energy,[17] and an examination of the published data on the reactions of ethyl radicals in the gas phase discloses no good evidence that the activation energy for ethyl radical combination is other than zero.[18] E_t was therefore assigned the value zero for this study, so that

$$E_p = E - {}^1/_2E_i \qquad (13)$$

Using the value of $E_i = 38.4$ kcal./mole, the values of E_p obtained for the systems studied are: acetylene 5.1, butadiene 4.9, ethylene 8.2 and propene 5.6 kcal./mole. The value for butadiene agrees well with previous values of 5.4[5] and 5.5[6] kcal./mole. The value for ethylene is in fair agreement with the value of 6.8 kcal./mole given by Raal and Danby.[2] However, the results of Raal and Danby depended upon the value of 9.7 kcal./mole for the activation energy for hydrogen atom abstraction from acetaldehyde by methyl radical. If the more recent value of 7.5 kcal./mole given by Volman and Brinton[19] is taken, however, the work of Raal and Danby indicates a value of 4.6 kcal./mole for the propagation activation energy in ethylene polymerization, which does not agree with our results. If the values for E_p obtained in this study are compared with those of Mandelcorn and Steacie previously cited,[8] it is seen that the correspondence is quite good in the cases of acetylene and propene and is certainly within experimental error for ethylene. Since their value for butadiene is a rough approximation, the discrepancy with our value is not significant.

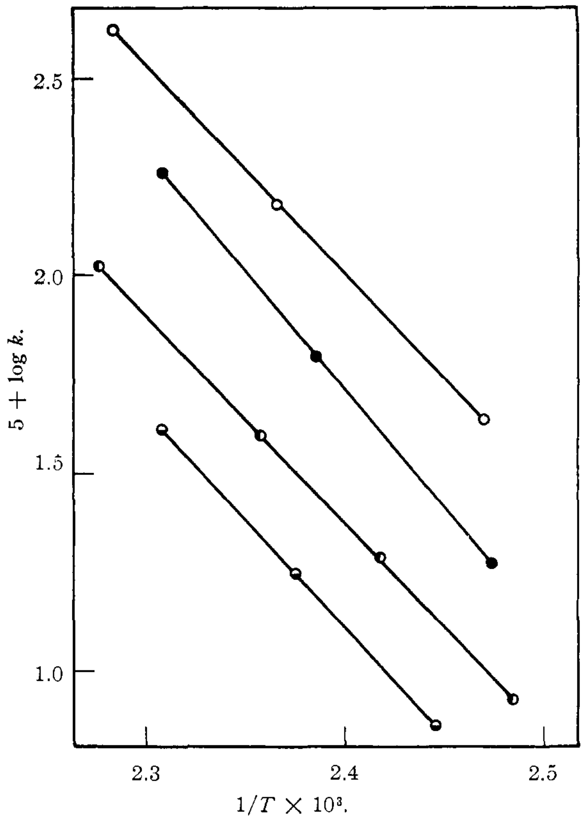

Fig. 1.—Effect of temperature on polymerization rate: ○, acetylene; ●, ethylene; ◐, butadiene; ◒, propene.

Acknowledgment.—The authors wish to express their appreciation to the Research Corporation for financial aid.

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[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORIES OF THE OHIO STATE UNIVERSITY]

The System Ammonia-Hydrazine-Ammonium Chloride

BY FORREST R. HURLEY AND HARRY H. SISLER[1]

RECEIVED JANUARY 5, 1957

A study of the solid-liquid equilibria in the general ternary system of ammonia, hydrogen chloride and hydrazine was restricted to that portion of the general diagram enclosed in the triangle NH_3-N_2H_4-NH_4Cl, and to pressures near one atmosphere. A ternary compound believed to be $NH_3 \cdot HCl \cdot N_2H_4$, but whose composition has not been established, melts incongruently at −2.5°. The conditions for removal of ammonium chloride from the system by crystallization were outlined.

Sisler and Mattair[2] have shown that hydrazine is formed when chloramine, produced from gaseous chlorine and ammonia, is dissolved in a large excess of liquid ammonia. Subsequent papers from this Laboratory[3] give additional details concerning this synthesis and the recovery of anhydrous hydrazine.

