

LIQUID AMMONIA RESEARCH—1942

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I. INTRODUCTION

This, the tenth paper in a series (11, 13, 57, 58, 59, 61, 64, 65, 67) initiated in 1933, is concerned primarily with researches described by American workers. With very few exceptions, information relating to publications which have appeared in foreign periodicals is essentially that which has been made available through the various abstracting services. Including patents, the number of publications which have appeared or have become available during the past year is approximately one-half the average number for the preceding nine years.

II. PHYSICOCHEMICAL STUDIES

Methods have been described for the investigation of the effects of inorganic electrolytes (45) and certain organic compounds (46) upon the electrocapillary curves of mercury in liquid ammonia at or near room temperature. In the application of these methods to the study of inorganic electrolytes, ammonium nitrate was employed as the stock electrolyte and solutions containing sodium chloride, sodium bromide, or potassium iodide were prepared and investigated. Liquid ammonia solutions of these electrolytes were found to shift the maximum in the electrocapillary curve in a manner comparable to, but to a degree greater than, that observed previously for the corresponding aqueous solutions. Calculation of the capacity of the electric double layer resulted in a value of 11 μF per square centimeter, which is considerably lower than the value of 17 to 18 μF per square centimeter found when water was used. It has been suggested that this result may be due to the lower dielectric constant of liquid ammonia. Although liquid ammonia solutions of ammonium nitrate containing toluene, xylene, mesitylene, ethylbenzene, propylbenzene, cyclohexane, naphthalene, or tetralin resulted in a decrease in interfacial tension, these solutions failed to produce any shift in the maximum of the electrocapillary curve. With increase in length of the side chain, adsorption on the surface of the mercury was found to increase.

Audrieth and coworkers (2) have provided comparative data relative to the catalytic influence of salts upon ammonolytic and aminolytic reactions of esters and have suggested that the effects heretofore designated as acid catalysis in basic solvents may be only a special case of a more general type of electrolyte catalysis. A related but independent investigation (36) has shown that catalytic effects of this type observed in connection with the ammonolysis of both esters and organic halogen compounds are accompanied by increases in energy of activation. These and subsequent studies (70) provide quantitative proof of the assumption that these effects should be classified as electrolyte catalysis rather than acid catalysis.

Using a differential manometer and a method permitting rapid and exact equalization of temperature in the two liquids, Kirshenbaum and Urey (31) have redetermined the vapor pressure differences of the isotopic ammonias, NH_3 and ND_3 . The results of their measurements have been found to be represented accurately by the expression

$$\log_{10} P_{\text{NH}_3}/P_{\text{ND}_3} = (46.25/T) - 0.14003$$

The triple point for ammonia (195.68°K.) was found to be in excellent agreement with the value reported by Overstreet and Giauque (60); however, that found for 98 per cent trideuterio-ammonia (198.79°K.) was lower than the value reported previously by de Bruyne and Smyth (16). Jaffe (29) has pointed out that the color of the light reflected from a saturated solution of lithium in liquid ammonia [which contains $\text{Li}(\text{NH}_3)_4$] is dependent upon the angle of incidence. Measurement of the Hall effect showed that the saturated solution contains one mobile electron for each atom of lithium and, in terms of this electron density, the observed color can be explained satisfactorily by the classical theory of dispersion of electrons. Procedures for the electroplating of gold from liquid ammonia solutions of gold salts have been described by Kushner (34).

III. INORGANIC REACTIONS

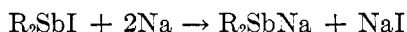
The preparation of bright red (and apparently amorphous) potassium cyanonickelate, $\text{K}_2\text{Ni}(\text{CN})_3$, in a pure condition has been accomplished by Eastes and Burgess (18) by the interaction of potassium and an excess of potassium cyanonickelate, $\text{K}_2\text{Ni}(\text{CN})_4$, in liquid ammonia at its boiling point. This product, which had not been isolated previously, was also produced by reactions effected in aqueous solutions. When the reduction of potassium cyanonickelate was effected in liquid ammonia, using an excess of potassium, there was obtained a yellow solid product having a composition represented by the formula $\text{K}_4\text{Ni}(\text{CN})_4$. These reduction products of the nickelate are of particular interest in that $\text{K}_3\text{Ni}(\text{CN})_4$ is presumably a compound of univalent nickel, while $\text{K}_4\text{Ni}(\text{CN})_4$ may perhaps be looked upon as a compound involving zerovalent nickel. Analogous reactions have been observed when potassium cyanonickelate was reduced by liquid ammonia solutions of calcium (19). On the other hand, the complex cyanides $\text{KAg}(\text{CN})_2$, $\text{K}_2\text{Cd}(\text{CN})_4$, and $\text{K}_3\text{Cu}(\text{CN})_4$ were reduced by liquid ammonia solutions of potassium to the pyrophoric elemental metals. For

