RESULTS

The results are given in Table I and shown graphically in Figure 1. The binodal area at 15° C. is considerably smaller than at 25° C., indicating the probability of a lower critical point at which the binodal area disappears. The total area under the two curves is strikingly similar, the only major difference being a slight reduction in the over-all solubility of the salt in water at the lower temperature.

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Solid Hydrates of Some Halomethanes

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A NUMBER of nonpolar gases and volatile liquids which are relatively inert form solid hydrates that are stable over a range of temperature extending in some cases to well above 0° C. Such hydrates have a fairly uniform and reproducible composition and are clathrate compounds, with the volatile component included in interstices in a water framework, which bears some resemblance to the structure of ice. Hydrates of this type have been found to form, for example, at temperatures well above the freezing point of water in pipelines carrying natural gas.

In this work phase equilibria, composition, and crystal structure of hydrates formed by some fluoromethanes have been studied. Halogenated methanes are commonly used as refrigerants, and therefore a problem of hydrate formation in refrigeration systems arises. Furthermore, it has been proposed that cyclic formation and decomposition of gas hydrates may be a means of purification of saline water. Aside from the practical significance of these materials, there is probably a relation between the simple gas hydrates and more complex hydrates which occur in biological systems. The relations between properties of the hydrate former and the structure and stability of the resulting hydrate deserve further exploration.

The materials were obtained from commercial sources as Freons; they are also commercially available as Genetrons. Hydrates prepared were those of Freon 11, trichlorofluoromethane; Freon 12, dichlorodifluoromethane; Freon 13B1, bromotrifluoromethane; and Freon 22, chlorodifluoromethane. Some properties of each of these halomethanes are given in Table I, along with the composition of each hydrate as calculated from phase equilibrium data in the manner described below. Previously available information on the hydrates of these materials includes mention of the existence of hydrates of trichlorofluoromethane and of dichlorodifluoromethane by von Stackelberg (*13*), and some phase data at temperatures above 0° C. for the hydrates of trichlorofluoromethane, dichlorodifluoromethane, and chlorodifluoromethane by Chinworth and Katz (*2*).

EXPERIMENTAL PROCEDURE FOR PHASE STUDIES

Several batches of each Freon investigated were employed in making the hydrates. The purity of each batch was checked by vapor pressure measurements, and, when the need was indicated by the results, the material was fractionated through a vacuum-jacketed, low-temperature column.

The samples of hydrate were prepared in a cylindrical metal chamber, about 6 inches long by ½ inch i.d., or, with Freon 11, which has a low vapor pressure, in a similar vessel of glass. The sample chamber was connected to a manifold, to which were attached the container of Freon, a pressure gage, and a vacuum connection. Depending on the vapor pressures of the particular Freon and hydrate, gages of range 100 or 200 p.s.i., graduated in 1-pound increments, were used. For pressures below atmospheric, a mercury manometer was used.

The chamber was immersed in an agitated water bath, which was cooled by refrigeration coils; the temperature was regulated to within 0.1° C. by a thermostat. The temperature was measured with mercury thermometers, graduated in tenths, one with a range from -2° to 50° C., and another from -38° to 2° C. The thermometers were calibrated against thermometers from the National Bureau of Standards.

In forming the hydrate, a quantity of demineralized water was placed in the chamber, which was connected to the manifold and immersed in the water bath. The chamber was then evacuated and the appropriate Freon was allowed to condense into it. Each of the Freons was more dense than water and settled to the bottom of the chamber. The pressure of the system now corresponded very closely to the vapor pressure of the liquid Freon at the working temperature. Hydrate formation, which usually did not occur spontaneously, was initiated by allowing some of the liquid Freon to evaporate, either by opening the valve to the atmosphere or by applying suction. Thus hydrate was formed as the bubbles of gas rose through the aqueous layer. The pressure of the system then decreased, after which release of vapor was repeated, sometimes several times, followed by a period of equilibration, until a constant and reproducible pressure was obtained. If the pressure was lowered still further by release of vapor, a portion

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Table I. Properties of Freons and Their Hydrates

