sim}{v}_{-p}} = \frac{\underset{\sim}{n}_{-p}}{\underset{\sim}{\sigma}} \sqrt{\frac{2}{\pi}} \exp- \frac{\underset{\sim}{v}^{2}_{-p}}{2\underset{\sim}{\sigma}^{2}} \qquad \text{CON08}$$

Here, $d\underset{\sim}{n}_{-p}/d\underset{\sim}{v}_{-p}$ is the limited number of vapor molecules having velocities away from the substrate of between $\underset{\sim}{v}_{-p}$ and $d\underset{\sim}{v}_{-p}$, $\underset{\sim}{n}_{-p}$ is the number of molecules per unit volume of atmosphere having components of motion away from the object of interest, and $\underset{\sim}{\sigma}$ is the standard deviation of the distribution.

This distribution, of course, is the negative half of a "normal" or Gaussian probability distribution. The most probable velocities normal to the substrate are very close to zero (quantum considerations eliminate true zero as a possibility). This means that even weak attractive forces can change the *–p* subscript of those molecules with low relative velocities to a *p* subscript. This increases the number of vapor molecules in the forced inflow population.

Inflow Categories: It is possible to group those vapor molecules that will impact on the surface of the substrate during some measure of time into four distinct categories:

1. Unforced Inflows: This category is composed of all of those vapor molecules that would impact on the surface of the substrate even if there were no forces of attraction.

2. Forced Inflows: This category is composed of all of those vapor molecules that impact on the surface of the substrate due to the forces of attraction of that substrate; but would not otherwise do so.

3. "Knock-Backs": This category is composed of those molecules escaping from the substrate that are "knocked back" into the substrate by collision with incoming air molecules. Collisions with incoming vapor molecules are not counted in this group, because it is assumed that they would impact on the surface anyway. The vapor-to-vapor collision simply represents a one-for-one exchange.

4. "Weaklings": This category is composed of those molecules that manage to break away from surface tension and leave the surface, but possess

insufficient escape velocity to escape the total of attractive forces. The
leave the surface with a parabolic trajectory that takes them back to that
surface instead of escaping to become vapor molecules.

Selection in Vapor Molecule Capture

The nature and degree of selectivity in vapor molecule capture by a substrate
depends upon which of the four above categories the incoming molecule
represents.

1. Unforced Inflow: There is no selective mechanism in the vapor molecules
    that make up unforced inflow.

2. Forced Inflow: For the vapor molecules in this group, selection favors the
    molecules that have slow velocities normal to the proximity axis. These
    molecules will be in the zone of attraction longer than those with greater
    sideways velocities, and thus stand a better chance of capture.

       The same principle holds true for those vapor molecules that are
    slowly moving away from the substrate. The slower they move, the more
    likely they are to be captured. This is because the forces of attraction are
    steadily diminishing that away velocity. If that molecule stays in the zone of
    attraction long enough, it will eventually possess a positive velocity toward
    the substrate.

3. Knock-Backs: These molecules simply become part of the unforced inflow
    or the forced inflow—depending upon their post-collision trajectory. If they
    become part of the forced inflow, the same selection mechanisms that apply
    to that group apply to the knocked-back molecules. If they become part of
    the unforced inflow, there is no selection.

4. Weaklings: No selection applies. The molecules return to the substrate with
    the same kinetic energy as they had when they left. The substrate neither
    gains nor loses enthalpy, and the mean kinetic energy of translation is
    unchanged.

Transfer of Enthalpy during Gross Condensation

When an atmospheric vapor molecule is captured by a substrate, enthalpy is transferred from the vapor phase of the atmosphere to the liquid or solid phase. The amount of enthalpy that is transferred is the sum of the amount of enthalpy that the molecule possessed before entering the zone of attraction plus whatever energy is added to the molecule before impact by those attractive forces. That is, their kinetic energies of translation along the proximity axis are increased by the acceleration of the intermolecular forces of attraction. Their energies of impact will be (on the average) equal to the energies that they possessed when the first crossed the zone boundary plus a kinetic energy of translation that is equal to the escape energy; i. e.,

$$\overline{u}_i^{impact} = \overline{u}_i^{initial} + u_i^{capture} \qquad \text{CON09}$$

Here, $\overline{u}_i^{impact}$ is the mean kinetic energy of translation of the inflow molecule at impact (directed toward the surface of the substrate along the proximity axis), $\overline{u}_i^{initial}$ is the mean kinetic energy of translation along that same axis that the molecules had when they first crossed the escape boundary, and $u_i^{capture}$ is the energy that the molecule gets from its acceleration along the proximity axis by the forces of attraction. For any given substrate, this is equivalent to the escape energy.

In *Gross Vaporization*, we saw that this escape energy amounted to some 1.17 x 10^{-20} Joules per molecule for a plane surface of water under laboratory conditions at NTP. At impact, all of this energy is manifested in the molecule's increased velocity along the proximity axis. Once the molecule is absorbed into the substrate, however, this energy is shared by collisions with surrounding molecules and must then be made manifest in all of the active degrees of freedom.