reasons not indicated, potassium cyanozincate, $K_2Zn(CN)_4$, was reduced by sodium rather than by potassium and in this case a non-pyrophoric precipitate of elemental zinc was obtained.

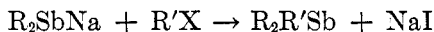
A study of reactions of certain oxides of cobalt and iron in liquid ammonia (44) has shown that, at room temperature, cobalt(III), cobalt(II), and iron(II) oxides are insoluble in and unreactive toward liquid ammonia. Cobalt(III) oxide was not attacked by liquid ammonia solutions of ammonium chloride or ammonium nitrate at $100^\circ C.$, while, under the same conditions, the oxides of divalent cobalt and iron were partially dissolved and in these cases the extent of reaction was found to be the more pronounced in the case of ammonium chloride solutions. The action of liquid ammonia solutions of potassium amide at room temperature upon these oxides was found to result in the formation of complex mixtures of soluble and insoluble products, of which only elemental cobalt could be separated and identified. By reaction with liquid ammonia solutions of potassium at $0^\circ C.$, cobalt(III) oxide was reduced first to cobalt(II) oxide and finally to elemental cobalt to an extent dependent upon the quantity of potassium employed in reaction with a given weight of oxide. Under similar conditions, iron(II) oxide was reduced only to a limited extent which was largely independent of the quantity of potassium employed. The comparative behavior of cobalt(III) and iron(II) oxides indicated that the reduction products of the former are much less effective catalysts for the conversion of potassium to potassium amide than is the elemental iron formed by the reduction of iron(II) oxide.

The addition of liquid ammonia to concentrated solutions of ammonium sulfate (formed by the interaction of gypsum and ammonium carbonate) has been suggested as a means of effecting precipitation in a manufacturing process which provides ammonium sulfate of 75 per cent purity (14).

A series of unsymmetrical organoantimony compounds (72) has been prepared in liquid ammonia by the reduction of disubstituted antimony(III) iodides,



followed by reaction of the resulting sodium salt with an appropriate organic halide,



Methods for the preparation of unsymmetrical organolead compounds have been described by Apperson (1) and Bindschadler (6). These compounds were studied in relation to their ease of cleavage by alkali metals, which was found to result in the formation of unsymmetrical organolead-sodium compounds. In the course of this investigation, one organolead compound containing divalent lead, $(C_2H_5)_2Pb$, was prepared. The order of decreasing ease of cleavage of the substituent groups was found to be allyl, benzyl, *sec*-butyl, butyl, ethyl, methyl, and phenyl. In connection with a general discussion of the chemistry of organobismuth compounds, Gilman and Yale (23) have called attention to the utility of liquid ammonia as a medium for the formation of salts of the type R_2BiM or

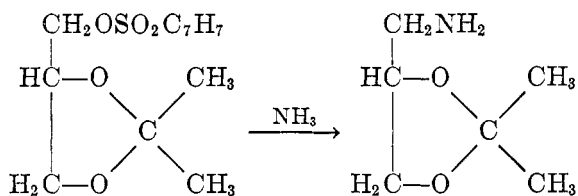
$(R_2Bi)_2M$ and their subsequent use in the preparation of unsymmetrical organobismuth compounds and of water-soluble organobismuth compounds of potential therapeutic value.

