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CANDIDATE CHEMICAL SYSTEMS FOR AIR COOLED,
SOLAR POWERED, ABSORPTION AIR
CONDITIONER DESIGN

PART II - SOLID ABSORBENTS,
HIGH LATENT HEAT REFRIGERANTS

MASTER

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CANDIDATE CHEMICAL SYSTEMS FOR AIR COOLED,
SOLAR POWERED, ABSORPTION AIR CONDITIONER DESIGN

PART II - SOLID ABSORBENTS, HIGH LATENT HEAT REFRIGERANTS

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SUMMARY

This report summarizes work done in attempting to qualify absorption refrigeration systems based on refrigerants with intermediate latent heats of vaporization. In practice, these comprise methanol, ammonia and methylamine. A wide variety of organic substances, salts and mixtures were evaluated in as systematic a manner as possible.

Several systems of interest were described:

1. $\text{LiClO}_3\text{-LiBr-H}_2\text{O}$. A good "back up" system to our first choice of an antifreeze additive system, thermodynamically promising but subject to some inconvenient materials limitations.
2. LiBr/ZnBr_2 - Methanol. Thermodynamically promising but requires additional kinetic qualification.
3. LiCNS - Ammonia/Methylamine with various other third components. Chemical stability does not appear to be adequate for a long lived system.

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1-0 INTRODUCTION

In the first report of this series, the conclusion was reached that the development of solar driven absorption chillers with air heat rejection would have an increased likelihood of technical and economic success if high latent heat refrigerants were used. Among those which should have high priority of consideration would be water, methanol and the lower molecular weight derivatives of ammonia. The few other high latent heat fluids available can generally be eliminated on the basis of corrosion, excessive toxicity or chemical reactivity.

1-1 SOME THEORETICAL CONSIDERATIONS

Absorption refrigeration is based on the fact that the vapor pressure of a volatile liquid, the refrigerant, can be reduced through appropriate use of a second substance, the absorbent. Most commonly this is through the formation of a solution between the volatile refrigerant and a much less volatile absorbent. Practical operating conditions dictate that the solution must show a partial pressure of refrigerant over the absorbent-refrigerant solution which is substantially less than would be predicted by Raoult's Law. Such "negative deviations from Raoult's Law" are explained in terms of forces between the absorbent and refrigerant molecules. If these forces are negligible, Raoult's Law is obeyed and as the magnitude of the forces increases the negative deviation becomes greater. In the limiting case these forces become sufficiently large to be recognized unambiguously as chemical bonds (as would occur if boron trifluoride were absorbed by an ether). In those systems of absorbent-refrigerant which deviate sufficiently from Raoult's Law to be of practical interest, the forces are generally sufficiently high to lead to interaction energies of a few kilojoules per gram-mole, in which case it is customary to describe the interaction as chemical bond formation. The strength of the chemical bond may be taken as a measure of the deviation from Raoult's Law. Thus, the absorption of a refrigerant can be described by means of a simple chemical reaction:

In principle, at least, the vapor pressure of refrigerant can be fixed at any desired value by selection of an absorbent with appropriate bond energy to the refrigerant.

Practical systems have thus far included only refrigerants with a high dipole moment (water and ammonia) and absorbents which interact with these dipoles by virtue of their own dipole moment (water) or by possession of an electrostatic charge (hydrogen ion, hydroxyl ion, metallic cations). Solid absorbents are customarily used as strong solutions of the solid in the refrigerant in order to obviate mechanical and heat exchange difficulties which would occur in circulating a solid absorbent through an absorption cycle.

In the present state of the art, the most satisfactory system for absorption refrigeration has been the use of water as refrigerant and a strong aqueous solution of lithium chloride or lithium bromide as the absorbent. These solutions have several properties which restrict their usefulness, principally the fact that the absorber solution must be kept relatively cool in order that the vapor pressure of refrigerant over the solution be low enough to permit practical operation.

When a refrigerant, such as water, is absorbed by an ionic absorbent, the strength of the resultant bond is determined primarily by the total dipole moment of the refrigerant molecule and the ionic potential (ratio of charge of ion to radius of ion), the bond strength increasing with both these quantities and hence giving larger deviations from Raoult's Law. Each ionic species can associate only with a small, integral number of refrigerant molecules (called the "coordination number") which will be arranged about the ion in a fixed geometric pattern. If the ratio of refrigerant molecules to absorbent ions present exceeds the coordination number, interaction between the two is still possible but the forces are much lower, as seen from the increase in vapor pressure over the absorbent solution.

A popular misconception is that all bonds formed between refrigerant and absorbent, within the limit of the coordination number, are of equal energy, in effect predicting that the vapor pressure of a refrigerant-absorbent solution cannot be reduced significantly by further increase in concentration of absorbent once the molar ratio of refrigerant to absorbent has decreased to the coordination number. There exist two well established theoretical methods which belie this assumption, but they need not be developed here.

It has sometimes been stated that no better absorbent for water than lithium bromide can be found. This is predicated on the lithium ion having the highest ionic potential of any cation which has not been rejected for some practical consideration such as toxicity, corrosion or low solubility. The prediction also implicitly includes the equal bond energies assumption in that the ratio of water molecules to lithium ions in a solution saturated at room temperature is just under four, the anticipated coordination number for the electronic configuration of lithium.

By rejecting this second postulate, there is opened the possibility of finding an absorbent superior to lithium bromide (for water, at least) by looking among those lithium salts whose solubilities are at least equal to the solubility of lithium bromide. It should be noted in passing that the numerical solubility scale, to be significant in terms of the preceding arguments, must be a measure of the relative number of moles of solvent and solute. The scale generally most convenient for this purpose is the molal scale, the number of gram formula weights per kilogram of solvent. The familiar percentage scale of solubility is not simply related to this mole ratio.

Five very soluble lithium salts are:

	<u>Solubility (20°C)</u>	
	<u>Weight, %</u>	<u>or Molal</u>
Lithium Chlorate	82.0	50.2
Lithium Nitrite	50.9	29.6
Lithium Chloride	45.8	19.9
Lithium Thiocyanate	54.6	18.5
Lithium Bromide	61.0	18.0

The "state of the art" prediction would be that all five would have similar vapor pressures since each solution contains fewer than four moles of water per formula weight of lithium salt. The "new" approach outlined above predicts that the above arrangement is in the order of increasing vapor pressure with lithium bromide solution having the highest vapor pressure of the set. Experimentally we find the order of vapor pressure to be:

which is not in agreement with either prediction.

It was from this evidence that a concept was deduced which does not seem to have previously been considered in the art; namely, that the effectiveness of an absorbent is determined, in part, by its degree of dissociation in solution. The association of ions such as nitrite, chlorate and thiocyanate, through their non-bonding electron pairs, to cations of high ionic potential, such as the lithium ion, is consistent with our general experience with chemical bond formation between ions in solution. This association, involving partial transfer of electrons through which the bond is formed, has the net effect of lessening the effective charge on the lithium ion and thus weakening the lithium-water bonds to which we attribute the marked reduction in water vapor pressure over lithium ion solutions. As a consequence, a high degree of association overcomes the beneficial effect of increased concentration and gives a rational explanation of the failure of the higher concentrations of lithium ions in the case of the nitrite, chlorate and thiocyanate salts to show a lower vapor pressure than the less soluble, but more completely dissociated, lithium bromide. The intermediate vapor pressure of the lithium chloride also fits suitably into the pattern because the chloride ion, being smaller than the bromide ions, would be expected to associate to a greater extent than bromide ion but to a lesser extent than the other three which are known to be strong "complex formers."

In summary, therefore, we assign the effectiveness of a metallic salt absorbent for polar refrigerants in regard to vapor pressure lowering to three factors, namely:

1. A high ionic potential of the cation favors a low vapor pressure.
2. A high solubility, particularly past the point where the mole ratio of refrigerant to absorbent becomes equal to the coordination number of the cation, favors a low vapor pressure.
3. Formation of bonds between the anion and cation in solution leads to increasing vapor pressure.

Unfortunately these three properties are interrelated in a generally unfavorable manner. For instance, as (1) becomes increasingly favorable, (2) and (3) tend to become less favorable. Similarly, as (2) increases there is a general tendency for (3) to become less favorable. Thus, it would be anticipated that some one salt would exist in which the best balance of these three quantities would exist, and the prevalent belief that trial and error procedures have disclosed this essentially optimum salt to be lithium bromide are probably correct.

Anticipating some of our later results and a few scattered reports by others, we find that it is not necessary for favorable values of all three factors to reside in the same substance. By combining salts which individually show a particularly favorable degree of one of these basic properties it is possible to achieve a mixture whose vapor pressure is substantially lower than can be achieved by attempting to maximize these three properties in the same substance.

In particular, a possible procedure would be to select a cation in which the best value of the ionic potential occurs (also considering such practical concepts as corrosion and toxicity), namely lithium, and improve the performance over the best present state of the art by mixing lithium salts in which high values of factors (2) and (3) are separately achieved.

