Atmospheric Exclusion Limits for Clouds of Water and Other Substances

JAMES E. McDONALD

Institute of Atmospheric Physics, University of Arizona, Tucson

Abstract. Clouds of liquid droplets or of crystals cannot exist in stable equilibrium at a level in the atmosphere where the temperature and pressure are such that the saturation vapor pressure of the cloud substance exceeds the ambient pressure. Using vapor pressure data for water and a number of substances commonly used in rocket propellant mixtures, the exclusion limits for the existence of persistent clouds of these substances are determined for the U. S. standard atmosphere.

Introduction. Schilling [1964] has discussed the limits of existence of clouds of water particles in the atmosphere and has pointed out the layers within which clouds cannot possibly be in stable equilibrium. I have independently considered the same problem and have extended the analysis to clouds of other substances than water.

That there are regions of our atmosphere within which it is not thermodynamically possible for clouds of water drops or ice particles to exist seems not to be widely appreciated. No textbooks to my knowledge, mention this interesting point, which depends simply on the fact that there are layers in the earth's atmosphere within which the air temperature is warm enough and the total pressure low enough so that the saturation vapor pressure of water (or ice) must exceed the ambient pressure. *Ludlam* [1957] mentions this point briefly in a discussion of noctilucent clouds; but I have seen no other earlier comment on the matter.

With increasing numbers of rockets launched to high altitudes, it becomes of considerable interest to know the conditions under which clouds may form, not only from water substance but also from various other substances that may be intentionally or unintentionally released into the upper atmosphere. For this reason, I have computed exclusion limits for water and ice as well as for a number of other substances currently used as rocket propellants.

Method of determining limits. Consider the case of water substance. By means of standard data on its saturation vapor pressure [*List*, 1951], along with temperature and pressure data for the *U. S. Standard Atmosphere* [1962], definite levels can be determined at which the temperature and pressure are such that liquid water drops maintained at that temperature have a saturation vapor pressure just equal to the ambient pressure. Such a level will then constitute either an upper or a lower limit of a *layer of exclusion* for liquid water drops. The same applies to ice or other substances.

This principle is made clear in Figure 1. Exclusion limits for both liquid water and ice are found near 43 km, and the upper part of Figure 1 displays how that limit can be located precisely by graphical means. The dashed curve exhibits the dependence of ambient air pressure p on altitude z in the vicinity of 43 km in the standard atmosphere. The solid curves are, effectively, plots of the saturation vapor pressures of liquid water, e_{sw}, and of ice, e_{si}, corresponding to the ambient temperature at successive levels in the standard atmosphere. For example, consider the 43.0-km level, at which the temperature is $-14.5°C$. At that temperature, $e_{sw} = 1.99$ mb and $e_{si} = 1.73$ mb, and these two values are the respective ordinates, at 43 km, for the plotted e_{sw} and e_{si} curves. By repeating such determinations for a number of altitudes, and hence ambient temperatures, the loci of the solid curves are established.

The ambient pressure necessarily decreases with increasing altitude; but near 43 km temperatures are increasing with altitude, inasmuch as the temperature maximum of the stratopause lies higher. Since saturation vapor pressures rise exponentially with increasing temperature, both the curve for e_{sw} and the curve for e_{si} slope

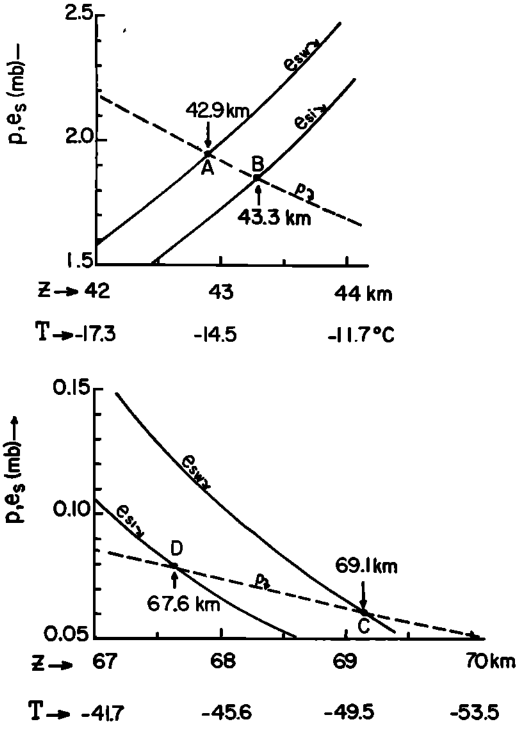

Fig. 1. Graphical method of determining cloud exclusion limits for water and ice in the U. S. standard atmosphere.