IV. ORGANIC REACTIONS

A. Ammonolysis

An extended study of the interaction of benzil and liquid ammonia or liquid ammonia solutions of potassium amide or ammonium chloride has provided information with regard to the identity and yields of the various products, together with methods for the separation and estimation of these products (37). Reaction with liquid ammonia at 35°C. was found to yield benzamide, 2,4,5-triphenyloxazole, "imabenzil," "benzilimide," and traces of tetraphenylpyrazine. The constitution of imabenzil and of benzilimide has not been definitely established. Addition of potassium amide resulted in an increase in the yield of benzamide, a decrease in the yield of imabenzil, and elimination of 2,4,5-triphenyloxazole from among the reaction products. At 103°C., benzamide, 2,4,5-triphenylglyoxaline ("lophine"), 2,4,5-triphenyloxazole, and small quantities of tetraphenylpyrazine were produced by the reaction between benzil and liquid ammonia, while in the presence of potassium amide the yield of benzamide was increased, that of lophine was decreased, and no 2,4,5-triphenyloxazole was obtained. The influence of ammonium chloride was not pronounced at either temperature.

In connection with the study of the preparation of *l*-glycidol from *d*(+)-acetoneglycerol, Sowden and Fischer (55) have shown that α -(*p*-toluenesulfonyl)-*d*-acetoneglycerol is ammonolyzed to *l*-1-aminoacetone-2,3-propanediol.



The ammonolysis was carried out by allowing the *p*-toluenesulfonyl derivative to react with anhydrous liquid ammonia at room temperature over a period of 98 hr.

B. Reactions of alkali amides

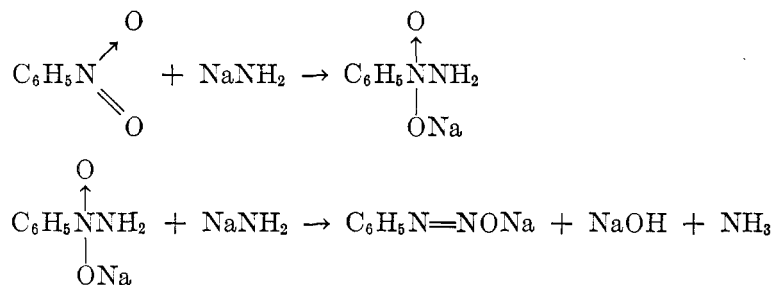
White and Bergstrom (68) have reported that 2-phenylquinoline-4-carbonamide reacts with potassium amide in liquid ammonia at room temperature to form 4-amino-2-phenylquinoline in approximately 45 per cent yield. If potassium nitrate is present during the reaction, the yield is almost quantitative. Only certain homologs of the above carbonamide reacted similarly to yield amines: *o*-benzoylbenzamide yielded small quantities of *o*-aminobenzophenone, while the other amides studied did not react. Since it is believed improbable that the $-\text{CONH}_2$ group is replaced directly by $-\text{NH}_2$, it has been suggested

that potassium amide reacts with RCONH_2 reversibly to form the ion RCON^{--} , which loses two electrons to potassium nitrate to form RNCO by rearrangement. The excess potassium amide converts this product to RNHK . The over-all reaction may be represented by the equation



Experiments conducted with isocyanates support the foregoing mechanism. 9-Amino-9-phenylfluorene was found to react with potassium amide and potassium nitrate to form 9-aminophenanthridine, the expected 9-phenylphenanthridine being converted to the 9-amino compound. Under similar conditions triphenylmethylamine yields benzamide, and in this reaction it is believed that benzophenone anil is first formed by rearrangement and subsequently cleaved by potassium amide to form benzamidine which, in turn, is hydrolyzed to benzamide.

An excess of potassium amide or sodium amide in liquid ammonia at -33°C . or at room temperature has been found to react with nitrobenzene to form a deep reddish brown solution from which a dark-colored precipitate separates slowly (4). At the same time, gaseous nitrogen is liberated in the approximate ratio of 0.5 mole per mole of nitrobenzene. Several other nitro compounds have been shown to react in a similar manner. Sodium amide or potassium amide in excess was found to react with nitrobenzene and 2-naphthol in liquid ammonia to form 1-phenylazo-2-naphthol in yields up to 30 per cent. Since it was shown that sodium benzenesidiazotate does not react with 2-naphthol in the presence of sodium amide, the normal diazotate ($\text{C}_6\text{H}_5\text{N}=\text{NONa}$) is probably the intermediate in the reaction. The following partial mechanism has been suggested:



Bergstrom and coworkers (5) have also shown that sodium, potassium, or barium diphenylamide (prepared by the action of the appropriate metal amide on diphenylamine in liquid ammonia) reacts with nitrobenzene to form *p*-nitrotriphenylamine in yields up to 45 per cent. The reaction may be carried out at -33°C . or at room temperature, using liquid ammonia or absolute ethyl ether as the solvent. *o*-Nitrotoluene was found to react with sodium diphenylamide in liquid ammonia at -33°C . to form 2,2'-dinitrobibenzyl in 36 per cent yield, while only small quantities of 4,4'-dinitrobibenzyl were obtained when *p*-nitrotoluene was employed under similar conditions.

