

NOTES AND CORRESPONDENCE

Cloud Formation on Descent Revisited

CRAIG F. BOHREN

Department of Meteorology, Pennsylvania State University, University Park, PA 16802

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In 1934 Brunt published a paper in which he pointed out that the high latent heat of vaporization of water is responsible for cloud formation in *ascending* air. If the latent heat were considerably smaller, clouds would form in *descending* air. Many years later, McDonald (1964) expanded on this "little-known paper." In particular, he argued that there might be planets with atmospheres containing vapors that would condense in adiabatic descent. His primary candidate was cyanogen (C_2N_2): "It seems quite possible that somewhere in the universe planetary atmospheres exist in which cyanogen clouds are forming in downdrafts." McDonald was followed by Ingersoll (1969), who asserted that "real clouds will form only on updrafts." His conclusion, however, was based on a list of properties of vapors on which cyanogen did not appear, a curious omission given McDonald's statement about this vapor. Nevertheless, McDonald was not correct, although through no fault of his own. In this note, I should like to revive the ascending-descending cloud controversy (this is probably too strong a word), point out how McDonald was misled, and consider the conditions under which cloud formation on adiabatic descent is possible. In so doing, I also shall show what previous authors seem to have missed: the same vapor can condense when adiabatically expanded *or* compressed. The ideas put forth by Brunt, McDonald, and Ingersoll are worth contemplating not because they necessarily have practical applications, but because they illustrate that what is familiar is not always inevitable.

Consider a vapor, possibly mixed with one or more gases. In an adiabatic process the saturation ratio S , defined as the ratio of the pressure of the vapor to its saturation vapor pressure, may be written compactly as

$$S = S_0 x \exp[L(x^{(1-\gamma)/\gamma} - 1)/RT_0], \quad (1)$$

where T_0 is the absolute temperature at the beginning of the process, L the latent heat of vaporization, R the gas constant, and x the ratio of the total pressure p to the initial total pressure p_0 . The mean ratio of the specific heats for the mixture, γ , is defined by

$$\gamma = \frac{\sum f_i c_{vi} \gamma_i}{\sum f_i c_{vi}}, \quad (2)$$

where f_i is the mole fraction of the i th component, c_{vi} its molar heat capacity for a constant-volume process, and γ_i the ratio of its specific heats.

The assumptions underlying (1) are that the entire mixture may be treated as an ideal gas, that the saturation vapor pressure is obtained by integrating the Clapeyron equation with the latent heat of vaporization independent of temperature, and that the specific volume of the vapor is much greater than that of the condensed phase. Two of these restrictions will be removed later; for the moment we proceed on the basis of (1). Whether condensation occurs on compression (x increases) or on expansion (x decreases), beginning at saturation ($S_0 = 1$), is determined by the sign of the derivative of S with respect to x at $x = 1$. It occurs (assuming suitable nuclei, of course) when the pressure increases if

$$\frac{L}{RT_0} < \frac{\gamma}{\gamma - 1}. \quad (3)$$

This criterion is the same as that derived by Brunt (1934) and McDonald (1964). Thus, for a sufficiently low latent heat, condensation does indeed occur upon compression (i.e., on adiabatic descent). McDonald's choice of cyanogen as a likely vapor was based on latent heats in the 40th edition of the *Handbook of Chemistry and Physics* (Hodgman, 1958). In more recent editions (e.g., the 64th), however, the latent heat for cyanogen is about ten times greater than the value listed in earlier ones. No reason is given for this large discrepancy, but the new value seems more in line with those for the more than 1000 organic compounds listed in the 64th edition (Weast, 1983, pp. C691-C695). McDonald's incorrect conclusion was therefore based on correct reasoning using incorrect data.

