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Clathrate Hydrates of Air in Antarctic Ice

Abstract. Measurements of the dissociation pressure of nitrogen hydrate and oxygen hydrate show that the clathrate hydrate of air with the formula \((N_2O_3)_2\cdot 6H_2O\) should exist below about 800 meters in the Antarctic ice sheet. This accounts for the disappearance of gas bubbles at depths greater than 1200 meters. The hydrate should exist from this depth to the bottom of the core and should comprise 0.06 percent of the ice.

Gow et al. (1) have described an Antarctic ice core (2164 m deep) and have observed air bubbles to a depth of 1200 m below which they disappear. Although no bubbles can be seen, air is still present since gas is evolving on melting the deep ice.

These observations can be accounted for on the basis of an air hydrate. The structure and properties of gas clathrate hydrates have been reviewed (2, 3), and the occurrence of various hydrates on the other planets in the solar system has been discussed (4). The structure of the air hydrate would be the same as that of \(N_2O_3\) and \(O_3\)—structure I hydrate with a cubic unit cell of 12 A, containing 46 water molecules and 8 cages for the gas molecules (5). This gives an ideal formula of \((N_2O_3)_2\cdot 5\cdot 6H_2O\), but the actual formula is approximately \((N_2O_3)_2\cdot 6H_2O\) because the cages are not completely filled with gas molecules (2, 6).

A hydrate of air is stable if the pressure in the bubble is equal to or greater than the dissociation pressure of the hydrate. These dissociation pressures can be considered analogous to vapor pressures of a liquid or solid in that the hydrate is unstable below the dissociation pressure, and all the gas is converted to hydrate above the dissociation pressure, provided there is sufficient water present.

The pressure at which the air hydrate begins to form is given approximately by (4)

\[
P_{\text{Air}} = P_{N_2}X_{N_2} + P_{O_2}X_{O_2}
\]

where \(P_{N_2}\) and \(P_{O_2}\) are the respective dissociation pressures of pure \(N_2\) and \(O_2\) hydrates, and \(X_{N_2}\) and \(X_{O_2}\) are the respective mole fractions in the gas phase. Since \(O_2\) is concentrated in the hydrate, the dissociation pressure where the gas bubble completely disappears is nearly that of pure \(N_2\) hydrate. The small amount of Ar and CO\(_2\) in air would not affect the dissociation pressure significantly. These gases as well as the traces of Ne, H\(_2\), and He would be incorporated into the air hydrate.

In order to estimate the dissociation pressure of the air hydrate at the ice core temperatures, I measured a dissociation pressure for \(N_2\) hydrate of 61.9 ± 0.5 atm at \(-35.04^\circ\)C (6,8). This value combined with the quadrupole point (6) of 141.5 atm and \(-1.3^\circ\)C gives

\[
\log P_{N_2} = 4.6849 - 688.9/T \quad (2)
\]

The \(O_2\) dissociation pressure is given by (9, 10)

\[
\log P_{O_2} = 4.673 - 717/T \quad (3)
\]

The temperatures and pressures in the ice core are shown in Fig. 1, along with the dissociation pressures of \(N_2\), \(O_2\), and air hydrates. The pressures in the core were calculated from the density data (1). The data in the figure show that the air hydrate should begin to form at approximately 800 m, and that by 850 m all the air should have formed hydrate, leaving no bubbles. At greater depths the temperature rises, thus requiring a high pressure to stabilize the hydrate, but since the pressure increase with depth is greater than this, the hydrate would be stable to the bottom of the ice core. Hydrate equilibrium should be attained in the core, since the rate of formation of \(N_2\) and \(O_2\) hydrates is rapid with finely divided ice, and large crystals of ice would be expected to form hydrate in times much shorter than the age of the ice at large depths.

[Diagram of temperature-pressure relationship for ice core, showing hydrate formation]

References and Notes
7. Supported by U.S. Office of Naval Research grant N00014-67-A-0108-0004, NSF grant OA 415, and New York State grant NSF 7. We thank Captain Kohler, officers, and crew of the R.V. Fenna for their assistance during the survey. The manuscript was critically reviewed by G. Bryan and D. Hayes, Lamont-Doherty Geological Observatorio Contribution 1351.
Although the discrepancy between the predicted depth for the disappearance of bubbles and the observed depth is not great, it might be accounted for by errors in the hydrate data, the ice temperature, density, or depth. The hydrate might also have decomposed to form bubbles in the 800- to 1200-m part of the core when the pressure was released on the ice because of the way the ice crystals were packed. The discrepancy is more likely to result from the pressure in the bubbles being less than the hydrostatic pressure. When air hydrate forms, the pressure in the bubble decreases. The restoration of the air pressure in the bubble to the value of the hydrostatic pressure will be slow because of the high viscosity of ice (11). The observation that gas is released only when the deep ice melts implies that the structural strength of the ice crystal mass is greater than the dissociation pressure of the hydrate (12).