In accordance with the equation

$$ClNH_2 + 2NH_3 = N_2H_4 + NH_4Cl$$

equivalent amounts of hydrazine and ammonium chloride are formed in the reaction. However, the over-all yield of hydrazine is reduced by its reaction with chloramine.

$$2ClNH_2 + N_2H_4 = N_2 + 2NH_4Cl$$

Therefore, the mole ratio of hydrazine to ammonium chloride in the product mixture is always less than unity. During the last stages of evaporation of excess ammonia, hydrazine, which has a lower volatility than ammonia, reacts with ammonium chloride in accordance with the equation

$$N_2H_4 + NH_4Cl = NH_3 + N_2H_5Cl$$

This reaction makes it difficult to distil the hydrazine from the reaction mixture since the ammonium chloride in the mixture is always in excess of the

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[1] Department of Chemistry, University of Florida, Gainesville.

[2] R. Mattair and H. H. Sisler, THIS JOURNAL, **73**, 1619 (1951).

[3] H. H. Sisler, *et al.*, *ibid.*, **76**, 3909 (1954); **76**, 3912 (1954); **76**, 3914 (1954).

hydrazine. If the mole ratio of ammonium chloride to hydrazine were reduced by fractional crystallization to a value less than one, a portion of the hydrazine (the excess over the equivalent of ammonium chloride) would thereby be made available for removal by simple distillation.

A study of the solid–liquid equilibria existing in the general ternary system of ammonia, hydrazine and hydrogen chloride was necessary in order to determine the most favorable conditions for crystallization of solid phases containing ammonium chloride but no hydrazine. The investigation was restricted to that portion of the general diagram enclosed in the triangle NH_3–N_2H_4–NH_4Cl, and further to pressures near one atmosphere. Phase diagrams for each side of the triangle were constructed prior to the investigation of the ternary system. The freezing point diagram for the NH_3–NH_4Cl side of the triangle was constructed from the solubility data compiled by Seidell[4] from the work of several investigators. The freezing point diagram for the NH_3–N_2H_4 system was constructed from solubility data published by Friedrichs.[5] Freezing points for various N_2H_4–NH_4Cl mixtures (the third side of the triangle) were determined as a part of this investigation.

Experimental

The solid–liquid equilibria in the binary system N_2H_4–NH_4Cl and the ternary system NH_3–N_2H_4–NH_4Cl were studied by the method of thermal analysis. The phase diagram of the N_2H_4–NH_4Cl system was investigated in the region from 60 to 100 mole % hydrazine. At lower concentrations of hydrazine the equilibrium pressure of the system is well in excess of one atmosphere. The ternary phase diagram was broken up into forty experimental sections for investigation. Each section was characterized by a fixed mole ratio of ammonia to ammonium chloride. Therefore, every ternary mixture investigated had a composition point falling on experimental sections which extended radially from the hydrazine corner to points on the NH_3–NH_4Cl side of the ternary phase diagram lying approximately between 10.5 and 98.7 mole % NH_3 (*e. g.*, see Figs. 3 and 4).

Apparatus.—All freezing point determinations were made in a glass freezing point cell shown in Fig. 1. The glass-spiral stirring rod was operated by intermittent magnetic interaction of a solenoid with the iron slug sealed into the top arm of the stirrer.

The time–temperature cooling curves were obtained by using a Leeds and Northrup Micromax Model S-40000 series self-recording potentiometer with a copper–constantan thermocouple immersed in the well of the freezing point cell. Petroleum ether (b.p. 30–60°) was used as a heat-transfer medium in the thermocouple well. The apparatus was calibrated at the freezing points of distilled water, carbon tetrachloride ($-22.6°$), chloroform ($-63.5°$), and the α- and β-forms of diethyl ether ($-116.3°$ and $-123.3°$).

A cooling rate of 1 to 2 degrees per minute was regulated by the choice of coolant, and the type of jacket used to control the rate of heat transfer from the freezing point cell to the cooling bath.