upward, crossing the p curve in points A and B at 42.9 and 43.3 km, respectively. Above 42.9 km a liquid water drop that might be expelled into the atmosphere would *instantaneously boil,* and so no *persistent* cloud of water drops can possibly exist above that level of the standard atmosphere. Similarly, an ice particle, if it found itself in the air above 43.3 km, would very quickly sublime away, just as solid carbon dioxide does at room temperatures. Regardless of the ambient water vapor pressure, cloud persistence is not possible in such cases. Indeed, the only condition under which a liquid-water cloud might exist even at a level of exactly 42.9 km in the standard atmosphere would be for the local atmosphere to consist solely of water vapor. That is certainly unlikely as a natural condition, and so natural water-droplet clouds are scarcely to be expected at as high an altitude as the 42.9-km limit. If water were artificially expelled from a rocket just at 42.9 km, for a short time the very boiling of the water would create a local pocket of pure water vapor as it expanded, pushing away the surrounding air. During this nearly explosive boiling and expansion, droplets could exist temporarily in vapor equilibrium. But, in a few moments, turbulent mixing with the ambient air would lower the actual vapor pressure below the saturation value and all the water would evaporate. Clouds of liquid droplets are possible at 42.9 km or above only as transient, nonequilibrium systems, not as 'persistent' systems.

All altitudes cited here refer specifically to the 1962 U. S. standard atmosphere. In any given situation, the departure of the actual lapse rate from the standard value will shift the prevailing exclusion limits somewhat, but use of the graphical method illustrated in Figure 1 will permit ready determination of the actually prevailing exclusion limits.

As one ascends from the neighborhood of the exclusion limits near 43 km, the temperature passes through its stratopause maximum and then begins to fall. Finally the temperature reaches low enough values so that, despite the concurrent fall of pressure with altitude, we again find levels at which the ambient temperature implies that water substance would have saturation vapor pressures just equal to the ambient pressure. The lower part of Figure 1 shows how the *top* of the exclusion layers for liquid water and for ice are determined as 69.1 km and 67.6 km, respectively.

As we consider still greater altitudes than the preceding, the ambient temperature remains cold enough, despite steadily falling pressures, so that equilibrium clouds of water or ice remain a thermodynamic possibility up to but not above the mesopause. An ultimate exclusion limit is then found near 94.7 km in the standard atmosphere for the case of *ice*. Because it is not likely that water droplet clouds will be found at such low temperatures as prevail near this limit region, and because saturation vapor pressures over supercooled water at such low temperatures are not reliably known, no exclusion limit for water drops above the mesopause has been determined. It seems sufficient to say that no water clouds of any kind can persist in the earth's atmosphere at altitudes appreciably higher than about 95 km.

Limits for some propellants. By means of the methods illustrated above for water, I have made estimates of cloud exclusion limits for