Thus, this concept leads to the prediction that the combination of a relatively highly dissociated salt such as lithium bromide, lithium nitrate or lithium chloride can be used in conjunction with a salt showing lesser dissociation but higher molal solubility, such as lithium nitrite, lithium chlorate, or lithium thiocyanate to obtain a mixed salt solution with a lower

vapor pressure than can be obtained with either salt separately, comparison being made between saturated solutions at room temperature. A variety of data has been taken in which virtually all pairs of the above mentioned salts have been examined and in each case the resultant vapor pressure-composition curve is in agreement with prediction.

The argument is not restricted to pairs of salts as it is possible to combine, for example, two salts having high solubility and low dissociation (i.e., LiClO_3 and LiNO_2) with a salt having lower solubility but higher dissociation (i.e., lithium bromide) and obtain lower vapor pressures than can be obtained with any single salt of the set. A few such instances have been examined perfunctorily with the result anticipated.

Of special interest would be combinations with lower vapor pressures than saturated lithium bromide solutions. As lithium bromide is one of the more highly dissociated of the reasonably soluble lithium salts, the obvious direction to look for improvement is to add salts in which the solubility factor is very high (necessarily at the expense of the dissociation). In this connection we might look for considerable improvement from the extremely soluble lithium chlorate and lesser improvements with lithium nitrite or chloride. This is precisely what has been observed.

The above treatment is, at least experimentally, restricted to systems in which water is absorbed by lithium salts. This I regard as the situation of most practical significance although the concept presented probably can, and should, be extended. Specific areas of possible extension are:

1. No experiments have been made in which cations of various ionic potential are mixed. An existing patent, however, teaches the use of caesium and rubidium salts (low ionic potential, high solubility and high dissociation) in conjunction with lithium salts (high ionic potential at expense of solubility and dissociation) to produce low vapor pressures.

2. It would seem that combinations of salts with lower vapor pressures than either constituent salt could be realized for cations other than lithium. Very few of these would be low enough to be of interest in absorption refrigeration.
3. It might be of interest to attempt to establish the previous pattern for refrigerants other than water. This could be a complex undertaking if the investigation were to achieve any width of scope.

1-2 LITHIUM BROMIDE - WATER

The system lithium bromide-water has been extensively developed and any candidate system which would supersede this combination for solar absorption would necessarily show improved vapor-pressure-solubility relationships. For reference purposes a copy of the Carrier Lithium Bromide Properties Chart, as edited for inclusion into the current ASHRAE Guide and Data book by Mr. Lowell McNeely, has been included as Figure 1.

FIGURE 1
EQUILIBRIUM CHART FOR AQUEOUS
LITHIUM BROMIDE SOLUTIONS

EQUATIONS

1. $t = At' + B$
2. $t' = (t - B)/A$
3. $A = -2.00755 + .16976X - (3.133362 E-3)X^2 + (1.97668 E-5)X^3$
4. $B = 321.128 - 19.322X + .374382X^2 - (2.0637 E-3)X^3$
5. $\log P = C + D/(t' + 459.72) + E/(t' + 459.72)^2$

$$6. t' = \frac{2E}{(-D - (D^2 - 4E(C - \log P))^{.5})} - 459.72$$

TEMP. RANGE (REFRIGERANT)	0	V	t'	230	°F
TEMP. RANGE (SOLUTION)	40	V	t	350	°F
CONCENTRATION RANGE	4%	V	X	70%	

$C = 6.21147$
 $D = -2286.373$
 $E = -337269.46$
 $t' =$ REFRIGERANT TEMP. °F
 $t =$ SOLUTION TEMP. °F
 $X =$ PERCENT LiBr
 $P =$ PSIA = (mm Hg)/51.715

2-0 EXPERIMENTAL RESULTS, SALTS AND WATER

2-1 SINGLE SALTS, SOLUTION VAPOR PRESSURES

A variety of lithium salts were prepared on a small scale, either by acid-base reaction or by double decomposition reactions between lithium chloride and the sodium salt of the desired anion. These were allowed to stand in contact with saturated water solutions for a day or two at 20°C to insure that a reasonable approach had been made to equilibrium. The saturated solution was then placed in a glass container communicating with a closed end manometer degassed with a vacuum pump, and the vapor pressures measured over a range of temperature. In general, the salts selected were either known from the literature to be particularly soluble or from the size and other properties of the anion were expected to be very soluble.

In Figures 2 and 3 are presented a representative sample of these lithium salts, of which it will be noted that only lithium chlorate appears to have any vapor pressure gain over lithium bromide. Figure 4 contains more detailed information about the vapor pressure of lithium chlorate in the form of a series of Duhring plots. Table I contains numerical data on which these curves are based. This material will be discussed further in Section 2-2, Mixed Salt Results.

Another salt of particular interest is lithium iodide which has a high solubility and low vapor pressure at elevated temperatures. Figure 5 shows a family of Duhring plots for aqueous solutions of this material superimposed on a solubility curve. It will be noted that (as a result of a series of hydrates in the solid phase at various temperatures) there is a "hump" in the terminations of the Duhring lines at the solidus curve. It would present a challenging design problem to construct a machine which could use the attractive high temperature properties of lithium iodide solutions without frequent solidification problems in "crossing the hump." For a more optimistic report, see "Vapor Press of Aqueous Lithium Iodide Solutions," Bach, R. O. and Boardmann, W. W., Jr. ASHRAE J. 33, November (1967).

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FIGURE 2
VAPOR PRESSURES OF SEVERAL
VERY SOLUBLE LITHIUM SALTS
SOLUTIONS SATURATED AT 20° C
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FIGURE 3

VAPOR PRESSURES OF SEVERAL
VERY SOLUBLE LITHIUM SALTS
SOLUTION SATURATED @ 20°C

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FIGURE 4
DÜHRING PLOT FOR THE SYSTEM
LITHIUM CHLORATE - WATER

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FIG. 5
DÜHRING PLOT
LITHIUM IODIDE / WATER SOLUTION

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TABLE I

Lithium Benzenesulfonate $\text{LiC}_6\text{H}_5\text{SO}_3$

Vapor pressure above saturated solution (20°C)

<u>T °C</u>	<u>mm Hg</u>	<u>kPa</u>	<u>mm Hg</u>	<u>kPa</u>
26.67	15.8	2.11	15.6	2.08
29.44	18.3	2.44	18.2	2.43
32.22	21.5	2.87	21.2	2.83
35.00	24.0	3.20	24.8	3.31

Lithium Hydrogen Phosphite

<u>T °C</u>	<u>mm Hg</u>	<u>kPa</u>
26.67	16.5	2.20
29.44	20.2	2.69
32.22	24.1	3.21

Lithium Nitrite

<u>T °C</u>	<u>mm Hg</u>	<u>kPa</u>
26.67	6.3	0.84
32.22	8.9	1.19
37.78	12.7	1.69
48.89	23.4	3.12
54.44	27.9	3.72

Lithium Hexfluorophosphate - Hydrolyzed on boiling

Lithium Tetrafluoroborate - Hydrolyzed rapidly

Lithium Sulfide - Hydrolyzed rapidly

LiBF_4

<u>T °C</u>	<u>mm Hg</u>	<u>kPa</u>
26.67	14.4	1.92
32.22	17.5	2.33

TABLE I (cont'd.)

Lithium Trifluoroacetate LiCF_3CO_2

<u>T °C</u>	<u>P mm</u>	<u>P (kPa)</u>
26.67	8.1	1.08
32.22	10.6	1.41
37.78	15.0	2.00
43.33	21.2	2.83

Lithium Trichloroacetate

<u>T °C</u>	<u>P mm</u>	<u>P kPa</u>
26.67	11.2	1.49
29.44	13.7	1.83
32.22	16.2	2.16
35.00	20.0	2.67
37.78	22.2	2.96
40.56	25.0	3.33

Lithium Dichloroacetate

<u>T °C</u>	<u>P mm</u>	<u>P kPa</u>
23.89	7.5	1.00
29.44	12.5	1.67

Lithium Thiocyanate

<u>T °C</u>	<u>P mm</u>	<u>P kPa</u>
26.67	7.8	1.04
32.22	10.9	1.45
37.78	14.7	1.96
43.33	20.3	2.71
48.89	25.0	3.33

TABLE I (cont'd.)

Lithium Thiosulfate

<u>T °C</u>	<u>P mm</u>	<u>P kPa</u>
26.67	8.7	1.16
32.22	11.2	1.49
37.78	15.3	2.04
43.33	20.6	2.75
48.89	24.7	3.29

Lithium Iodide Data D.P. (°C) = $m T_{sol} + b$

	<u>m</u>	<u>b</u>
50%	0.93500	-12.683
60%	0.95152	23.572
65%	0.90370	-33.893
70%	0.77777	-37.531
75%	0.70513	-42.621
80%	0.68831	-52.251
85%	0.70000	-67.000

Crystallization Curve

<u>Solution Axis °C</u>	<u>D.P. Axis °C</u>
10.00	-6.67
21.11	0.00
32.22	4.44
37.78	6.11
43.33	7.78
54.44	11.11
65.56	16.94
71.11	17.78
78.06	9.44
82.22	-0.28
93.33	3.33
104.44	8.89
118.33	14.44

VAPOR PRESSURES OF LITHIUM CHLORATE SOLUTIONS

TABLE I (cont'd.)

