

## Freezing of Water Droplets in Equilibrium with Different Gases

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(Manuscript received 26 August 1968)

### ABSTRACT

Water droplets in thermal equilibrium with gases of different solubilities were frozen at temperatures between  $-4$  and  $-14^{\circ}\text{C}$ , in order to observe the influence of the volume of dissolved gas on the shattering of the droplet.

In air, which has a low solubility in water, no shattering was produced. In methane with a slightly higher solubility, 5% of the droplets shattered. In mixtures of carbon dioxide and air, the frequency of shattering is a function of the temperature and the concentration of carbon dioxide, attaining under the most favorable conditions a value of 40%. However, a large volume of gas is not a sufficient condition to produce shattering. In acetylene, which has nearly the same solubility as carbon dioxide, and in sulfur dioxide, the solubility of which is more than one order higher, shattering was not observed, either in the pure gas or in mixtures with air. When the released gas is readily dissolved in the remaining solution (as for droplets in acetylene or low concentrations of sulfur dioxide) or the gas is separated in a solid phase as a hydrate (as for droplets in high concentrations of sulfur dioxide), the gas does not contribute to an increase of the internal pressure, thus eliminating the possibility of shattering.

### 1. Introduction

The behavior of water droplets during freezing, and whether they eject splinters or shatter, producing a large number of ice particles, is a problem of fundamental importance in cloud physics. Splintering has been invoked to explain certain observations in clouds whose concentration of ice particles is larger than expected from the ice nuclei count on the ground (Koenig, 1963; Braham, 1964; Mossop *et al.*, 1962). Also, splintering has been suggested as an important charging mechanism in thunderstorms (Latham and Mason, 1961).

The shattering of water droplets when freezing in air was observed by Mason and Maybank (1960). The frequency of shattering was quite high at low super-coolings but negligible below  $-9^{\circ}\text{C}$ .

Dye and Hobbs (1968) could not reproduce these results when the droplets were in thermal equilibrium with the environment. They related the probability of shattering to the rate of freezing and the degree of symmetrical heat transfer from the droplets, and they calculated the rate of freezing for droplets in different gases. Since the rate of freezing values for hydrogen at 1 atm and air at 0.1 atm were higher than for air and carbon dioxide at normal pressure, shattering should have been more frequent in the first two cases. However, the experimental results showed that 1) no shattering was produced in air whatever the pressure, 2) shattering in hydrogen was observed only at temperatures  $< -9^{\circ}\text{C}$ , and 3) shattering in carbon dioxide was quite frequent. In Fig. 1 are indicated, as a function of temperature, the volumes of different gases contained in one volume of water; it can be seen that at 1 atm the volume of

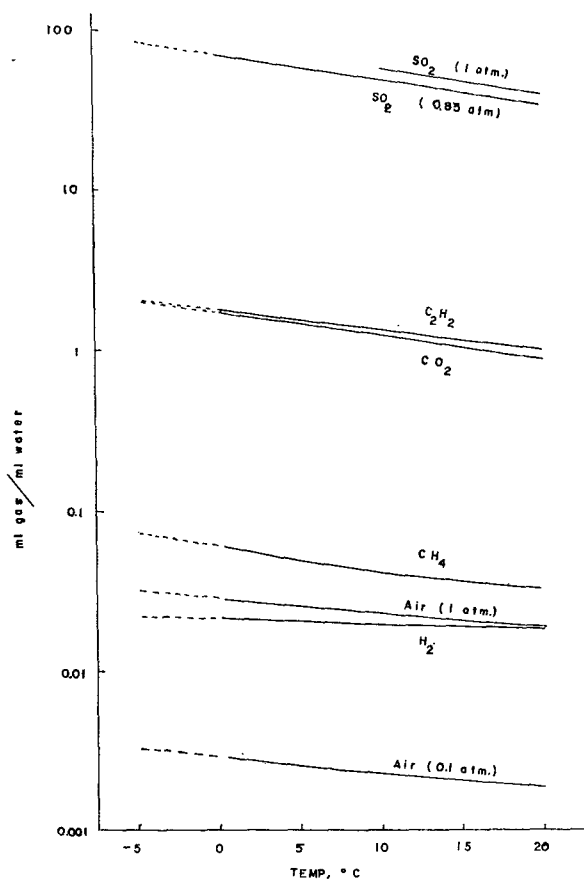


Fig. 1. Volume of gas at 0°C and 1 atm in one volume of water, at different temperatures.