Designation	Freon 11	Freon 12	Freon 13B1	Freon 22
Formula	CCl_3F	CCl_2F_2	$CBrF_3$	$CHClF_2$
B.P., ° C.	23.8	−29.8	−57.8	−40.8
Soly. in H_2O, g./(CC.-p.s.i.a.)	...	1.06×10^{-5}	...	7.08×10^{-4}
Molar vol., cc.	92(17.2°)	81.5(−30°)	76.1(−59°)	58.2(−69°)
ΔH_a, kcal.	11.571[a]	7.793	6.985[a]	6.998
ΔH_b, kcal.	35.447[a]	30.144	29.417[a]	25.099
Moles H_2O/mole Freon in hydrate	16.6	15.6	15.6	12.6

[a] Uncorrected. See text.

of the hydrate decomposed, since the liquid Freon phase was now used up, and the pressure rose again to the equilibrium value. By simply changing the temperature and repeating the process, a series of pressure-temperature values was obtained. If the temperature of a measurement was lower than that of the previous measurement, it was usually not necessary to reform the hydrate, but only to release sufficient vapor and observe the rise to the equilibrium pressure caused by the partial decomposition of the hydrate.

In investigating the behavior below 0° C., the problem of ice formation arose. Thus it was necessary to reform the hydrate at each temperature, for as the hydrate decomposed, a layer of ice formed over its surface. Hydrate, rather than ice alone, was shown to be present, by dropping a portion of the solid into a beaker of water. As the solid decomposed, bubbles of gas were liberated. Furthermore, if allowed to decompose in air, the solid "foamed" in a manner which has been observed to be characteristic of gas-hydrate decomposition.

The phase equilibrium results are summarized in Table II.

TREATMENT OF PHASE EQUILIBRIUM DATA

Figure 1 is a Typical phase diagram, plotted from the data for dichlorodifluoromethane. Curve I represents the variation of the vapor pressure of the water-saturated liquid Freon with temperature. This closely resembles the vapor pressure of the pure Freon, for the solubility of water is low. For three of the Freons studied, published vapor pressure data are available (*7*).

Curve II represents the variation of pressure with temperature for the equilibrium

$$F \cdot x\,H_2O\ (s) \rightleftarrows F\ (g) + x\,H_2O\ (s) \quad \Delta H_a \qquad (1)$$

Curve III represents the variation of pressure with temperature for the equilibrium

$$F \cdot x\,H_2O\ (s) \rightleftarrows F\ (g) + x\,H_2O\ (l) \quad \Delta H_b \qquad (2)$$

Between these three curves, I, II, and III, the hydrate is stable. The point marked *T* is the critical decomposition temperature, since above this temperature hydrate can not be formed at any pressure. Curve IV simply represents the water-ice equilibrium.

The number of moles of water associated with 1 mole of Freon may be calculated from the heats of reaction for Equations 1 and 2, together with the heat of fusion of water, 1437 cal. per mole at 0° C., according to a procedure described by von Stackelberg (*12*). This treatment assumes that over the range of temperature and pressure for data in the computation, the composition of the hydrate is constant, and that the hydrate is insoluble in liquid water. If Equation 1 is subtracted from 2, there results:

$$x\,H_2O\ (s) \rightleftarrows x\,H_2O\ (l) \qquad (3)$$

ΔH for Equation 3, which is the observed difference between ΔH for Equation 2 and ΔH for Equation 1, is numerically equal to x times the heat of fusion for water. The heats of reaction for Equations 1 and 2 are calculated by applying the Clausius-Clapeyron equation to the pressure-temperature data for the respective equilibria. The heats of reaction thus calculated vary only slightly with temperature, as indicated by the nearly straight-line plot of $\log p$ against $1/T$ which is shown in Figure 2 for the hydrate of Freon 12. In fact, calculations were made from the slopes of the lines near 0° C.

The values of ΔH thus obtained are not exact because of approximations implicit in the Clausius-Clapeyron equation. Corrections may be made because the gas is nonideal, because the gas is saturated with water vapor, and because Freon is slightly soluble in liquid water. Together, these correction factors amount to only a few per cent, and to some extent they cancel each other. For the hydrate of Freon 12, the uncorrected values of ΔH_a and ΔH_b were 7.881 and 30.126 kcal., compared to corrected values of 7.793 and 30.144; for Freon 22 the uncorrected values were 7.180 and 26.312, and the corresponding corrected values are 6.998 and 25.099. A more detailed treatment of the application of the corrections is given by von Stackelberg (*12*). Equations of state and solubility

