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**Mixed Clathrates for Cool
Storage Applications**

J. J. Carbajo

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MARTIN MARIETTA ENERGY SYSTEMS, INC.
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NOMENCLATURE

C	number of components
F	degrees of freedom
(g)	gas
h	heat of change of state, J/g
H	hydrate
(ℓ)	liquid
m	mass, g
M	molecular weight
N	number of molecules of water
P_i	pressure, kPa
P	number of phases
Q ₁	quadruple point 1
Q ₂	quadruple point 2
R	refrigerant
(s)	solid
T	temperature, °C
x	mole fraction

Subscripts

p	PARTIAL
T	TOTAL
11	Refrigerant-11
12	Refrigerant-12
114	Refrigerant-114

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ABSTRACT

Mixtures of refrigerants have been used to produce mixed-gas hydrates or clathrates at different pressures and temperatures. A clathrate at atmospheric pressure and at a temperature of 9.2°C (48.6°F) was obtained by using a mixture of Refrigerant-12 (R-12) and Refrigerant-11 (R-11). In addition, mixtures of R-12 and Refrigerant-114 (R-114) and of R-11 and R-114 have been tested. For these cases R-114 did not enter into the clathrate. Mixed hydrates or clathrates open new possibilities as the storage media for either cool or heat storage systems.

1. INTRODUCTION

Conventional space-cooling demands in residential and commercial buildings produce large peak loads on the electrical utilities during the hottest part of the summer days. There is a need to manage the load of the utilities, reducing the high peak loads during the summer days by shifting some of the power demand to off-peak hours during the nights. A solution to this problem is distributed cool storage systems that can be charged during the night and discharged during the day, using little on-peak electricity.

There are some commercial storage systems using either chilled water or ice as the storage medium.¹ These systems, however, have been proven to be inefficient when compared with conventional systems. Chilled water systems, for example, require a very large volume for storage while ice systems have a reduced compressor performance² and high heat gains because of the low temperature of the storage tank. Salt hydrates have also proven to be inefficient.³ These drawbacks have focused attention on gas hydrates or clathrates as the cool storage medium.^{4,5} Gas hydrates, for example, have a heat of fusion comparable to, and a melting temperature higher than, ice. Therefore, they are suited for storage

in air conditioning units with less heat gain into the storage tank and higher evaporator temperatures.

Three refrigerants that form gas hydrates for cool storage applications have been selected in this study: Refrigerant-11 (R-11), or trichloromonofluoromethane; Refrigerant-12 (R-12), or dichlorodifluoromethane; and Refrigerant-21 (R-21), or dichloromonofluoromethane. These refrigerants combine with water to form, according to the reaction, a gas hydrate crystal,



The number of molecules of water N — between 15.6 and 16.9 — needed to form the gas hydrate crystal per molecule of refrigerant is given in Table 1. Also given in Table 1 are the heat of formation per unit mass of the gas hydrate h and the upper temperature and the pressure at which the gas hydrate forms Q_2 . Extensive testing has been performed at Oak Ridge National Laboratory (ORNL) with R-12 (Refs. 6 and 7), which forms the gas hydrate at a pressure >1 atm (449 kPa or 65.4 psia), and with R-11, which forms the gas hydrate at an absolute pressure <1 atm (59 kPa or 8.6 psia). From an economic viewpoint it is desirable to use a gas hydrate at atmospheric pressure because a storage tank designed for a working pressure of 1 atm is cheaper than a tank designed for higher or lower pressure. An economic study of cool storage systems⁸ indicates that the storage tank contributes significantly to the total cost of the system.

Table 1. Refrigerants considered in this study

Refrigerant	Q_2 [°C (°F), kPa (psia)]	M	N_{H_2O}	h [J/g (Btu/lb)]
R-11 (CCl ₃ F)	8.7 (47.6), 59 (8.6)	137	16.6	281.7 (121.2)
R-12 (CCl ₂ F ₂)	12.1 (53.8), 449 (65.4)	121	15.6	270.4 (116.6)
R-21 (CHCl ₂ F)	8.6 (47.5), 101 (14.7)	103	16.9	276.6 (118.9)
R-114 (C ₂ Cl ₂ F ₄)	No hydrate	171		

Refrigerant-21 produces a gas hydrate at precisely atmospheric pressure (Table 1). However, this refrigerant is very chemically active and would be appropriate for a closed storage system, also called indirect-charged, indirect-discharged system (Fig. 1). In this system the refrigerant and the water plus the surfactant added to aid mixing will be in a completely closed system that can be manufactured of materials chemically resistant to R-21. Since this system will be charged indirectly by the coil at the top (Fig. 1) and also will be discharged indirectly by the coil or heat exchanger at the bottom, the refrigerant will not be in contact with seals of either pumps, compressors, or valves. However, R-21 could not be used in the more efficient direct-contact-charged, direct-contact-discharged system (Fig. 2) because it would eventually corrode the system's compressor seals, discharge pump seals, and valve seals. In this study an alternative to using R-21 was found by mixing R-11 and R-12 to obtain a mixed clathrate at atmospheric pressure. In the mixed clathrate (or mixed-gas hydrate) both refrigerants enter into the gas-hydrate crystal at a temperature and pressure determined by the composition of the refrigerant mixture. For a specific composition the mixed-gas hydrate forms at an invariant pressure and temperature.

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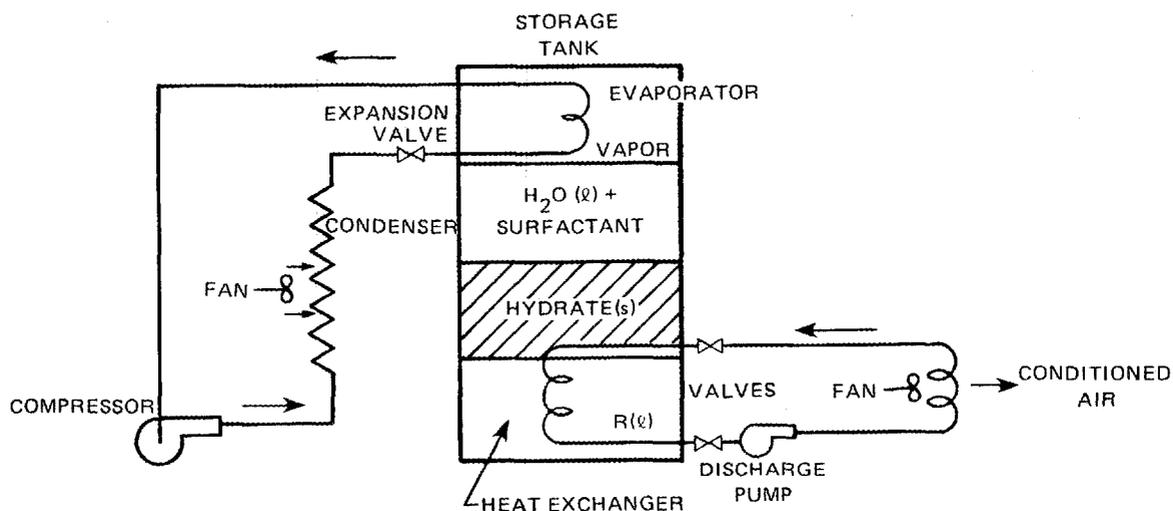


Fig. 1. Indirect-charged, indirect-discharged hydrate cool storage system.