FIG. 2. Successive photographs of freezing of a water droplet in air.

carbon dioxide is 60 times the volume of air, and the volume of hydrogen at 1 atm is almost 10 times the volume of air at 0.1 atm, suggesting that, for the same value of the rate of heat transfer, the volume of gas contained in the water droplet is a determinant factor in its shattering.

As a droplet shatters it produces some hundred ice particles (Mason and Maybank, 1960). If the shattering is stimulated by a large volume of gas contained in the water droplets, it would be sufficient to increase the gas content in the cloud droplets in order to multiply the number of ice particles in the clouds. For very soluble gases it is possible to obtain solutions containing a large volume of gas with very low partial pressures. Table 1 indicates the partial pressures necessary to obtain a solution containing one volume of gas per volume of water for four gases at 0C.

The present study consisted of the observation of the freezing of water droplets in equilibrium with gases covering a wide range of solubilities.

## 2. Experimental method

The device employed consisted of a cylindrical glass chamber of 10 cm length and 5 cm diameter. The gas in which the droplets were frozen was cooled in two coils before entering the chamber. When a mixture of gas and air was used, the flow of each gas was measured with respective flowmeters and the mixture precooled in ice in order to reduce the water contained in the air.

The glass chamber and the coils were placed in a cold box, whose temperature could be lowered to  $-15^{\circ}\text{C}$ . The droplets were observed and photographed through a microscope with low magnification. Bi-distilled and de-ionized water was employed. With the device used, no

TABLE 1. Partial pressures (atm) required to obtain a solution containing one volume of gas per volume of water at 0C.

Gas	$p$
CO <sub>2</sub>	0.58
C <sub>2</sub> H <sub>2</sub>	0.57
SO <sub>2</sub>	0.0126
NH <sub>3</sub>	0.0009

freezing was observed at temperatures  $> -15^{\circ}\text{C}$ . The water droplet was placed with a syringe on a thermocouple of copper and constantan wires of 0.004 inch diameter, the thermocouple being covered with shellac. The diameter of the droplets varied from 1–2 mm.

The thermocouple with the droplet was placed in the glass chamber through which the appropriate gas was continuously flowing at a rate of  $80\text{ cm}^3\text{ min}^{-1}$ , equivalent to a velocity of  $0.05\text{ cm sec}^{-1}$ . Another thermocouple was placed in the chamber, very near the droplet. Both temperatures, that of the droplet and that of the environment, were registered on Speedomax recorders. When the temperature of the droplet was the same as the environment and when no less than 5 min had elapsed since the droplet was put in place, freezing was produced by the introduction of some silver iodide nuclei through a syringe placed near the droplet.

## 3. Results

### a. Freezing of water droplets in air

Ninety droplets were frozen at temperatures between  $-4$  and  $-15^{\circ}\text{C}$ . No shattering was observed in any case. Spikes were formed more frequently at temperatures  $> -9^{\circ}\text{C}$  (40% of the droplets formed spikes) than at lower temperatures (20%). The maximum length of the spikes was 0.6 mm. In many cases gas was observed to be expelled from one or several points of the frozen surface. Fig. 2 shows successive photographs of a droplet freezing in air at  $-7^{\circ}\text{C}$ .

### b. Freezing of water droplets in methane

Sixty droplets were frozen over the same temperature interval as for air. The shape, sizes and frequency of spikes were similar to those in air. Three droplets shattered and five produced a significant crack during the freezing.

### c. Freezing of droplets in carbon dioxide

The freezing of water droplets was observed in mixtures of air and carbon dioxide and in pure carbon dioxide. It was possible to separate the results according to the temperature at which the freezing was produced.

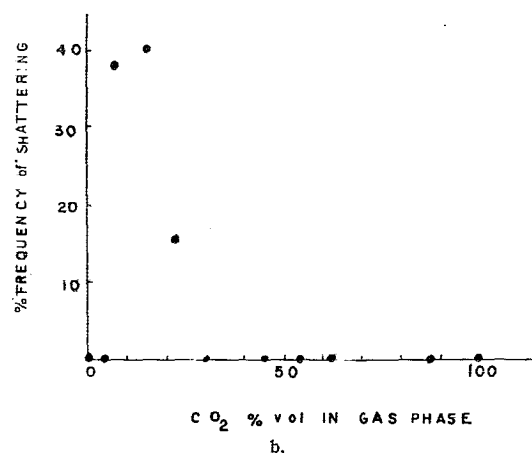
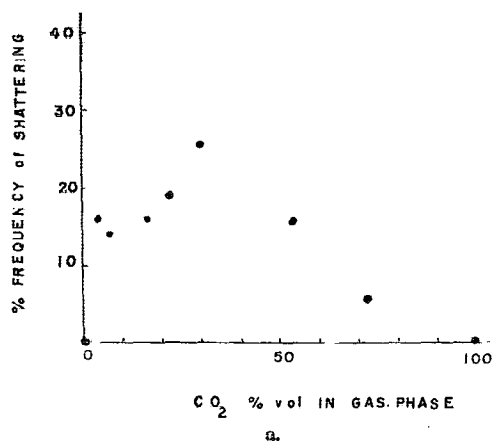