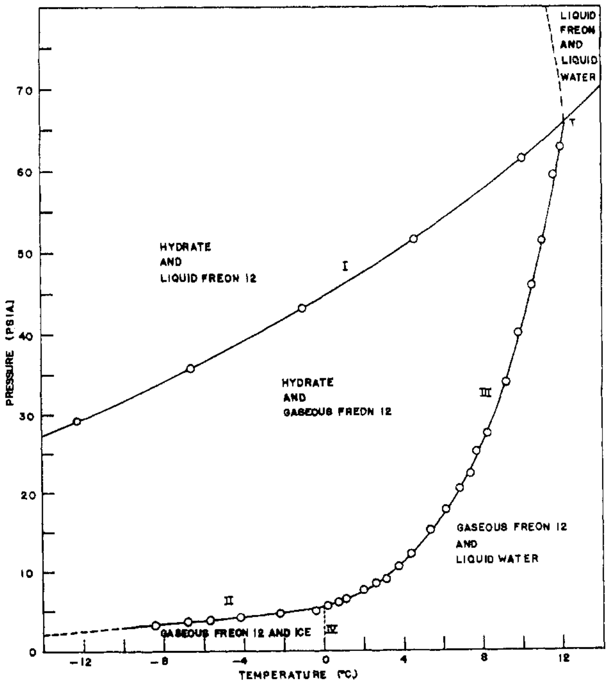

Figure 1. Phase diagram for system water-dichlorodifluoromethane

Figure 2. Plot of equilibrium pressure data for the system water-dichlorodifluoromethane illustrates application of Clausius-Clapeyron equation

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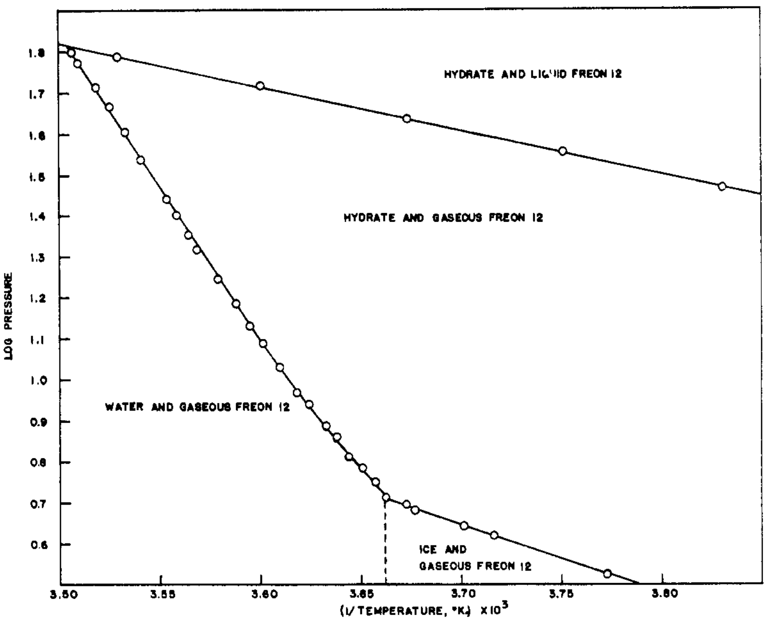

data required for the corrections were available in the literature only for Freons 12 and 22 (*9, 10*).

COMPOSITION OF THE HYDRATES

Phase data for the hydrate of Freon 12 are plotted in Figure 1; this hydrate has the composition $CCl_2F_2 \cdot 15.6\ H_2O$ and may exist up to 12.1° C. Freon 11 forms a hydrate stable up to 8.5° C., with composition calculated to be $CFCl_3 \cdot 16.6\ H_2O$. This hydrate exists at pressures well below atmospheric. The critical decomposition temperature of the hydrate of Freon 13B1, having composition $CBrF_3 \cdot 15.6\ H_2O$, is estimated to be 10° to 12° C., although measurements were not extended to the maximum temperature. Freon 22 forms the hydrate $CHClF_2 \cdot 12.6\ H_2O$ with critical decomposition temperature of 16.3° C. The enthalpies of formation for these hydrates from water and the Freon are presented in Table I.