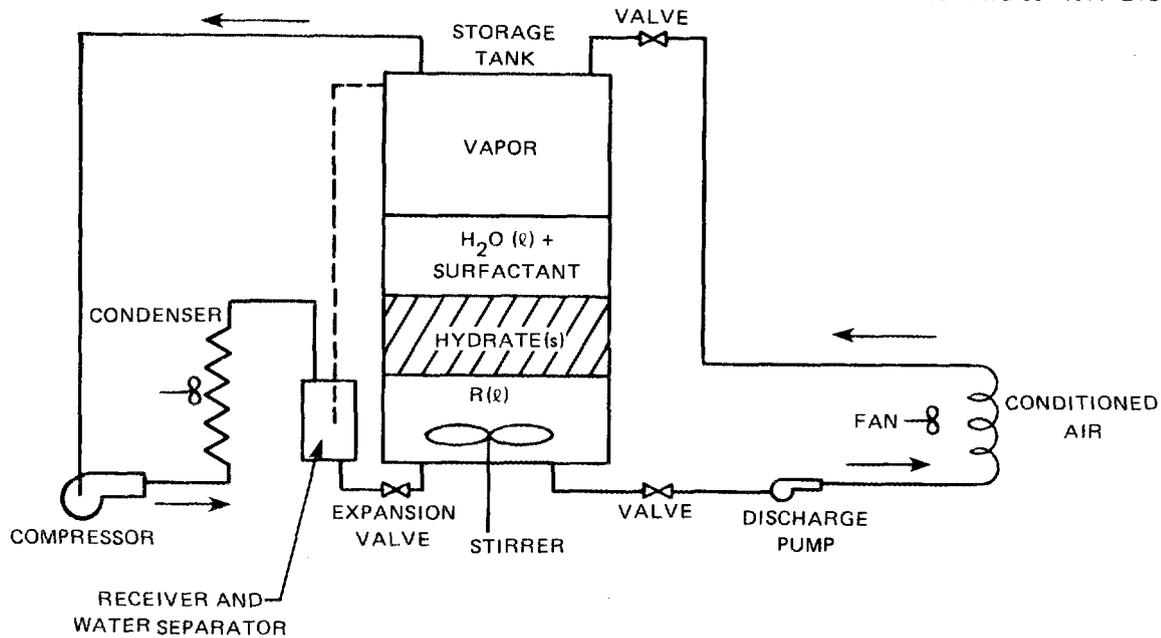


Fig. 2. Direct-contact-charged, direct-contact-discharged hydrate cool storage system.

There have been some previous experiments with mixed hydrates. For example, mixed hydrates have been formed with mixtures of monochloroethane (C_2H_5Cl or R-100) and three other chlorinated hydrocarbons: trichloromethane ($CHCl_3$ or R-20) and two different isomers of dichloroethane (CH_3CHCl_2 and CH_2Cl-CH_2Cl).⁹ Mixed hydrates of methane and isobutane¹⁰ and mixed hydrates of mixtures of other hydrocarbons -- specifically, methane, ethane, and propane, as well as mixtures of methane and carbon dioxide or methane and hydrogen sulfide¹¹ -- also have been identified.

2. THEORETICAL BACKGROUND

When a single refrigerant such as R-12 is used in a gas hydrate, cool storage system, the gas hydrate is formed at point Q_2 of the phase diagram of the refrigerant/water system (Fig. 3). The pressure and temperature of this point correspond to that shown in Table 1. In a cool storage system, gas hydrate (solid) will coexist with some water (liquid), some refrigerant (liquid), and a gaseous portion containing both the refrigerant saturated vapor and water vapor. This system has two components (water and refrigerant) and four phases (liquid refrigerant, liquid water, solid hydrate, and vapor). According to the phase rule,¹²

$$F + P = C + 2 .$$

(2)

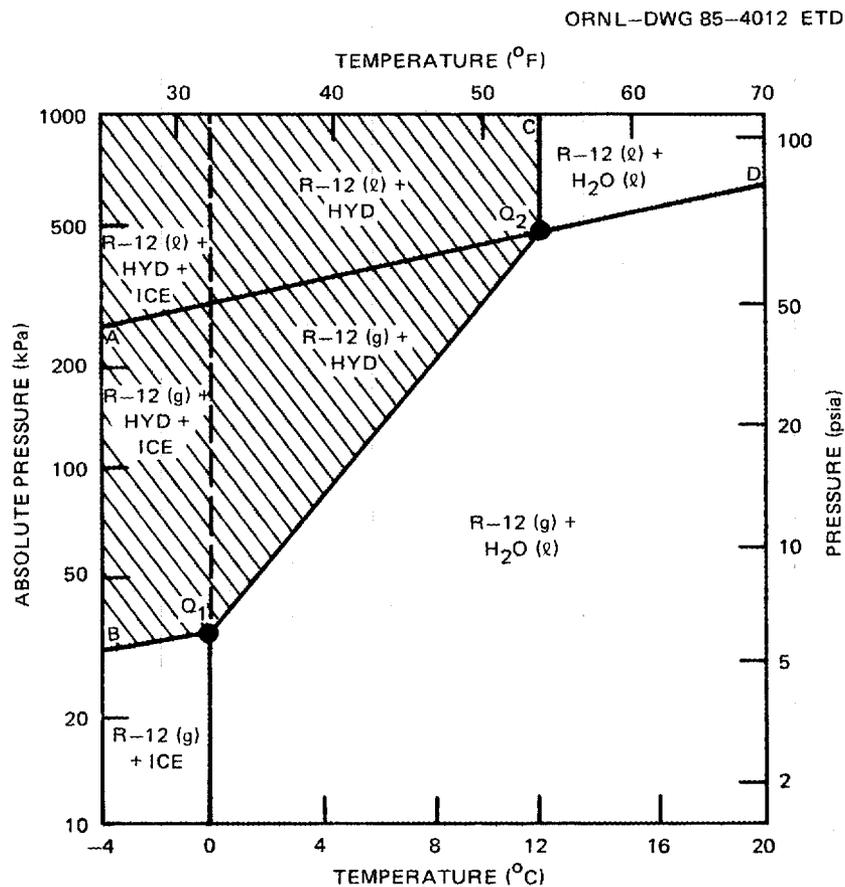


Fig. 3. Phase diagram for R-12/H₂O mixtures.

For the cool storage system with a single refrigerant the phase rule yields

$$F = C + 2 - P = 2 + 2 - 4 = 0 . \quad (3)$$

Therefore, no degrees of freedom are available, and the system, when in equilibrium, has to operate at the invariant point Q_2 (Fig. 3), where R-12(l), R-12(g), $H_2O(l)$, and gas hydrate can coexist.