Mixtures of N_2H_4 and NH_4Cl.—A weighed amount of ammonium chloride was transferred to the freezing point cell through a side arm which was then capped with a vaccine bottle stopper. It was necessary to cool the cell and ammonium chloride below $-40°$ before hydrazine was added since a small amount of hydrazine coming in contact with solid ammonium chloride releases a considerable quantity of gaseous ammonia which could cause excessive pressures. Purified hydrazine was transferred to the freezing point cell from a glass syringe fitted with a No. 26 gage stainless steel hypodermic needle, 1.5 inches long. A glass syringe affords a convenient means of transferring and weighing hydrazine with a minimum of exposure to the atmosphere. At atmospheric pressure as many as 10–15 punctures of the Arthur H. Thomas No. 2330 vaccine bottle stoppers could be made without significant leakage. A freezing point of the mixture was obtained only after the contents of the cell was warmed sufficiently to completely melt the mixture. All freezing points were determined at least twice. The precision obtained was always within 0.5°. Successive additions of hydrazine were made so that freezing points of several compositions were obtained for one addition of ammonium chloride.

Mixtures of NH_3, N_2H_4 and NH_4Cl.—A weighed amount of ammonium chloride was transferred to the freezing point cell. Anhydrous ammonia was slowly distilled into the cell and condensed over the ammonium chloride by cooling the cell in a Dry Ice bath. The amount of ammonia condensed with the ammonium chloride was determined by one or both of the following methods: (1) by the difference in weight of the cell, and (2) by the freezing point of the binary mixture of ammonia and ammonium chloride. The first method was used in all cases where the mole per cent. of ammonia was less than 75. Both methods could be used for mixtures containing from 75 to 88 mole % ammonia, being restricted only by the ammonia pressure developed at the temperature of the measurement. For compositions greater than 88 mole % ammonia, the freezing point of the mixture was used as a measure of concentration, the percentage of ammonia being determined from the NH_3–NH_4Cl phase diagram (Fig. 5).

After the ammonia was added, the freezing point cell was sealed with a vaccine bottle stopper. Several additions of hydrazine were made in the manner described above. It was always necessary to cool the mixture with a Dry Ice bath before each addition of hydrazine.

Materials.—Synthetic anhydrous ammonia was obtained from the Verkamp Corporation. The ammonia was slowly distilled from a 50-pound cylinder through a glass wool plug, and condensed directly into the freezing point cell. Under these conditions the distilled ammonia froze at -77.5 to $-78°$ which agrees well with the literature value.

Matheson Coleman and Bell anhydrous hydrazine was allowed to stand over flaked sodium hydroxide for 24 hours and then distilled. The distillate froze at 1.5 to 2.0° which agrees with the freezing point of hydrazine recorded in the literature.[6] The purified hydrazine was stored in the distillation receiver and under dry nitrogen at one atmosphere. A short side arm attached to the receiver was capped with a rubber vaccine bottle stopper so that the purified hydrazine could be pulled through the hypodermic needle into a glass syringe without exposure to the atmosphere.

Mallinckrodt Analytical Reagent grade ammonium chloride was dried overnight at 105°, and stored in a desiccator.

Results and Discussion

The System N_2H_4–NH_4Cl.—The freezing point diagram for mixtures of hydrazine and ammonium chloride is given in Fig. 2. Since it is known that the reaction $N_2H_4 + NH_4Cl \leftrightarrows NH_3 + N_2H_5Cl$ takes place, and since no satisfactory analyses of the equilibrium solid phase associated with the peritectic point could be obtained, there is uncertainty concerning the interpretation of these data. For the purpose of our study, we have assumed that the system N_2H_4–NH_4Cl is a quasi-binary section of the general ternary diagram NH_3–HCl–N_2H_4. For this assumption to be strictly valid, no ammonia or hydrazine must escape into the vapor phase, and the composition of the solid phases must be an additive compound of N_2H_4 and NH_4Cl. Under the conditions under which the system was studied, the amount of ammonia and hydrazine in the vapor phase was negligible. It is our belief that, in the presence of an appreciable concentration of ammonia, the more basic character

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(4) A. Seidell, "Solubilities of Inorganic and Metal Organic Compounds," Vol. I, D. Van Nostrand Co., Inc., New York, N. Y., 1940, pp. 1091–1092.

(5) F. Friedrichs, *Z. anorg. allgem. Chem.*, **127**, 221 (1923).

(6) P. H. Mohr and L. F. Audrieth, *J. Phys. Colloid Chem.*, **53**, 901 (1949); D. W. Scott, *et al.*, THIS JOURNAL, **71**, 2293 (1949).