FIG. 3. Frequency of shattering as a function of the concentration of carbon dioxide in the gas mixture: temperatures between  $-4$  and  $-9.4^{\circ}\text{C}$ , a., between  $-9.4$  and  $-14^{\circ}\text{C}$ , b.

At temperatures between  $-4$  and  $-9.4^{\circ}\text{C}$  shattering was observed for every concentration between 4 and 75% by volume of carbon dioxide in the gas mixture. In Fig. 3a the frequency of shattering is represented as a function of the composition of the gas mixture. At low concentrations of carbon dioxide, very long and transparent spikes were formed, attaining a maximum length of 3 mm. During the freezing a large quantity of small or large bubbles were formed inside the droplet

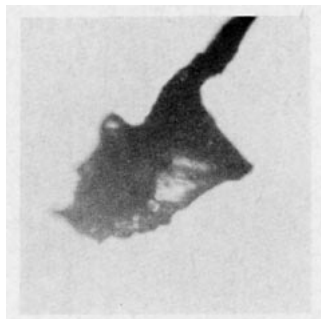


FIG. 4. Shattering of a droplet in 40% of carbon dioxide.



FIG. 5. Freezing of a droplet in 30% of carbon dioxide showing formation of a spike, a., and partial fragmentation, b.

and were pushed toward the extremity of the spike; they were sometimes ejected from the droplet. In many cases a large crack was produced; in others total shattering (Fig. 4) or a partial fragmentation of the droplet was observed (Fig. 5).

As the concentration of carbon dioxide increased, very large bulges were formed instead of spikes (Fig. 6). These bulges grew at a very fast rate, generally expelling gas, shrinking and forming again as new gas arrived. At the same time the frequency of shattering became lower and at 100% carbon dioxide it was zero.

At temperatures between  $-9.5$  and  $-14^{\circ}\text{C}$ , shattering was observed only in the range of concentrations between 7 and 22% of carbon dioxide (Fig. 3b), and the frequency was slightly higher than that for the higher temperatures. Bulges and spikes were formed less frequently, but gas was expelled in almost every case.

At all the temperatures studied the sizes of the bulges increased as the concentration of carbon dioxide increased, i.e., a greater volume of gas was evolved. The fact that the frequency of shattering became smaller for higher concentrations indicates that the gas trapped by the ice modifies its mechanical properties making it more pliable. At lower temperatures, when the rate of freezing is greater with more gas being trapped, this effect is more noticeable.

The three gases considered show two common features: a) gas bubbles are built up inside the droplet and expelled during the freezing, and b) the shapes of

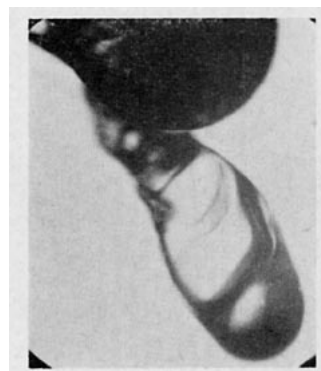


FIG. 6. Large bubble formed in a droplet freezing in 60% of carbon dioxide.

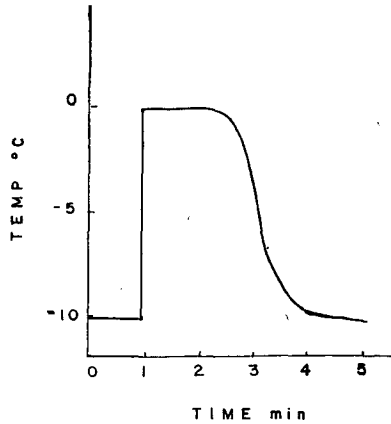


FIG. 7. Temperature of a droplet freezing in 60% of carbon dioxide as a function of time.

the curves showing droplet temperature as a function of time during freezing are similar. Fig. 7 demonstrates such a curve obtained with a 1.7-mm diameter droplet freezing in 60% carbon dioxide at  $-10^{\circ}\text{C}$ . As freezing is initiated the temperature rises to nearly  $0^{\circ}\text{C}$  and remains at this temperature until the freezing is almost complete. The observed time of freezing is in agreement with that obtained by assuming that the rate of freezing is controlled by the rates of heat and vapor transfer (Mason, 1956).