If two completely miscible refrigerants are used to form a mixed clathrate, the situation changes. Now, the system has three components (water and two refrigerants) but the same four phases as in the previous case. The degrees of freedom that are available now are

$$F = C + 2 - P = 3 + 2 - 4 = 1 . \quad (4)$$

One degree of freedom indicates that the pressure-temperature relationship for the mixed hydrate is uniquely dependent on the composition of the mixture of refrigerants. Mixed-hydrate formation should occur at a point between the two Q_2 points of the single refrigerants in the mixture, a fact confirmed by previous experiments.⁹ If, however, only one refrigerant is used, the hydrate will form at the end of this line corresponding to the Q_2 point of the refrigerant used.

If a mixture of two refrigerants — one that does not form a hydrate [like Refrigerant-114 (R-114)] and the other one entering into the hydrate — is used, the same situation as the one given by Eq. (4) occurs. Still, three components and four phases will be present, and, therefore, one degree of freedom will be available. Hydrate will be formed at different pressures and temperatures, depending on the composition of the mixture, with only the hydrate-forming refrigerant entering into the hydrate. Inactive R-114 and the remaining water, if any, will not combine and will remain as liquid coexisting with the solid hydrate.

3. TEST PROCEDURE

Tests were performed in small (0.023-m-ID), glass test tubes and also in a larger (0.127-m-ID) test section with indirect charging and direct-contact discharging.

The glass test tubes, designed for a maximum pressure of 1.37 MPa (200 psia), were installed with a thermocouple and a pressure gauge so that the temperature and the pressure of the mixture could be measured. Different mixtures of R-11 and R-12 were tested ranging from pure R-11 to pure R-12. In addition, mixtures of R-12/R-114 and R-11/R-114 were tested. The mole fraction of the mixture was calculated by

$$x_{11} = \frac{m_{11}/M_{11}}{M_{11}/M_{11} + M_{12}/M_{12}}, \quad (5)$$

$$x_{12} = \frac{m_{12}/M_{12}}{M_{11}/M_{11} + M_{12}/M_{12}} = 1 - x_{11}, \quad (6)$$

where M is molecular weight (Table 1), and m is the mass (g) of R-11 or R-12. The mass of water needed to form hydrate was calculated by

$$m_{\text{H}_2\text{O}} = M_{\text{H}_2\text{O}} \left(16.6 \frac{m_{11}}{M_{11}} + 15.6 \frac{m_{12}}{M_{12}} \right). \quad (7)$$

Most of the tests were performed with a combined mass of ~13 g for both refrigerants and ~25 g of water.

Before the mixture was placed into the glass tube, the air was removed by using a vacuum pump. Once the vacuum inside the tube was obtained, the desired amount of water was introduced. The refrigerant with the lower vapor pressure (R-11) was added next, and, finally, the refrigerant with the higher vapor pressure (R-12 or R-114) was added. When a mixture of R-12 and R-114 was tested, R-114 was placed inside the tube before R-12.

After the mixture of refrigerants and water was inside, the glass tube was placed in a controlled-temperature bath. Occasionally, the tube

was agitated to mix the refrigerants and the water. The temperature and the pressure were recorded during both the hydrate-forming process and the hydrate-melting process. For each mixture of R-11 and R-12, temperature and pressure were found to be constant during the complete melting process, which took place outside of the bath and was observed visually. However, the temperature and pressure of mixtures of R-11 and R-114 or R-12 and R-114 changed during the hydrate-melting process; that is, a "plateau" for the pressure or the temperature as a function of time was not obtained.

The bigger test section, the crystallizer, has been described in previous publications^{6,7} and has been used extensively for direct-contact-charged tests. The crystallizer consisted of a cylinder made of plexiglass, 0.914 m (36 in.) high with an inside diameter of 0.127 m (5 in.), and surrounded by thermal insulation. A small slot of this insulation could be removed to observe the clathrate-forming or -melting process. For the tests in the present study, a coil was added at the top of the crystallizer so that the system could be charged indirectly (Fig. 4). Cold water at $\sim 1^{\circ}\text{C}$ (34°F) or alcohol at approximately -6°C (20°F) was circulated inside the coil to remove heat from the crystallizer. The system was usually charged by using cold alcohol, and a stirrer in the crystallizer provided agitation to the mixture. The system was discharged by using a pump connected to the bottom of the crystallizer to circulate liquid through a heat exchanger and return it to the top of the crystallizer⁷ (Fig. 4).

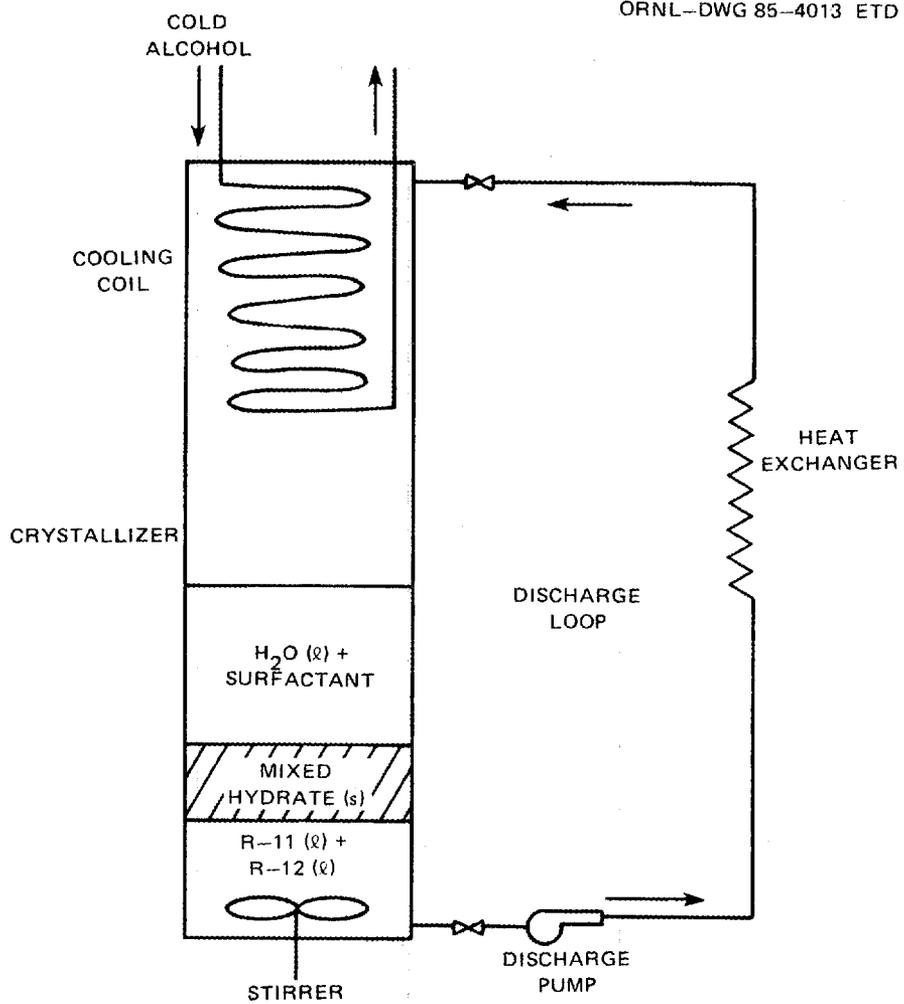


Fig. 4. Indirect-charged, direct-discharged test facility.

