

Paul Withers

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Chemistry of the Solar System Paper

Thermodynamics and Microphysics of Clouds on Jupiter

The thermodynamics controlling cloud condensation on Jupiter are discussed with reference to the major reactions and a scheme for calculating the cloud structure is outlined. Cloud microphysical processes are introduced and the extent to which they modify the results of the thermodynamic equilibrium model is discussed. The NH_3 cloud is found to be weakly precipitating and similar to terrestrial cirrus clouds. The H_2O cloud is found to be weakly precipitating and similar to terrestrial cumulus clouds. Terrestrial analogies suggest the classical picture of three compositionally distinct cloud layers on Jupiter may not be accurate.

1 - Vertical Structure of an Atmosphere

The vertical structure of an atmosphere is a description of how its pressure, temperature and chemical composition vary with distance from the centre of the planet.

The temperature structure is controlled by radiation, conduction and convection in response to heat sources and sinks. It can be used to divide the atmosphere into three regions.

- i) The troposphere lies deepest in the atmosphere. Temperature decreases rapidly as height above the warm surface increases and convection occurs. The temperature gradient is adiabatic.
- ii) The mesosphere lies above the troposphere and is not convecting. Temperature increases as height above the surface increases in response to the input solar flux and the downward transport of heat from the thermosphere above.
- iii) The thermosphere lies at the top of the atmosphere. Temperature asymptotes to a constant value as the atmosphere becomes too tenuous to support temperature gradients.

The pressure structure is simply controlled by the weight of the atmosphere above the height level. It is often a good approximation to have the pressure decreasing exponentially as height increases.

Figure 1 shows pressure-temperature profiles for the four giant planets. Note the troposphere below ~ 0.1 bar, the mesosphere above it and the asymptoting thermosphere at the lowest pressures.

The chemical composition structure in the absence of chemistry is kept constant by eddy mixing up to the homopause. This level lies above the troposphere. Above this level mixing is weak and the species separate, with the lighter ones becoming more abundant relative to the heavier ones. Chemistry modifies this situation. Solar radiation initiates chains of photochemical reactions and changes in equilibrium constants with temperature can alter the abundances of species. Condensation of gases can occur. When a gas's partial pressure exceeds its saturation vapour pressure it can condense. This will significantly reduce its number density. Figure 2 shows the effect of condensation on H_2O , H_2S , and NH_3 and diffusive separation of H_2 , He, and CH_4 above the homopause (called turbopause in this figure). Altitude is measured from the 400 K level.

Condensation to form clouds has significant effects on the vertical structure of an atmosphere. It is therefore vital to have some understanding of this process.

2 - Calculation of Cloud Structure

(After Lewis, 1969; Weidenschilling and Lewis, 1973; Atreya and Romani, 1985)

An atmospheric cloud structure can be calculated in the following manner:

Assume thermodynamic equilibrium.

Assume hydrostatic equilibrium. This specifies how pressure changes with altitude.

Assume an adiabatic temperature gradient.

Begin deep in the atmosphere with a specified temperature, pressure and chemical composition.

Increment the altitude and calculate the new temperature and pressure.

Calculate the new partial pressures of each constituent from the total pressure and its mole fraction.

Calculate the saturation vapour pressure of each constituent from the temperature and empirical equations.

If the saturation vapour pressure of a constituent exceeds its partial pressure form condensate until the partial pressure is reduced to the saturation vapour pressure. Calculate new mole fraction.

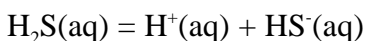
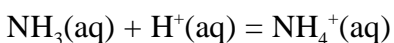
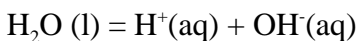
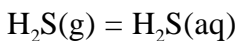
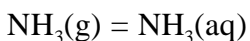
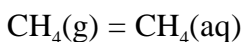
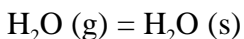
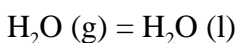
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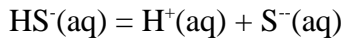
The main compounds of importance in the cloud forming regions of Jupiter are H₂, He, CH₄, H₂O, NH₃, and H₂S. Jupiter's atmosphere can be modeled as having solar composition but there is evidence that it is enriched in heavy elements, e.g. C, N, O, and S (Carlson, Rossow and Orton, 1988). The enrichment is limited to less than an order of magnitude by measurements of the Jovian gravitational moment (Stevenson, 1982). Uncertainty in the chemical composition lead to uncertainties in the results.

H₂ and He make up the bulk of the atmosphere but are not important participants in cloud formation, except for the thermal changes (both latent heat and specific heat) involved in para to ortho conversion of H₂ (Massie and Hunten, 1982). These changes are difficult to model accurately.

CH₄ undergoes photochemical reactions and reactions with hydrogen to produce a wide variety of hydrocarbons (Atreya and Romani, 1985). However Jupiter is not cold enough to permit CH₄ condensation.

H₂O forms ice and liquid water, allowing aqueous chemistry.