To make this analysis more rigorous, I shall go beyond Brunt and McDonald. Accurate vapor pressures of pure substances are often specified not by their latent heats (which, after all, are temperature dependent) but by the constants in the Antoine equation (e.g., see Boublik et al., 1984):

$$\log e_s = A - \frac{B}{t + C}, \quad (4)$$

where e_s is the saturation vapor pressure in kPa, t the temperature in degrees Celsius, and A , B , C are constants determined by fitting (4) to measurements over a limited range of temperatures. By using this equation, the saturation ratio can be written

$$S = S_0 x \exp\left(B' \left[\frac{1}{T_0 x^{(\gamma-1)/\gamma} + C'} - \frac{1}{T_0 + C'} \right]\right), \quad (5)$$

where $B' = 2.3026B$ and $C' = C - 273$. Note that when $C = 273$, (5) is identical with (1) and B' is the latent heat divided by the gas constant. From (5) we obtain the criterion corresponding to (3):

$$\frac{B'}{T_0} < \frac{\gamma}{\gamma-1} \left(1 + \frac{C'}{T_0}\right)^2. \quad (6)$$

The only assumption underlying (6) is that the mixture of vapors and gases is ideal to good approximation. That this assumption is valid can be shown from the van der Waals equation of state in the form

$$p = \frac{RT}{v} \left[1 + \frac{v_c}{v} \left(\frac{1}{3} - \frac{9}{8} \frac{T_c}{T} \right) + O(v_c^2/v^2) \right], \quad (7)$$

where p is the pressure, v the molar volume, v_c the critical molar volume, and T_c the critical temperature. According to the table of critical data compiled by Epstein (1937, p. 15), T_c for several common organic vapors (including diethyl ether, *n*-pentane, and *n*-hexane, which will be discussed later) ranges from about 450 to 650 K. Critical molar volumes range from about 250 to 500 cm³. Those for common gases such as nitrogen and oxygen are comparable, but critical temperatures for these gases are usually less. For pressures near one atmosphere and temperatures of 300–400 K, the molar volume v is on the order of 100 times greater than the critical molar volume. Thus, it is clear from (7) that at normal terrestrial temperatures and pressures, the ideal gas equation is in error by, at most, a few percent.

In the context of the preceding paragraph, I must comment on Ingersoll's (1969) assertion that "McDonald has applied" the ideal gas law "to saturated vapors close to their critical points," where it is "certainly invalid." Not only was this criticism of McDonald not substantiated by adducing values of appropriate pressures, temperatures, and volumes, it was not warranted. Although McDonald was in error, he was misled by an incorrect handbook value of a latent heat, not by applying the ideal gas law outside of its range of validity.

I have perused a large catalog of vapor pressures (Boublik, et al., 1984) without finding any obvious candidates that satisfy (6). The value of C is almost invariably less than 273, sometimes even negative, which imposes an even severer restriction on the latent heat (i.e., B') than does (3). Thus, this would seem to

imply, in agreement with Ingersoll, that cloud formation on descent is not possible.

But this conclusion is based on the tacit assumption that γ is appropriate to one of the common diatomic or triatomic gases (or a mixture of them). The ratio of specific heats was shown by Jeans (1954, p. 185) to have the form

$$\gamma = 1 + \frac{1}{3(1+\beta)}, \quad (8)$$

where β is the ratio of the internal to translational energy of a molecule. The greater the number of atoms in a molecule, the greater β is expected to be. Many attempts have been made to relate γ to the number of atoms in a molecule (e.g., see Partington and Shilling, 1924, p. 23). No single rigorous expression has emerged, but the trend is clear: the larger the molecule the closer γ is to 1. Thus, if a high molecular weight vapor is *not* mixed with gases having a relatively high value of γ (for air it is about 1.4), then condensation on compression is possible. This was recognized by Brunt (1934), who stated that it is "well known in petrol engine practice." If γ is close to 1, compressing a vapor does not appreciably raise its temperature; hence its saturation vapor pressure does not increase appreciably either. The work of compression is converted mostly into internal molecular energy (vibrational and rotational) rather than translational kinetic energy (i.e., temperature). Compression always increases the vapor pressure. Therefore, for γ sufficiently close to 1, condensation can occur on compression.