A group of diethyl α -(alkoxyethyl)alkylmalonates, $[\text{CH}_3\text{CH}(\text{OR})\text{CR}'(\text{CO}_2\text{C}_2\text{H}_5)_2]$, have been prepared by the reaction of α -chloroethyl alkyl ethers with the sodium salts of diethyl alkylmalonates in benzene-ether solution. The sodium salts were prepared by adding the alkylmalonic esters to liquid ammonia solutions of sodium amide at temperatures below the boiling point of ammonia (41). The use of liquid ammonia as a medium for the amination of heterocyclic bases by alkali amides has been discussed in considerable detail by Leffler (35). Applications involving the use of ammonia as the reaction medium are based almost entirely upon the investigations of Bergstrom and his coworkers (62).

C. Reactions of solutions of metals

Freudenberg and coworkers (22) have made an extensive investigation of the action of liquid ammonia solutions of potassium at room temperature upon sprucewood meal, beechwood meal, and spruce lignin. In order to obtain comparative data useful in the interpretation of the observations recorded, they have also studied the reactions of ammonia solutions of potassium upon a number of "model substances" including phenol ethers, glucosides, coumarone, coumaran, and chroman derivatives. Treatment of sprucewood meal with a solution of potassium over a period of several hours resulted in degradation to a small ammonia-soluble fraction (which consisted of phenolic decomposition products of lignin) and an ammonia-insoluble portion. The latter was separated into a methanol-insoluble fraction (which was subsequently divided into carbohydrate and lignin fractions) and a methanol-soluble fraction containing most of the lignin present in the original sample of wood. This lignin was found to have a relatively high —OH content, which is attributed to the cleavage of phenolic ethers with resultant formation of new —OH groups. In the case of beechwood meal, a somewhat more complicated reaction produced a larger ammonia-soluble fraction and the size of the other fractions was found to vary considerably with the concentration of potassium employed. Treatment of cuproxam lignin with potassium in ammonia converted all of the lignin to forms soluble in either liquid ammonia or methanol. The interpretation of these and other similar observations has been based largely on the over-all behavior of the model substances toward solutions of potassium rather than on any detailed study of the reactions of each of these substances.

A study of the reduction of benzoxazole and benzothiazole (32) has shown that their reactions with liquid ammonia solutions of sodium at -33.5°C . result in the rupture of the heterocyclic rings and formation of sodium salts as the primary reduction products. These salts were converted to the corresponding Schiff bases by treatment with ammonium bromide or ethyl bromide or to the aminophenols or thiophenols by hydrolysis of the sodium salts (or the Schiff bases). More extensive reduction at the same temperature was effected by reducing liquid ammonia solutions of the oxazole or thiazole by the hydrogen generated by the interaction of sodium and ammonium bromide. Thus, benzoxazole was reduced by hydrogen to *o*-(methylamino)phenol. In connection with this work, limited information relative to the reduction of 2-phenylbenzoxazole and 2-chlorobenzothiazole has also been recorded.

Greenlee and Fernelius (24) have suggested that the formation of pure *trans*-olefins by treatment of dialkylacetylenes with sodium in liquid ammonia proceeds through a mechanism in which the *trans* configuration is established by electrostatic repulsion. An analogy between this mechanism and the Walden inversion is suggested. Hennion and Murray (25) have described certain catalytic addition reactions of acetylenic alcohols which were prepared, as described previously (63), by the condensation of the appropriate aldehyde or ketone with sodium acetylide in liquid ammonia.