4. RESULTS

Different mixtures of R-11 and R-12 were tested in both the glass test tubes and the larger crystallizer. Mixed clathrates at different pressures and temperatures were obtained. The different test mixtures and the equilibrium temperatures (T) and pressures (P) for the mixed-clathrate formation are given in Table 2 and plotted in Fig. 5. As can be seen from Fig. 5, the resulting P-T values are in a line between the two Q_2 points of R-11 and R-12. This line is not straight in either linear coordinates (Fig. 5) or semilog coordinates (Fig. 6).

With a mixture composition of $x_{11} = 0.88$ and $x_{12} = 0.12$ (mole fractions in the liquid portion), a mixed hydrate at atmospheric pressure and

Table 2. Mixed clathrates formed with mixtures of R-11 and R-12

Molar fractions		T	P_T
x_{11}	x_{12}	[°C (°F)]	[kPa (psia)]
1.00	0.00	8.7 (47.6)	59 (8.6)
0.95	0.05	8.5 (47.8)	62 (9.0)
0.92	0.08	8.8 (47.9)	69 (10.0)
0.90	0.10	9.0 (48.2)	84 (12.2)
0.88	0.12	9.2 (48.6)	101 (14.7)
0.83	0.17	9.5 (49.1)	122 (17.8)
0.80	0.20	9.6 (49.4)	136 (19.8)
0.78	0.22	9.7 (49.5)	144 (21.0)
0.75	0.25	9.8 (49.7)	155 (22.5)
0.70	0.30	10.0 (50.0)	172 (25.0)
0.64	0.36	10.2 (50.3)	192 (28.0)
0.64	0.36	10.3 (50.5)	199 (29.0)
0.60	0.40	10.3 (50.5)	210 (30.5)
0.57	0.43	10.6 (51.0)	213 (31.0)
0.57	0.43	10.6 (51.0)	220 (32.0)
0.54	0.46	10.7 (51.2)	234 (34.0)
0.50	0.50	10.8 (51.5)	247 (36.0)
0.42	0.58	11.1 (51.9)	275 (40.0)
0.25	0.75	11.3 (52.4)	314 (45.7)
0.17	0.83	11.4 (52.5)	330 (48.0)
0.04	0.96	11.9 (53.5)	433 (63.0)
0.00	1.00	12.1 (53.8)	449 (65.4)

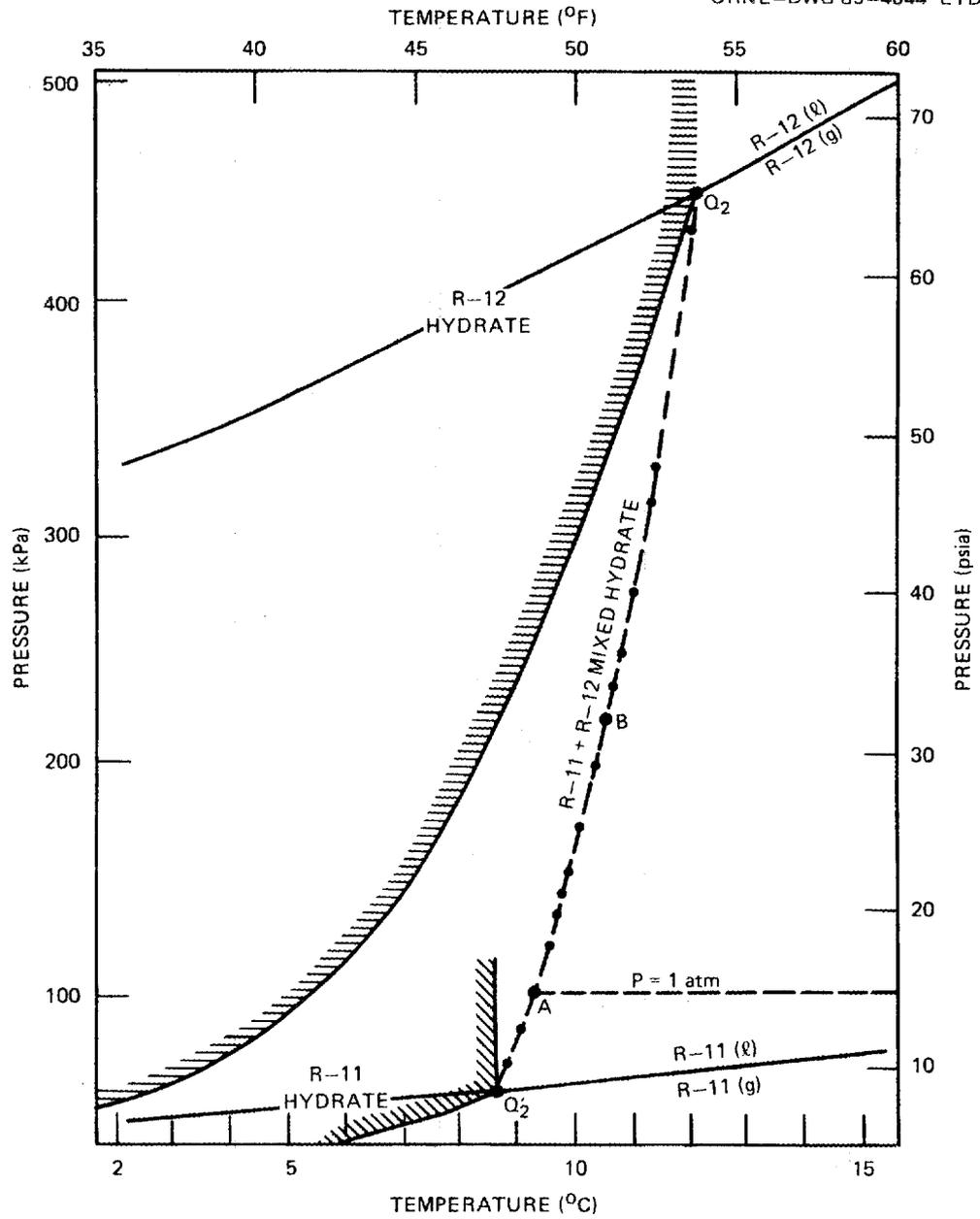


Fig. 5. Phase diagram for R-11 + R-12 + H₂O mixed-hydrate mixtures.