#### d. Freezing of water droplets in acetylene

Water droplets were frozen as in the other cases, in six different concentrations of acetylene: 3, 5, 10, 26, 58 and 100%. For mixtures up to 10% the droplets formed a thin spike and one or several small protuberances. For higher concentrations only the protuberances were observed (Fig. 8). Neither the build-up of gas bubbles nor shattering were observed in any case. Curves showing droplet temperatures as a function of time for three different concentrations of acetylene are shown in Fig. 9. Note that the temperature rise which occurs on the initiation of freezing decreases with increasing concentration, and is always less than  $0^{\circ}\text{C}$ . The shape of the curves and the times of freezing differed from those obtained with the other gases cited above.

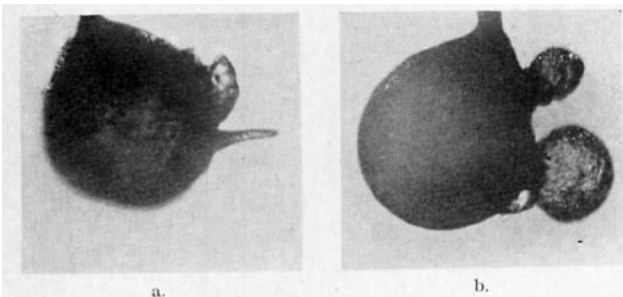


FIG. 8. Freezing of a droplet in 10% of acetylene, a., in 58%, b.

As the solution of acetylene in the droplet in equilibrium with pure acetylene is approximately 0.08 molar, the lowering of the freezing temperature is more than likely not due to an influence of the solute in the freezing temperature of water, but to a modification in the rate of freezing of the droplet, which is no longer regulated by the rate of heat and vapor transfer. Fig. 9 suggests that more heat is transferred to the environment than is released by the freezing, acetylene thus acting as an inhibitor for the growth of ice.

#### e. Freezing of water droplets in sulfur dioxide

Mixtures of sulfur dioxide and air of the following volume concentrations were used: 3.4, 5.3, 12.5, 20, 59 and 100%. The lowest freezing temperature was set at  $-9^{\circ}\text{C}$ , taking into account the fact that sulfur dioxide liquifies at  $-10^{\circ}\text{C}$ .

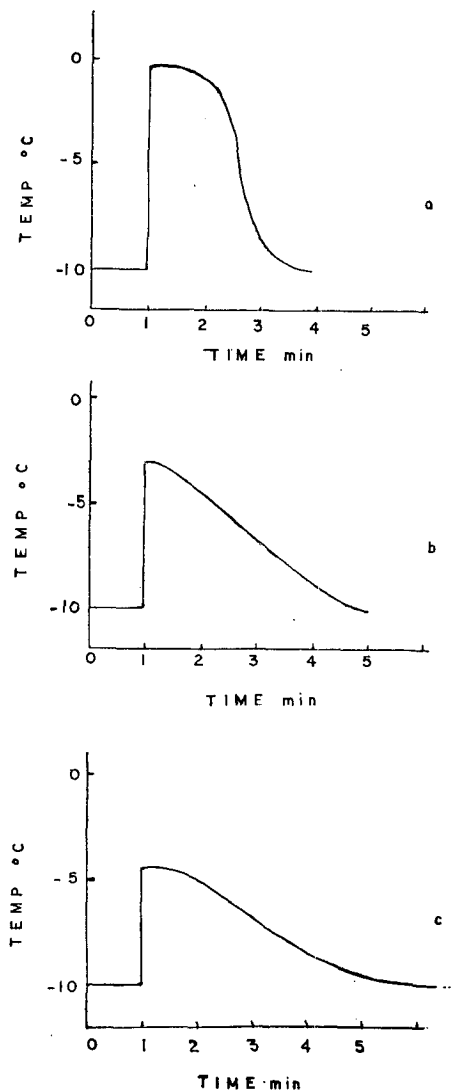


FIG. 9. Temperature as a function of time for droplets freezing in 5% of acetylene, a., 58%, b., and 100%, c.