Certain dextrans isolated from corn sirup have been methylated completely by sodium and methyl iodide, using liquid ammonia as the reaction medium (39). This now rather generally well known method was found to yield better results than other methods which were tried. Similarly, the dextran obtained from sucrose by the action of *L. mesenteroides* has been methylated completely, i.e., to a methoxyl content of 45.6 per cent (38). Liquid ammonia may be used as a medium for the introduction or removal of alkyl or other substituent groups. The methyl group of *dl*-methionine may be removed by treatment in liquid ammonia with the calculated quantity of sodium (56). If this treatment is followed by addition of benzyl chloride, *S*-benzyl-*dl*-homocysteine is obtained. This series of reactions is the reverse of that employed by du Vigneaud and Patterson (12) for the preparation of methionine from homocysteine. If an excess of sodium is employed in the reduction of *dl*-methionine, followed by addition of benzyl chloride, *N*-dibenzyl-*S*-benzyl-*dl*-homocysteine is formed.

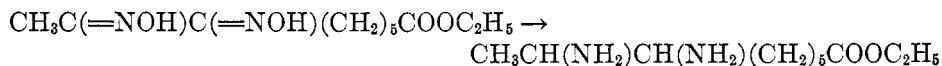
The liquid ammonia-sodium method for the analysis of organic substances for halogens has been used in the determination of chlorine, bromine, and iodine in a series of *p*-*s*-alkylhalobenzenes (26).

D. Other organic reactions

In a study of evidence bearing upon the structure of salts of hydroxyanthraquinones, Scholl and coworkers (54) have prepared a considerable number of ammonium salts by the interaction of the various hydroxyanthraquinones and liquid ammonia. It has been shown that these salts are predominantly ionic, and particular attention has been directed toward the relationship between the colors of these (and other) salts and the electronic structures of the corresponding anions.

A series of ferrihemochromogens has been prepared by dissolving crystalline or amorphous insulin in anhydrous liquid ammonia, followed by treatment of the resulting solutions with varying amounts of ferriheme chloride (3). Insulin was found to combine with ferriheme up to a maximum ratio of 1:8, indicating a relationship of one insulin nitrogen to one ferriheme iron atom. The physiological activity of this conjugate proved to be no different from that of ordinary insulin. When commercial curare is added to liquid ammonia, more than one-half of the total amount passes into solution as inert material, leaving the active principles undissolved (53). If the ammonia-insoluble fraction is treated with an equal weight of glycine, it becomes more potent, prolonged in its action, and less toxic than curare. In connection with studies relating to the establishment of the structure of biotin, du Vigneaud and coworkers (17) have converted

ethyl ζ, η -dioximinopelargonate to ethyl ζ, η -diaminopelargonate by hydrogenation over Raney nickel in a solvent medium consisting of liquid ammonia containing a small quantity of methanol.

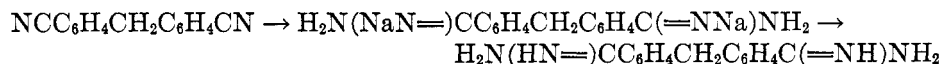


In an attempt to produce plastics from inexpensive domestic materials, Roberts (51) has prepared plastic elastomers by treatment of proteins such as casein or gluten and rubber latex with liquid ammonia. Removal of the ammonia was found to leave plastics having the desirable properties of toughness, resiliency, and hardness. The structure or mode of formation of these products is not known.

V. PATENTS

Previous papers in this series have called attention to numerous patents relating to processes for the large-scale production of melamine. More recent patents issued describe improvements in the design of equipment suited to the production of melamine from liquid ammonia and cyanamide or dicyanamide (71), conditions of temperature and concentration favorable to the formation of melamine from liquid ammonia and dicyanodiamide (69), and a method for the production of liquid ammonia solutions of cyanamide (15) suitable for use in the production of melamine. In this latter process cyanamide is produced, for example, by the interaction of calcium cyanamide and ammonium carbonate in the presence of liquid ammonia which serves as a solvent for the liberated cyanamide.