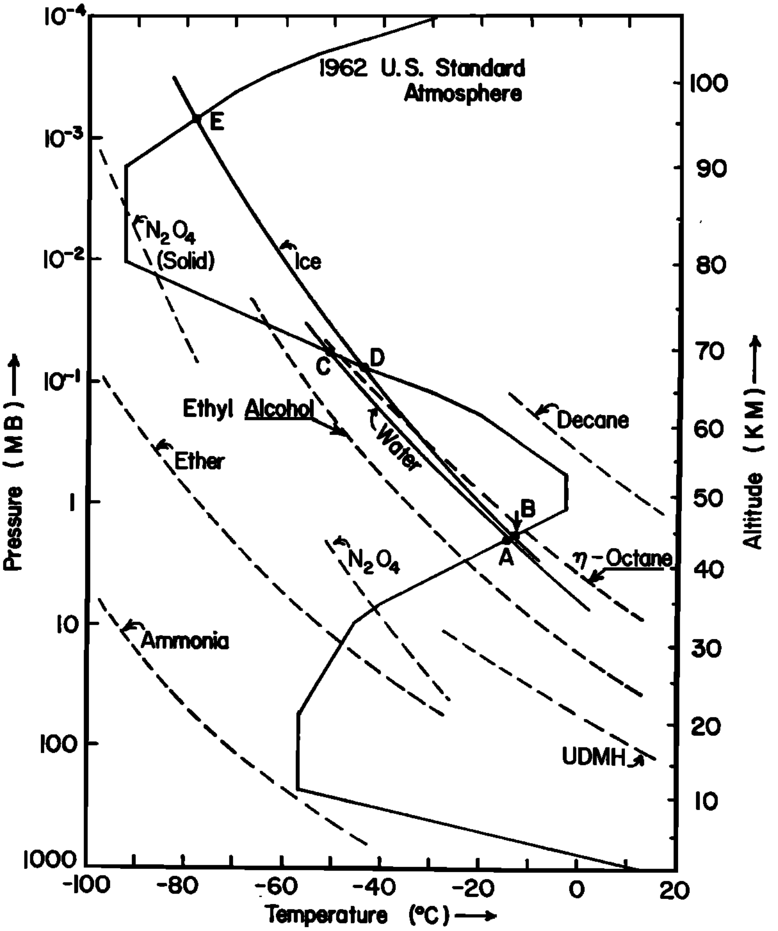

Fig. 2. Cloud exclusion limits of a number of substances in the U. S. standard atmosphere.

seven fuels and rocket propellants. Saturation vapor pressure data were taken from the *International Critical Tables* [*Washburn*, 1926], from *Kit and Evered* [1960], and from other standard chemical tables. For some of the substances of interest, the data were for temperature ranges that permitted only a rough estimate of exclusion limits (e.g., UDMH = unsymmetrical dimethylhydrazine). However, the results suffice to show, in general, which common fuels and propellants can form persistent clouds and which cannot possibly be expected to yield persistent clouds.

The results are shown in Figure 2. The 1962 U. S. standard atmosphere is plotted there, with both pressure and altitude ordinates on a single temperature abscissa. All other curves represent plots of the saturation vapor pressures of the given substances, the temperatures being those of the abscissa and the saturation vapor pressures being read on the left-hand pressure scale. Wherever one of these saturation vapor pressure curves intersects the standard atmosphere locus, either an upper or lower exclusion limit occurs, the sense of each limit being clear from the principles outlined above.

Discussion. The water exclusion limits implicit in Figure 2 are those already elaborated in discussing Figure 1 and need little further comment. It is of interest, however, to point out that the roughly 43-km base of the exclusion layer for water clouds coincides almost exactly with the photogrammetrically determined altitude of the remarkable ring cloud that appeared over Flagstaff, Arizona, near sunset on February 28, 1963 [*McDonald*, 1963*a*, 1963*b*]. This is only one of a number of extremely puzzling aspects of that cloud which I am still studying. It is also to be briefly noted that noctilucent clouds of ice or ice-coated dusts are thermodynamically possible in the thin layer near 80 km where they are observed to occur; and nacreous clouds of drops or ice particles are also seen to be entirely possible in their roughly 20- to 25-km layer of occurrence.

We see from Figure 2 for the curves for decane and *n*-octane that, if gasoline were released into the upper atmosphere, its less-volatile components could form persistent droplets from which the more-volatile components would quickly boil off. Kerosene, composed largely of aliphatic hydrocarbons even less volatile than decane, can yield clouds that are persistent in the present sense at all altitudes up to well above 100 km.

Drops of ethyl alcohol would rapidly boil away if released into any part of the alcohol-cloud exclusion layer from about 41 to 72 km. Unsymmetrical dimethylhydrazine that might be jettisoned or exploded from a rocket would not yield a persistent cloud at any altitude above about 35 km. Nitrogen tetroxide, a common oxidizer for fuels such as UDMH, would not form liquid-droplet clouds above about 34 km; but the curve for its solid form indicates slim possibility of formation of a cloud of nitrogen tetroxide crystals in a shallow permitted layer near 80 km. Ether droplets would boil away if released at altitudes above about 30 km, and it can be seen from Figure 2 that ether is so volatile that at no greater altitude does our standard atmosphere again become cold enough to lower the saturation vapor pressure of that substance below the ambient pressure. Finally, ammonia has the interesting property that nowhere in the standard atmosphere does it satisfy the persistence requirement; droplets of it would boil at any and all levels. However, with a very cold tropopause, a very thin permitted layer for ammonia droplets might exist.

For any other substances for which saturation vapor pressure data are available, similar exclusion limits are easily assigned. Also for other atmospheres, exclusion limits are similarly determinable. The atmosphere of Mars is of interest. If the atmosphere of Mars proves to have a surface pressure near 80 mb, as many investigators suspect, both water droplet clouds and ice crystal clouds can be persistent at low elevations. But if recent suspicions that the surface pressures of Mars may be nearer to 8–10 mb are correct, students of the meteorology of Mars should keep in mind the fact that the temperatures of Mars may be high enough at certain latitudes, seasons, and levels to imply water-cloud exclusion limits.

Acknowledgment. The work reported here has been done with the support of the Office of Naval Research.

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(Manuscript received June 8, 1964.)