Certain observations of interest were made during the preparation of the hydrates. The ease of formation of the hydrates varied, as did their readiness to decompose. The hydrate of $CHClF_2$ formed most readily: It was sufficient in some cases merely to lower the pressure once in order to initiate hydrate formation. CCl_3F and CCl_2F_2 were intermediate in ease of hydrate formation. At the other extreme, liquid $CBrF_3$ often completely evaporated before any hydrate was formed. Also, the hydrate of $CBrF_3$ decomposed most readily; in some cases no more than two pressure readings at two different temperatures could be made before the hydrate was lost. The hydrates of CCl_2F_2 and $CHClF_2$ were sufficiently stable so that the entire range of temperature from zero degrees to the critical decomposition temperature could be investigated with one sample. Probably one factor in determining the relative stability of the hydrate is the molecular size of the Freon. According to von Stackelberg (*12*) the upper limit for the molar volume in the liquid state of the volatile component at which hydrate formation is possible is 85 cc. The data given in Table I show that $CHClF_2$ has the most favorable molar volume for hydrate formation.

Attempts were made to form the hydrate of Freon 114, dichlorotetrafluoroethane, in the range −2° to 10° C. This substance has a molar volume of 111.5 cc. at 0° C. which, according to von Stackelberg's rule, is too large for hydrate formation. This was verified, since hydrate did not form within this temperature range.

Table II. Pressure-Temperature Data for Hydrate-Water-Freon Equilibria

CCl_3F		CCl_2F_2		$CHClF_2$	
Temp.., ° C.	Pressure, p.s.i.a.	Temp., ° C.	Pressure, p.s.i.a.	Temp., ° C.	Pressure, p.s.i.a.
8.3	9.05	11.9	62.7	16.3	112.2
7.2	6.62	11.6	59.2	15.8	102.7
6.8	6.14	10.9	41.6	15.5	99.7
6.1	5.15	9.8	40.2	15.0	91.7
5.7	4.66	9.1	34.4	13.6	77.2
5.3	4.08	8.2	27.4	12.4	66.2
4.2	3.17	7.7	25.2	12.0	62.2
3.5	2.50	7.3	22.4	11.5	58.7
2.5	1.95	6.9	20.7	10.6	52.7
1.8	1.72	6.2	17.9	10.0	48.2
0.7	1.33	5.4	15.2	9.1	43.2
−0.5	1.08	4.4	12.8	8.4	39.2
−2.7	1.08	3.7	10.6	7.7	35.7
−4.4	0.88	3.1	9.3	6.9	31.7
−6.6	0.74	2.8	8.6	6.1	28.7
		2.0	7.6	5.4	26.2
$CBrF_3$		1.1	6.5	4.8	24.2
7.2	60.5	0.8	6.1	3.7	21.2
6.4	49.2	0.2	5.6	3.1	19.7
4.5	34.2	−0.3	5.2	2.6	18.2
3.0	23.5	−2.2	4.9	2.0	16.9
1.7	18.7	−4.2	4.2	0.7	14.3
0.8	15.2	−5.7	3.8	-0.3	12.7
−0.9	12.0	−6.8	3.7	−2.2	11.2
−2.5	11.2	−8.3	3.3	−3.1	11.2
−5.0	9.8			−4.5	10.3
−7.0	9.2			−5.5	9.7

X-RAY DIFFRACTION STUDIES

Von Stackelberg (*14*) and Claussen (*4, 5*) were able to work out, on the basis of x-ray data and formulas, two crystal structure types, to which all of the hydrates they observed could be assigned. Each of these structures has cubic symmetry. Structure I has a lattice constant of about 12 A., and the unit cell contains 46 water molecules with two small voids of coordination number 20 and six larger voids of coordination number 24. Structure II has a lattice constant of about 17 A. and 136 water molecules per unit cell with 16 small voids, similar to the small voids in I, and eight large voids with coordination number 28. It is in the voids of various sizes, surrounded by water molecules, that the gas molecules are trapped, forming the solid hydrate.

If only the larger voids of II are filled, the ideal composition ratio would be eight molecules of hydrate former to 136 molecules of water, corresponding to the empirical formula $F \cdot 17\ H_2O$. The hydrates of Freon 11, Freon 12, and Freon 13B1 are apparently examples of this structure, as indicated by their composition.

If only the larger voids of structure I are filled, the formula should by $F \cdot 7.67\ H_2O$, while if all the voids are filled, the formulas for I and II, respectively, would be $F \cdot 5.75\ H_2O$ and $F \cdot 5.67\ H_2O$. Thus the formula alone of the hydrate of Freon 22 does not allow a structure to be assigned to this hydrate. It was thus felt desirable to determine the identity of the crystal structures of several of the hydrates by means of x-ray deffraction measurements.