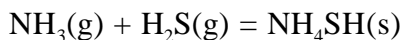
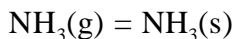




Acid-base chemistry between H_2S and NH_3 is important in the aqueous phase. H_2S readily dissolves to $\text{HS}^-(\text{aq})$. The presence of this anion allows an increased amount of NH_3 to dissolve to $\text{NH}_4^+(\text{aq})$ and $\text{NH}_3(\text{aq})$. If H_2S was absent, $\text{NH}_4^+(\text{aq})$ would have to be charge-balanced by $\text{OH}^-(\text{aq})$ and less $\text{NH}_3(\text{g})$ would dissolve.

The presence of aqueous ammonia solution is a complication. Its vapour pressure in the required concentration and temperature range is complicated and not accurately constrained by existing laboratory data (Atreya and Romani, 1985). Extrapolations of uncertain accuracy have to be made.

NH_3 is extremely important for cloud formation undergoing the following reactions in addition to its aqueous reactions.



$\text{H}_2\text{S}(\text{g})$ does not condense as $\text{H}_2\text{S}(\text{s})$ but as $\text{NH}_4\text{SH}(\text{s})$. Without this reaction $\text{H}_2\text{S}(\text{g})$ is expected to be abundant in the Jovian atmosphere and, until Jovian cloud theory was developed, observers were at a loss to explain why they did not detect it (Lewis, 1969).

Calculation of the adiabatic temperature gradient illustrates the connections between temperature, pressure and chemical composition.

Conservation of energy relates changes in temperature, pressure and amount of condensates present. Hydrostatic equilibrium relates changes in pressure to changes in altitude. The Clausius-Clapeyron equation relates changes in amount of condensates present to changes in temperature and altitude. Thus we have an expression relating changes in temperature to changes in altitude.

This model's prediction for upper tropospheric clouds on Jupiter is given in figure 3.

The topmost cloud layer is formed by simple condensation of NH_3 vapour near 130 K. It has a low mass density.

The intermediate cloud layer consists of crystalline NH_4SH clouds formed by chemical reaction between gaseous NH_3 and H_2S near 210 K. It has an intermediate mass density. The bottom cloud layer consists of ice crystals and water droplets near 280 K. The liquid droplets contain dissolved NH_3 . It has a large mass density.

This approach can be applied to the other gas giant planets (figures 4, 5, 6). CH_4 condensation becomes possible as you move further from the Sun and become cooler. More recent work with improved pressure-temperature profiles and compositional information predicts H_2S condensation above the NH_3 cloud layer but below any CH_4 cloud layer.

3 - Validity of this Approach

The assumptions must be justified.

Thermodynamic equilibrium - this neglects solar radiation induced photochemistry, physics of cloud formation and atmospheric dynamics. It leads to a static solution.

Large observed PH_3 tropospheric abundances lead to the conclusion that PH_3 is not oxidising to P_4O_6 and dissolving in H_2O as predicted but is being transported upwards faster than its reaction timescale into a less oxidising region where it can photochemically shield the NH_3 cloud layer (Atreya and Romani, 1985). So observations show us that equilibrium models cannot tell the whole story.

Hydrostatic equilibrium - this is likely to be a good approximation.

Adiabatic temperature gradient - this is likely to be a good approximation except for upwelling wave activity which is clearly seen on Voyager temperature profiles in figure 7.

Also, not knowing the bulk chemical composition exactly contributes significant uncertainties (Carlson, Rossow and Orton, 1988).

It is known from terrestrial observations that cloud formation is a dynamical process. I now investigate how cloud microphysics modify the results of the above model.

4 - Cloud Microphysics

(After Rossow, 1978). There are five major processes involved in cloud evolution

4a - Condensation

Conversion of vapour into a particle (liquid or solid) can occur when the saturation vapour pressure of a constituent exceeds its partial pressure. Nucleation theories predict which sizes of pre-existing condensate drops ("embryos") can grow further and which must evaporate. The saturation vapour pressure over a curved surface like an embryo is increased above its nominal value - measured near a flat surface of condensate - due to surface tension and small embryos with a sharply curved surface evaporate while large embryos with a flatter surface are stable. The embryos are formed by density fluctuations in the vapour. Embryo growth can occur in a number of ways.

i) Homogeneous nucleation

Molecules simply collide and merge with embryos. There is no help around the "curved surface" energy barrier and nucleation by other processes is more efficient.

ii) Chemical nucleation

Chemical reactions in the vapour can produce large, stable embryos which can grow rapidly.

iii) Heterogeneous nucleation

Embryos form around cloud condensation nuclei. These are other small particles in the atmosphere. As vapour is condensing onto a surface of different composition there is no increase in the saturation vapour pressure. Condensation by this process can occur rapidly at the saturation vapour pressure.

The characteristic time constant, τ_{cond} , of the condensation growth of an particle population is the time required for its mass to increase by a factor of e.