Sol. T °C	<u>LiClO₃ 80.5%</u>		<u>71.5%</u>	
	<u>P (kPa)</u>	<u>T Dew Pt. (°C)</u>	<u>P (kPa)</u>	<u>T Dew Pt. (°C)</u>
26.67	--	--	0.43	-4.8
32.22	0.25	-11.6	0.51	-2.6
37.78	0.33	-8.0	0.76	3.0
43.33	0.47	-3.6	0.96	6.4
48.89	0.68	+1.5	1.35	11.4
54.44	0.93	6.0	1.95	17.1
60.00	1.35	11.4	2.45	20.8
65.56	1.85	16.3	3.08	24.5
76.67	2.87	23.35	3.63	27.3
82.22	3.55	27.55		

80.5% LiClO₃

$$T_{\text{ref}} = 0.78622 T_{\text{sol}} - 37.03$$

71.5% LiClO₃

$$T_{\text{ref}} = 0.71027 T_{\text{sol}} - 23.71$$

TABLE I (cont'd.)

Vapor pressures of LiClO_3 Solutions (cont'd.)

63.2%		81.3%		73.4%	
Sol. T °C	Dew Pt.	Sol. T °C	Dew Pt.	Sol. T °C	Dew Pt.
38.9	15.6	71.1	20.2	61.1	23.1
41.1	17.4	68.9	18.5	58.9	21.1
43.3	19.3	65.6	15.9	56.7	19.3
45.6	21.2	62.2	13.3	54.4	17.5
47.8	23.0	58.9	10.7	52.2	15.6
50.0	24.9	55.6	8.1	48.9	12.6
51.3	26.0	52.2	5.7	46.7	10.8
		48.9	3.2	44.4	8.9
		47.8	2.4	43.7	8.2
		56.7	9.3		
		61.1	12.8		
		65.5	16.3		

$$63.2\% \quad T_{\text{H}_2\text{O}} = 0.83851 T_{\text{sol}} - 17.035$$

$$73.4\% \quad T_{\text{H}_2\text{O}} = 0.85216 T_{\text{sol}} - 28.984$$

$$81.3\% \quad T_{\text{H}_2\text{O}} = 0.76919 T_{\text{sol}} - 34.432$$

$$T_{\text{ref}} = [0.97327 - 0.0024601 (x)] T_{\text{sol}} + 50.96 - 1.0706 (x)$$

where T is temperature, °C.

x is solute concentration, weight percent.

2-1.1 Other Salts and Salt-like Materials

There are few cations whose effective ionic potential is as high as lithium. Those which might be examined are beryllium salts which would be eliminated on the basis of toxicity and cost. In the second row of the periodic table, we find sodium and magnesium, neither of whose salts show the solvating ability of lithium. The last remaining cation in the upper left of the periodic table is hydrogen, and the affinity of the hydrogen ion, in the form of strong acids, for water is well known. No data on these strong acids are included on the basis that their corrosive properties render them improbable candidates for absorption refrigeration.

Some of the lighter transitional metals, notably zinc and to a lesser extent cadmium show high effective ionic radii because of their polarizability. We will look at these in our section on mixed salts.

One last possible single salt-like class would be the very soluble alkali metal (except lithium) hydroxides in which the anion shows very strong coordinating power to water. Following below are some Duhring plots and a solubility diagram for sodium-hydroxide water. Its thermodynamic promise is marginal and the generally corrosive properties of strong caustic soda lead to a decision to reject. Considerable property data are available:

"Caustic Soda" Solvay Technical and Engineering Service, Bulletin No. 6, Allied Chemical Company, New York.

Bertetti, J. W. and McCabe, W. L., "Sodium Hydroxide Solutions: Heat of Dilution," Ind. Eng. Chem. 28, 247 (1936)

Ibid "Specific Heats" 28, 375 (1936).

Hayward, A. M. and Perman, E. P., "Vapor Pressure and Heat of Dilution - Part VII Vapor Pressures of Aqueous Solutions of Sodium Hydroxide and of Alcoholic Solutions of Calcium Chlorate," Trans. Faraday Soc. 27, 60 (1931).

Figure 6 presents some Duhring curves for sodium hydroxide solutions in water and Figure 7 gives crystallization temperatures for the various solid phases of sodium hydroxide.

47 0702

K&E 10 X 10 TO THE INCH 10 X 15 INCHES
KEUFFEL & ESSER CO. MADE IN U.S.A.

SATURATION TEMPERATURE °C

-20-

-20-

FIGURE 7
SOLUBILITY OF SODIUM HYDROXIDE IN WATER

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CARRIER CORPORATION

CONTRACT EG-77-C-03-1587 (SAC 2)

2-2 MIXTURES OF SALTS

A considerable body of mixed salts with water have been suggested for use as absorption refrigeration systems. Unfortunately, most of these have been qualified only with respect to vapor pressure and such problems as heat transfer coefficients and chemical stabilities have not been addressed adequately. There does not seem to be any systematic way of covering such systems and our presentation will be pretty much at random, covering some of the more interesting or well known systems in detail and leaving the others as items in which the reader may find utility which this author overlooked.

2-2.1 Lithium Chlorate/Lithium Bromide-Water

This chemical combination was explored in considerable detail by the Research Division of Carrier Corporation as a promising candidate for a gas fired-air cooled absorption cooling cycle. Two patents⁽¹⁾ cover the use of lithium chlorate alone or in mixture, as an absorbent.

Figure 8 shows the variation of Dew Point as a function of the mole fraction LiBr in the LiBr/LiClO_3 solute, comparing solutions at 60°C and having a common crystallization point of 25°C . These data indicate that the optimum composition is around $N_{\text{LiBr}} = 0.43$ and subsequent discussion assumes this concentration ratio of salts.

Figure 9 shows the vapor pressure variation of $\text{LiClO}_3/\text{LiBr}$ solutions in the form of a family of Duhring plots. Figures 10 and 11 present differential heats of dilution and specific heat capacities. Numerical data (vapor pressures only in part) leading to these figures are collected as Table II. Table II also includes some absorber film heat transfer coefficients which, with appropriate heat transfer additives turn out to be not much worse than lithium bromide, and also some experimentally measured corrosion rates on possible materials of construction.

(1) U.S. Patents 3,316,728 and 3,316,736. W. J. Biermann. "Absorption Refrigeration Systems" Granted 5/2/67. Assigned to Carrier Corporation.

FIGURE 8
SATURATION TEMPERATURE
FOR THE SYSTEM LiBr/LiClO₃ - H₂O
AS A FUNCTION OF MOLE FRACTION
LiBr IN THE SOLUTE
SOLUTION TEMPERATURE 60°C
CRYSTALLIZATION TEMPERATURE 25°C

47-0702

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KEUFFEL & ESSER CO. MADE IN U.S.A.

SATURATION TEMPERATURE °C

FIGURE 11
SPECIFIC HEATS OF $\text{LLClO}_3/\text{LLBr}$
SOLUTIONS, $N_{\text{LLBr}} = 0.433$
WENDELL BIERMANN
ENERGY SYSTEMS DIVISION
CARRIER CORPORATION
CONTRACT EQ-77-C-03-1587 (SAC 2)

TABLE II

Properties of LiClO₃/LiBr/H₂O

Vapor Pressure Curve for a solution temperature of 60°C and crystallization temp. of 25°C as function of mole fraction LiBr in the solute.

N_{LiBr}	Dew Point (60°C)
0.0	11.1
0.300	6.33
0.395	4.22
0.430	3.33
0.450	4.39
0.500	6.33
0.650	8.78
1.00	15.22

Specific Heats of LiClO₃/LiBr/H₂O solutions.

