"REVIEWED"

THE SURFACE TEMPERATURE OF DRY ICE, SOLID CO_2

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Abstract. A common misconception of dry ice temperature under cloud seeding operations has been pointed out. The widely known temperature of -78.2°C occurs only when the dry ice is under equilibrium with CO_2 gas of 1 atmosphere. The temperature of falling dry ice pellets in air is decided by a steady state balance of heat conduction to and the CO_2 gas diffusion from the surface. Under the free fall condition of cloud seeding, the temperature is about -100°C and is fairly insensitive to the pellet and the environmental conditions.

1. INTRODUCTION

In this journal, Vonnegut (1981) wrote a short article to correct the misconception about cloud seeding with dry ice. Unfortunately, he did not straighten the widespread misconception for the surface temperature. Although the problem has already been resolved explicitly in a theoretical treatment (Fukuta et al., 1971) and in an experiment (Kochtubajda and Lozowski, 1985), there exists a widespread misunderstanding about the temperature. It is, therefore, the purpose of this brief paper to explain the theoretical basis that leads to the surface temperature of dry ice under cloud seeding conditions which is different from the commonly quoted value.

2. THE THERMODYNAMIC TEMPERATURE

The vapor pressure of a condensed phase is known to obey the Clausius-Clapeyron equation and is a function of temperature alone under the atmospheric condition. Fig. 1 shows the vapor density of dry ice instead of the vapor pressure as a function of temperature. Also shown at the top of the figure is the vapor density of CO_2 gas under a pressure of 1 atmosphere as a function of the temperature. The interception between the two curves shows the commonly quoted temperature of dry ice, -78.2°C. It is equivalent to the boiling temperature of water under 1 atmosphere vapor, i.e., 100°C. When dry ice is kept in a semi-enclosed condition such as in a box, the gas sublimes from the dry ice and the surface becomes surrounded by the gas under the pressure. Thus, the dry ice temperature that gives CO_2 pressure of 1 atmosphere is -78.2°C.

3. THE KINETIC TEMPERATURE

It is well recognized that the temperature of wet-bulb thermometer drops considerably below that of the air under low relative humidity. However, the wet-bulb temperature is often defined in meteorology as the temperature to which air is cooled by evaporation of water at constant pressure until the saturation is reached (thermodynamic definition). This has nothing to do with the temperature of the wet-bulb thermometer, although both happen to be close to each other. It is unfortunate that the terminology has been confusing and misleading in this regard.

The temperature of wet-bulb thermometer is determined by a kinetic process of heat and water vapor transportation around the wet-bulb. The process was first treated properly by J.C. Maxwell. Being faced with the drier environment, water evaporates and diffuses out from the wet-bulb. The evaporation cools the wet-bulb until such a condition has been reached that the heat conduction, which determines the rate of water evaporation by supplying the latent heat, matches the latent heat removal rate by evaporation. The water vapor pressure of the wet-bulb is a sole function of temperature and may be expressed by the Clausius-Clapeyron equation (Fukuta and Walter, 1970).

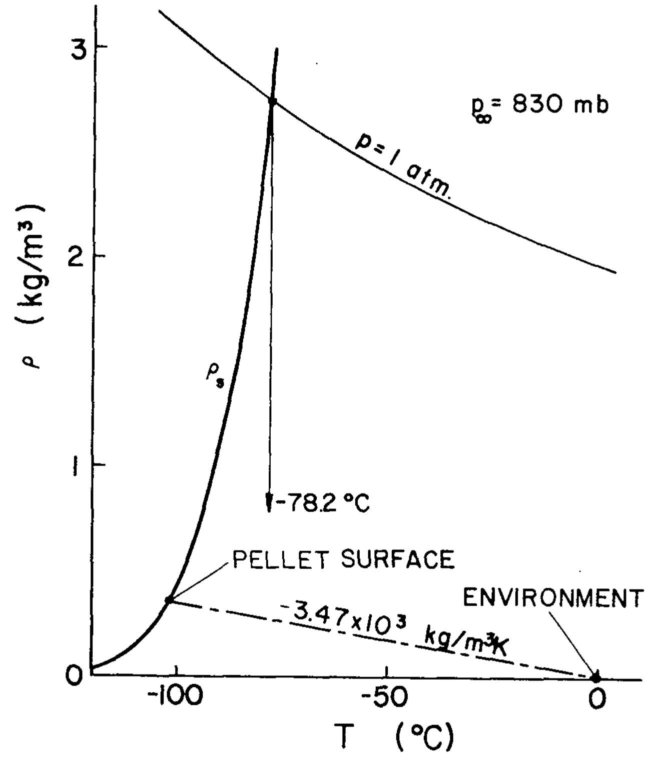

Fig. 1. Saturated vapor density of dry ice plotted as a function of temperature.