For concentrations up to 20%, small spikes or protuberances were formed at the beginning of the freezing, the temperature rise on initiation of freezing again decreasing with increasing concentration, remaining below 0C, and changing continuously with time during freezing (curve AB in Fig. 10a). At a certain temperature, variable from droplet to droplet, a second increase of temperature was observed (curve BC) accompanied by a sudden increase in the opacity of the droplet. The behavior for the higher concentrations is illustrated in Fig. 10b. In this case, the first increase of temperature corresponded to the increase in opacity, and was generally to a value higher than 0C, while the second, as in the lower concentrations, was to a value of -2.4C. Spikes were observed only after the second rise of temperature (Fig. 11).

In any case there were no observations of shattering, formation of gas bubbles or expelling of gas.

4. Discussion

We shall begin by discussing the behavior of the droplets freezing in mixtures of sulfur dioxide and air,

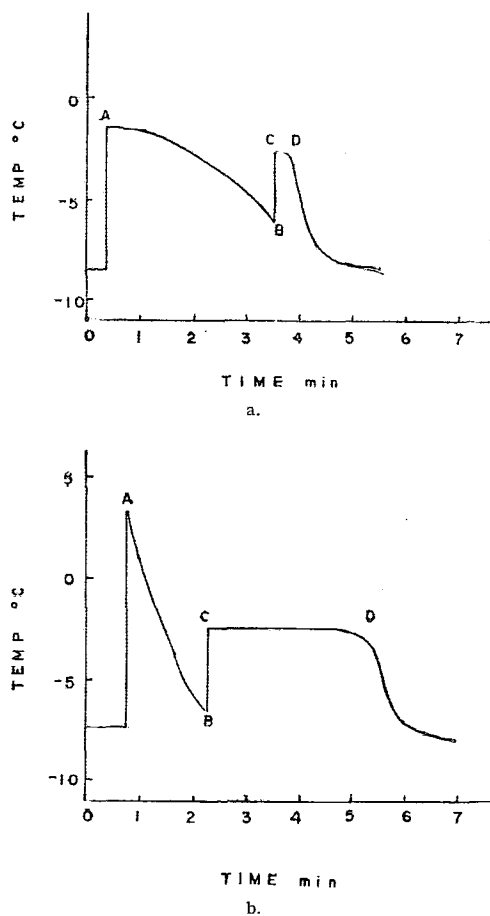


Fig. 10. Temperatures as a function of time of droplets freezing in 20%, a., and 70%, b., of sulfur dioxide.

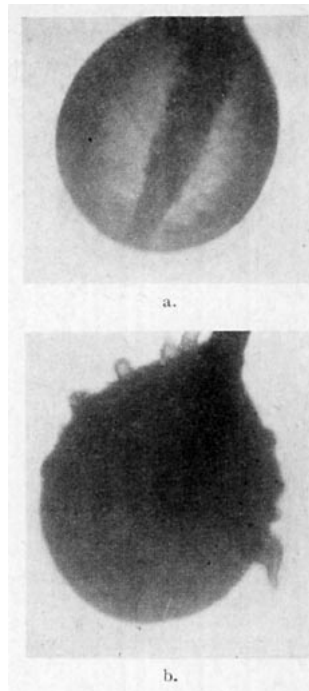


Fig. 11. Droplet containing 20% SO<sub>2</sub> by volume frozen at -9C, before the second raise of temperature, a., and the same droplet, after the second raise of temperature, b.

for which more information is available. The phase diagram of the system SO<sub>2</sub>-H<sub>2</sub>O was studied by Terres and Rühl (1934). We have reproduced in Fig. 12 this diagram for partial pressures of SO<sub>2</sub> up to 1 atm and have also indicated, with dotted lines, the solubilities of the gas for different partial pressures.

If we consider a droplet in equilibrium with a mixture in which the partial pressure of the gas is 0.2 atm (20% by volume), the diagram indicates that the equilibrium freezing point A for this droplet is -1.5C. While the experiment indicated that it remains supercooled at much lower temperatures, the temperature does rise to this value if the freezing is induced artificially; note from Fig. 11a that ice began to be separated with a continuously changing temperature in good agreement with the diagram. The eutectic temperature (point C of Fig. 12) was then observed when freezing was completed.

For mixtures of sulfur dioxide with a partial pressure higher than 0.275 atm, a hydrate (SO<sub>2</sub>·6H<sub>2</sub>O) is separated as the freezing is induced, the remaining solution increasing its concentration in water; the eutectic temperature is then observed when hydrate formation was completed. This was exactly what we observed, again with different degrees of supercooling (Fig. 10b).