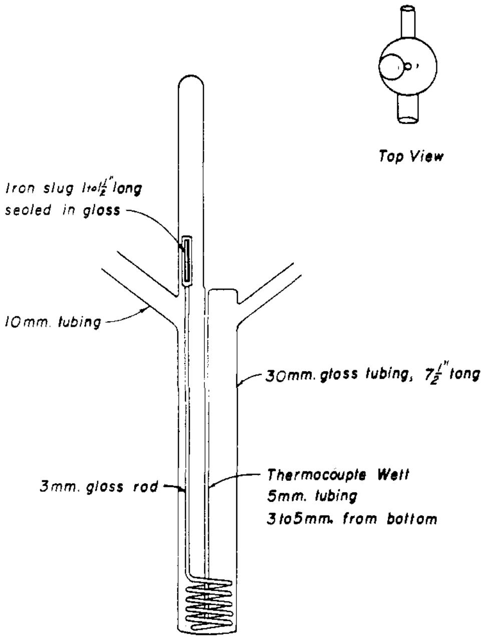

Fig. 1.—Freezing point cell.

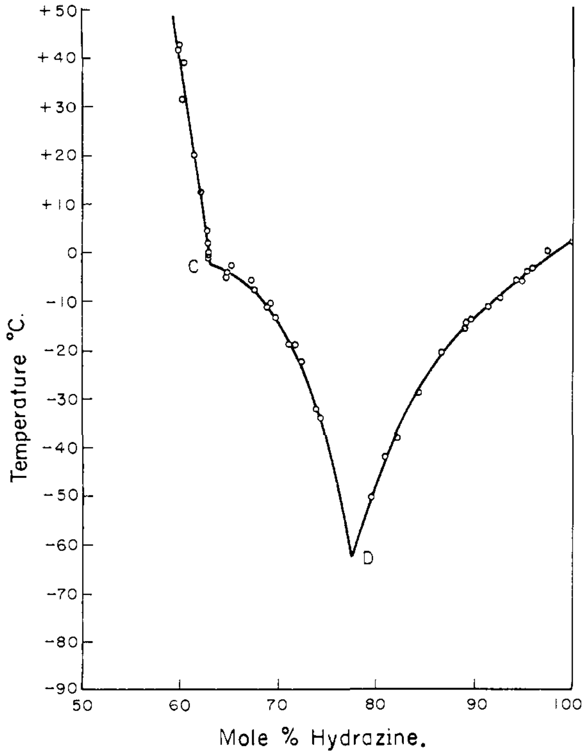

Fig. 2.—Freezing point diagram for the binary system N_2H_4–NH_4Cl.

of ammonia over hydrazine will inhibit the conversion of hydrazine and ammonium chloride mixtures to ammonia and hydrazine hydrochloride. In any case, these uncertainties concerning the interpretation of the N_2H_4–NH_4Cl section do not in any way invalidate the important synthetic implications involved, for the results obtained in this study help to form the experimental basis for an interesting and unique method for isolating anhydrous hydrazine.