Mole Fraction LiBr = 0.433 Reliability $\pm$ 5%

<u>Concentration</u> <u>Weight Percent</u>	<u>Temperature</u> <u>°C</u>	<u>Specific Heat</u> <u>kJ/kg</u>	<u>Precision</u>
65.5	26.1	2.13	$\pm$ 0.02
70.0	28.9	1.98	$\pm$ 0.02
	83.9	2.07	$\pm$ 0.04
75.0	25.0	1.83	$\pm$ 0.04
	83.9	1.88	$\pm$ 0.03
80.0	83.9	1.68	$\pm$ 0.01

TABLE II(Continued)

Dew Point Measurement $N_{LiBr} = 0.45$

Wt% solute 79.7		Wt% solute 75.72		77.0	
Solution T(°C)	Dew Pt(°C)	Sol T°C	T _{D.P.} °C	Sol T(°C)	T _{D.P.} (°C)
82.2	18.6	75.6	19.33	82.2	22.00
81.1	17.7	74.4	18.53	81.1	21.22
80.0	16.9	73.3	17.72	80.0	20.42
78.9	16.1	72.2	16.61	78.9	19.47
77.8	15.2	71.1	15.78	77.8	18.69
76.7	14.4	70.0	15.00	76.7	17.69
75.6	13.7	68.9	14.14	75.6	16.85
74.4	12.7	67.8	12.88	74.4	15.86
73.3	11.9	66.7	12.44		
72.2	11.2	65.6	11.64	72.2	14.28
71.1	10.3	64.4	10.78	71.1	13.50
70.0	9.6	63.3	9.89	70.0	12.58
68.9	8.7	62.2	9.06	68.9	11.81
67.8	7.8	61.1	8.19	67.8	10.94
66.7	7.0	60.0	7.33	66.7	10.06
65.6	6.1	58.9	6.50	65.6	9.28
64.4	5.4	57.8	5.61	64.4	8.42
63.3	4.5			63.3	7.56
79.50 wt%				62.2	6.71
82.2	17.50			61.1	5.86
81.1	16.61			60.0	4.96
80.0	15.89				
78.9	15.19	79.70%			
77.8	14.06	T _{D.P.} = 0.74255	T _{sol} - 42.50		
76.7	13.28	75.72%			
75.6	12.58	T _{D.P.} = 0.76927	T _{sol} - 38.85		
74.4	11.83	77.00%			
73.3	11.06	T _{D.P.} = 0.76609	T _{sol} - 40.98		
72.2	10.17				
71.1	9.42	79.50%			
70.0	8.61	T _{D.P.} = 0.72141	T _{sol} - 41.89		
68.9	7.69				
67.8	6.94				
66.7	6.06				
65.6	6.22				
64.4	4.39				
63.7	3.89				

TABLE II (Continued)

Dew Point Measurement $N_{LiBr} = 0.43$

76.16 st% Solute		77.60 ut%		80.7%	
T (sol) °C	Dew Pt(°C)	T (sol) °C	T _{D.P.} °C	Tsol	D.P. °C
73.3	15.4	75.6	15.3	87.8	18.97
72.2	14.7	74.4	14.3	86.7	18.22
71.1	13.9	73.3	13.4	85.6	17.46
70.0	13.1	72.2	12.6	84.4	16.56
68.9	12.3	71.1	11.9	83.3	15.67
67.8	11.3	70.0	11.0	82.2	14.89
66.7	10.4	68.9	10.3	81.1	14.19
65.6	9.6	67.8	9.3	80.0	13.25
64.4	8.8	66.7	8.5	78.9	12.58
63.3	8.0	65.6	7.6	77.8	11.61
62.2	7.1	64.4	6.8	76.7	10.89
61.1	6.2	63.3	5.9	75.6	10.16
60.0	5.4	62.2	5.1	74.4	9.39
58.9	4.4	60.0	3.3	73.3	8.58
57.8	3.6			73.1	8.44

78.94% Solute

77.77

82.2	17.6
81.1	16.8
78.9	14.9
77.8	13.9
76.7	13.3
75.6	12.4
74.4	11.6
73.3	10.8
72.2	9.9
71.1	9.0
70.0	8.2
68.9	7.4
67.8	6.6
66.7	5.8
65.6	4.8
64.9	4.5

85.6	22.77
84.4	21.97
83.3	21.14
82.2	20.29
81.1	19.50
80.0	18.72
78.9	17.86
77.8	17.04
76.7	16.14
75.6	15.16
74.4	14.39
73.3	13.67
71.1	12.00
70.0	11.12
68.9	10.29
68.3	9.90
67.8	9.39
66.7	8.58
66.3	8.33

76.16%	
T _{D.P.} = 0.76670	T _{sol} = 40.65
77.60%	
T _{D.P.} = 0.76041	T _{sol} = 42.23
80.7%	
T _{D.P.} = 0.72079	T _{sol} = 44.32
78.94%	
T _{D.P.} = 0.75749	T _{sol} = 44.79
77.77	
T _{D.P.} = 0.75295	T _{sol} = 41.59

General Equation:

$$T_{sol} = [1.1931 - 0.0055198(X)]^{T_{sol}} + 50.658 - 1.20057(X)$$

TABLE II (Continued)

Differential Heats of Dilution LiClO₃/LiBr - Hz ^NLiBr = 0.433

Wt% Solute	Heat of Dilution kJ/kg water		
	60°C	104°C	160°C
60	164.8	239.1	278.5
65	232.1	308.7	352.8
70	292.4	385.3	443.3
75	373.7	464.2	533.8
80	454.9	557.0	636.0
85		636.0	728.8

Corrosion Studies 350°F, air free

90/10 Cupronickel	486 mdd
Inconel	5.5 mdd
Titanium	0.2 mdd
Zircalloy	0.0 mdd
Copper	1340.0
Carbon Steel	0.3 - 0.5 mdd*

*See text for explanation.

Heat Transfer Coefficients, Film side

Vertical Tube Absorber

Absorbent	Concentration	Additive	No (^W _m -2 °C)
LiBr	58%	octyl alcohol	1817
LiBr/LiClO ₃	76%	none	369
LiBr/LiClO ₃	75%	amine	1334

Horizontal Tube Absorber

LiBr	58%	none	1022
LiBr	58%	octyl alcohol	1789
LiBr/LiClO ₃	76%	none	625
LiBr/LiClO ₃	74%	amine	1334

Experimental Boiling Point

Wt% Solute (N = 0.43 LiBr)

Normal Boiling Point
°C (+ 1°C)

76.16	185.6
77.6	189.6
78.94	193.5
80.7	198.4

Figure 12 gives an approximate cycle calculation at the assigned conditions of 95°F ambient air and 230°F collector leaving temperature. A COP of 66% is predicted with individual component loadings being not significantly different than we are accustomed to seeing with water cooled lithium bromide. An improved heat exchanger or allowing the collector leaving temperature to rise by another 10°C (giving a concentration spread of 69.4% to 77.5%) would further improve the performance.

This system was never developed because the highly aggressive nature of lithium chlorate, a powerful oxidizing agent even when somewhat inhibited by 0.1% lithium hydroxide, could not be reliably controlled in the presence of the chlorate. Occasionally an inclusion in the iron would allow a couple to be set up, resulting in catastrophic local corrosion. In practice there seemed to be no reasonable way of avoiding this sort of thing, so with copper and iron both eliminated as constructional materials, first cost projections became unacceptably high for the market then existing.

A second problem was that of a supply of lithium chlorate. Presently the experimental amounts sold are made by reacting lithium sulfate with barium chlorate, filtering off the resultant barium sulfate and concentrating the lithium chlorate by evaporation. This is not economically practical if a product line were to be supported. We had a reasonable measure of success in an electrolytic process, using a proprietary electrode, preparing lithium chlorate on a semi-pilot scale.

For solar use, the system $\text{LiClO}_3/\text{LiBr}-\text{H}_2\text{O}$ may look more promising since first cost can be absorbed by reduced collector area if one has a high COP system. On balance of all factors the antifreeze additive system presently under development remains the most promising a priori. Should there be some unexpected obstacle, $\text{LiClO}_3/\text{LiBr}$ may be a good back-up system.

Figure 12

System LiBr/LiClO₃ - H₂O ($N_{\text{LiBr}} = 0.43$)

- 32 -

1. Superheated Ref. Vapor
2. Liquid Refrigerant
3. Saturated Ref. Vapor
4. Weak Sol. to HX
5. Weak Sol. to Gen.
6. Strong Sol. to HX
7. Strong Sol. to Abs.

Solar Collectors, $T(\text{out}) = 110^\circ\text{C}$
Assume 70% efficient HX

Point	Temp. °C	[X] Wt % abs.	W kg/kg-ref.	h kJ/kg	W _h kJ/kg-ref	Pressure kPa	Dew Pt °C	Q kJ/kg-ref	Q' ($Q_E=10\text{kW}$ 15.6kg ref/hr)
1	107	0	1	2693	2698		47	$Q_E = 2313$	$Q_E = 10 \text{ kW}$
2	47	0	1	197	197		47	$Q_C = 2501$	$Q_C = 10.8 \text{ kW}$
3	7	0	1	2510	2510		7	$Q_A = 3174$	$Q_A = 13.7 \text{ kW}$
4	49	69.40	18.79				7	$Q_G = 3493$	$Q_G = 15.1 \text{ kW}$
5	85.56	69.40	18.79				47	$Q_{HX} = 1408$	$Q_{HX} = 6.1 \text{ kW}$
6	107	73.30	17.79				47		
7	66.4	73.30	17.79				7	COP = 66.2%	

$$Q_E = (3) - (2) = 23.13 \text{ kJ/kg ref. circulated}$$

$$Q_C = (2) - (1) = 2501 \text{ kJ/kg ref. circulated}$$

$$Q_{\text{Str}} (\text{max.}) = 17.79 \times 1.95 \times (107 - 49) = 2013.0 \text{ kJ/kg ref. circulated}$$

$$Q_{\text{wk}} (\text{max.}) = 18.79 \times 2.05 \times (107 - 48) = 2234.1 \text{ kJ/kg ref. circulated}$$