If we assume the six-plus degrees of freedom for a water molecule shown in **Table WSV06** in *Water: Some Useful Values*, this gives an acceleration equal to an astonishing increase in that molecule's "temperature" of 847°C! However, our astonishment must give way to understanding when we consider that that is exactly the drop in molecular "temperature" experienced during a molecular escape.

Naturally, this increased energy is quickly shared with the other water molecules in the substrate. With trillions of collisions each second, this doesn't take long.

At any rate, we see that gross condensation results in a loss of enthalpy by the vapor phase and an increase in enthalpy by the liquid or solid phase. Moreover, the enthalpy gain by the liquid or solid phase is far greater than the enthalpy loss by the vapor phase. This imbalance requires a drawdown on the latent heat account.

Note that the heat is added to the liquid or solid phase, and removed from the vapor phase. Why then, does the temperature of that vapor phase increase during condensation?

Latent Heat of Condensation: The answer to this question lies in the selective nature of forced inflow. When condensation occurs, it is the "cooler" molecules that are most likely to condense out of the vapor phase. Since temperature is an average, this leaves those that remain with a higher average temperature.

This is the exact complement of the vaporization process. In that process it is the "hotter" molecules that escape, leaving those that remain behind with a lower average temperature.

There is no transfer of heat to the gaseous atmosphere during condensation (see *The Latent Heat Fallacy*). Instead, there is a transfer of heat (enthalpy) to the condensate instead. The temperature increase of the gaseous atmosphere during condensation is due to the selective removal of "cooler" vapor molecules.

Let me offer an analogy. Imagine a large room containing a considerable number of people. Each individual has a certain amount of money on their person. The **total** amount of money in the room is analogous to the heat content of a mass of humid air. The **average** amount per person is analogous to the temperature of our mass of humid air. We request that every individual with less than a certain amount of money step into the lobby for a moment. After they leave, the total amount of money in the room is diminished, but the average has gone up.

So it is during changes of phase. The change from a solid to a liquid involves the liquification of the most vigorous molecules first. The change from a liquid or a solid to a gas involves the vaporization of the most vigorous molecules

first. The change from a gas or vapor to a liquid or a solid involves the least vigorous molecules first. The change from a liquid to a solid involves the least vigorous molecules first.

We should not assume that the energy that a particular water molecule loses in escaping one atmospheric substrate is equal to the energy gained when condensing on a second atmospheric substrate. The mathematics of probability mandate against this. In point of fact, most atmospheric water condenses out at a much lower temperature than that which it had at evaporation. This is one way in which the atmosphere is heated (see *The Hydrologic Heat Pump*).

Dynamic Equilibrium: Both logic and mathematics tell us that, under conditions of dynamic equilibrium, molecular inflow should equal molecular outflow, and the net number of molecules escaping the surface should equal the net number being captured by that surface.

But here we get into the area of net vaporization and net condensation. That subject deserves its own essay.

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Summary of Condensation Concepts

01. Gross condensation takes place on every surface of any substance (except for those that actively repel water) exposed to the free atmosphere.

02. Although intermittent on the molecular level, this process may be considered to be virtually continuous on the macroscopic level. Such gross condensation is not always visible to the naked eye, nor measurable by our relatively crude instruments, but it is always occurring.

03. For condensation to occur most readily, a little assistance seems to be required in the form of surfaces that attract water vapor. This attraction can be any one or any combination of attractive forces. It can be physio-chemical, as in the attraction of water to silica and in the absorption of water by salt and sulfates. And, it can be electrostatic, as in the case of both simple ions and ionized surfaces.

04. Surrounding every object that attracts water vapor is a zone of attraction. Vapor molecules that enter that zone will have their trajectories modified by those forces of attraction. Most will continue to pass through the zone. Some, however, will be captured and become part of the substrate. Faster molecules are most likely to pass through; slower ones are most likely to be captured.

05. In condensation studies, it is extremely important to distinguish between "unforced" and "forced" inflows of vapor molecules toward the substrate. All the interactions that would occur if the substrate involved had no attraction for the vapor molecule can be considered "unforced". Those that occur solely because of some attraction for the vapor molecule (and would not occur otherwise) must be considered "forced".

06. In still air, the unforced flow rate of molecular impulses is a function of the number density of molecules with a component of motion toward the object of interest and the mean molecular speed of those molecules toward that object of interest.

07. In moving air, the number of molecules impacting upon the object of interest is inversely proportional to the wind velocity in laminar flow.

08. Forced inflows are a function of the total attractive forces of the substrate, as well as the number density and the molecular speeds along the proximity axis.

09. The capture of vapor molecules in forced inflows is selective, with the cooler (slower-moving) molecules being the ones most likely to be captured by the substrate.

10. During condensation, enthalpy is transferred from the gaseous phase to the liquid or solid phase.

11. The selective removal from the gaseous phase of those molecules that have lower kinetic energies of translation results in an increase in temperature in the remaining gaseous phase.

12. This temperature increase does not indicate a transfer of heat to the gaseous phase, but a loss of enthalpy by that gaseous phase and a transfer of that enthalpy to the liquid or solid phase.

13. The liquid or solid phase also gains enthalpy by the increase in incoming velocity due to the attractive forces of the substrate.

14. This enthalpy gain may or may not equal the enthalpy loss at vaporization.