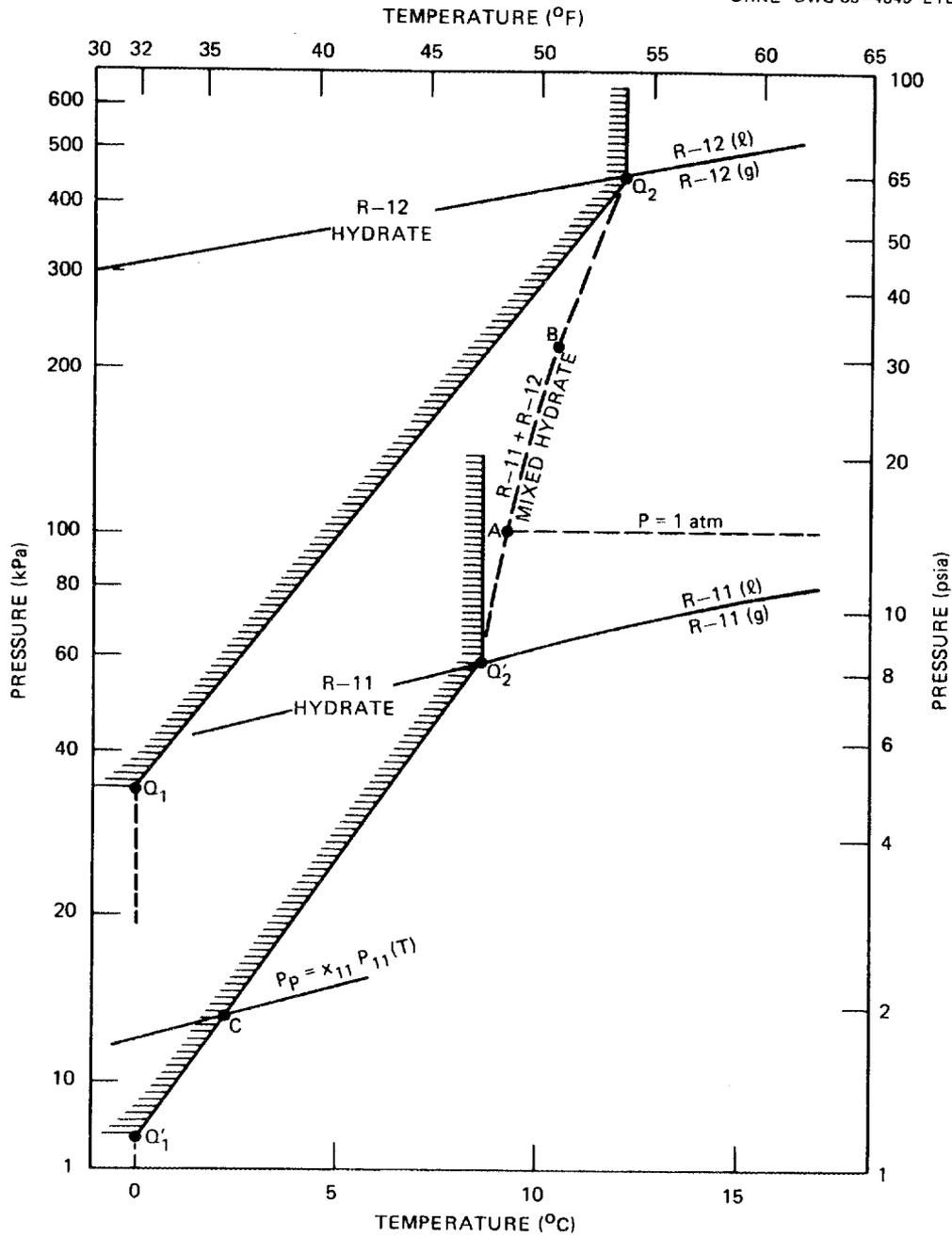


Fig. 6. Phase diagram for R-11 + R-12 + H₂O mixed-hydrate mixtures (semilog scale).

9.2°C (48.6°F) was obtained, corresponding to point A of Figs. 5 and 6. This composition corresponds to weight fractions of 0.9 and 0.1 and volume fractions of 0.89 and 0.11 for the R-11 and R-12, respectively.

The composition of an ideal mixture at a known pressure and temperature can be obtained from Raoult's law;¹² mixtures of R-11 and R-12 are almost ideal. A mixture at a pressure of 1 atm [101 kPa (14.7 psia)] will have the following mole fraction for its liquid components at a temperature of 9.2°C (48.6°F):

$$P_T = 101 = x_{11}P_{11} + x_{12}P_{12} + P_{H_2O} , \quad (8)$$

with

$$x_{11} + x_{12} = 1 , \quad (9)$$

where P_T is the total pressure of the mixture and P_{11} , P_{12} , and P_{H_2O} are the pressures of pure R-11, pure R-12, and pure H_2O at a temperature of 9.2°C (48.6°F). From Eqs. (8) and (9) $x_{11} = 0.88$ and $x_{12} = 0.12$ are obtained. The contribution from the water vapor (P_{H_2O}) is very small and can be neglected in most cases.

Mixed clathrates or hydrates of R-11 and R-12 can exist on the line $Q_2Q'_2$ of Fig. 4. For instance, if a mixed clathrate at a pressure of 220 kPa (32 psia) is desired (point B), the corresponding temperature of the hydrate is 10.6°C (51°F) (Fig. 5), and the composition of the mixture, calculated using Raoult's law (Eq. 8), is $x_{12} = 0.44$ and $x_{11} = 0.56$.

The heat of formation of mixed hydrates can be estimated by a weighted average of the heats of formation of the single hydrates forming the mixed hydrate. For instance, the mixed hydrate formed at atmospheric pressure with a composition of 0.1 and 0.9 by weight for R-11 and R-12, respectively, will have a heat of formation of

$$h = 281.7 (0.9) + 270.4 (0.1) = 280.6 \text{ J/g} . \quad (10)$$

Mixtures of R-11 and R-114 were also tested (Table 3). In this case, only R-11 entered the gas hydrate, and R-114 remained as a liquid without combining with water. When pure R-114 was used, ice was formed

Table 3. Tests performed with mixtures of R-11 and R-114

x_{11}	x_{12}	T [°C (°F)]	P_T [kPa (psia)]
0.00	1.0	0 (32)	87 (12.7)
0.26	0.74	1.8 (35)	80 (11.6)
0.35	0.65	3.5 (38)	81 (11.7)
0.49	0.51	5.0 (41)	78 (11.4)
0.74	0.26	7.2 (45)	71 (10.3)
1.00	0.00	8.7 (47.6)	59 (8.6)

at a $T = 0^\circ\text{C}$ (32°F). The resulting pressure for the gas hydrates formed with the R-11/R-114 mixtures was always below atmospheric.

The higher the mole fraction of R-11, the higher the temperature of the gas hydrate. In the mixture the higher the mole fraction of R-11, the higher the partial pressure P_p of R-11:

$$P_p = x_{11} P_{11}(T) . \quad (11)$$

The temperature for the gas hydrate formation can be obtained as the intersection of the line $Q_1' Q_2'$ of Fig. 6 and Eq. (11). For instance, for a mole fraction of R-11, $x_{11} = 0.3$, the temperature of hydrate formation, given by point C of Fig. 5, is $T = 2.2^\circ\text{C}$ (36°F).