$$Q_{\text{HX}} = 2012.0 \times 70\% = 1408.4$$

$$t_7 = 107 - 0.70 (107 - 49) = 66.4^\circ\text{C}$$

$$t_5 = 1408.4 / (18.79)(2.05) + 49 = 85.56^\circ\text{C}$$

$$Q_{\text{abs}} = (h_l, 49^\circ) - h(v, 7^\circ) + \Delta H_D (71\%, 49^\circ) - (66.4 - 49) \times 17.79 \times C_p (57^\circ, 73\%)$$

$$= (205 - 2505) - 280 - 594$$

$$= -3174 \text{ kJ/kg ref. circulated}$$

$$Q_G = (1) - h(l, 107^\circ) - \Delta H_D (71\%, 107^\circ) + 18.79 \times (107 - 85.56) \times C_p (96^\circ, 69\%)$$

$$= (2698 - 449) + 390 + 854 = 3493 \text{ kJ/kg water}$$

$$\sum Q_X = 131 \text{ kJ, or } 5\% \text{ of } Q_E$$

2-2.2 Lithium Acetate-Lithium Chloride

This system was studied as a good example of a mixture of one strongly dissociated salt (the chloride) with a less completely dissociated salt. As shown on Figure 13, over a range of mole fraction lithium acetate (N_{LiOAc}) from 0 to about 0.2 mixtures of lithium chloride and lithium acetate, saturated at 20°C, show lower vapor pressures than does lithium chloride when saturated under the same conditions. Table III, below, summarizes the 60°C information.

TABLE III

EFFECT ON VAPOR PRESSURE LOWERING, ADDITION OF LiOAc to LiCl

	<u>Vapor Pressure</u> <u>kPa (60°C)</u>	<u>Saturation Temp.</u> <u>($T_{sol} = 60^\circ\text{C}$)</u>	<u>Composition (20°C Sat.)</u>
$N_{LiOAc} = 0$	2.05	15.4°C	48.0% LiCl
$N_{LiOAc} = 0.125$	1.35	11.0°C	41.2% LiCl 9.0% LiOAc

The magnitude of saturation temperature gain did not justify any additional work.

2-2.3 Other Lithium Salt Mixtures

Figure 14 shows vapor pressures at 60° for mixtures of lithium nitrite/lithium chlorate, lithium thiocyanate/lithium bromide⁽¹⁾ and lithium thiocyanate/lithium chloride. It will be noticed that the less dissociated lithium thiocyanate shows a pronounced minimum in the region of 0.5 mole fraction with the strongly dissociated lithium bromide, but with the less dissociated chloride the minimum is not as well defined. With two salts of the less dissociated type, the nitrite and chlorate, no minimum is seen. These data are consistent with the hypothesis guiding our search, but the solutions were not considered to be candidates for development.

(1) R. A. Macriss, "Physical Properties of Modified LiBr Solutions," Symposium on Absorption Air Conditioning Systems, American Gas Association, Chicago 1968, for further discussions of lithium bromide/lithium thiocyanate and other systems.

VAPOR PRESSURE kPa, (20°C CRYSTALLIZATION)

3

2

1

0

.1

.2

.3

.4

.5

.6

.7

.8

.9

1.0

N_{LiDAC} - MOLE FRACTION OF LITHIUM ACETATE (1 - N_{LiCl})

FIGURE 13
VAPOR PRESSURES OF VARIOUS
MIXTURES OF LITHIUM CHLORIDE -
LITHIUM ACETATE, SATURATED
@ 20°C, MEASURED @ 60% C

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FIGURE 14

VAPOR PRESSURES OF SEVERAL
LITHIUM SALT MIXTURES.
SATURATED AT 20°C
VAPOR PRESSURES AT 60°C

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(SAC 2)

Mixtures of lithium chloride and lithium bromide show a pronounced reduction in vapor pressure over either salt, compared at identical crystallization and test temperatures.⁽¹⁾ The magnitude of the gain is only a few degrees in dewpoint, not large enough to be of significant help.

The system lithium bromide/lithium iodide-water has also appeared in the literature several times.^{(2),(3)} Our own evaluation of this system has disclosed no advantages over lithium bromide, when crystallization temperatures near usual ambient are considered.

-
- (1) U.S. Patent 2,091,983. S. B. Heath and L. R. Minger. Granted 9/7/37. "Dehumidifying Solution," Assigned to Dow Chemical.
 - (2) "The Absorption Cooling Process," Institute of Gas Technology Research Bulletin # 14, page 3 (Chicago 1957)
 - (3) U.S. Patent 3,524,815. Hensel, W. E. Jr. and Harlowe W. H. Jr., "Lithium Bromide-Lithium Iodide Compositions for Absorption Refrigeration System," Assigned to Arkla Industries, Inc., August 18, 1970.

2-3 LITHIUM SALTS, WITH NON-LITHIUM SALTS

The number of combinations of lithium salts with non-lithium salts is potentially very large, but the number in which significant amount of interaction can be expected, or has been observed, is small. Generally, the second salts which have aroused any interest have been either highly dissociated halide salts (from cations toward the lower left of the Periodic Table) or are transitional metal halides, usually from Groups 1b or 2b.

Examples of the use of highly dissociated halide salts are the use of caesium bromide with lithium bromide⁽¹⁾ and calcium bromide and/or calcium chloride^{(2),(3),(4),(5)} with lithium halides. The vapor pressure gains are not impressive and no information is available in print about heat transfer properties, corrosion rates, etc., which in the practical case are equally important.

-
- (1) U.S. Patent 3,004,919. W. L. Rush & W. G. Watters, "Absorbent Composition for any Absorbent Refrigeration System," Granted 10/17/61, Assigned to Borg-Warner.
 - (2) U.S. Patent 2,143,007. S. B. Heath and L. R. Minger, "Dehumidifying Solution," Granted 1/10/39. Assigned to Dow Chemical
 - (3) U.S. Patent 2,143,008. S. B. Heath, "Composition for Dehumidifying Gases," Granted 1/10/39, Assigned to Dow Chemical
 - (4) U.S. Patent 2,033,934. Grebe, J. and S. M. Stoesser, "Dehumidifying Solution" Granted 3/17/36. Assigned to Dow Chemical Company
 - (5) U.S. Patent 1,992,177.

Among the transitional metals, zinc salts have been uniquely important. We will review these in Section 2-3.1.

We did a large number of semi-quantitative experiments in which very soluble salts were mixed with lithium bromide in various approximate mole ratios and then the vapor pressures of saturated solutions were measured over a short temperature interval.

<u>Added Salt</u>	<u>Minimum?</u>	<u>Interaction Anticipated</u>
Cadmium bromide	No	$[\text{CdBr}_4]^-$
Nickel Nitrate	Yes, Small	$[\text{NiBr}_4]^-$
Iron (III) Bromide	No	$[\text{FeBr}_4]^-$
Iron (III) Chloride	Yes, Small	$[\text{FeBr}_4]^-$
Sodium Chlorate	No	Strong Salt
Sodium Nitrite	No	Shot in Dark
Sodium Bromide	No	Strong salt
Sodium Thiocyanate	No	Shot in Dark
Sodium Iodide	No	Strong Salt
Calcium Bromide ⁽¹⁾	Very Small	$[\text{CaBr}_4]^-$
Calcium Chloride	No	$[\text{CaCl}_4]^-$
Manganese (II) Nitrate	No	$[\text{MnBr}_4]^-$
Potassium Thiocyanate	No	Shot in Dark
Magnesium Chloride	No	Strong Salt
Magnesium Bromide	No	Very soluble material
Magnesium Iodide	No	Very Soluble
Ammonium Chloride	No	NH_4^+ Ion Similar to Rb^+
Ammonium Nitrate	No	NH_4^+ Ion Similar to Rb^+

(1) A ternary phase diagram (Blidin, V. P., "An Investigation of Solubility in Systems of CaBr_2 , (BaBr_2) - $\text{LiBr}-\text{H}_2\text{O}$ " Collection of Articles on General Chemistry, 1, 88-96 (1953) in Russian) suggests that our minor gain in vapor pressure was smaller than should have been observed. The author points out, however, that the extreme viscosity of these systems makes the attainment of equilibrium extremely slow -- perhaps our limited degree of interest was reflected in an inadequate number of days to reach time equilibrium.

<u>Added Salt</u>	<u>Minimum?</u>	<u>Interaction Anticipated</u>
Ammonium Bicarbonate	Yes, Slight	NH_4^+ Ion Resemblance to Rb^+
Ammonium Thiocyanate	Yes, Slight	NH_4^+ Ion Resemblance to Rb^+
Ammonium Bromide	Yes, Slight	NH_4^+ Ion Resemblance to Rb^+
Caesium Bromide	Yes, Slight	Strong Salt
Manganese Iodide	Yes, Significant	$[\text{MnX}_4]^-$
Iron (III) Thiocyanate	No	$[\text{FeX}_4]^-$

2-3.1 Zinc Halides

Virtually every combination of zinc, calcium, lithium, chloride and bromide ions has been suggested for use in absorption refrigeration. Using vapor pressure of solutions as the sole criterion for evaluation of systems, many members of this general group show great promise. The following short table, abstracted from a body of data collected by the Carrier Research Division, will illustrate some of the potential which these systems demonstrate.