The conclusion is that in spite of the high volumes of gas involved, no gas is expelled from the droplet during the freezing, since as the freezing proceeds in the higher concentration range, the solutions became more diluted in sulfur dioxide, and for the lower concentrations all the gas separated from the ice is immediately dissolved

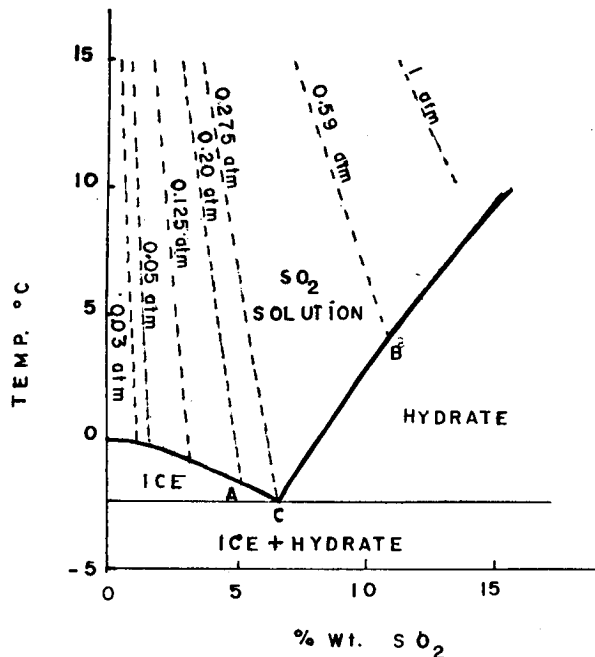


FIG. 12. Phase diagram of the system sulfur dioxide-water. In dotted lines are represented the solubilities of sulfur dioxide in water, at different partial pressures of the gas.

in the remaining solution as the diagram of Fig. 12 predicts and Fig. 10a indicates.

Droplets in equilibrium with acetylene do not form gas bubbles during freezing, suggesting a similar behavior to that of sulfur dioxide, i.e., the gas released is dissolved in the remaining solution. In addition, the inhibitory effect of acetylene in the growing of ice reduces the rate at which the gas is released. When droplets are in equilibrium with air, methane or carbon dioxide, the volume of gas contained in the droplet is smaller than that for the case of sulfur dioxide; however, gas bubbles are formed and are expelled from the droplets, indicating that the released gas is not immediately dissolved in the remaining solution. Like sulfur dioxide, methane, carbon dioxide and acetylene form hydrates, which have the structure of polyhedras (Jeffrey and McMullan, 1967) with water molecules in the corners and with large void spaces in which the gas molecules are enclosed. While the phase temperature-composition diagrams, were not studied for these gases, it is claimed (Clausen and Polglase, 1952) for hydrocarbons that these structures or "icebergs" are present even in the liquid solution. If we assume that the closer conditions are for the hydrate formation the more likely these structures will be formed, and the more easily the gas will be dissolved, then under the conditions of our experiment and according to Table 2, the gases would be ordered from increasing to decreasing solubility as sulfur dioxide, acetylene, carbon dioxide and methane. This is in good agreement with our observation of gas bubbles formed in the freezing droplets.

TABLE 2. Hydrate decomposition pressures and temperatures.

	Hydrate decomposition pressure at 0°C (atm)	Hydrate decomposition temperature at 1 atm (°C)
Methane	26.0	-29
Carbon dioxide	12.3	-15.4
Acetylene	5.5	-13.4
Sulfur dioxide	0.39	+7.0

## 5. Conclusions

The results of the freezing of water droplets in equilibrium with different gases show that the larger the volume of gas contained in the droplets the larger the probability of shattering; no shattering in air, 5% in methane and 40% in carbon dioxide, according to the order of the solubilities. However, a larger volume of gas is not a sufficient condition when:

- 1) The released gas is readily dissolved in the remaining solution, as for droplets in acetylene and low concentrations of sulfur dioxide.
- 2) The gas is separated in a solid phase as a hydrate, as for droplets in high concentrations of sulfur dioxide.
- 3) The released gas is trapped by the growing ice modifying its mechanical properties, as for droplets in high concentrations of carbon dioxide. In this case the frequency of shattering is reduced in spite of the greater amount of dissolved gas.

*Acknowledgments.* This research was supported by National Science Foundation Grant GA-777.

We thank Dr. R. Lavoie who read the manuscript and made many useful comments.

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