Table 4 shows the mole fraction of R-11 required to form gas hydrate at different temperatures. The mole fraction of R-11, x_{11} was calculated by

$$x_{11} = \frac{P_{Q_1' Q_2'}(T)}{P_{11}(T)} , \quad (12)$$

where $P_{Q_1' Q_2'}(T)$ is the pressure as a function of temperature given by line $Q_1' Q_2'$ of Fig. 6, and $P_{11}(T)$ is the saturation pressure of pure R-11 as a function of temperature. The calculated values of Table 4 agree with the measured values given in Table 3. The total pressure of the gas

Table 4. Thermodynamic state of mixtures of R-11 and R-114

T [°C (°F)]	$P_{Q_1 Q_2}$ [kPa (psia)]	$P_{11}(T)$ [kPa (psia)]	x_{11}^a
0 (32)	8.2 (1.2)	40.0 (5.83)	0.21
1.1 (34)	9.9 (1.45)	42.0 (6.11)	0.24
2.2 (36)	13.1 (1.9)	44.0 (6.40)	0.30
3.3 (38)	17.2 (2.5)	46.1 (6.71)	0.37
4.4 (40)	22.7 (3.3)	48.2 (7.02)	0.47
5.6 (42)	28.9 (4.2)	50.5 (7.35)	0.57
6.7 (44)	37.8 (5.5)	52.8 (7.69)	0.72
7.7 (46)	48.8 (7.1)	55.2 (8.04)	0.88
8.6 (47.6)	59.0 (8.5)	59.0 (8.5)	1.00

^aMolar fraction of R-11 needed to form hydrate at indicated temperature.

hydrate formed with the mixture of R-11 and R-114 can be calculated by using Raoult's Law in the form

$$P_T = x_{11}P_{11}(T) + x_{114}P_{114}(T) + P_{H_2O}(T) \quad (13)$$

Values for different temperatures are given in Table 5. The total pressure of the mixture-forming gas hydrate is always below atmospheric and reaches a maximum pressure of 81 kPa (11.8 psia) for the gas hydrate forming at 4°C (39°F).

Finally, tests were also performed with mixtures of R-12 and R-114. As found with mixtures of R-11 and R-114, R-114 did not enter into the clathrate. Molar concentrations, as well as pressures and temperatures of the gas hydrates formed, are given in Table 6. The higher the concentration of R-12, the higher the pressure and the temperature of the resulting gas hydrate.

The gas hydrate forms on the line $Q_1 Q_2$ of Fig. 6 as given by the partial pressure of R-12 in the mixture. Therefore, as in the case of R-11, the mole fraction of R-12 required to form gas hydrate in a mixture of R-12 and R-114 is

$$x_{12} = \frac{P_{Q_1 Q_2}(T)}{P_{12}(T)} \quad (14)$$

Table 5. Gas-hydrate temperature and pressure for mixtures of R-11 and R-114

T [°C (°F)]		x_{11}	x_{114}	P_T [kPa (psia)]
0	(32.0)	0.21	0.79	78 (11.3)
2.0	(35.6)	0.28	0.82	80 (11.65)
4.0	(39.2)	0.42	0.58	81 (11.80)
6.0	(42.8)	0.64	0.36	77 (11.20)
8.0	(46.4)	0.92	0.08	65 (9.40)
8.6	(47.6)	1.00	0.00	59 (8.60)

Table 6. Tests performed with mixtures of R-12 and R-114

Molar fractions		T [°C (°F)]	P_T [kPa (psia)]
x_{12}	x_{114}		
1.13	0.87	0.6 (33.0)	124 (18)
0.2	0.8	3.6 (38.5)	151 (22)
0.4	0.6	7.2 (45.0)	234 (34)
0.42	0.62	7.5 (45.5)	240 (35)
0.5	0.5	7.8 (46.0)	261 (38)
0.6	0.4	8.9 (48.0)	296 (43)

Calculations from Eq. (14) are given in Table 7. The experimentally measured values of Table 6 agree with the calculated values of Table 7.

Based on this analysis, mixtures of R-12 and R-114 should form a gas hydrate at atmospheric pressure and at $T = -3.3^\circ\text{C}$ (26°F) with a composition of $x_{12} = 0.12$ and $x_{114} = 0.88$. This composition was obtained by solving the equation of line BQ_1 of Fig. 3 with the equation of the partial pressure of R-12. The last equation is given by

$$P_p = x_{12} P_{12}(T) \quad (15)$$

Gas hydrates at temperatures below 0°C (32°F) are formed simultaneously

Table 7. Thermodynamic state of mixtures of R-12 and R-114

T [°C (°F)]	$P_{Q_1 Q_2}$ [kPa (psia)]	$P_{12}(T)$ [kPa (psia)]	x_{12}^a
0 (32)	35.7 (5.2)	307.8 (44.8)	0.12
1.1 (34)	44.0 (6.4)	318.8 (46.4)	0.14
2.2 (36)	55.0 (8.0)	330.5 (48.1)	0.17
3.3 (38)	65.3 (9.5)	342.8 (49.9)	0.19
4.4 (40)	79.7 (11.6)	355.2 (51.7)	0.22
5.6 (42)	103.1 (15.0)	367.6 (53.5)	0.28
7.2 (45)	151.1 (22.0)	387.5 (56.4)	0.39
10.0 (50)	298.9 (43.5)	421.8 (61.4)	0.71
12.1 (53.8)	449.0 (65.4)	449.0 (65.4)	1.00

^aMolar fraction of R-12 needed to form hydrate at indicated temperature.

with ice (Fig. 3). Gas hydrates formed with mixtures of R-12 and R-114 at temperatures above -3.3°C (26°F) will always be above atmospheric. Therefore, for cool storage applications with a temperature above 0°C (32°F), a mixture of R-12 and R-114 would not produce a hydrate at atmospheric pressure.

Table 8 shows Q_2 points (temperatures and pressures) of refrigerants forming hydrates. By combining two of them, mixed hydrates can be obtained over a wide variety of temperatures and pressures. Specifically, different gas hydrates can be formed at atmospheric pressure by mixing two refrigerants, one with a Q_2 point below and one with a Q_2 point above atmospheric pressure. The temperature and pressure of the resulting mixed hydrate will be between those of the Q_2 points of the single hydrates acting alone.