TABLE IV

SOLUBILITY/DEW POINTS ZINC AND CALCIUM CHLORIDES

<u>Solute Composition</u>	<u>% Solids, 25°C Solidification</u>	<u>Vapor Pressure at 43°C kPa</u>
LiBr	62.4	0.61
ZnCl_2 (n = 1)	79.0	0.40
ZnCl_2 (n = 0.95) CaCl_2 (n = 0.05)	85.0	0.31
ZnBr_2 (n = 1)	82.0	0.67
ZnBr_2 (n = 0.83) CaBr_2 (n = 0.17)	83.0	0.37
ZnBr_2 (n = 0.33) CaBr_2 (n = 0.67)	73.0	0.33

where n indicates mole fraction.

There is no denying the vapor pressure gains, over lithium bromide that are obtainable with zinc based systems. What is also true is that these are very nasty solutions to work with. Because of their very high viscosities (we have literally stood stirring rods up vertically in beakers of saturated solutions), they are very slow to reach any sort of equilibrium --

solubility, vapor pressure, thermal -- and would have incredibly low heat transfer coefficients.

A second problem is hydrolysis: $\text{Zn}^{++} + \text{H}_2\text{O} \longrightarrow \text{Zn}(\text{OH})^+ + \text{H}^+$ which renders these solutions highly acidic and very corrosive. Any attempts to adjust the acidity by adding hydroxides would merely further increase the viscosity by the formation of chainlike structures due to bridging hydroxyl coordination compounds which will be formed with zinc ions.

Because of these limitations, the writer has firmly resisted any major investigations involving aqueous zinc salts.

A very complete study of the innumerable combinations possible among the ions under discussion was carried out by David Aronson⁽¹⁾ who recites a multitude of solubility and vapor pressure data for ternary and quaternary systems.

(1) U.S. Patent 3,478,530 to David Aronson for "Absorption Refrigeration System," assigned to Worthington Corporation. Granted November 18, 1969.

3-0 REFRIGERANTS OTHER THAN WATER

As pointed out earlier, there exist some potential refrigerants whose latent heats of evaporation, while lower than water, are significantly higher than those of the halocarbon refrigerants considered in the first volume of this report. Among these are:

<u>Refrigerant</u>	<u>ΔH_v (kJ kg⁻¹)</u>
Methanol	1009.6 (100°C)
Ammonia	1372.0 (-33°C)
Methylamine	830 (-6°C)

In addition to the loss of latent heat of vaporization, with its consequences associated with an increased pumping rate, some other disadvantages must also be considered. Primarily, these are flammability, which leads to significant safety code problems, toxicity and poorer heat transfer characteristics than with water based systems. These must be regarded as limitations rather than insurmountable obstacles.

3-1 METHYL ALCOHOL - LITHIUM BROMIDE

Vapor pressures of a few lithium bromide-methyl alcohol solutions were determined and the results, in the form of a family of Duhring plots, are presented in Figure 15.

A second series of solutions using lithium bromide and zinc bromide in a 2:1 mole ratio as the absorbent for a methanol system were also studied. The Duhring plots determined from the vapor pressure data are presented in Figure 16.

No detailed follow up to these systems was made even though the solubility-vapor pressure depression appeared to be more than adequate to support an air cooled system. The primary reason for this was a series of film side heat transfer coefficient measurements done in the absorber simulation equipment. These results showed very low heat transfer in the

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FIGURE 15
DÜHRING PLOTS OF
LITHIUM BROMIDE - METHANOL
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FIGURE 16
DÜHRING PLOTS OF
LITHIUM BROMIDE / ZINC BROMIDE
(MOLE RATIO 2:1) IN METHANOL
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falling film, which was interpreted as a high activation energy to mass transfer from the vapor to the solution indicating the need for a heat transfer additive analogous to 2-ethyl hexanol in aqueous systems.

Since that time, the writer has had indications that this poor heat transfer rate might be in error and it is our intention to repeat these experiments in the course of the present program.

3-2 AMMONIA AND METHYLAMINE AS REFRIGERANTS

Ammonia has proved to be an excellent refrigerant in absorption cooling principally because it has a high latent heat of vaporization and because it is able to enter into strong associations, resulting in large negative deviations from Raoult's Law, with a variety of compounds which may be utilized as an absorbent. Methylamine is quite similar to ammonia as shown in the following table in both physical properties and chemical behavior. Ammonia has a higher heat of vaporization; however, when used with water as an absorbent, methylamine has a greater concentration spread ($\sim 38\%$ wt) than ammonia ($\sim 25\%$ wt) under similar operating conditions. The comparison of ammonia and methylamine as refrigerants is illustrated in Figure 17. It is our conclusion that there is little to choose between the two compounds as refrigerants.

For our experimentation, methylamine was preferred to ammonia because of the lower pressures involved and the greater flexibility the compound allowed in choosing absorbents among organic compounds. Being a stronger base than ammonia, methylamine would be expected to form stronger associations with acidic absorbents and, therefore, greater negative deviations from Raoult's Law and greater dew point depressions.

Physical Properties of NH_3 and CH_3NH_2

	<u>NH_3</u>	<u>CH_3NH_2</u>
1. Molecular Weight	17.03	31.06
2. Boiling Point	-33.35°C	-6.32°C
3. Critical Temperature	132.9°C	156.9°C
4. Ionization Constant at 25°C ($\times 10^5$)	1.8	~ 45

80

FIGURE 17

70 DÜHRING PLOTS FOR AMMONIA AND METHYLAMINE
DISSOLVED IN WATER

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3-2.1 Ammonia/Methylamine with Organic Absorbents

Since methylamine is a strong organic base, organic acids should be good absorbents. There are a very limited number of organic Lewis acids which have suitable physical properties, however, and our attention was focused on the protonic type; carboxylic acids, phenols, active hydrogen-containing compounds and hydroxy and mercapto-compounds are some of the more common protonic organic acids.

Many salts of carboxylic acids are known to be thermally unstable (especially carboxylic ammonium salts) due to decarboxylation. This was found to be true for benzoic acid when mixed with methylamine; carbon dioxide was evolved at about 50°C. For this reason carboxylic acids would not be suitable absorbents for methylamine.

Large dew point depressions were observed with solutions of methylamine and various phenols. However, the adducts of phenol and methylamine seemed to decompose at temperatures of about 150°C. This decomposition was noticed also with methyl p-hydroxybenzoate. The addition of water as a second absorbent had the effect of stabilizing the amine-phenol adducts. Since the resulting ternary systems are quite similar to the presently operated water-ammonia machine, no further exploration was done in this area. Some of the data obtained using phenols as absorbents for methylamine are given in Table V.

Typical compounds containing active hydrogens include β -diketones, β -keto esters, imides, acetylenes, etc. In these molecules, hydrogens are "active" because the presence of neighboring electron-withdrawing groups makes them more protonic. Among the active hydrogen compounds, only the β -diketones and β -keto esters were examined. Since multiple bonds tend to undergo thermal catalytic polymerization, the acetylenes were not considered. The imides, such as succinimide and phthalimide, are usually high melting solids which are not very soluble in methylamine and tend to decompose at moderate temperatures. Table VI gives vapor pressure data of methylamine and some organic esters with active hydrogens. The dew point depressions are generally good but unfortunately their thermal stabilities are all doubtful at temperatures above 150°C, probably due to ammonolysis or other types of thermal decomposition.

Aliphatic polyhydroxy compounds appeared to be the most promising group among the binary organic systems. Typical data for this group are shown in Table VII. The effectiveness of the OH group in association with methylamine can be demonstrated when comparing the vapor pressure data of glycerol, trimethylene glycol, glycol and diethylene glycol solutions. It was found that on a mole basis, adding one more hydroxyl group to an aliphatic molecule would lower the vapor pressure to a degree which would more than compensate for the increase in molecular weight. An ether group was found to be less effective in association with methylamine.