In addition to those indicated above, a number of recently issued patents have been concerned with the use of liquid ammonia in the production of other organic nitrogen compounds. Hill (27) has described the details of a process for the liberation of aliphatic bases such as guanylurea from their salts (e.g., the sulfates) by treatment with liquid ammonia or alkali metal amides in the presence of ammonia. By the selective hydrogenation of acyclic dinitriles in liquid ammonia and in the presence of a nickel catalyst, Rigby (49) has developed a process for the preparation of acyclic monoaminonitriles, such as ω -aminocapronitrile. Improved yields resulting from a more selective control over extent of hydrogenation have been realized through the use of cobalt-containing catalysts having relatively mild catalytic activity (50). On the other hand, dinitriles have been converted to the corresponding diamidines (20) by reaction with sodium amide in liquid ammonia. This conversion may be indicated as follows:



The use of liquid ammonia as a reaction medium is claimed but is not illustrated in the description of a patented process for the production of unsaturated amines of the acetylene series by the interaction of ammonia and acetylene in the presence of heavy-metal catalysts which are capable of forming acetylides, e.g.,

copper, silver, and mercury (48). Addition compounds of epinephrine and glycine, or glutamic acid, dextrose, ascorbic acid, lactic acid, cholesterol, urea, gelatin, etc., have been produced by bringing the two reactants together in liquid ammonia at -33.5°C . under anhydrous conditions (52). The conjugates so obtained have been found to produce an increase in blood pressure of greater duration than may be obtained through the use of epinephrine or epinephrine hydrochloride.

Patented processes for the production of non-nitrogenous organic substances include a method for the preparation of substituted ethynylcarbinols of high molecular weight (8). Ketones such as myristone, laurone, stearone, *p*-biphenyl heptadecyl ketone, etc. are condensed with an alkali metal acetylide (or substituted acetylide) in liquid ammonia and the resulting alkali metal salts are hydrolyzed to afford the corresponding ethynylcarbinols. Condensation products of allyl or substituted allyl halides (30) have also been produced by condensing, for example, allyl chloride with itself or its derivatives by treatment with liquid ammonia solutions of alkali or alkaline-earth metals. Additional patents have been issued in connection with the use of liquid ammonia as a medium for the formation of alkaline-earth metal salts of cellulose from carbohydrate materials such as cotton or wood pulp and the utilization of these salts (or the alkali metal salts) in the production of cellulose acetate (43). Salts formed similarly from partially substituted cellulose may be used in the formation of more highly substituted products, e.g., diethylpropylcellulose from the reaction between diethylcellulose and sodium in liquid ammonia, followed by interaction of the resulting sodium salt and propyl bromide (7).

A process for the separation of carboxylic acids from polybasic inorganic acids (28) has been based upon the fact that, upon treatment with liquid ammonia, the carboxylic acids form soluble ammonium salts. The salts of the organic acids are recovered by filtration, followed by evaporation of the solvent ammonia. Muskat and Ayers (47) have developed a method for the purification of sodium hydroxide through the removal of silica by treating concentrated caustic solutions with a quantity of liquid ammonia sufficient to precipitate most of the silica present but insufficient to cause separation of two liquid phases, while maintaining the temperature at a level such that separation of solid sodium hydroxide does not occur. Liquid ammonia has also been used as a medium for the incorporation of sensitizers into chlorate or perchlorate explosives (9). Provision has been made for the synthesis of ammonia by bringing together the constituent gases in a liquid medium, which may consist of liquid ammonia, in which a suitable catalyst is dispersed, immersed, or dissolved (40). Other recent patents involving the use of liquid ammonia are concerned with the production of sulfonamides (e.g., by the interaction of paraffin wax sulfonyl chloride and liquid ammonia) suitable for use in the compounding of lubricants (10) and with the removal of asphaltic materials from lubricating oils (42). In the latter process, the oil is treated with liquid propane together with a quantity of liquid ammonia sufficient to permit precipitation of a substantial quantity of non-paraffinic constituents.

VI. GENERAL

Accounts of experiments on the use of liquid ammonia solutions of acetylene as a motor fuel (21, 33, 66) indicate that a solution containing 22 per cent of acetylene provides a fuel having a high octane number and providing an ammonia-free exhaust. Danger of explosion arises only if the liquid phase contains 30 per cent by weight (or more) of acetylene, while gaseous mixtures of acetylene, ammonia, and air must contain at least 15 per cent of acetylene if complete combustion of the acetylene is to be realized. The fuel is prepared by passing gaseous acetylene into tank cars of liquid ammonia and, during use, the fuel is carried in light alloy-steel tanks which are not subject to corrosion by the acetylene-ammonia mixture. In connection with the study of the flammability of this gasoline substitute, the vapor pressures of the system acetylene-ammonia have been studied at -33° , 0° , 25° , and 40°C . as a function of the composition of both the gaseous and the liquid phases.

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