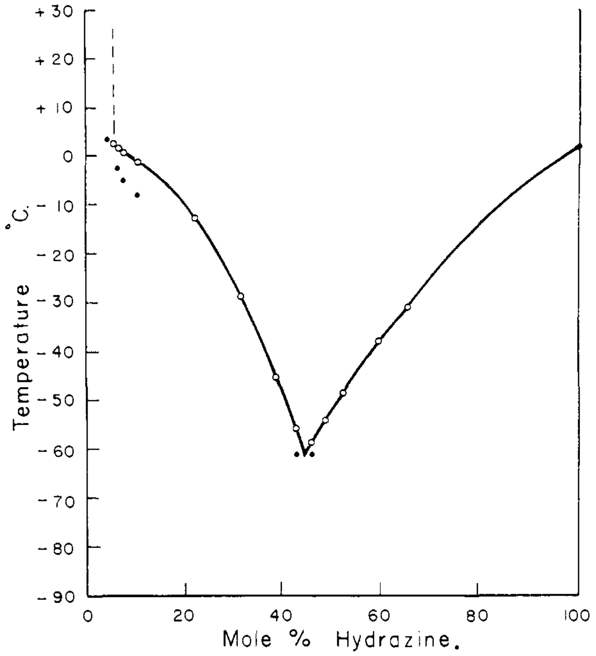

Fig. 3.—T–C section at 69.8/30.2 mole ratio NH_3/NH_4Cl

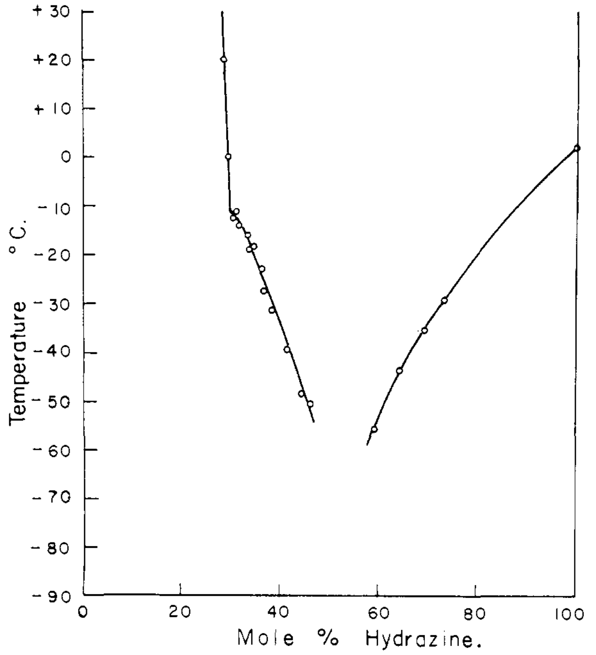

Fig. 4.—T–C section at 56.5/43.5 mole ratio NH_3/NH_4Cl.

The freezing point diagram shows two invariant points for the system. A peritectic point is located on the diagram at −2.5° and 63.0 mole % N_2H_4. The crystals which melt incongruently at this invariant point have been tentatively assigned the formula NH_4Cl–N_2H_4, but, for the reasons stated above, the composition of this phase is uncertain. The eutectic composition and temperature were not accurately established because of the viscous nature of the solutions in the vicinity of the eutectic point. However, the eutectic point has been estimated to be about −60° and 77.5 mole % N_2H_4. The significance of these two invariant points to the general ternary system NH_3-HCl-N_2H_4 will be discussed in the next section.

The Ternary System NH_3-N_2H_4-NH_4Cl.—The freezing points of various ternary mixtures of ammonia, hydrazine and ammonium chloride are not listed in this paper because of the voluminous amount of data[7] taken. A temperature–composition diagram was constructed for each group of freezing point data having a common mole ratio of ammonia to ammonium chloride. Forty such diagrams were prepared from the freezing point data. Two of these T–C Sections are shown in Figs. 3 and 4. The breaks in these diagrams are points at which the ternary liquidus is saturated with respect to two solid phases.

All the compounds and invariant points which occur in the binary systems NH_3-NH_4Cl, NH_3-N_2H_4 and N_2H_4-NH_4Cl also appear in the ternary system. The freezing point diagram for the condensed system N_2H_4-NH_4Cl has been given in Fig. 2 and already discussed. The freezing point diagram for the binary system NH_3-NH_4Cl is given in Fig. 5. Whereas the composition of the binary compound $NH_4Cl·3NH_3$ is well established, its melting point has been variously reported as 7, 7.6, 9.8 and 10.7°. The maximum in the curve in Fig. 5 occurs at 9.8°; however, Watt and McBride[8] in a recent paper seemed to prefer a lower value. Neither of the two eutectic points of the system are well defined by the data. The ammonia-rich eutectic point is estimated to be at *ca.* −81° and 0.5 mole % NH_4Cl, and the other eutectic point estimated to be at +8° and 27.5 mole % NH_4Cl. The phase diagram for the binary system NH_3-N_2H_4 is given in Fig. 6. No binary compound is formed; the eutectic point is at −80° and 7.36 mole % N_2H_4.