The amount of hydrate can be calculated on the assumption that 10 percent of the volume of the ice is gas bubbles when the snow is compacted into ice. On the basis of the formula \( \text{N}_2 \) \( \text{H}_2 \text{O} \) \( \cdot \text{H}_2 \text{O} \) \( \cdot \text{H}_2 \text{O} \) \( \cdot \text{H}_2 \text{O} \) \( \cdot \text{H}_2 \text{O} \), 0.06 percent of the ice would be in hydrate form. This amount of cubic crystals of air hydrate would not be easily detected in the presence of hexagonal ice.

This is the first example of the natural occurrence of clathrate hydrates on the earth (13), although methane hydrate has long been known to occur in natural-gas pipelines (14).

**Potentiality Lethal Radiation Damage: Repair by Mammalian Cells in Culture**

**Abstract.** Less than optimum conditions with regard to cell division after \( \gamma \)-irradiation provide the necessary environment in which mammalian cells can repair potentially lethal radiation damage. The kinetics of repair suggest that, during the repair process, a transient, unstable cellular state occurs which prevents cell division in complete growth medium. The capacity for repair appears to be dependent on cell age.

When mammalian cells are exposed to ionizing radiation, molecular perturbations occur which, if of sufficient magnitude, result in the registration of damage. This damage results in disturbances in the economy of the cell, the eventual expression of which is dependent upon the quality and quantity of radiation damage and the capacity for repair by the cell. In general, three classes of damage may be defined: (i) lethal, when registered suppression of colony formation occurs under any circumstance; (ii) potentially lethal, which may be repairable to a nonlethal level if suitable conditions are provided; if repair does not take place, conversion to a lethal state occurs and colony formation is suppressed; and (iii) sublethal; cells having this level of damage eventually form colonies.

The kinetics of repair of sublethal radiation damage have been extensively studied (1), and this repair capacity appears to be present in a variety of cells (2). To study sublethal damage repair, one must irradiate cells a second time. Survival, measured as a function of time between irradiations, is compared with survival found with the total dose delivered in one exposure; the kinetics observed are those for the repair of damage which would have been expressed as nonlethal had not the second dose been applied, and as modified by the progression of surviving cells through the cell cycle after irradiation.

Repair of radiation damage which would have been expressed as lethal has been less extensively studied. If the initial registration of damage produces injury states which are either nonlethal or lethal and the latter cannot be converted to a nonlethal injury state, survival will be independent of environment after irradiation. However, if survival is dependent upon the environment after irradiation, some part of the registered damage may exist in a labile injury state which may be fixed to a lethal event (3) or repaired permitting colony formation. There is evidence (3–5) that survival of mammalian cells irradiated in culture is dependent upon culture conditions after irradiation.

We now demonstrate the repair capability dependent on cell age of cells having experienced potentially lethal radiation damage. The cell line used was a clone (V79-103A) derived from lung cells of a female Chinese hamster (6). Surface-attached cells were maintained in Eagle’s minimal essential medium supplemented with Eagle’s nonessential amino acids, glutamine, NCTC-109 (4 percent), penicillin, streptomycin, and fetal calf serum (15 percent). Maintained in this medium (FS-15) at 37°C in a humidified atmosphere of 3 percent CO\(_2\), cells grew with a doubling time of 8.5 to 9 hours.

Exponentially growing cell populations were dispersed with 0.05 percent trypsin in Puck’s saline A and diluted with FS-15; the cells were then counted in a hemacytometer. Appropriate numbers of cells were plated onto 9-cm glass petri dishes to yield about 200 colonies in control and experimental dishes.

**References and Notes**

7. This measurement was made with finely divided ice, and the dissociation pressure was approached from both the high- and low-pressure side of the equilibrium. Equilibrium was approached with a \( t_2 \) of about 10 hours. Most of the measurements on \( \text{N}_2 \) and \( \text{O}_2 \) hydrates are above 0°C (6, 8) for the equilibrium involving water \(+\) hydrate \(+\) gas. The measurements below 0°C for the equilibrium involving ice \(+\) hydrate \(+\) gas extend to 
9. Equation 3 for \( \text{O}_2 \) hydrate is based on the quadruple point at \(-10.0^\circ\text{C}\) and 109.2 am (6) and the value of \( \Delta H_{\text{f}} \) above \( -40^\circ\text{C}\) \( =0.13 \text{ kcal (ice-hydrate-gas)} \) calculated by Plateauwe and van der Waals (10).
12. A. J. Gow (personal communication) has noticed that the deep cores have developed small cracks in the otherwise clear ice after storage for several months at \(-30^\circ\text{C}\).
13. I am proposing the name craigite for the naturally occurring air hydrate, after Harmon Craig.
15. Suppored by grant No. GB 8056 from the National Science Foundation.

24 February 1969; 15 April 1969