One of the lowest values of γ that I could find was for diethyl ether (C₄H₁₀O; also called ethyl ether), a value of 1.08 (Washburn, 1929, p. 81). The constants in (4) for this vapor are $B = 1061$, $C = 228$ over the temperature range -28° to 55°C , which were obtained by Boublik et al. (1984, p. 284) by fitting (4) to measurements of Ambrose et al. (1972). At a temperature of 308 K, the vapor pressure of diethyl ether is 1 atm. It follows from these values and (6) that if pure diethyl ether is compressed, beginning at a temperature of 308 K, it will condense (given suitable condensation nuclei). This is shown in Fig. 1. Now suppose that a small amount of gas is added, sufficient to increase γ of the mixture to 1.1. For this case, S has a minimum, and condensation occurs on either compression or expansion. If a bit more gas is added, condensation occurs only on expansion.

Diethyl ether is by no means the only vapor that can condense on compression (I chose this vapor as an example because it is rather common and because its molecular weight is not remarkably high). There are other such vapors, which follows from values of B and C compiled by Boublik et al. (1984), values of γ given by Washburn (1929), and the criterion (6). For example, methylal (C₃H₈O₂), *n*-pentane (C₅H₁₂), and *n*-hexane (C₆H₁₄) are vapors that can condense when compressed at temperatures around 300 K; their sat-

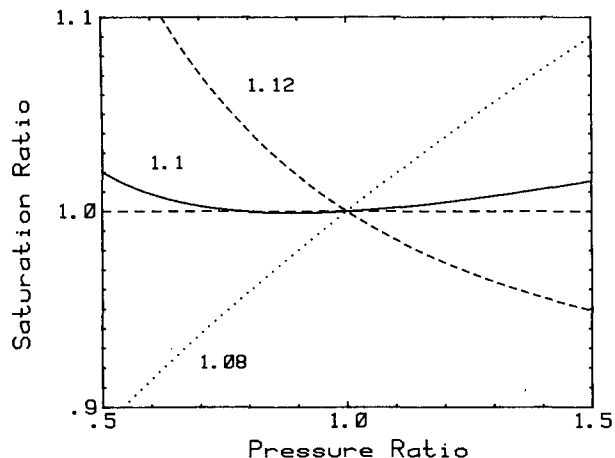


FIG. 1. Saturation ratio of diethyl ether subjected to adiabatic compression or expansion. The initial temperature is 308 K. The numbers noted on the curves are values of γ , the ratio of specific heats. $\gamma = 1.08$ corresponds to pure diethyl ether. The other two values may be realized by mixing it with small amounts of a diatomic or triatomic gas.

uration vapor pressures are 1 atm or less. As evidenced by (8), other vapors could be added to this list. There are undoubtedly a great many organic vapors with sufficiently high molecular weights and hence with γ close enough to 1 to satisfy (6).

Thus, we conclude that in an atmosphere consisting entirely or almost entirely of organic vapors with moderate or high molecular weights (admittedly, the probability of finding such an atmosphere in the universe seems small—but not necessarily less than that of finding life) clouds can form on compression (i.e., on descent). And if the mixture is just right, clouds of the same droplets can form on both ascent and descent.

A footnote to this note is Brunt's motivation for considering cloud formation on descent in the first place. He states that "iridescent clouds occur at heights of 20 to 30 km, the iridescent colours indicating that the clouds are formed of liquid drops." Thus he was

led to consider why liquid droplets were formed. Iridescence does not infallibly signal the presence of liquid droplets, however. The scattering diagram, for angles near the forward direction, for large (compared with the wavelength), randomly oriented cylinders is nearly identical with that for spheres (e.g., see van de Hulst, 1957, p. 110). Nor, as is stated in the *Glossary of Meteorology* (Huschke, 1959, p. 315), does iridescence infallibly signal the presence of ice crystals.

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