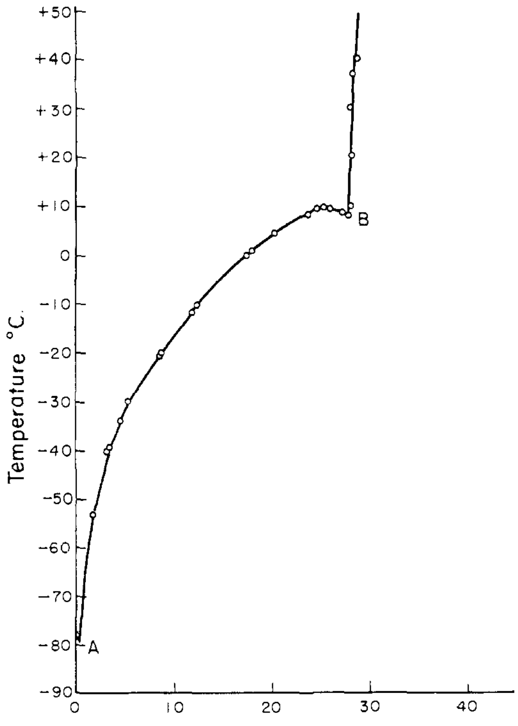

Fig. 5.—Freezing point diagram for the binary system NH_3-NH_4Cl.

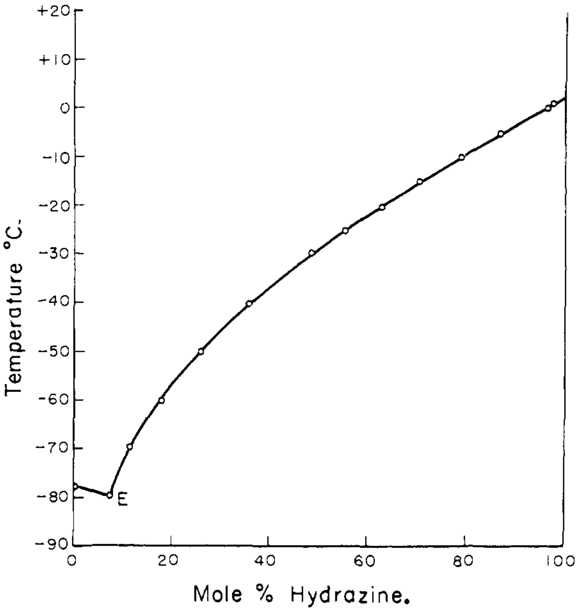

Fig. 6.—Freezing point diagram for the binary system NH_3-N_2H_4.

The invariant points in these binary systems are points of origin for curves of twofold saturation which divide the ternary liquidus into various primary fields of crystallization. The positions of these curves in the ternary phase diagram are set by the ternary breaks established by the ternary T–C Sections. The ternary phase diagram thus constructed appears in Fig. 7. Five primary fields of crystallization appear in the ternary system NH_3-N_2H_4-NH_4Cl. The primary fields of crystallization for the congruent melting hydra-

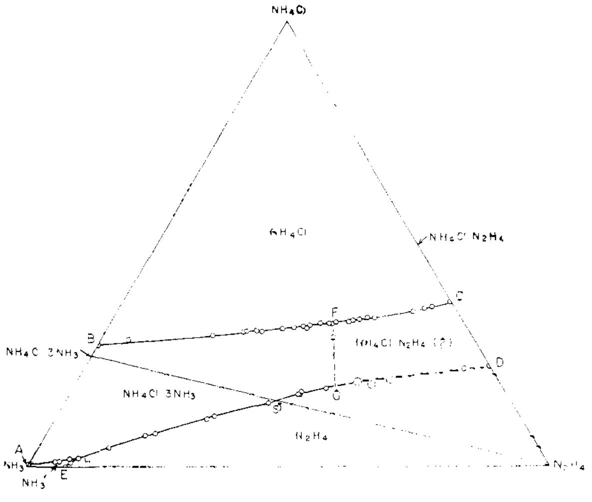

Fig. 7.—Phase diagram for the system NH_3-N_2H_4-NH_4Cl.

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[7] F. R. Hurley, Thesis, Ohio State University, 1954.