TABLE V

ABSORBENTS - PHENOLS
REFRIGERANT - CH_3NH_2

<u>Reaction</u>	<u>Absorbent</u>	Dew Point Lowering at Solution Temp.			<u>Average Slope of Duhring Line</u>
		<u>50°C</u>	<u>100°C</u>	<u>150°C</u>	
1	Phenol	Unstable			
2	p-OH Methyl Benzoate wt 15.7%		105	117.5	0.64
3	8% Aq. Phenol Sol's wt 21.0%		(85)	90	
4	15% Aq. Phenol Sol's				
	A. wt 8.9%		99	102	0.93
	B. wt 16.0%		87	95	0.86
	C. wt 30.5%	68	71	73	0.93
	D. wt 38.6%	51.5	57	62	0.90
	E. wt 46.6%	43.5	48.5		0.90
	F. wt 50.3%	37	43		0.86

TABLE VI

ABSORBENTS - ORGANIC ESTERS WITH ACTIVE HYDROGEN
REFRIGERANT - CH_3NH_2

<u>Reaction</u>	<u>Absorbent</u>	Dew Point Lowering at Solution Temp.			<u>Average Slope of Duhring Line</u>
		<u>50°C</u>	<u>100°C</u>	<u>150°C</u>	
1	Methyl Cyanoacetate	Unstable			
2	Methyl Acetoacetate wt 18.1% mol 45.2%		105	Decomp.	(0.77)
3	Dimethyl Malonate wt 21.1% mol 53.2%		93.5	107	0.74
4	Ethyl Dichloroacetate wt 11.3% mol 39.1%		109	118.5	0.82
5	Butyl Lactate				
	A. wt 15.0% mol 45.5%		117.5	137	0.60
	B. wt 29.0% mol 65.8%	53	70	87.5	0.66
	C. wt 36.9% mol 73.4%	31.5	52	68	0.68

TABLE VII

ABSORBENTS - POLYHYDROXY COMPOUNDS
REFRIGERANT - CH_3NH_2

<u>Reaction</u>	<u>Absorbent</u>	Dew Point Lowering at Solution Temp.			<u>Average Slope of Duhring Line</u>
		<u>50°C</u>	<u>100°C</u>	<u>150°C</u>	
1	Glycerol				
	A. wt 25.6% mol 50.5%	56.6	63.5	80	0.77
	B. wt 42.8% mol 70.5%	29	33	-	0.90
	C. wt 60.7% mol 83.2%	0.2			
2	Trimethylene Glycol				
	wt 25.9% mol 46.2%	45	56	70	0.77
3	Diethylene Glycol				
	A. wt 19.4% mol 45.2%	61.5	66	82	0.75
	B. wt 31.4% mol	37	43	-	0.88
4	Glycol				
	A. wt 10.9% mol 19.9%	77	97	115	0.60
	B. wt 22% mol 36.2%	55	68	88	0.60

3-2.2 Inorganic Salts as Absorbents for Methylamine

The results obtained by other researches indicated that metal salts in general are effective vapor pressure depressants for ammonia and methylamine. Our investigation was centered on the use of salts of alkali and transition metals as cations and chlorides, bromides, iodides* and thiocyanates as anions while avoiding the unstable nitrates and chlorates and considerably less soluble alkaline earth salts. The results of the most promising systems are summarized in Tables VIII and IX.

The nature of the association between methylamine and metal salts is believed to be coordination of methylamine with the metal ions, and to a lesser extent from the interaction between methylamine and the pi-orbitals (if any) of the anionic group. Of the metal salts studied, lithium thiocyanate, which would be expected to coordinate very well with methylamine, proves to be the most soluble salt and the greatest vapor pressure depressant for methylamine.

Large negative deviations from Raoult's Law were observed with transition metal salts of thiocyanates and chlorides, but these were found to be the result of incompletely reversible reactions producing some metal-amine complex salts relatively insoluble in methylamine. The results are plotted in Figure 18. Attempts to find a system employing a solvent to obtain complete reversibility proved futile.

* U.S. Patent 3,312,077 Absorption Refrigeration System to W. L. McHale, et al., assigned to Robertshaw Controls. No data included.

TABLE VIII

METHYLAMINE AND HEAVY METAL THIOCYANATES

Metal Thiocyanates	Wt. % CH_3NH_2	Temp. (°C) at Vapor Pressure										827 kPa	Dew Pt. Lowering of CH_3NH_2 at 100°C
		138	207	276	345	414	483	552	621	690	758		
	100		13	19	25	30	35	38	42	46	50		0
$\text{Zn}(\text{SCN})_2$	43.5						30	33	36	38	44	48	Negative
$\text{Ni}(\text{SCN})_x$	34.4	77	100	114	130	145							89°C
	66.5		9	21	27	33	37	40	46	48			5°C
$\text{Co}(\text{SCN})_2$	19.7	100	117	131	142	150	157						100°C
	31.6	85	95	106	115	120	127	133	138	143	147	152	85°C
	37.0	65	77	88	97	104	110	117	122	127	131	135	73°C
CuSCN	21.0						128	133	141	146	152		81°C
	27.9						108	115	121	128	133	139	70°C
	34.9						81	87	93	97	101	105	52°C
	40.5						63	70	74	78	82	86	36°C
$\text{Cu}(\text{SCN})_2$	39.2						82	85	92	96	100	105	50°C
	51.0						50	54	57	61	64	68	15°C

TABLE IX

METHYLAMINE AND ALKALI METAL THIOCYANATES

<u>Metal Thiocyanate</u>	<u>Wt. % CH₃NH₂</u>	<u>Temp. at Vapor Pressure, °C</u>										<u>827 kPa</u>	<u>Dew Pt. Lowering of CH₃NH₂ at 100°C</u>
		<u>138</u>	<u>207</u>	<u>276</u>	<u>345</u>	<u>414</u>	<u>483</u>	<u>552</u>	<u>621</u>	<u>690</u>	<u>758</u>		
	100.0		13	19	25	30	35	38	42	46	50		0
NaSCN	50.0	50	60	67	75	82	87	91	95				51.0°C
	61.1	27	36	43	50	55	60	64	68	72			21.0°C
	68.1	15	24	32	38	44	48	53	58	62	65		14.0°C
LiSCN	48.2	94	105	114	122	130	135	142					92.0°C
	54.3		81	88	95	102	107	114	119	124	129	134	71.5°C
	63.0		50	57	63	68	73	79	83	88	93	96	43.5°C
80% NaSCN } 20% LiSCN }	30.6	66	78	87	97	106	113	122	128	136			73.0°C
	42.8	54	66	74	82	89	95	101	106	111			61.5°C
	53.4	39	50	58	65	72	78	84	89	93	97		48.0°C
62% NaSCN } 38% LiSCN }	26.4	100	112	122	132	141	148						95.0°C
	42.1	72	82	91	100	107	114	120	125	131			75.0°C
	49.3	64	73	82	88	95	101	106	110	116			66.0°C
	54.3	48	58	67	72	79	84	89	94	98	102		52.5°C

- CH_3NH_2
- — CH_3NH_2 IN $\text{Zn}(\text{SCN})_2$
- △ — CH_3NH_2 IN CuSCN
- ▽ — CH_3NH_2 IN $\text{Cu}(\text{SCN})_2$
- — CH_3NH_2 IN $\text{Ni}(\text{SCN})_x$
- CH_3NH_2 IN $\text{Co}(\text{SCN})_2$
OR $\text{Co}(\text{SCN})_2 \cdot 3\text{H}_2\text{O}$

FIGURE 18
TRANSITIONAL METAL THIOCYANATES
IN METHYLAMINE

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Figure 19 presents a series of Duhring plots for sodium thiocyanate and methylamine along with the crystallization limits. For the standard air cooled conditions we have adapted for screening purposes, we find that the strong solution (107°C solution temperature, 47°C dew point) would be 51.7% LiSCN and the weak solution (47°C solution, 7°C dew point) 46.0% NaSCN. This is a usable concentration spread, but unfortunately skirts so close to saturation that the cycle would probably be highly prone to crystallization.

Lithium thiocyanate, with a room temperature solubility of about 52 weight percent appeared to be a very favorable candidate for an air cooled absorption system with methylamine. A major qualification program was undertaken between the Institute of Gas Technology and the Research Division of Carrier Corporation. Figure 20 presents a Duhring plot based on data determined during this program.*

Based on these Duhring plots, one projects a concentration spread of 39.75% to 36.85% under our provisional air cooled rating curves, and a safe 12% displacement of the strong solution from the crystallization line.

The lithium thiocyanate program was terminated following the observation that a reaction took place, at an easily measurable rate, between copper or iron surfaces and the lithium thiocyanate-methylamine solution. This observation was made in carefully dried solutions.

Figure 21 shows some unsmoothed vapor pressure data, presented in Duhring plot form, for two lithium thiocyanate solutions in ammonia. The vapor pressure depressions are similar to those observed for methylamine but the absolute pressure would, of course, be much higher. No stability studies were made but there is no reason to expect sufficient stability improvement over methylamine to permit successful system operation.

* Macriss, R. A., Punwani, D., Rush, W. F., and Biermann, W. J. ,
"Thermodynamic and Physical Properties of Monomethylamine-Lithium
Thiocyanate System," J. Chem. Eng. Data 15, 466 (1970).

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FIGURE 19

SODIUM THIOCYANATE IN METHYLAMINE

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FIGURE 20
DÜHRING PLOTS FOR THE SYSTEM
LITHIUM THIOCYANATE - METHYLAMINE
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3-2.3 Ternary Refrigerant-Absorbent Combinations

3-2.3.1 Two Inorganic Salts

The large vapor pressure depression effect of lithium thiocyanate and its high solubility in methylamine appeared to make the methylamine-lithium thiocyanate pair an attractive absorption refrigeration system. This system, however, has the disadvantage of being viscous and having a small concentration spread (see 3-2.2). Therefore, sodium thiocyanate was utilized as a viscosity reducing diluent. Our results indicated that for this (CH_3NH_2 -LiSCN-NaSCN) ternary system, the optimum ratio of LiSCN to NaSCN should be approximately 4:6 in weight. For such a solution, the concentration spread is improved; the solution is clear and comparatively nonviscous, but further investigation would almost certainly disclose chemical instability with metals of construction.