The powder technique was employed to obtain the diffraction patterns of the hydrates of Freon 12 and Freon 22. The samples of hydrate were prepared on a vacuum line connected by a spherical joint to a capillary about 8 cm. long and 1 mm. i.d. The system was evacuated, and water was condensed in the capillary by bringing up around it a Dewar flask containing liquid air. The ice which formed in the capillary was next melted, and then the Freon was condensed into the capillary in the same manner. When sufficient quantities of both materials were present, the capillary, still dipping into the liquid air bath, was sealed off under vacuum, using the method developed by Cole (*6*).

Before an exposure, the capillary was again immersed in liquid air in order to form sufficiently small crystals of hydrate by rapid cooling, and then it was transferred to the precooled camera. During the exposure, the temperature of the capillary was maintained at about 2° C. by directing against it a stream of nitrogen gas which had passed through a metal coil immersed in an acetone-dry ice bath. To permit the cold gas to enter the camera, it was necessary to uncover the camera and to cover the film with a strip of black paper. Exposure times of 4 to 6 hours were required, and the capillary was rotated during the exposure. Two cameras were used, one having a circumference of 180 mm. and the other a circumference of 360 mm. The x-ray tube had a copper target and the radiation was filtered with a nickel filter.

In most of the patterns, lines characteristic of ice were also observed. These could be distinguished not only by comparison with known values of diffraction angles but also by their appearance. The lines for ice were spotty, while those for the hydrate were uniform and somewhat diffuse. Thus the crystallite size of the hydrate is appreciably smaller than that of ice.

The two hydrates lattices described above have the following space groups: I, $O_h^3 P_m 3_n$; II, $O_h^7 F_d 3_m$ (*14*). The conditions limiting the possible reflections for these structures can be obtained from tables (*8*), and the allowed reflections matched with the observed lines. To make a more thorough test of the assignment of indices to the observed lines, the lowest measured value of the angle θ was successively assigned to every integral value of Σh^2 from 1 to 12, and for each of these assignments values of Σh^2 were then calculated for the remaining lines in the pattern. The series was selected which gave the best fit to the condition that Σh^2 be an integer for each line. Once this assignment had been made, the lattice constant a was calculated for each reflection, using the equation applicable to the cubic system (*3*):

$$a = 0.7695\ (\Sigma h^2/\sin^2 \theta)^{1/2} \tag{4}$$

The calculated value of the lattice constant, 17.13 A., together with the observed extinctions for the hydrate of Freon 12 confirmed the assignment to this hydrate of structure II.

Table III. X-Ray Data for Hydrate of Chlorodifluoromethane

θ	Intensity	Σh^2	Indices	a, A.
5°12′	Weak	2	110	11.99
8°24′	Weak	5	210	11.78
10°42′	Weak	8	220	11.72
13°24′	Weak	13	320	11.97
13°45′	Strong	14	321	12.11
14°45′	Medium	16	400	12.09
15°18′	Very weak	17	322, 410	12.02
15°51′	Very weak	18	330, 411	11.95
23°11′	Medium	38	532, 611	12.05
23°41′	Medium	40	620	11.96
24°6′	Medium	41	443, 540	12.07
30°6′	Weak	73	661	11.97

The average value of a for the hydrate of Freon 22 was calculated to be 11.97 A. which, with the observed extinctions, allows structure I to be assigned to this hydrate. The assignment of lines and corresponding values of a are given in Table III. Thus the hydrate of Freon 22 should have the ideal formula of either $CHClF_2 \cdot 5.75\ H_2O$ or $CHClF_2 \cdot 7.67\ H_2O$, while $CHClF_2 \cdot 12.6\ H_2O$ is actually the formula, or perhaps more correctly $0.609 CHClF_2 \cdot 7.67\ H_2O$. Thus there is a deficiency of Freon 22 in this hydrate—that is, some of the voids are unoccupied by Freon molecules. In structure I, which is usually assumed by hydrates of small molecules, the two types of voids have diameters of 5.2 and 5.9 A. respectively. If a Freon molecule is free to rotate inside a void, then the spherical volume occupied, calculated from covalent radii, has a diameter of 5.50 A. Thus the smaller voids of structure I cannot be occupied by Freon 22 molecules. In addition, there are apparently some vacancies in the larger voids. This is not surprising in view of thermodynamic considerations which have indicated that the gas hydrates may be nonstoichiometric (*1, 11*).

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