[8] G. W. Watt and W. R. McBride, THIS JOURNAL, **77**, 1317 (1955).

zine, ammonium chloride and ammonium chloride 3-ammoniate were assigned by inspection to those areas in which their composition points lie. The remaining area in the ternary phase diagram is assigned as the primary field of crystallization for the incongruent melting compound which, as stated above, we have assumed but not yet proved to be $NH_4Cl \cdot N_2H_4$. The hydrazine field was further confirmed by the secondary temperature breaks in the thermal analysis curve. Mixtures having constant NH_3/NH_4Cl ratios in the hydrazine field showing the same secondary temperatures breaks have composition points which form a series of straight lines passing through the N_2H_4 corner of the ternary diagram.

A summary of all the invariant points in the ternary phase diagram is given in Table I.

TABLE I

INVARIANT POINTS

Point	Solids	Liquid composition, % NH₄Cl	NH₃	N₂H₄	Temp., °C.
A	$NH_3 + NH_4Cl \cdot 3NH_3$	0.5	99.5	...	*ca.* −81
B	$NH_4Cl \cdot 3NH_3 + NH_4Cl$	27.5	72.5	...	+ 8
C	"$NH_4Cl \cdot N_2H_4$" + NH_4Cl	37.0	...	63.0	− 2.5
D	N_2H_4 + "$NH_4Cl \cdot N_2H_4$"	22.5	...	77.5	*ca.* −60
E	$NH_3 + N_2H_4$	..	92.64	7.36	−80
F	$NH_4Cl + NH_4Cl \cdot 3NH_3$ + "$NH_4Cl \cdot N_2H_4$"	32.3	25.0	42.7	−17
G	$N_2H_4 + NH_4Cl \cdot 3NH_3$ + "$NH_4Cl \cdot N_2H_4$"	18	32	50	*ca.* −67
H	$NH_3 + NH_4Cl \cdot 3NH_3 + N_2H_4$	2.0	89.0	9.0	−83
S	$NH_4Cl \cdot 3NH_3 + N_2H_4$	15.0	44.9	40.1	−60

Point F, a ternary peritectic point, is at −17° and 42.7 mole % N_2H_4, 32.3 mole % NH_4Cl. The invariant reaction occurring at this point is

$$\text{Liquid} + NH_4Cl = NH_4Cl \cdot 3NH_3 + \text{"}NH_4Cl \cdot N_2H_4\text{"} + \text{heat}$$

The curves FG and GD are dashed lines because the viscous nature of the solutions in this area of the phase diagram made it difficult to obtain freezing points. Point G, a ternary eutectic point, is estimated to be at −67° and 50 mole % N_2H_4, 18 mole % NH_4Cl. Point H, a ternary eutectic point, is at −83° and 9.0 mole % N_2H_4, 2.0 mole % NH_4Cl.

The temperature along the twofold saturation curve between the ternary eutectic points G and H passes through a maximum at point S which is called a saddle point. The temperature at the saddle point is −60°. The composition points for $NH_4Cl \cdot 3NH_3$ and N_2H_4 are points of maximum temperature in their respective areas, and with the saddle point form a straight line known as a quasi-binary section line of the ternary system.

In order to make clear the importance of the results presented in this paper to the synthesis of anhydrous hydrazine, the following example is given: A typical hydrazine reaction mixture may be composed of 99 mole % NH_3, 0.4 mole % N_2H_4 and 0.6 mole % NH_4Cl. This composition point lies in the field of crystallization for ammonium chloride 3-ammoniate. The equilibrium ternary liquid compositions along the curve GH represent the practical limits for fractional crystallization of ammonium chloride from these solutions. An equilibrium liquid composition near the saddle point S may be obtained by proper adjustment of the ammonia concentration of the ternary mixture by evaporation and cooling to crystallize ammonium chloride 3-ammoniate. At the saddle point where the equilibrium temperature is −60° the mole ratio of hydrazine to ammonium chloride in the liquid phase is 2.7:1. At this mole ratio about 63% of the hydrazine is in excess over the equivalent ammonium chloride in solution, and this excess hydrazine can be separated in the anhydrous form by distillation. The maximum mole ratio of hydrazine to ammonium chloride is obtained if less ammonia is evaporated and crystallization of the 3-ammoniate is carried to the ammonia-rich ternary eutectic point H; however, more refrigeration is required since the equilibrium temperature is −83°. The N_2H_4 to NH_4Cl mole ratio in the liquid phase is 4.5:1. Thus, a maximum (theoretical) of about 78% of the hydrazine can be freed by this procedure.

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