As mentioned above, the thermodynamic temperature of dry ice under 1 atmosphere of CO_2 gas is equivalent to the boiling temperature of water under 1 atmosphere. Then, an isolated dry ice pellet becomes equivalent to a boiling water drop placed in a completely dry air under 100°C and 1 atmosphere. From the drop, water evaporates and the surface temperature lowers so that now thermal conduction from the air can supply the heat necessary to maintain steady state balance of the evaporation. An identical situation develops when a dry ice pellet is transferred from the storage box to the outside air where the partial pressure of CO_2 is zero. However, unlike the case of boiling water or that of subliming dry ice being surrounded by its own vapor of 1 atmosphere (where the controlling factor of the temperature of the condensed phases is the pressure) the temperature of a dry ice pellet isolated in air depends on the boundary conditions and the constants involved in the transport processes of heat and vapor which are also a function of the environmental variables.

Suppose a dry ice pellet is placed quiescently in an air environment of temperature T_∞ and pressure p_∞. The heat transport rate to its surface is expressed by Fourier's law of heat conduction

$$\frac{dQ}{dt} = A \cdot K \cdot \frac{dT}{dr} \quad , \qquad (1)$$

where Q, t, A, K, and r are respectively the heat energy, the time, the surface area, the heat conductivity of air and the pellet radius.

Similarly the rate of CO_2 gas removal from the pellet is given by Fick's law of diffusion

$$\frac{dm}{dt} = - A \cdot D \cdot \frac{d\rho}{dr} \quad , \qquad (2)$$

where m, D and ρ are respectively the mass of CO_2, the diffusion constant of CO_2 gas in air and the CO_2 gas density. The removal rate of the latent heat of sublimation from the pellet surface is given as

$$\frac{dQ}{dt} = L_d \frac{dm}{dt} \quad , \qquad (3)$$

where L_d is the latent heat of sublimation of CO_2 gas from dry ice. Using equations (1) through (3), we have

$$- \frac{d\rho}{dT} = \frac{K}{L_d D} \quad . \qquad (4)$$

When the pellet falls, the air surrounding it moves and the pellet is ventilated. The ventilation makes both the temperature and the vapor field steeper. The modification of each field is expressed by the so-called "Ventilation Factor", f_h, for the temperature field, and, f_v, for the vapor field. As a result, equation (4) modifies to

$$- \frac{d\rho}{dT} = \frac{K f_h}{L_d D f_v} \quad , \qquad (5)$$

(see Fukuta et al., 1971 for detail). The ventilation factors are a function of non-dimensional fluid dynamical numbers. At p_∞ = 0.83 atm. and T_∞ = 0°C, the ratio $f_h/f_v \simeq 0.932$, and is almost independent of the pellet size. Since the transport processes of heat and vapor are largely controlled by the condition existing near the pellet, the transport constant values are taken at the dry ice surface temperature, which we shall find later as about -100°C. The $d\rho/dT$ value thus estimated is -3.47×10^{-3} kg/m³K as shown in the figure. A line with this slope must satisfy the environmental condition (T_∞ = 0°C, ρ_∞ = 0 N/m²) and the dry ice surface condition on the saturation vapor density line expressed by ρ_s. Thus, the surface temperature of dry ice is the temperature of the interception between the ρ_s curve and the line passing through (T_∞, ρ_∞) with $d\rho/dT$ slope mentioned above. As can be seen in the figure, the surface temperature of dry ice thus obtained is a little below -100°C under the condition taken here. Considering uncertainty involved in various constants taken, -100°C is sufficiently representative. In addition, the fact that the ratio f_h/f_v is nearly independent of the pellet size and the environmental conditions, the $d\rho/dT$ slope is very low and ρ_s is standing, indicates that the surface temperature does not change appreciably depending on the environmental conditions.