A mixture of R-11 and R-12 in the proportion 0.9/0.1, respectively, by weight (0.88/0.12-mol fraction) with water and surfactant was tested inside the crystallizer. The mixture was cooled by circulating cold alcohol in the cooling coil above the sample. Figure 7 shows the resulting temperature and pressure of the mixture inside the crystallizer as a function of time during the charging cycle. The mixture cooled from room

Table 8. Gas-hydrate-forming refrigerants

Refrigerant	Q ₂ point		
	T [°C (°F)]	P	
		kPa (psia)	atm
R-140 (C ₂ H ₃ Cl)	1.15 (34.1)	182 (26.5)	1.8
R-160B1 (C ₂ H ₅ Br)	1.4 (34.5)	22 (3.2)	0.22
R-150 (CH ₃ CHCl ₂)	1.5 (34.7)	9 (1.3)	0.09
R-20 (CHCl ₃)	1.7 (35.0)	9 (1.3)	0.09
R-30 (CH ₂ Cl ₂)	1.7 (35.1)	21 (3.1)	0.21
R-40I1 (CH ₃ I)	4.3 (39.7)	23 (3.4)	0.23
R-160 (C ₂ H ₅ Cl)	4.8 (40.6)	78 (11.3)	0.77
R-12B2 (C Br ₂ F ₂)	4.9 (40.8)	51 (7.4)	0.5
R-21 (CHCl ₂ F ₂)	8.6 (47.5)	101 (14.7)	1.0
R-11 (C Cl ₃ F)	8.7 (47.6)	59 (8.6)	0.58
R-22B1 (CHBrF ₂)	9.9 (49.8)	268 (38.9)	2.65
R-12B1 (CBrClF ₂)	10.0 (50.0)	169 (24.5)	1.67
R-13B1 (CBrF ₃)	11.0 (51.8)	1141 (166.1)	11.3
R-12 (CCl ₂ F ₂)	12.1 (53.8)	449 (65.4)	4.44
R-142b (CH ₃ CCl ₂ F ₂)	13.1 (55.6)	231 (33.7)	2.29
R-40B1 (CH ₃ Br)	14.7 (58.5)	152 (22.2)	1.51
R-152a (CH ₃ CHF ₂)	14.9 (58.8)	434 (63.2)	4.3
R-22 (CHCl ₂ F ₂)	16.3 (61.3)	768 (111.7)	7.6
R-31 (CH ₂ ClF)	17.9 (64.2)	286 (41.6)	2.83
R-41 (CH ₃ F)	18.8 (65.8)	3232 (470.4)	32.0
R-40 (CH ₃ Cl)	20.5 (68.9)	495 (72.0)	4.9
R-161 (C ₂ H ₅ F)	22.8 (73.0)	808 (117.6)	8.0

temperature and reached point B, the invariant point for the mixed gas-hydrate formation, 1.46 h after the test was started. However, gas hydrate did not form, and the mixture subcooled until point C [7.2°C (45°F) and 94 kPa (13.7 psia)] was reached at 1.6 h. At that time, gas-hydrate started forming, and the temperature and pressure of the mixture started

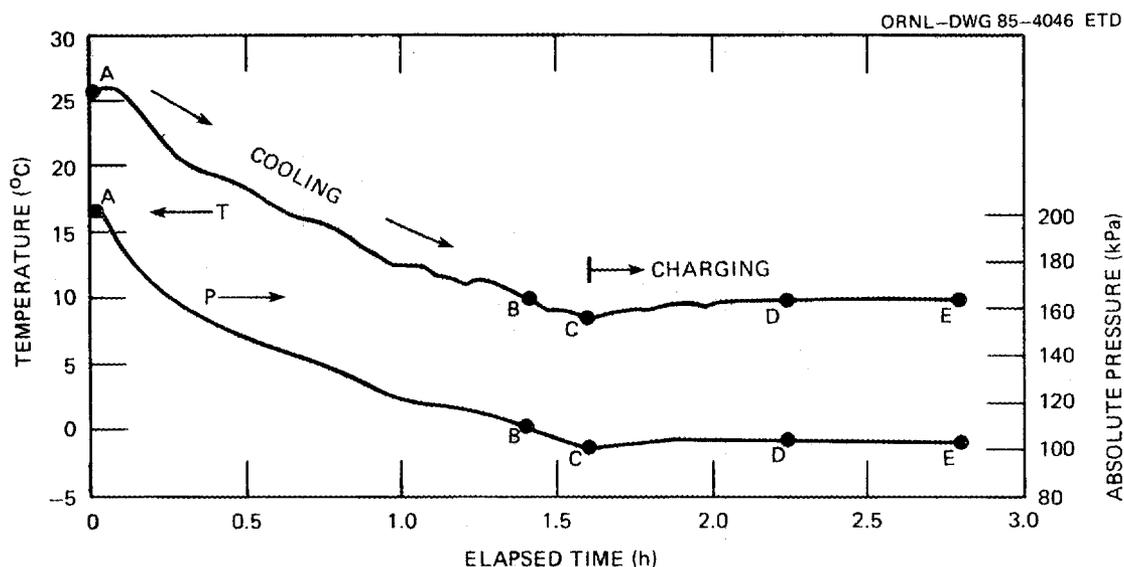


Fig. 7. Pressure and temperature vs time during charging cycle in crystallizer.

rising until the invariant point of gas hydrate formation was reached (point D). Based on the composition used, this invariant point for mixed gas-hydrate formation was 9.2°C (48.6°F) and 101 kPa (14.7 psia), corresponding to earlier measurements in glass test tubes (Table 2).

The charging cycle was stopped at point E of Fig. 7, 2.75 h after the test was started. Figure 8 shows the points A, B, C, D, and E of Fig. 7 on a P-vs-T graph. Points B, D, and E correspond to the invariant point of gas-hydrate formation.

The discharge cycle was initiated immediately after the charging cycle was stopped (point E of Figs. 7 and 8). The discharge pump located at the bottom of the crystallizer, as shown in Fig. 4, was turned on after the valves of the discharge loop were opened. The liquid refrigerant discharged from the crystallizer was circulated through a heat exchanger where it was heated and then returned to the crystallizer. As a result of the heat gains through the heat exchanger (Fig. 4), the liquid refrigerant pumped back to the crystallizer had a higher temperature than that discharged from the crystallizer. The higher temperature of the liquid refrigerant pumped back to the crystallizer increased the pressure inside the crystallizer.