4b - Evaporation

This is strongly related to condensation, being the reverse physical process.

The characteristic time constant, τ_{evap} , of the evaporation of an particle population is the time required for its mass to decrease by a factor of e .

4c - Sedimentation

The descent of aerosols due to gravity into a higher temperature, evaporation region or onto a planetary surface. The characteristic time constant, τ_{fall} , of sedimentation is the time required for a particle to fall one atmospheric scale height at its terminal velocity.

4d - Coagulation

The formation of a single particle from two colliding particles, where the collision is caused by the Brownian motion of the particles. The collision kinetic energy is less than the surface energy, leading to the formation of a single particle. This is one of two major collisional processes. The characteristic time constant, τ_{coag} , for coagulation is the inverse of the rate of coagulation collisions for particles of mean mass.

4e - Coalescence

Collisions between particles caused by the different sedimentation velocities of different size particles. This is the other major collisional processes. This process can result in formation of a single particle or disruption into many particles, depending on whether the collision kinetic energy is respectively lesser than or greater than the surface energy. This process determines the maximum particle size. The characteristic time constant, τ_{coal} , for coalescence is the inverse of the rate of coalescent collisions between particles of mean mass and one-half mean mass.

Collisions between solid particles and between liquid particles are different. Solid particles can bounce off one another, liquid particles cannot. There are also differences between types of solid particles. Non-porous dust-like particles fall so fast that hydrodynamic forces prevent them from coalescing. However, on Jupiter, the solid particles in clouds are all porous ices. These fall slower than dust-like grains and can undergo coalescence.

5 - Application of Cloud Microphysics to Jovian Clouds

(After Rossow, 1978 and Carlson, Rossow and Orton, 1988). Results of the work of the previous section are usually displayed in the form of graphs of the microphysical time

constants versus mass-weighted mean particle radius (i.e., the radius of the particle with mean mass) for a constant mass cloud (cf figure 8).

There are several important features of this type of diagram.

a) Since collisional growth processes conserve total mass, the curves representing τ_{coag} and τ_{coal} are approximate evolutionary tracks for the mean particle radius of a constant mass cloud.

b) Condensation does not conserve total particle mass, hence the curve for τ_{cond} is not an evolutionary track. The curve instead represents the growth time as a function of particle size and can be used to approximate the time required by a cloud to attain a particular mean particle size by integrating from smaller to larger size. The growth time is such a strong function of particle size that the time taken to reach a particular size is only slightly longer than the growth time at that size, given by the τ_{cond} curves.

Curves for τ_{evap} are parallel to those for τ_{cond} . $\tau_{\text{evap}} \sim 3$ orders of magnitude smaller than τ_{cond} .

NH₃ Cloud

From figure 8 it can be seen that the mean particle size increases by condensation until it reaches $\sim 10\mu\text{m}$ in times $\sim < 10^4$ s. At this point coalescence, one of the collisional growth processes, takes over and the particles may increase in size. Sedimentation limits growth to a factor of a few increase in particle size from the end of condensation. As the sedimenting particles are only a few times larger than the size they reached by condensation, they will evaporate before falling a significant distance. The NH₃ cloud is only weakly precipitating. It is similar to a terrestrial cirrus cloud.

NH₄SH Cloud

Data for this cloud were not found in a literature search. However, Carlson, Rossow and Orton noted that, from a microphysical standpoint, the NH₄SH clouds were intermediate in

nature, having mass densities and precipitation rates midway between the NH_3 and H_2O cloud values.

H_2O Cloud

From figure 9 it can be seen that the mean particle size increases by condensation until it reaches $\sim 10\mu\text{m}$ in times < 100 s. Coalescent growth increases the size to $\sim 50\mu\text{m}$ in ~ 100 s. Coalescent disruption prevents further growth and sedimentation then occurs on timescales $\sim 10^4$ s. As the sedimenting particles have grown to their full size before being removed by sedimentation, they will fall a significant distance before evaporating. The H_2O cloud is moderately precipitating. It is similar to a terrestrial cumulus cloud.

6 - Conclusions

(After Carlson, Rossow and Orton, 1988). Thermodynamic equilibrium models are capable of providing some useful constraints on the composition, potential structure and chemical complexity of Jovian clouds, as well as the condensate abundance. Microphysical studies, in conjunction with analogies to terrestrial clouds, extends our understanding of the likely nature of these clouds.

For all Jovian clouds, the microphysical timescale is much shorter than the dynamical timescale and vapour cannot be supplied to the cloud level as rapidly as it is converted to precipitation. The cloud mass density is smaller than the equilibrium thermodynamic prediction and the ascending air is dried effectively.

Rapid formation of precipitation leads to significant latent heat feedback on dynamics and the drying of downdraughts. On Earth, this feedback can lead to the formation of other cloud layers well above the main thermodynamic layer. The possibility exists that the same is true on Jupiter, The classical picture of three compositionally distinct cloud layers on Jupiter may not be accurate.

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