4. SURFACE TEMPERATURE IN THE LITERATURE

After the style of Vonnegut's paper, we list the following excerpts as examples of the surface temperature quotation:

"...The first, discovered by Schaefer (1946), consists of dropping into a supercooled cloud pellets of solid CO_2 (dry ice, -78°C) which chill the droplets formed by condensation to well below the temperature for homogeneous freezing and so produce a cloud of tiny ice-crystals in the wake of the pellets." (Fletcher, 1962)

"...Dry ice has a very low temperature (-109 degrees (Fahrenheit)). Various scientists began to wonder what would happen if they dropped dry ice pellets into a very cold part of a cloud." (Gallant, 1967 reviewed by J. Spar)

"...The first successful 'seeding' of clouds was carried out by Schaefer (1946) who used solid carbon dioxide (Dry Ice) rather than artificial ice nuclei. Dry Ice, which has a temperature of -78°C, causes large numbers of ice crystals to form in its wake by homogeneous nucleation when it is dropped through air." (Hobbs, 1974)

"...Dry ice - solid carbon dioxide at a temperature of about -80°C - was used by Schaefer (1946) in his initial experiments that started the modern era of weather modification." (Holroyd, III et al., 1978)

"...Schaefer quickly realized that the extremely low temperature near the surface of the dry ice pellet (-78°C) had caused the droplets along its path to freeze." (Dennis, 1980)

"...Dry ice, i.e., solid carbon dioxide (CO_2) has a very low surface temperature while subliming (-78°C) and in pellet form will create many ice crystals in its wake as it falls through a cloud." (Kopp et al., 1983)

"...To seed a cloud they dropped crushed pellets of dry ice (solid carbon dioxide) from a plane. Because dry ice has a temperature of -78°C (-108°F), it acts as a cooling agent. Small pellets dropped into the cloud cool the air to the point where new liquid droplets are able to form." (Ahrens, 1985)

"...Dry ice, which is frozen carbon dioxide, has a temperature as low as -112°F (80°C). When dropped into a cloud from an airplane, pellets of dry ice lower the temperature of supercooled water." (Wendland, 1986)

Although the surface temperature of falling dry ice pellets was first computed with a sufficient accuracy by Fukuta et al. (1971), some skepticism was expressed to this author by a Soviet scientist at the Tashkent WMO Weather Modification Conference in 1973. So, after returning from the Soviet Union, an experiment was carried out which confirmed the result of the prior computation. Although we did not bother to report the result in an open literature, the following is an excerpt of the letter sent to the scientist explaining the finding:

> November 12, 1973
>
> Dr. V.P. Bakhanov
> Ukrainian Hydrometeorological
> Research Institute
> Kiev, Prospect Nauki 105, U.S.S.R.
>
> Dear Dr. Bakhanov:
>
> ----. Concerning the promise I made to you about the measurement of dry ice (solid CO_2) temperature in air, I would like to tell you the result. We moulded a copper-constantan thermocouple of 0.076 mm diameter in a dry ice sphere of 9.5 mm diameter. Then, the dry ice sphere was placed on a pile of dry ice in a Dewar vessel where dry ice temperature at Denver altitude of 1.65 km (pressure: 0.82 atm.) was about -81°C. As soon as the moulded dry ice sphere was pulled out of the Dewar vessel, the temperature of the thermocouple showed -100°C. The error of the measurement was probably ± 1°C, or smaller. We repeated the experiment, and the result was highly reproducible. The air ventilation did not appear to be affecting the temperature significantly. Therefore, theoretically and experimentally, the dry ice surface temperature in still air is about -100°C and the ventilation affects the temperature relatively little. ----
>
> Yours sincerely,
>
> Norihiko Fukuta

A recent paper by Kochtubajda and Lozowski (1985) reported a measured surface temperature of ventilated dry ice pellet to be at -96°C. The air temperature for the pellet evaporation test was not described but was presumably above 0°C which was used in their experiment most of the time. If this were the case, as can be seen in the figure, ventilation with a 0°C air could have cooled the pellet close to -100°C.

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