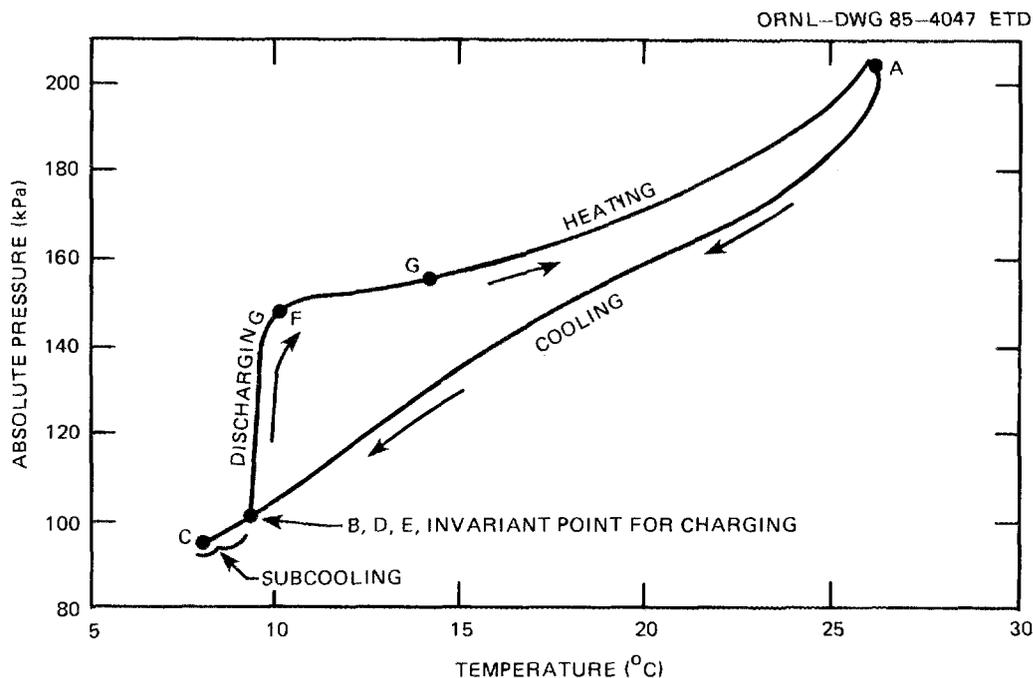


Fig. 8. Pressure vs temperature for charging and discharging cycles in crystallizer.

However, the temperature of the mixture of liquid and hydrate at the bottom of the crystallizer did not change; it remained at 9.2°C (48.6°F) for as long as hydrate was present. The hydrate melted slowly, cooling the hotter liquid returning from the discharge loop. Figure 9 shows the pressure and the temperature of the liquid mixture at the bottom of the crystallizer during discharge as a function of time. Once all of the gas hydrate was melted (point F), both the temperature and the pressure of the mixture started rising. The discharge pump was stopped after 1 h of operation, which corresponds to point G of Fig. 9. The crystallizer was then allowed to warm slowly by the heat gained from the environment, and the data acquisition was stopped 13 h after the discharge test was initiated.

The P-vs-T of the discharge cycle is also plotted as points E, F, G, and A (Fig. 8). The end point of the discharge cycle, point A, is the same as the initial point of the charging cycle and corresponds to a temperature of 25.7°C (78.3°F) and a pressure of 204 kPa (29.7 psia).

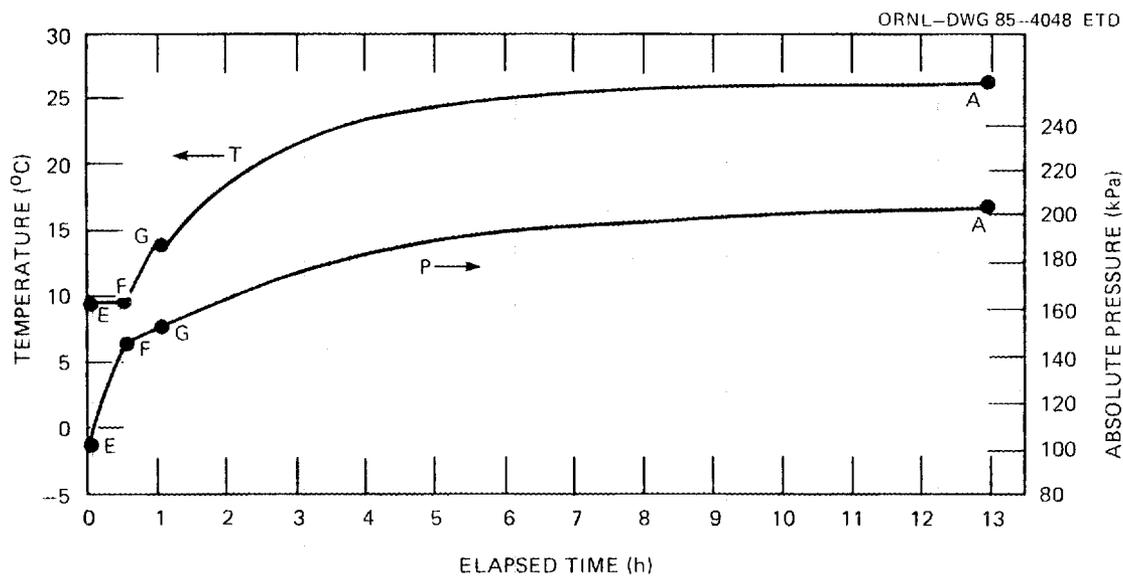


Fig. 9. Pressure and temperature vs time during discharging cycle in crystallizer.

Although the mixed-gas hydrate formed at atmospheric pressure, a pressure below atmospheric occurred during the subcooling process (point C of Figs. 7 and 8). Pressures above atmospheric also occurred when the mixture warmed during discharge [>2 atm at 25.7°C (78.3°F), point A of Figs. 7, 8, and 9].

Other mixtures of R-11 and R-12 were also tested in the crystallizer, and mixed hydrates at pressures above and below atmospheric were formed. The temperature and pressure of hydrate formation were the same as measured in the tests performed inside the glass test tubes (Table 2).

5. CONCLUSIONS

Mixed-gas hydrates of R-11 and R-12 have been produced in laboratory tests. By varying the composition of the mixture, different gas hydrates at different temperatures and pressures may be obtained. Specifically, a gas hydrate at atmospheric pressure [101 kPa (14.7 psia)] and at a temperature of 9.2°C (48.6°F) can be formed by mixing R-11 and R-12 in the proportion 0.9/0.1, respectively, by weight or 0.89/0.11, respectively, by volume, equivalent to mole fractions of $x_{11} = 0.88$, and $x_{12} = 0.12$. As a 1-atm, cool-storage compound, this R-11/R-12 hydrate is a better alternative than the chemically active R-21 refrigerant hydrate.

Gas hydrates of a mixture of R-11 and R-114 have also been formed; only R-11 entered the gas hydrate. By varying the composition of the mixture, gas hydrates over a range of temperatures and pressures were obtained. All of the hydrates formed at pressures below atmospheric and temperatures below 8.7°C (47.6°F).

Finally, gas hydrates from mixtures of R-12 and R-114 were also produced. Apparently, only R-12 entered into the clathrate structure, as in the case of mixtures of R-11 and R-114. For temperatures $>0^{\circ}\text{C}$ (32°F), all of the gas hydrates formed with R-12 and R-114 are at pressures above atmospheric.

Mixed-gas hydrates can be formed for any other mixtures of refrigerants that form gas hydrates. Their pressures and temperatures of formation will be between the pressures and the temperatures of hydrate formation for each refrigerant (Q_2 points).

Mixed-gas hydrates open new possibilities as the storage material in cool storage systems. They may be obtained at pressures around atmospheric and temperatures in the range of 7 to 10°C (45 to 50°F), which are more adequate than ice for air conditioning purposes. Mixed hydrates forming at pressures around atmospheric and high temperatures can also be obtained. Thus, many new possibilities of storage media for heat storage systems are opened by the mixed hydrates. In fact, several gas-hydrate-forming refrigerants can be mixed, and the resulting gas hydrate will be between the Q_2 pressure and temperature values of the single refrigerants in the mixture.

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