3-2.3.2 With Two Organic Compounds

Mixtures of two types of organic compounds have been tested as absorbents for methylamine. The purpose was to see the effect of the third component on the solubility of the main absorbent and on the concentration spread. Combinations such as methylamine-phenol-glycol and methylamine hydroquinone-dimethylformamide have been examined. The results indicate no advantage or improvement over binary organic systems.

3-2.3.3 Inorganic Salts and Organic Solvents*

The above investigations show that for methylamine:

- A. The organic absorbents give very poor dew point depressions with moderate concentration spreads.
- B. Alkali metal salts of halides or pseudohalides are good dew point depressants, but yield small concentration spreads.
- C. Mixtures of two alkali metal salts give both good dew point depression and improved concentration spreads.

* U.S. Patent - 1,734,278, Refrigerant to J. G. Tandberg, Assigned to Electrolux Servel.

Therefore, it was decided to use high boiling organic solvents as a third component in an attempt to increase the concentration spread of the methylamine-alkali salt system, hoping to retain the magnitude of the dew point depression. The hypothesis is that if a polar organic solvent is a good coordination agent, it would compete with methylamine in solvating the alkali metal ion. An equilibrium would then be established such that at low methylamine concentrations the equilibrium would favor the metal-ion-solvent complex formation. At high methylamine concentration, formation of a methylamine-metal ion complex would be favored according to the mass action law. The concentration spread should be increased if the above premise is correct. The results of our first experiments with methylamine-lithium thiocyanate-tetraethylene glycol dimethyl ether proved that the expected dew point depression and increased concentration spread was obtainable. Because of this result an extensive investigation was performed in the following directions.

3-2.3.3.1 Solvent Effect

Different high boiling organic solvents were tested with methylamine and lithium thiocyanate in order to determine the effect of solvent polarity, dielectric constant, and functional groups. When 37.5% LiSCN and 62.5% of each of several solvents were used as absorbents for methylamine, the following concentration spreads were obtained: (Reference Conditions for this section: 150°C generator, 47°C condenser and absorber, 6°C evaporator).

Tetraethylenic glycol dimethyl ether	22 wt % (19-41)	or methylamine
Diethylene glycol	18 wt % (37-19)	"
1, 4-butanediol	20 wt % (40-20)	"
2-aminoethanol	12 wt % (14-26)	"
N, N-dimethyl formamide	~12 wt %	"
Trimethyl glycol	21 wt % (42-21)	"
Ethylene glycol	18 wt % (36-18)	"

The Duhring plot of CH_3NH_2 -LiSCN-tetraethylene glycol dimethyl ether is given in Figure 22 as a typical example. In Figure 23 the results are plotted in the form of Raoult's Law plot at 100°C . In this plot the design condition corresponds to a pressure range from 40 to 100 psia. One can see that the system with tetraethylene glycol dimethyl ether has the flattest curve across this range. This is consistent with its largest concentration spread in the group.

3-2.3.3.2 Concentration Effect

The relative concentrations of the components in CH_3NH_2 -LiSCN-solvent system can affect the change in concentration spread, as one would expect. When lithium thiocyanate was mixed with different amounts of tetramethylene glycol dimethyl ether, the following methylamine concentration spreads were obtained under reference conditions:

<u>Weight Ratio Ether/LiSCN</u>	<u>Wt % Conc. Spread (CH_3NH_2)</u>
0.83	16 (42-26)
1.25	16 (38-22)
1.67	22 (41-19)
11.7	11 (25-14)

Similar results with other solvents are:

<u>Weight Ratio 2-aminoethanol/LiSCN</u>	<u>Wt % Conc. Spread (CH_3NH_2)</u>
0.67	22 (39-17)
1.67	12 (26-14)
<u>Dimethyl Formamide/LiSCN</u>	
0.67	18 (41-23)
1.67	12

The above data indicate that:

1. For the ether as solvent, the optimum weight ratio of TEGDM ether to lithium thiocyanate is approximately 1.25.

FIGURE 22

DUHRING PLOT FOR THE SYSTEM
(37.5% LITHIUM THIOCYANATE AND 62.5%
TETRAMETHYLENE GLYCOL DIMETHYL ETHER)
WITH METHYLAMINE

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FIGURE 23
 RAOULT'S LAW FOR THE SYSTEM
 LITHIUM THIOCYANATE - METHYLAMINE
 WITH VARIOUS THIRD COMPONENTS

THIRD COMPONENT USED:

O - $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_4\text{CH}_3$

□ - ETHYLENE GLYCOL

Δ - 1, 4 - BUTANEDIOL

▽ - 2 - ETHANOLAMINE

◇ - DIMETHYLFORMAMIDE

X - 5.8 g LiSCN WITHOUT
 THIRD COMPONENT

DATA AT 100° C

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2. For solvents of smaller molecules, such as 2-aminoethanol or dimethyl formamide, a smaller amount of solvent is required to achieve the optimum concentration spread. In terms of mole fraction or functionality (the number of functional groups in the solvent), the ratio of LiSCN to solvent is somewhat constant for solutions of largest concentration spreads. The effect can also be explained in terms of the Raoult's Law plot as shown in Figure 24.

3-2.3.3.3 Anionic Effect

When 37.5% of LiBr and 62.5% of tetraethylene glycol dimethyl ether was tested as an absorbent, a methylamine concentration spread of 20 wt % was obtained. This is similar to the result with LiSCN as salt. But the range of concentration spread being 34-14 in comparison with 41-19 for LiSCN as salt, indicates loss of some dew point depression. This is consistent with the fact that the LiBr formula weight is greater than LiSCN.

37.5% LiCl and 62.5% H₂O was tested as absorbent for methylamine. A 21 wt % (38-17) concentration spread was obtained. Water was used in this case because of the expected low solubility of LiCl in methylamine. Comparing this system with the above system, it is interesting to note that although such a large mole fraction of water was present, the dew point depression was still greater.

3-3 METHYLAMINE/AMMONIA, CONCLUSIONS

In a paper on "Vapor Pressure of Ammonia and Methylamine in Solutions for Absorption Refrigeration Systems," published by J. P. Robertson in ASHRAE (1966), the conclusion was reached that the use of ammonia in an absorption system using a nonaqueous absorbent appeared quite promising. The following systems were cited:

1. Ammonia and sodium thiocyanate
2. Ammonia and a mixture of sodium thiocyanate and iodide
3. Ammonia and a mixture of sodium thiocyanate and 1,4-butanediol.

VAPOR PRESSURE, kPa

1241

1103

965

827

689

551

414

276

137.8

0.0

0.1

0.2

0.3

0.4

0.5

0.6

0.7

0.8

0.9

1.0

LLSCN

MOLE FRACTION REFRIGERANT

CH₃NH₂

FIGURE 24
EFFECTS OF CONCENTRATION OF THIRD
COMPONENT

DATA AT 100°C

WEIGHT RATIO

CH₃O(CH₂CH₂O)₄CH₃ / LLSCN

x - 0.00

▽ - 0.85

△ - 1.25

○ - 2.0

□ - 4.0

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The Carrier work described here has led us to conclude that sodium thiocyanate is not quite soluble enough to support an air cooled absorption cycle. The work cited does suggest that an "antifreeze additive" could be found which would permit the construction of such a machine based on methylamine or ammonia, with sodium thiocyanate and one of several antifreeze additives. Because of the several disadvantages (costs, latent heat, heat transfer properties) of ammonia and methylamine as compared to water, it appeared more advantageous to follow up by developing a water-salt-antifreeze system instead.

The exploratory work done with lithium thiocyanate indicated that this material would be a very promising material to develop with methylamine, particularly in some of the mixtures. The chemical instability with regard to containment materials, discovered only after considerable effort had been expended in glass containers or with only short time exposures to metal, makes any further efforts with lithium thiocyanate too high a risk to justify any efforts, in the writer's judgment.

4-0 CONCLUSIONS AND RECOMMENDATIONS

In the search area described in this volume, Part II - Solid Absorbents, High Latent Heat Refrigerants, we have identified three systems which could be used for developing an air cooled, solar driven, absorption machine.

- A. Lithium chlorate/lithium bromide-water with an amine heat transfer additive. The system has, in its favor, sufficient thermodynamic information to justify optimism regarding its thermodynamic and heat transfer suitability for this application. The two major disadvantages are the limitations on materials of construction and the lack of commercial availability of lithium chlorate.

This system is a viable alternate, should our present antifreeze additive candidate system prove to have some unforeseen obstacle.

- B. The possible use of lithium bromide and methyl alcohol will be re-examined as another possible alternate.
- C. Ammonia/methylamine with lithium thiocyanate (perhaps lithium bromide) and an anti-crystallization additive could be developed. Our concerns with this system are the long term stability of the thiocyanate ion in the environment obtaining in an absorption machine and the limitations involved in using a refrigerant which is both flammable and toxic.

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